

**Determination of NO_x and SO₂ concentration levels in
Nairobi city, Kenya by use of passive samplers**

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Chemistry in the Jomo Kenyatta University of Agriculture and Technology**

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university.

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DEDICATION

This research work is dedicated to my grandmother Alina Nanyama, my mother Jedrix Nasimiyu, my dear wife Annastarciah Kawembe, to my children; Catherine, Bossy, Cavesh, Sosyne, Joyne and Mark, my late sister in- law Mwikali and to all my friends who inspired me to be what I am.

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LIST OF ABBREVIATIONS

A	Absorbance
ANOVA	Analysis of variance
AQM	Air quality monitoring
AU	Absorbance Unit
c	Velocity of light in a vacuum
d	Diameter
CBS	Central Bureau of Statistics
CRD	Completely Randomized Design
CO_x	Oxides of carbon
DSM	Dichloro-sulphitomercurate
DOAS	Differential optical absorption system
E	Energy
FP	Fine particle
GK	Government of Kenya
h	Planck's constant
H₀	Null hypothesis
HDS	Hydro-desulphurization
i.d	Internal diameter
J	Mass flux of gas
JKUAT	Jomo Kenyatta University of Agriculture and Technology

KEMRI	Kenya Medical Research Institute
KENGO	Kenya Energy and Environment Organizations
KNH	Kenyatta National Hospital
ℓ	Length
M	Molarity of a solution
NEDA	N-(1-Naphthyl)-ethylenediamine dihydrochloride
NEMA	National Environment Management Authority
nm	Nanometer
NYS	National Youth Service
NED	N-(1-Naphthyl)-ethylenediamine dihydrochloride
NO_x	Oxides of nitrogen
PAHs	Polycyclic aromatic hydrocarbons
PAN	Peroxyacyl nitrate(s)
PM	Particulate matter
PNA	Polynuclear ammonium
PRA	Pararosaniline
SPSS	Statistical Package for Social Scientists
SO_x	Oxides of sulphur
T	Transmittance
TCM	Tetrachloromercurate
TEA	Triethanolamine

TSP	Total Suspended Particulates
$\mu\text{g}/\text{m}^3$	Microgram per cubic meter
UV/Vis	Ultraviolet and visible
UVF	Ultraviolet fluorescence
ν	Frequency
VOCs	Volatile organic compounds
λ	Wavelength
WHO	World Health Organization

ABSTRACT

This research work describes the determination of the levels of nitrogen monoxide, nitrogen dioxide (termed as NO_x) and sulphur dioxide (SO_2) in Nairobi city by use of passive sampling method. In this technique, Triethanolamine (TEA) and potassium tetrachloromercurate (TCM) solutions were used as trapping agents and air samples which were sampled from twelve sites within Nairobi city were analyzed spectrophotometrically. The detection limit of passive sampling method was found to be $7\mu\text{g}/\text{m}^3$ and $4\mu\text{g}/\text{m}^3$ and precision was $4\mu\text{g}/\text{m}^3$ and $3\mu\text{g}/\text{m}^3$ for NO_2 and SO_2 , respectively for a 24-hour sampling. The highest 24-hour mean concentrations of NO_x and SO_2 were recorded at City Kabanas site along Nairobi-Mombasa road with $300.61 \pm 8.21\mu\text{g}/\text{m}^3$ and $181.35 \pm 2.46\mu\text{g}/\text{m}^3$, respectively and the lowest mean concentrations of NO_x and SO_2 were recorded at Githurai site with $169.92 \pm 6.12\mu\text{g}/\text{m}^3$ and $85.60 \pm 0.78\mu\text{g}/\text{m}^3$, respectively. The overall mean levels for these air pollutants were; $82.87 \pm 6.13\mu\text{g}/\text{m}^3$ for NO, $136.78 \pm 9.72\mu\text{g}/\text{m}^3$ for NO_2 and $127.66 \pm 10.45\mu\text{g}/\text{m}^3$ for SO_2 . The recorded level of NO_2 in Nairobi troposphere was found to be above the WHO value of $100\mu\text{g}/\text{m}^3$, that of SO_2 was within the WHO value of $125\mu\text{g}/\text{m}^3$ and that of NO was below the WHO value of $400\mu\text{g}/\text{m}^3$. Furthermore, it was found that levels of NO_x and SO_2 recorded during the dry season were higher than those of the wet season. The trend of levels of NO_x and SO_2 followed the vehicular density and areas with high vehicular traffic and industrial activities had high levels of NO_x and SO_2 .

CHAPTER ONE

1.0 INTRODUCTION

Clean air is considered to be a basic requirement for human health. However, air pollution continues to pose a significant threat to health worldwide. According to a WHO assessment of the burden of disease due to air pollution, more than 2 million premature deaths that occur each year can be attributed to the effects of urban outdoor and indoor air pollution. More than half of this disease burden is borne by the populations of developing countries (WHO, 2005).

Nairobi is the Capital city of Kenya, the biggest town in the Country. It is a commercial as well as industrial centre of the country. Nairobi's population has grown from an estimated 1.1 million in 1985 to around three million currently with the numbers set to rise to about 3.8 million by 2015 (UNEP/WHO, 2000). It is reputed to be the fastest growing city in the World after Guadalupe, Mexico City and Maputo (Mulaku and Kariuki, 2001).

In most cases, Nairobi troposphere is full of dust and smoke as it can be seen in plate 1. No wonder the area of Nairobi and its outskirt occasionally have a phenomenon of fog formation (especially Kikuyu area).



Plate 1: A photograph of part of Nairobi city. The smoky troposphere is an evidence of air pollution

The major sources of air pollution in Nairobi city are burning of fossil fuels in stationary combustion and industrial processes, automobiles and domestic emissions as shown in plates 2, 3, 4 and 5. Domestic solid fuel use such as biomass and burning of used tyres and plastic materials also presents a significant source of these pollutants in the atmosphere particularly in the slum areas. Open burning of solid wastes is also a common phenomenon in Nairobi city (a lot of air pollutants are released into troposphere), especially in neighbourhoods of the city centre.

One of the major sources of air pollution in the city is vehicle emissions as shown in plate 4. Statistics from the Central Bureau of Statistics of 2000 show that in the years 1992 and 1999, the number of imported motor vehicles into Kenya was 385,636 and

585,624, respectively. Most of these cars had been used for a number of years in their countries of origin, mainly Dubai and Japan, before resale to local buyers in Kenya.



Plate 2: A photograph of part of Nairobi industrial area



Plate 3: A photograph of motor vehicles on Nairobi-Mombasa road



Plate 4: A photograph of smoke from burning waste in the outskirts of Nairobi city



Plate 5: A photograph of smoke from burning tyres

They are known to emit far higher air pollutants than new and properly maintained vehicles. The level of motor vehicle related air pollution is expected to be highest in Nairobi city than other urban centers in the country due to the fact that most of these imported vehicles are used mainly in Nairobi city (Maina, 2004).

The effects of air pollutants on human health vary according to intensity, duration of exposure, age and health status of population for example, the young, elderly and those already suffering from respiratory, cardiopulmonary disease and hyper-responders. Ozone, nitrogen dioxide and sulphur dioxide, fine particulates and smoke cause reddening of eyes, inflammation of pharynx and throat and impair functioning of lung which reduces resistance to diseases leading to respiratory infections. Existing illnesses can worsen resulting to an increase in emergency consultations and hospital admissions for respiratory problems and premature deaths (World Health Organization, 1996; www.who.int/peh.htm, May 2008).

Furthermore, presence of NO_x , SO_2 , and hydrocarbons in the atmosphere lead to photochemical reactions particularly on sunny days, for instance, areas in warmer sunny locations with high traffic densities tend to be prone to net formation of ozone and other photochemical products from precursor emissions. This is due to high levels of air pollutants in the atmosphere (www.nl/products/aerosol.html, May 2008).

In view of this, the major objective of this study was to determine the current levels of NO_x and SO₂ in ambient air in Nairobi city and in the light of the findings recommendations would be made to relevant authorities. In this study, passive samplers with TEA and TCM as absorbents were used in sampling process and air samples were analyzed spectrophotometrically.

This method has several advantages such as simplicity, low cost, portability, no need for electricity and air flux calibration when compared to conventional techniques. Results from passive measurements were derived in form of time-weighted average concentration and there was no need to know the sampled air volume. These features make this kind of sampler suitable not only for monitoring individual exposure but also for application to environmental atmosphere, including remote areas, where there is no electric power and other techniques cannot be used (Palmes *et al.*, 1976).

However, passive samplers show some disadvantages such as not providing instantaneous concentrations, not commercially available for several atmospheric compounds, not allowing sampling rate to vary, thus hindering concentration and dilution during sampling. But accuracy of passive samplers has been tested in comparison with active methods and good agreement has been observed for average concentrations in measured periods (Parrah and Linda, 1988).

Lastly, in this research work it was demonstrated that activated charcoal has ability of absorbing NO_x and SO₂ from the troposphere.

1.1 Statement of the problem

Nairobi city does not have any regular air quality management system yet and any measurement of air pollution has been done on an ad hoc basis. Indeed, out of 20 cities mainly from developing countries sampled for a UN study on air quality management capability, Nairobi's capacity was rated as the worst (WHO Regional Publications, 1999).

Some of the reasons for high levels of air pollutants in the city are; use of poor quality fuels such as sulphur containing fuels, uncontrolled growth of vehicles and industries some of which are unworthy. The National Environment Management Authority (NEMA) is charged with the role of formulating and enforcing air quality regulations and standards, but data on air pollution in Nairobi are scanty and there is need to come up with simple method of monitoring air quality on a daily basis. Progress has, however, been slow due to lack of funding (Langwen, 2006).

In view of this, there was need to carry out a study to determine current levels of NO_x and SO_2 concentrations in ambient air in Nairobi city and find out whether their levels meet the WHO air quality guidelines or not.

1.2 Justification of the study

Currently there is no air pollution monitoring programme in the city, as the measurement of air pollution is not done on a regular or routine basis but is undertaken as need or opportunity arises. Also there are no national air quality standards in Kenya only specific standards are formulated from World Health Organization guidelines. For instance, World Health Organization (WHO) guidelines are used for affected industries as the need arises to control air pollution (Langwen, 2006).

One major consequence of lack of air quality management in Nairobi city is the lack of data on air pollution, which often gives the illusion that, this is not serious problem. This is far from the truth and only contributes to the concealment of a very significant public health problem. “Nairobi lacks a comprehensive physical development plan and neither does it have an environmental policy addressing circumstances peculiar to the city. The formulation of these policy instruments would go a long way in addressing the issues, especially the poor quality human settlements, pollution and waste management” Dick Wathika, who was then mayor of Nairobi was quoted in (UNEP/WHO, 2000). It was therefore decided to carry out a study to establish the current levels of NO_x and SO_2 in ambient air in Nairobi city. Passive sampling technique was considered because it is applicable to anywhere including areas with no electricity, its apparatus are portable and are easy to setup

and the low sampling unit cost makes it applicable for large scale measurements. However passive sampling technique gives average value since sampling is carried over a period of twenty four hours.

1.3.0 Objectives of the study

1.3.1 General objective

The objective of this study was to determine 24-hour mean levels of NO_x and SO₂ in ambient air in Nairobi city and its environments.

1.3.2 Specific objectives

The specific objectives of this study were:

1. To compare results obtained by use of passive sampling method with those results of active sampling method.
2. To determine current levels of NO and NO₂ in ambient air using passive sampling.
3. To determine current levels of SO₂ in ambient air using passive sampling.
4. To compare results obtained by use of activated charcoal with those results of TEA and TCM.

1.3.3 Hypothesis of the study

1. The levels of NO_x and SO₂ in ambient air of Nairobi city are higher than WHO air quality values.
2. The TEA and TCM absorbing agents' results do vary from those of activated charcoal.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1.0 Air quality and air pollution

Pure air comprises oxygen (21%) and nitrogen (78%) and a number of rare gases, of which argon is the most plentiful (0.99%). Carbon dioxide (CO₂) is present at a lower percentage concentration (0.03%) than argon (0.93%). Water vapour, up to 4% by volume, is also present. Oxygen is produced by plants as a by-product of photosynthesis and the earth's atmosphere is now described as oxidant or oxidizing, in comparison with the hydrogen-rich reducing atmosphere that was present before life began (Research Triangle Park, 1976).

Air pollution is an atmospheric condition in which certain substances are present in such concentrations and duration that they may produce harmful effects on man and his environment. Common air pollutants include oxides of carbon, nitrogen and sulphur, volatile organic compounds, ammonia, heavy metals, a wide range of polycyclic aromatic hydrocarbons (PAHs) and suspended particulate matter which includes dust, smoke, pollen and other solid particles (Research Triangle Park, 1993).

Most of these substances occur naturally in low (background) concentrations and are harmless. Nevertheless they become pollutants only when their concentrations

are relatively high compared to the background value and begin to cause adverse effects (Rao, 1991). Their concentrations vary widely depending on the sources of pollution and their distribution, meteorological conditions and the topographical features in the vicinity (Mulaku and Kariuki, 2001).

The industrial revolution precipitated rapid industrialization, motorization, rapid growth of urban centres and a greater dependence on fossil fuel. The use of fossil fuels brought about an increase in emissions of harmful pollutants into the atmosphere. Pollution of the atmosphere affects the lives of millions of people in all parts of the world, especially those living in large industrialized cities like Nairobi city. The World Health Organization (WHO) lists some of the major environmental problems of urban and industrial areas and their surroundings as; unpleasant fumes and odours, reduced visibility, injury to human health and crops, damage to property by dust and corrosive gases (WHO, 2005).

2.1.1 World health organization guidelines for air quality

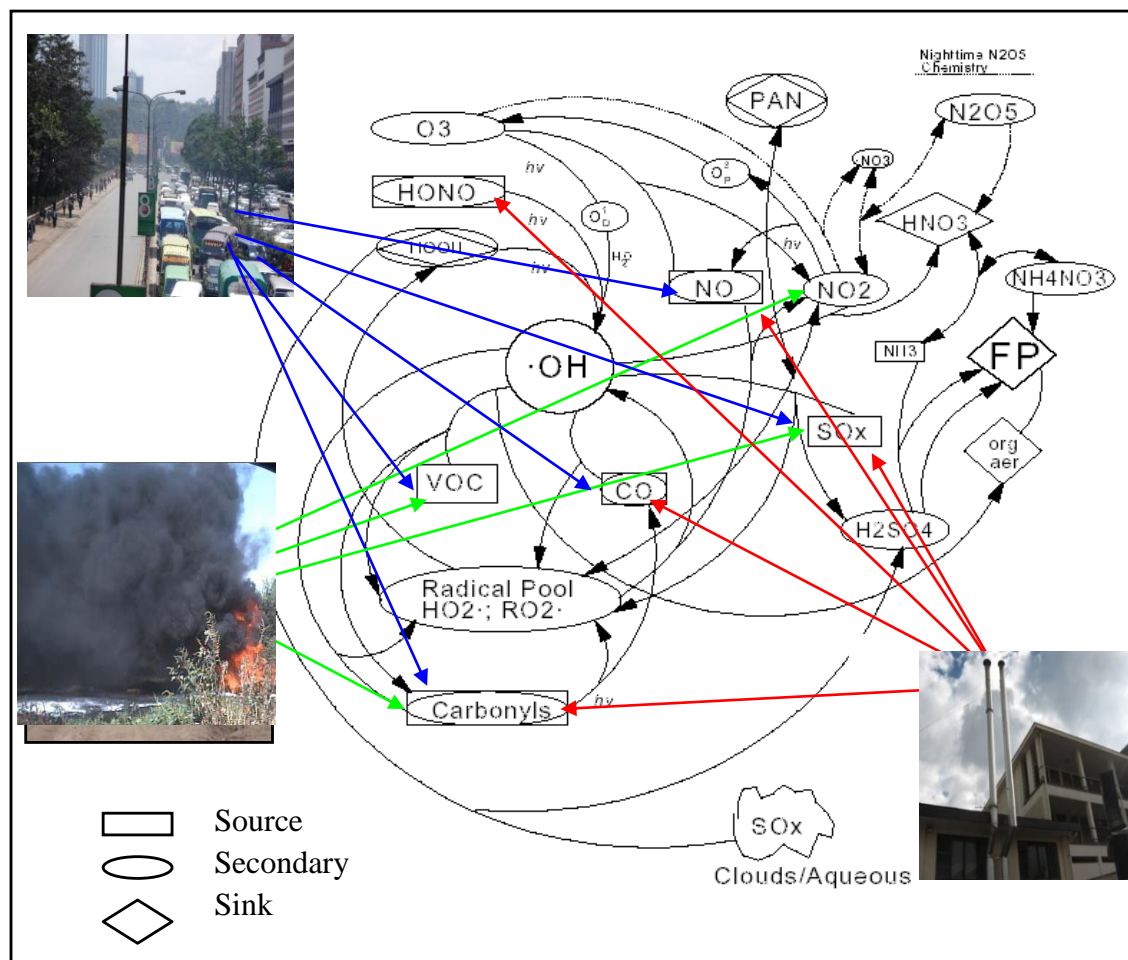
The WHO air quality guidelines are designed to offer guidance in reducing the health impacts of air pollution. They were first produced in 1987 and recent revised air quality guideline was released in 2006 (Appendix VII). These guidelines are based on expert evaluation of current scientific evidence. Given the wealth of new studies on the health effects of air pollution that have been published in the

scientific literature since the completion of the second edition of the air quality guidelines for Europe (WHO, Regional Office for Europe, 1995), including important new research from low-and middle-income countries where air pollution levels are at their highest, WHO has undertaken to review the accumulated scientific evidence and to consider its implications for its air quality guidelines. The WHO air quality guidelines cover a wide range of pollutants. These guidelines indicate the level and exposure time at which no adverse effect on human health is expected to occur. They are designed to protect human health and are legally enforced (World Health Organization, 2000; World Health Organization, 1994).

2.2.0 Oxides of Nitrogen

Nitrogen dioxide (NO_2) is a reddish brown, pungent, acidic gas which reacts with water and other compounds in ambient air to form nitric oxide (NO), nitrogen trioxide (NO_3), nitrate (NO_3^{-1}), nitrogen pentoxide (N_2O_5), nitrous acid (HNO_2), nitric acid (HNO_3) and peroxyacetyl nitrate ($\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) as shown in the scheme 1. Anthropogenic NO_2 is produced along with NO by the oxidation of molecular (N_2) in high temperature combustion processes including motor vehicles and fossil fuelled power stations, boilers and domestic appliances. The proportion of NO to NO_2 from these sources is typically 90-95% NO.

The interactive relationship between NO and NO₂ and their involvement in photochemical smog reactions has generated the common term of “oxides of nitrogen” (NO_x). NO_x is normally considered on a mass basis where NO is calculated as if it had been oxidized to NO₂. NO is a colourless, odourless, tasteless gas which is relatively non-irritating and non toxic at atmospheric levels but is readily oxidized to form NO₂ as a secondary pollutant.



Scheme 1: A schematic diagram showing a link between oxidant chemistry, fine particle formation in polluted troposphere and sources of air pollution

NO is primarily oxidized by ozone (O_3) but this reaction is reversed by short wavelength sunlight. NO is also slowly oxidized directly by oxygen (O_2) and photochemically by hydrogen species such as the hydroxyl radical ($OH\cdot$), hydrogen dioxide (HO_2) and hydrogen peroxide (H_2O_2) (Vesilind, *et al.*, 1990).

Nitrogen dioxide is an important pollutant gas, not only because of its health effects but also because; (a) it absorbs visible solar radiation and contributes to impaired atmospheric visibility; (b) as an absorber of visible radiation it could have a potential direct role in global climate change if its concentrations are to become high enough; (c) it is, along with nitric oxide (NO), a chief regulator of the oxidizing capacity of the free troposphere by controlling the build-up and fate of radical species, including hydroxyl radicals; and (d) it plays a critical role in determining ozone (O_3) concentrations in the troposphere because the photolysis of nitrogen dioxide is the only key initiator of the photochemical formation of ozone, in polluted atmosphere (Matsuo, 1981).

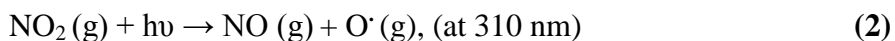
The schematic of photolytic equations illustrated in scheme **1**, shows NO_x cycle in polluted troposphere within 24-hour duration. The three steps involved are;

Step 1

In the troposphere, nitric oxide gas is oxidized to nitrogen dioxide gas as shown in equation **(1)**;



In day time, nitrogen dioxide molecules (NO_2) absorb energy in the form of ultraviolet light and break into nitric oxide molecules (NO) and reactive oxygen atoms (O^\cdot) as shown in equation (2);



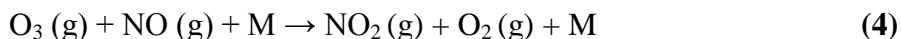
Step 2

The atomic oxygen atoms react with atmospheric oxygen gas to form ozone gas, as a secondary pollutant, (M is an atom or a molecule that absorbs excess energy of the reaction) as shown in equation (3).



Step 3

The ozone reacts with NO to yield NO_2 and O_2 and the cycle gets completed as shown in equation (4).



This cycle gets disrupted when both water vapour and volatile organic compounds (VOCs) are present because of their ability to form hydroxyl and organic radicals that react with either the reactive oxygen atoms (O^\cdot) produced in equation (2) or the ozone produced in the equation (3). The most likely reaction is that between O^\cdot and organic radicals, because it takes place 10^8 times faster than the one between O_3 and organic radicals (Tyagi and Mehra, 1990). The reaction between O^\cdot and O_2 is faster

than that between oxygen atoms and organic radicals, but the latter reaction still proceeds fast enough to upset the cycle.

The product of a reaction between O[·] and organic radicals is a very reactive intermediate species which can further react with a number of different species including NO, NO₂, O₂, O₃, and hydrocarbons. Some known facts about these free radicals are; free radicals can react with hydrocarbons and oxygen species to produce additional undesirable organic compounds as shown in equations (5), (6) and (7).

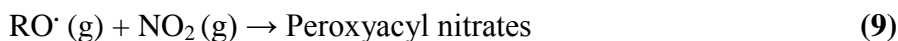


Free radicals (RO₃[·] in equation (6)) react rapidly with NO to produce NO₂ as shown in equation (8).

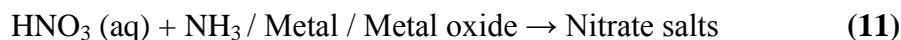


The consequence of this is that, with NO removed from the cycle, the normal mechanism for O₃ removal as shown in equation (4) is eliminated and the concentration of O₃ in the ambient air is increased.

Finally, free radicals (RO[·]) produced in equation (5) react with NO₂ to form peroxyacyl nitrates (PAN) as shown in equation (9).



The mixture of products resulting from organic radicals' interference in the NO₂ photolytic cycle is called photochemical smog. It consists of accumulation of O₃, CO, nitrate salts, PAN, and other organic compounds, including aldehydes, ketones, and alkyl nitrates (Research Triangle Park, 1995). However, presence of water vapour leads to formation of hydroxyl radicals which later combine with NO₂ molecules and metals or metal oxides to form fine (nitrate) particles (FP) as shown in equations (10) and (11).



2.2.1 Health effects of NO₂

The available evidence suggests that ambient exposure may result in both acute and chronic effects, especially in susceptible population subgroups with asthma. NO₂ primarily acts as an oxidizing agent that may damage cell membranes and proteins. At high concentrations, the airways may become acutely inflamed (WHO Regional Publications, 1999).

In addition, short-term exposure may predispose towards an increased risk of respiratory infection (Research Triangle Park, 1993). For acute exposure, only very high concentrations (>1880 µg/m³, 1 ppm) affect healthy people; however, people with asthma or chronic obstructive pulmonary disease are more susceptible at lower

concentrations. Based on the best available clinical evidence, a 1-hour guideline of $200 \mu\text{g}/\text{m}^3$ and a 24-hour guideline of $100 \mu\text{g}/\text{m}^3$ have been set by World Health Organization (WHO (2005)).

2.3.0 Sulphur (IV) dioxide

Sulphur dioxide is a colourless, pungent, irritating, water-soluble, and reactive gas. It is produced by both natural and man-made sources. Sulphur dioxide in the city troposphere is associated with human activities; in this case the combustion of sulphur-rich fuels and petrochemicals (fossil fuels), steel mills, refineries, pulp and paper mills and from non-ferrous smelters (Jain, *et al.*, 1993).

Combustion of sulphur containing material produces two oxides of sulphur as given in equations (12) and (13).

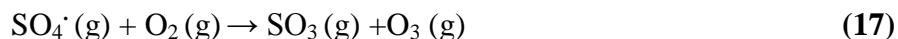


In the troposphere, SO_3 reacts with water vapour to form droplets of sulphuric acid according to equation (14).

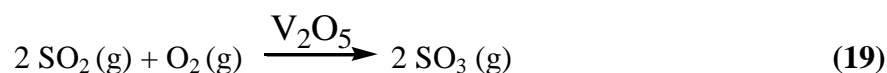


Once in the troposphere, SO_2 is partially converted to SO_3 and then to H_2SO_4 by various photolytic reactions according to equations (15), (16), (17) and (18)





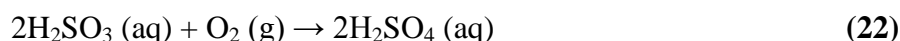
However, in presence of a catalyst (like vanadium (V) oxide) SO_2 is oxidized to SO_3 as shown in equation (19).



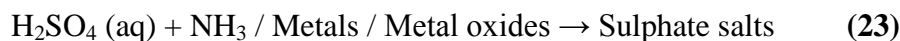
Furthermore, SO_3 gas reacts with water vapour in atmosphere to form sulphuric acid which is the main component of acid rain as shown in equation (20)



Also, sulphur dioxide in ambient air combines with water vapour to form sulphurous acid which is further oxidized to sulphuric acid by oxygen gas as shown in equations (21) and (22).



The amount of SO_2 oxidized to SO_3 in equations (15) and (19), depends upon a number of factors including: the amount of moisture present, the light intensity, duration and spectral distribution of sunlight, and the amounts of catalytic sportive and alkaline materials present (Alloway and Ayres, 1993). Presence of metals, ammonia or metal oxides in troposphere lead to formation of sulphate salts in the form of fine particulates (see scheme 1) as shown in equation (23).



2.3.1 Health effects of Sulphur dioxide

The major health concerns associated with exposure to high concentrations of sulphur dioxide include effects on breathing, respiratory illness, irritation of eyes, alterations in pulmonary defenses and aggravation of existing cardiovascular disease. Children, the elderly, and people with asthma, cardiovascular disease or chronic lung disease (such as bronchitis or emphysema), are most susceptible to adverse health effects associated with exposure to SO₂. When sulphur dioxide irritates the respiratory tract it causes coughing, mucus secretion, aggravates conditions such as asthma and chronic bronchitis and makes people more prone to respiratory tract infections. Sulphur dioxide attaches itself to particles and, if these particles are inhaled, they cause more serious effects. In case of short-term high exposure, a reversible effect on lung functioning occur, according to individual sensitivity (Vesilind et *al.*, 1990).

The secondary product H₂SO₄ primarily influences respiratory functioning. Its compounds, such as polynuclear ammonium (PNA) salts or organo-sulphates, act mechanically in alveoli and, as easily soluble chemicals, they pass across the mucous membranes of the respiratory tract into the organism. Particulate aerosol formed by the gas-to-particle formation has been found to be associated with numerous health effects. On environment, sulphur dioxide combines with water vapour in atmosphere to form sulphuric acid which is the main component of acid

rain. When acid rain falls it causes deforestation, acidify waterways to the detriment of aquatic life and corrode building materials and paints (Kasper-Giebl and Puxbaum, (1999).

2.4 Methods of measuring air pollution

There are four main methods available to measure air pollution namely active sampling, automatic sampling, remote sensors and passive sampling. Active sampling involves the collection of samples, by physical or chemical means, for subsequent laboratory analysis. Typically, a known volume of air is pumped through a filter or chemical collector for a known period of time and the collection medium is then subjected to laboratory analysis (Sivertsen, *et al.*, 2005). This method is not suitable for continuous or near-real time air quality monitoring.

Automatic sampling is the most sophisticated method of air quality analysis, producing high-resolution measurement data of a range of pollutants. The pollutants that can be measured include, but are not limited to, NO_x, SO₂, CO, O₃, VOC's, particulate matter (PM), carbon black, Hg, benzene and so on. The air quality is continuously sampled and measured on-line and in real-time. The real time data is stored, typically as one hourly average, with data being collected remotely from individual monitoring stations by telemetry. Remote control of the monitoring and

data system is also possible as is remote diagnostics for most of the analyzers (Elsevier Science, 1996).

Remote sensors (long-path monitoring systems) are available for the measurement of some air pollutants including CO₂, O₃, NO, NO₂ and SO₂, but the methodology is less well established than that for automatic point monitors. The accuracy and precision of the data from these instruments are, therefore, much more difficult to determine. The method does not conform to ISO 7996 and to ISO 7996 (Research Triangle Park, 1977; World Health Organization, 1994). Careful attention is needed to be given to instrument calibration and quality assurance to obtain meaningful data.

Passive sampling is based on the property of molecular diffusion of gases, hence the term passive (also referred to as diffusive) sampling. The gas molecules diffuse into the sampler where they are quantitatively collected on an impregnated filter or an absorbent material. Plastic tubes open at one end to the atmosphere and with a chemical absorbent at the other, collect a sample for subsequent analysis in the laboratory (Hargreaves, 1990; Krochmal and Kalina, 1997).

The low cost per tube allows sampling at a number of points and is useful in highlighting "hotspots" where more detailed study may be needed. The quality and

accuracy of the data from passive sampling tubes does not make them suitable for precise measurements but they can give useful long term trend data (Glasius *et al.*, 1999)

In this study, the passive sampling technique was considered in sampling the three air pollutants. Passive samplers using TEA and TCM as absorbents were used in sampling process and air samples obtained were analyzed spectrophotometrically.

2.5 Passive samplers

Passive samplers have been used for workplace air monitoring for many years and in many cases have been found to be valid and cost-effective alternatives to conventional pumped or 'active' samplers. A passive sampler is a device which is capable of taking gaseous pollutants from the atmosphere at a rate controlled by diffusion process through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler (De Santis, *et al.*, 1997).

Passive sampling in the occupational environment dates back to the 1930s when qualitative devices were described, but the first serious attempt to apply science to quantitative passive sampling was in 1973 when Palmes described a tube-form sampler for sulphur dioxide (Palmes and Gunnison, 1973). Since then, a wide

variety of samplers have been described, some relying on diffusion through an air-gap, while others relying on permeation through a membrane and some using both techniques, for the rate-controlling process in sampling (Gair, *et al.*, 1991; Hangartner, *et al.*, 1989). Many of these devices are commercially available.

The theoretical basis for passive sampling is now well established. Diffusion and permeation processes can both be described in derivations of Fick's first law of diffusion, which result in expressions relating the mass uptake by the sampler to the concentration gradient, the time of exposure, and the sampler area exposed to the pollutant atmosphere (Palmes and Gunnison, 1976).

Expressions have also been derived for the application of Fick's Law to passive sampling in the "real" world. For instance, taking into account non steady-state sampling, the effects of fluctuating concentrations, sorbent saturation, wind velocity and turbulence at the sampler surface, temperature, pressure, and so on (Atkins, 1986). Except for sorbent saturation, which may lead to reduced (although sometimes predictable) uptake rates, these modifications to the basic Fick's Law expression do not lead to significant errors for well-designed samplers. Such samplers may be regarded as truly integrating devices with accuracies similar to those of active samplers (www.euro.who.int/air/activities, August 2008).

2.6 Environmental monitoring potential of passive sampling

In conventional environmental monitoring technology such as active sampling, it is common to sample many litres of air in order to have sufficient sensitivity. Such volumes can only be sampled in reasonable periods by means of a sampling pump. On the other hand, passive samplers operate at an equivalent of a few millilitres a minute.

The latter are only practical, therefore, if blanks can be made extremely low by meticulous attention to cleanliness; by having much increased sensitivity in the analytical stage (relative to the blank or by sampling for very long times). The last option can be a very useful one, for whilst sampling with an electrically driven pump is impractical for more than a day or so without a dedicated power supply, passive samplers can be exposed indefinitely, at least in principle. The trade-off is of course lack of time-resolution in the integrated result. An air concentration can therefore be deduced from a measured mass uptake (which is usually the analytical result) if the time of exposure is known. It is important, therefore, that the sampling rate is constant, i.e. does not change with pollutant concentration or time of exposure.

The fundamental equation describing diffusion is Fick's first law. From this, it can be deduced that the sampling rate of a diffusive sampler is directly proportional to the diffusion coefficient of the particular pollutant in air, the concentration and the

time of exposure, provided the concentration gradient is maintained. It is also proportional to the cross-sectional area of the diffusion path and inversely proportional to its length. The diffusion coefficient can be ascertained from the literature, is not expected to be concentration-dependent, at least at concentrations below 1000 ppm. However, the concentration gradient can be reduced if the sorbent begins to reach saturation.

For a pumped sampler, sampling efficiency will be reduced or 'breakthrough' will occur if the sorbent becomes saturated. A similar phenomenon occurs with passive samplers, and may occur earlier than full saturation (depending on the shape of the adsorption isotherm), if a significant vapour pressure exists at the sorbent surface relative to the ambient concentration of pollutant. For most sorbents used in environmental monitoring, this is not a problem. However, for organic vapours sampled on thermal desorption tubes, it is sometimes difficult to have sorbents which are both strong enough to provide negligible back-diffusion and weak enough to be convenient for thermal desorption. Even so, for environmental monitoring concentrations, passive sampling rates remain fairly constant even when non-ideal sorbents are used, as can be shown from a computerized model developed by Rao (1994).

Passive sampling rates can also be affected by air movement external to the sampler. Most studies have examined the effect of low air velocities (Plaisance, 2002). For the concentration gradient to be maintained as the driving force for diffusion, external air movement has to be sufficient to reduce the 'boundary layer' effectively to zero. Another way of looking at this is to imagine that at low air velocities, a static layer of air external to the sampler will cause 'starvation' or an extension of the diffusive path and hence a flattening of the concentration gradient (Helleday, 1993).

Experiments on samplers exposed to air velocities typical of the workplace suggest that the 'face velocity' effect is small provided a minimum of about 0.1 d s linear air velocity is maintained (Gair, 1995). This is unlikely to be a problem in measuring ambient air element (Palmer and Gunnison, 1973). Gair (1995) reports lowering the detection limit to 30 ppb/hr (blank 7 ppb/hr) by replacing the acrylic tube with stainless steel and changing to ion chromatographic analysis. Gair also found reversible adsorption of NO₂ on the walls of the perspex sampler and storage problems with the stainless steel sampler. Gair (1995) found a similar detection limit and blank by preparing tubes in situ with ultra clean reagents. An increase in blank level of about 34 ppb/hr for each week of storage was noted and was ascribed to permeation of NO₂ through the walls of the tubing. Contamination did not increase in tubes stored in the freezer (Gair, 1995).

Helleday (1993) found that peroxyacetyl nitrate (PAN) was a positive interferent for NO₂ using TEA coated (pumped) cartridges and HPLC-UV detection. However, Gair *et al* (1991) found only a <6% positive interference which they considered non-significant.

2.7 Validation of passive samplers

Gerboles and Amantini (1993) reported a good agreement between Palme's tubes and a chemiluminescent method in measuring NO₂ in houses, but presented only limited data. Kirby (2000) included some 50 comparisons of Palme's tube results with a chemiluminescent monitor, measuring NO₂ levels in homes. The overall correlation coefficient was 0.93. Biases of up to 30% were observed in particular locations, but as the conventional of each method was estimated at about 10%, these differences are probably not significant.

A detailed comparison between diffusion tubes and chemiluminescent monitors used for ambient air monitoring has also been published (Atkins, 1986). It covered the low ppb range (2-35 µg/m³) and compared weekly diffusion tube measurements with means of hourly concentrations measured by the monitors. The authors concluded that there were no significant differences between the two methods. Other workers have reported similar results (Hangartner and Burri, 1987).

Passive samplers have been found to be valid and cost-effective alternatives to conventional pumped or 'active' samplers. For instance, Hangartner and Burri, used passive samplers in measuring NO₂ and SO₂ in ambient air. TEA was used as absorbing medium for NO₂ and a mixture of TEA and glycol in ratio 3:1 used as absorbing medium for SO₂. They found out that sampling efficiency of the passive sampler for NO₂ was not affected by meteorological factors like wind, precipitation and temperature under usual range of weather conditions (e.g. 0.5 to 4 m/s, wind speed and -10 to 25⁰C). This was not the case with SO₂. The standard deviation of NO₂ and SO₂ were 0.00281 and 0.00147 and the lower detection limit were 4µg/m³ for NO₂ and 2µg/m³ for SO₂ for a 24-hour exposure.

Parrah and Linda (1988) determined the performance of passive sampling for NO₂ in ambient air. The results of passive sampling were compared to those of automatic analyzer (chemiluminescent) and in their calibration experiments, passive samplers had strong correlation to active monitor: $r = 0.9539$ for a 24-hour exposure period.

Annika *et al* (1999) validated passive samplers for NO₂, both in laboratory and outdoor test using TEA as absorbing medium. The analysis was performed by a flow injection analysis technique. There was no effect of NO₂ concentration or relative humidity on sampling rate and the influence of sampling time was found to be very small, which does not influence the usefulness of the method. The detection

limit was $4\mu\text{g}/\text{m}^3$ for a 24-hour sampling and the capacity was high enough to allow sampling of $150\mu\text{g}/\text{m}^3$ for 7 days. The overall uncertainty of the method was 24%. The sensitivity and capacity of the method make it suitable for personal sampling for 2-8 hour in working environments.

Waterhouse *et al* (2000) determined the reliability of nitrogen dioxide passive samplers for ambient measurement (*in situ* properties of TEA). They were able to show that, for a range of aqueous TEA solution (0-20% H_2O), no freezing occurred even at $-10.0\text{ }^\circ\text{C}$. NO_2 collection efficiency was unlikely to be impaired by low temperature exposure and the recovery of TEA from the meshes of exposed samplers was $\sim 98\%$, even after 42-day exposure, showing that the stability *in situ* of TEA is unaffected by long-term exposure.

Licia *et al* (2005) carried out a laboratory validation of a passive sampler for SO_2 atmospheric monitoring. The performance of a passive sampler was tested under exposure in Teflon chamber. The SO_2 trapped in impregnated filter with 1.0×10^{-2} M Na_2CO_3 solution was extracted in ultrasound bath with H_2O_2 solution for 15 min and determined as SO_4^{2-} by ion chromatography. The sampler presented good performance except for air in total stillness condition (0 ms^{-1}), for very short exposure periods (30 min), for atmosphere with $3 >150\text{ }\mu\text{g}/\text{m}^3$ and for high concentrations of reduced sulphur compounds. The relative humidity of the air (20 -

80%) and the exposure to zero concentration did not affect the sampler performance. It showed stability for one month at 4 °C or for one week at about 25 °C. Its precision varied within 3.5 to 23% depending on the SO₂ concentration and the accuracy varied from 91 to 100% (www.rsc, Org/Journal of environmental monitoring).

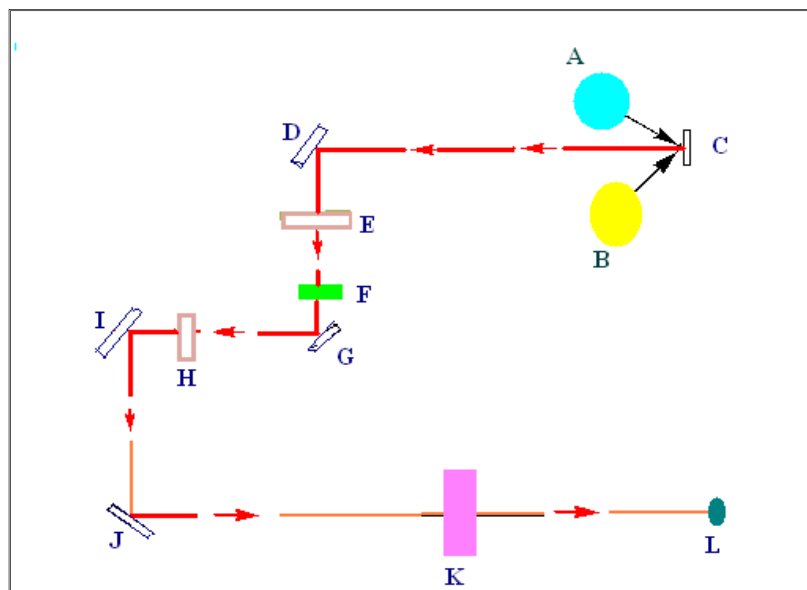
Gerboles *et al* (2005) carried out laboratory and field comparison of measurements using passive samplers for ozone and nitrogen dioxide in ambient air. For NO₂, the results of the laboratory experiments showed that most of the passive samplers were affected by extreme exposure conditions. The agreement between the samplers and reference method was better for the field tests than for the laboratory ones. The agreement between O₃ measured by the passive samplers and by the reference method was satisfactory for one week exposure. The field tests showed that the majority of passive samplers fulfill the 25% uncertainty requirement of the NO₂ and the 30% uncertainty requirement of the O₃ European Directive for one week exposure.

2.8.0 Theory of single-beam UV-Vis spectrophotometer

Single-beam spectrophotometer is an instrumentation which is very sensitive and relatively cheap. It is suitable for trace organics analysis/monitoring, suitable for colorimetric and specular reflection measurements. It is dispersive designed, uses a

monochromator that converts the white light produced by the light source into a single wavelength of light. This single wavelength is then passed through the sample and detected. When light falls upon a sample, a portion of the light is absorbed and the rest is passed on to the monochromator which allows only wavelength of interest to reach the detector.

Single beam ultraviolet and visible spectrometry is almost entirely used for quantitative analysis; that is, the estimation of the amount of an analyte present in a sample. In this single beam design, it is necessary first to zero the instrument (to establish the I_0 value) and then to measure the analyte/sample in aqueous state. The following is a schematic diagram of single-beam ultraviolet/visible spectrophotometer (Hopke and Markowitz, 2002).



Scheme 2: Schematic diagram of single-beam ultraviolet/visible spectrophotometer

In the scheme 2, **A** is a deuterium bulb for UV range radiation and **B** is a tungsten bulb for the visible range. When a device scans a range of frequencies it simply uses one bulb for visible, then switches to the other bulb for the UV. The beam is focused onto a mirror **C** for source change and later focused onto mirror **D** then sends a beam through a filter wheel **E**. A filter wheel rotates sending off different frequencies of light at entrance slit **F** where the beam of radiation is sharpened and sends to monochromator **G** which is a wavelength-fixed filter. A beam of radiation with specific wavelength leaves and passes through exit slit **H** to mirror **I**, mirror **J** and finally focused to sample **K**. When white light of specific wavelength passes through sample **K**, a portion of the light is absorbed and the balance passes to detector **L** (Stephen, 2000).

2.8.1 Principles of single-beam UV-VIS spectrophotometer

The most important principle in absorption analysis is the Beer–Lambert Law. The Beer-Lambert Law states that the concentration of a substance in aqueous state is directly proportional to the absorbance A of the solution. The law is only true for monochromatic light (light of a single wavelength) because absorptivity ϵ is a constant for each molecule for each wavelength and also provided that the physical or chemical state of the substance does not change with concentration (Henry, *et al.*, (1990). When monochromatic radiation (intensity of the incident radiation I_0) passes through a homogeneous analyte solution in a cuvette, the intensity of the emitted

radiation I depends upon the cuvette length l and the concentration C of the analyte solution as shown in figure 1.

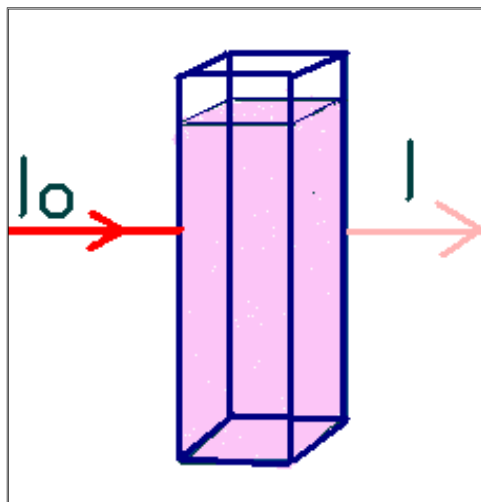


Fig. 1: Monochromatic radiation passing through a cuvette with analyte solution

The ratio I/I_0 is called transmittance and sometimes it is expressed as a percentage and referred to as % transmittance according to equations (24) and (25).

$$T = I/I_0 \quad (24)$$

$$\%T = I/I_0 \times 100 \quad (25)$$

Mathematically absorbance (A) is related to percentage transmittance (% T) as shown in equations (26) and (27);

$$A = -\log_{10}(T/100) \quad (26)$$

$$= \log(100/T) \quad (27)$$

Therefore, if wavelength, cuvette length and physical or chemical states of analyte remain unchanged, there is a linear relationship between concentration of analyte and absorbance (A) as shown in equation (28)

$$A = \epsilon C \ell \quad (28)$$

Where,

A = Absorbance

ϵ = Absorptivity of the analyte

C = Concentration of the analyte

ℓ = Cuvette length

If ϵ and ℓ are kept constant for a given set of experiments, a plot of the analyte absorbance against the concentration should give a straight line. In practice, a calibration curve is prepared by plotting the absorbance of a series of standard analyte as a function of their concentration. If the absorbance of an unknown analyte is then measured, the concentration of the absorbing component can be assessed from this graph. Another consequence of the Beer–Lambert law is that it is possible to change the path length to affect the absorbance (Stephen, 2000).

This is useful where lower detection limits are required as the cuvette length can be increased (longer path length cuvettes are available) or, where the absorbance is too high to be measured on the instrument, the cuvette length can be reduced. Alternatively, it is possible to reduce the absorbance by diluting the analyte but one has to take care when dealing with chemically active analytes, particularly enzyme-

based solutions, as this may have a profound effect on the activity (Hopke and Markowitz, 2002).

2.8.2 Limitation and alternative of single-beam UV-VIS spectrophotometer

A single beam device works much the same way, with slits, mirrors and diffraction gratings just as a double beam device does, but does not have a chopper mirror or two cell slots. In this case, the reference (blank) spectrum for the solvent is taken separately before the sample and reference spectrum is deducted from the sample spectrum to get the sample UV-VIS spectrum. Single-beam instruments are used mainly on grounds of cost. They have poorer noise specifications compared with their dual-beam and double-beam counterparts and are prone to drifting with time. This makes accurate kinetics and applications involving repetitive sampling over time more difficult. The cheaper models often lack the spectral resolution demanded by some chemical applications, for example porphyrin analysis.

Double-beam UV-VIS spectrophotometer has a single detector usually called a photomultiplier (a phototube). The beam is then sent alternately through sample and reference positions using a chopper wheel or vibrating mirror. The electronics in the instrument are also able to synchronize the beam switching with the detector so that it can distinguish whether the detector is measuring the sample or reference beam at any one time.

Even in complete darkness, a photomultiplier will output a signal. This is known as the dark current. As a result, the beam shuttling device will also have some means of temporarily blocking the light from both beams so that this residual signal (the dark current) can be measured and subtracted from each sample and reference measurement (Khopkar, 1995).

Dual-beam spectrophotometer is an alternative to the double-beam design. In this design, the beam is split using a half-silvered mirror (beam splitter) into its sample and reference components. Each beam has its own detector. This design is only practical with solid-state detectors and gives equivalent results compared with a double-beam system for most analyses. The design removes the need for a mechanical beam shuttling device to improve reliability and, as solid-state detectors are used, there is no need for a high-tension power supply to provide the high voltages which are required to set the photomultiplier gain. The design also produces very good baseline noise characteristics. If the design has a weakness, it is at very high absorbance over 3 absorbance unit as the photomultiplier is able to detect lower light levels than solid-state detectors where a single monochromator instrument is limited by its stray light. If analytes exceed the upper absorbance limit of a spectrophotometer, they can either be diluted or a shorter path length of cuvette can be used (Stephen, 2000).

In view of the nature of air pollutants targeted in the study and availability of single-beam spectrophotometer, UV-Vis Spectrophotometer was considered in analyzing nitrite ions and sulphite ions in this research work.

2.9.0 Activated charcoal

Activated charcoal, also called activated carbon is a general term which covers carbon material mostly derived from charcoal. For the word "activated" is sometimes substituted with "active". It is a material with an exceptionally high surface area. Just one gram of activated charcoal has a surface area of approximately 500 m², typically determined by nitrogen gas adsorption, and includes a large amount of micro-porosity. Sufficient activation for useful applications may come solely from the high surface area, though often further chemical treatment is used to enhance the absorbing properties of the material (<http://en.org/Activated-carbon.htm>. June 2008).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1.0 Area of study

Nairobi city is located 10° S and 40° E at a mean altitude of 1700 m and covers an area of 700 Km². To the east, the ground is flat, while to the west, southwest and northwest, the ground is high and gradually emerging into farming areas further into the countryside. There are three seasons; warm and dry season, long rainy season and cool dry season. The annual mean temperature ranges between 11.0 – 20.0 °C and the average annual rainfall is 600-900mm (Njogu, 1998).

Nairobi city was selected as an area of study because it is an urban centre with high population of over 2 million people, many industries and vehicles on its roads which most of them being second hand in poor state than any other town in the country (Mulaku and Kariuki, 2001). These are major sources of air pollution in Nairobi city. Yet, there is no national programme on air pollution measurements. Thus this study was carried out to ascertain the current levels of NO_x and SO₂ in the city troposphere.

The study was conducted at road sites in the city center, industrial areas and outskirts of the city center that are prone to high vehicle emissions based on the preliminary study results which were obtained within the month of October, 2006. Eleven sites and one control site were selected and are described in Table 1 and the

map in figure 2, gives a picture of the spatial distribution of these sampling sites. Passive samplers were used to sample NO, NO₂ and SO₂ in ambient air at the selected sites to ascertain the levels of NO, NO₂ and SO₂ in different microenvironments of Nairobi city (road sides, urban background and industry area) in order to calculate the mean concentration of each air pollutant in the troposphere.

Table 1: Sampling sites for NO, NO₂ and SO₂ passive samplers.

Site name	Nature of site	Main emission sources	No. of samplers per exposure			Time (hrs)
			NO	NO ₂	SO ₂	
KNH's gate	Outskirt/ road side	traffic	5	5	5	24
Dagorett Corner	Outskirt/ road side	traffic	5	5	5	24
Country Bus Stage	City centre/ road side	traffic	5	5	5	24
Co-op. Bank house	City centre/ road side	traffic	5	5	5	24
Savora Parafric	City centre/ road side	traffic	5	5	5	24
Globe cinema R.	City centre/ road side	traffic	5	5	5	24
City Kabanas	Industrial area/ road side	Industry/ traffic	5	5	5	24
Tetra pak Comp.	Industrial area/ road side	Industry	5	5	5	24
Pangani Roundabout	Near to city centre/road side	traffic	5	5	5	24
NYS HQ.'s gate	Outskirt/ along the road	traffic	5	5	5	24
Githurai oundabout	Outskirt/ road side	traffic	5	5	5	24
Control site	urban back- ground/ rd. side	traffic	5	5	5	24

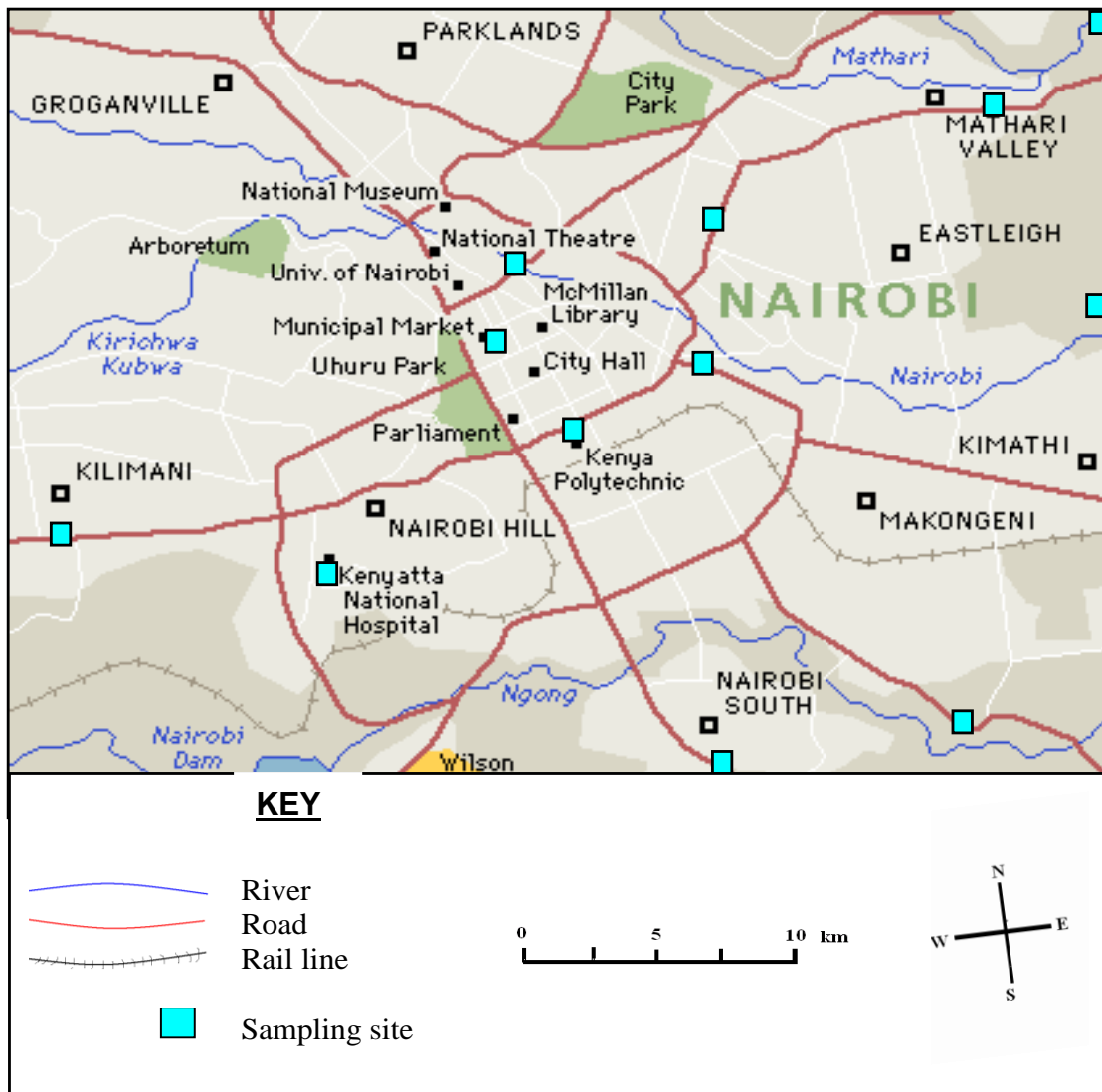


Fig. 2: A map of Nairobi city showing sampling sites of the study

3.1.1 Numbers of sites and selection

Air pollutant concentration differs depending on the location and time. However, pollutant concentration at each measurement point changes in accordance with the existence of local pollution sources and the existence of man made structures such

as buildings and roads and the height of the measurement point. Eleven sites were selected; four sites in the city centre, two sites in industrial area, five sites in the outskirts and one control site, all were located at road side. These numbers of sampling sites were considered to give necessary data to build up a reasonable data on the levels of NO_x and SO₂ in the Nairobi city troposphere.

These sampling sites were selected based on preliminary results which were obtained earlier within the month of October, 2006 (sites with high levels of air pollutants) and dispersion of the pollutants under study. The other factors which were put in consideration were weather and land topography given that they strongly influence the dispersion of air pollutants and affect the production of secondary pollutants in the atmosphere.

3.1.2 Sampling protocol

Sampling was done twice per site per week from November 2006 to September 2007. Triplicate samples of each NO, NO₂ and SO₂ were sampled from each sampling site. A total of twenty samples per air pollutant were sampled from each sampling site; the first ten were sampled during the dry season and the other ten during the wet season.

3.2.0 Experimental

3.2.1 Equipment and apparatus

Pyrex distiller was used for distilling water. Elegestant micro deionizer cartridge type MC-DC was used for de-ionizing water. UV-Spectrophotometer (Nova-spec II, model 80) was used in the determination of amount of nitrite ions and sulphite ions in the both standard solutions and samples. Analytic weighing balance (CHYO JL-180) was used in the weighing of reagents. Refrigerator with deep freezer is where unstable reagents at room temperature were kept.

Volumetric flasks (class A) were used in preparation of standard reagent solutions. Beakers and conical flasks were used as reaction vessels. Pipettes and burette were used in the transferring fixed volume of reagents into vessels. Reagents bottles and water bottles were used for storing reagents and water, respectively. Measuring cylinders were used in the measuring volume of reagents. Separating funnels were used in the separating immiscible reagents. Test tubes were used as reaction vessels and test tube rack was used to hold test tubes upright. Filter papers (whatman No. 42) were used as absorbing pads and passive samplers were used in the sampling process.

3.2.2 Cleaning of glassware

All apparatus mentioned in the above were thoroughly cleaned with warm water mixed with detergent, rinsed with deionized water and twice with 4% nitric acid solution. It was then rinsed with distilled water and finally with deionized water. The glassware and passive samplers were then dried in an oven for two hours at 105.0 °C and 80.0 °C, respectively. This was done in order to minimize systematic errors in the results.

3.3.0 Reagents

The analytical grade reagents were used in this research work. The following reagents were obtained from Kobian Kenya limited, Nairobi, Kenya: triethanolamine used as absorbing agent; acetone was used to destroy interferences in analysis of NO₂; activated charcoal used as absorbing agent; concentrated sulphuric acid and potassium dichromate used in the preparation of acidified potassium dichromate (NO-oxidizing agent); sodium nitrite used in the preparation of standard nitrite solutions; N-(1-Naphthyl)-ethylenediamine dihydrochloride, glacial acetic acid and sulphanilic acid used in the preparation of NO₂-colouring agent; sulphamic acid used to destroy interferences in analysis of SO₂; formaldehyde used as medium for the reaction of sulphite ions; sodium sulphite used in the preparation of standard sulphite solutions; mercuric chloride, ethylenediamine tetraacetic acid (EDTA) and potassium chloride used in the

preparation of TCM absorbing agent and 1-butanol, pararosaniline hydrochloride dye, phosphoric acid (AR) and concentrated hydrochloric acid (AR) used to make PRA solution.

The aim of obtaining analytical reagents from known supplier was to avoid purchasing reagents which give unreliable results.

3.3.1.0 Preparation of reagents

3.3.1.1 Triethanolamine solution (TEA-20%)

TEA of 20% (NO₂-absorbing reagent) was prepared by mixing 50.0 ml of TEA with 200.0 ml deionized water in a 250 ml volumetric flask. The solution was stored in a well stopper brown bottle in a refrigerator at 5.0 °C to avoid decomposition. Fresh solution was prepared after three months.

3.3.1.2 Sulphanilic acid (0.029M)

0.029M sulphanilic acid (NH₂C₆H₄SO₃H.H₂O) was prepared by dissolving 5.500g of sulphanilic acid crystals in 600 ml of de-ionized warm water in a 1000 ml volumetric flask. 140.0 ml of glacial acetic acid was added and then diluted up to the mark with deionized water. The solution was stored in brown bottle in a refrigerator at 5.0 °C. Fresh solution was prepared after one month.

3.3.1.3 N-(1-Naphthyl)-ethylenediamine dihydrochloride solution (0.1%)

0.1% of N-(1-Naphthyl)-ethylenediamine dihydrochloride (NED) solution was prepared by dissolving 0.100 g of N-(1-Naphthyl)-ethylenediamine dihydrochloride in 100.0 ml of deionized water in a 100 ml volumetric flask. The stock solution was kept below 5.0 °C in a refrigerator. Fresh solution was prepared after three months.

3.3.1.4 NO₂-colouring producing reagent

Fresh NO₂-colouring producing reagent solution was prepared per experiment. Sulphanilic acid solution was mixed with NED stock solution in a 10:1 ratio (10 part sulphanilic acid solution to 1 part NED stock solution) in a 100 ml conical flask.

3.3.1.5 Nitrite stock solution (1000 µg/ml)

Sodium nitrite crystals (NaNO₂) were dried in an oven for four hours at 105.0 °C to remove water of crystallization. Then 0.375 g of anhydrous sodium nitrite was dissolved in 150.0 ml of de-ionized water in a 250 ml volumetric flask and made up to the mark with deionized water. The solution was stored in a brown bottle in a refrigerator at 5.0 °C. Fresh solution was prepared weekly.

3.3.1.6 Working solution of nitrite (1 µg/ml)

Fresh working solution was prepared per experiment. 0.1 ml of stock nitrite solution was transferred into a 100 ml volumetric flask and diluted to the mark with deionized water.

3.3.1.7 Acetone solution (30%)

30.0 ml of Acetone (99% by volume) solution was transferred into a 100 ml volumetric flask and diluted up to the mark with deionized water. The solution was transferred into a stopper brown bottle and stored in a refrigerator at 5.0 °C. Fresh solution was prepared weekly.

3.3.1.8 Acidified potassium dichromate solution (0.1M)

0.1M acidified potassium dichromate solution was prepared by dissolving 14.710g of potassium dichromate ($K_2Cr_2O_7$) crystals in 800.0 ml of deionized water in a 1000 ml volumetric flask and then 100.0 ml of 1M H_2SO_4 was added before making up to the mark with deionized water. The solution was transferred into a bottle and stored in a refrigerator at 5.0 °C. Fresh solution was prepared after fortnight.

3.3.1.9 Sulphamic acid (0.6%)

0.6% of sulphamic acid was prepared by dissolving 0.600 g of sulphamic acid in 100.0 ml of deionizer water in a 100 ml volumetric flask. Fresh reagent was prepared daily.

3.3.1.10 Formaldehyde (0.2%)

0.2% of formaldehyde (CH₂O) was prepared by diluting 0.5 ml of formaldehyde (40 percent) solution to 100.0 ml with deionized water in a 100 ml volumetric flask. Fresh reagent was prepared daily.

3.3.1.11 Sulphite stock solution (0.005M)

0.005M sulphite solution was prepared by dissolving 0.315g of anhydrous sodium sulphite Na₂SO₃ in 500.0 ml of deionized water. 1.0 ml of this solution contain sulphite ions equivalent to 400 µg SO₂. The solution was transferred into a stopper brown bottle and stored in the refrigerator at 5.0 °C. Fresh solution was prepared weekly.

3.3.1.12 SO₂-Absorbing reagent (0.04 M TCM)

0.04 M potassium tetrachloromercurate K₂HgCl₄ (TCM) was prepared by dissolving 10.860 g mercuric chloride, 0.066 g EDTA, and 6.000 g potassium chloride in 800.0 ml of deionized water in a 1000 ml volumetric flask and diluted up to mark

with deionized water. The solution was transferred into stopper brown bottle and stored in the refrigerator at 5.0 °C. Fresh solution was prepared weekly.

3.3.1.13 Sulphite-TCM solution (5.0 X10⁻⁶ M)

0.1 ml of the standard sulphite solution was transferred into a 100 ml volumetric flask and diluted to volume with 0.04 M TCM solution. 1.0 ml of the solution contain sulphite ions equivalent to 0.4 µg SO₂. The solution was kept in a refrigerator at 5.0 °C. Fresh solution was prepared per experiment.

3.3.1.14 Stock PRA solution

100.0 ml each of 1-butanol and 1 M HCl was placed in a 250 ml separator funnel and allowed to equilibrate (certain batches of 1-butanol contain oxidants that create an SO₂ demand). 0.100 g of pararosaniline hydrochloride dye was placed into a 100 ml beaker. 50.0 ml of the equilibrated acid (drained from the bottom part of acid layer) was added to the beaker and left to stand for 10 minutes. 50.0 ml of the equilibrated 1-butanol (drawn from the top part of 1-butanol layer) was transferred into a 250 ml separator funnel and the acid solution in the beaker containing dye was added into the separator funnel. The mixture was carefully shaken to extract the dye and enable violet impurity to be transferred to organic phase.

The lower aqueous phase was transferred into another separator funnel and 20.0 ml of the equilibrated 1-butanol was added for further extraction. This procedure was

repeated three times with three more 10.0 ml portions of equilibrated 1-butanol which had remained in the separator funnel. After the final extraction, the acid phase was filtered through a cotton plug into a 50ml volumetric flask and was brought to the mark with 1 M HCl solution. The stock PRA solution was stored in a well stopper volumetric flask in the refrigerator at 5.0 °C. Fresh solution was prepared after three months (Dasgupta and Decesare 1982; West and Gaeke 1956).

3.3.1.15 Pararosaniline reagent (0.2%)

20.0 ml of stock PRA solution was transferred to a 250 ml volumetric flask and then 25.0 ml of 3M phosphoric acid was added and diluted to volume with deionized water. The reagent was stored in the refrigerator away from heat and light. Fresh solution was prepared after three months.

3.4.0 Preparation of samplers

3.4.1 Passive samplers

Passive samplers used in this study were acrylic industrial grade. This model was chosen because it has several advantages over other kinds of samplers. For instance, all its parts are reusable, different filter loading reagents can be packed in, it minimizes the effect of turbulence, it is a simple sampler model and absorbing pad is well protected from direct sunlight and rain as shown in plate 6.

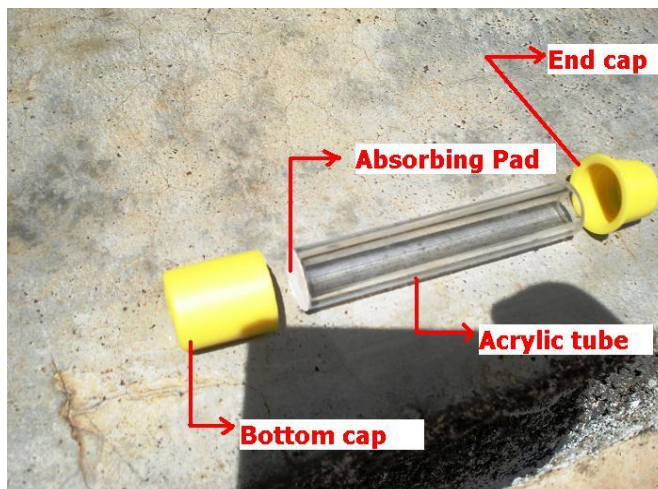


Plate 6: A photograph of parts of passive sampler

This device is capable of taking gaseous sample from ambient air at a rate controlled by a diffusion process through a static air layer in the tube according to Fick's First Law of diffusion, that is the sampling rate of a diffusive sampler is directly proportional to the diffusion coefficient of the air pollutant in ambient air, the concentration and the time of exposure, provided the concentration gradient is constant (Hargreaves, 1990; Shooter, *et al.*, (1997).

In this study, filter papers were soaked in triethanolamine (TEA) solution in the case of absorbing NO_2 and in potassium tetrachloromercurate (TCM) solution in the case of absorbing SO_2 . NO_2 and SO_2 were trapped as nitrate ions and sulphite ions and were measured spectrophotometrically.

The average concentration of a gas in ambient air determined by exposing a passive sampler is estimated according to Fick's First Law as shown in equation (29);

$$J = D \times A \times (C - C_0) / L \quad (29)$$

Where,

J = Mass flux of gas ($\mu\text{g/s}$)

D = Diffusion coefficient of the gas in air (m^2 / s)

A = Cross-sectional area of the diffusion path of the monitor (m^2)

C = External concentration of the gas in air ($\mu\text{g}/\text{m}^3$)

C_0 = Concentration of the gas at the interface of the sorbent ($\mu\text{g}/\text{m}^3$)

L = Diffusion length (m)

For a certain exposure time the total amount of absorbed gas can be defined as shown in equation (30);

$$Q = J \times t \quad (30)$$

Where:

Q = Total amount of absorbed gas (μg)

J = Average mass flux during exposure time t ($\mu\text{g/s}$)

t = Exposure time (s)

If the concentration (C_0) above absorbing surface is zero, then equations (29) and (30) when combined we obtain equation (31);

$$C = \frac{Q \times R_t}{A \times t} \quad (31)$$

Where,

C = Average concentration during exposure ($\mu\text{g}/\text{m}^3$)

R_t = Entrance filter resistance

In equation (31), $(A \times t)/R_t$, is equivalent to the volume of the air from which the gas was sampled. Thus, the calculation of concentration of a gas in ambient air sampled with passive sampler is expressed as shown in equation (32);

$$C = \frac{M \times \ell}{D \times A \times t} \quad (32)$$

Where:

C = External concentration of the gas in ambient air ($\mu\text{g}/\text{m}^3$)

M = Mass of gas collected (μg)

ℓ = Diffusion length (cm)

D = Diffusion coefficient of the gas in ambient air (cm^2/s)

A = Cross-sectional area of the diffusion path of the monitor (cm^2)

t = Sampling time in second (s)

To express the concentration in $\mu\text{g}/\text{m}^3$, equation (32), is multiplied by 10^6 and this derivation of equation (32) agrees with the work reported by Atkins (1986), Bjarne *et al*, (2005) and Chacha and Frenzel (2005).

3.4.2 Preparation of samplers for exposure

Five cleaned dried circular Whatman filter papers ($d = 1\text{cm}$) were soaked in 2.0 ml of TEA solution in a 100 ml beaker for ten minutes to obtain NO_2 -absorbing pads and other five more filter papers were soaked in 2.0 ml of TCM solution in a 100 ml beaker for a duration of ten minutes to obtain SO_2 -absorbing pads. Then, each absorbing pad was placed at one end of a passive sampler as shown in the plate 6 above before closing both ends with caps tightly.

In the case of NO , samplers were prepared in a similar way as those of NO_2 , but the only difference is that, a plastic screen soaked in acidified potassium dichromate solution was placed at the opening end of the sampler. Acidified potassium dichromate solution was used in order to oxidise ambient NO to NO_2 before reaching TEA-coated pad at the other end of the sampler tube.

For samplers with activated charcoal, 0.600g of dried activated charcoal crystals were placed on a circular sticker paper per sampler instead of TEA and TCM and were exposed in the similar way as described in the above.

For each set, six samplers each with absorbing pad were labeled with a waterproof marker and two samplers as blanks were left unmarked. Then, all samplers were placed in an airtight plastic bag together with blanks before they were taken to the sampling site.

3.5.0 Air pollutants sampling

3.5.1 Exposing passive samplers

At each sampling site, samplers were exposed by attaching two samplers to the sampler holder and hanged about 1.5 m above the ground and left for 24 hours as shown in plate 7. Blank samplers with closed caps intact were exposed together with the other. At the end of the sampling period all exposed samplers were closed, placed in an airtight plastic bag together with blanks and taken to the JKUAT Chemistry laboratory for analysis within two hours.

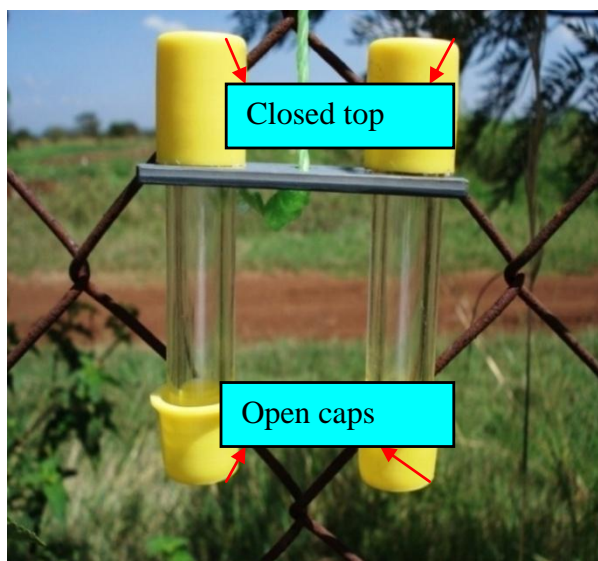


Plate 7: A photograph of exposed passive samplers

3.5.2 Active sampling

50 ml of TEA 20% solution was transferred into a 250 ml conical flask and connected to air sampling pump as shown in plate 8. The ambient air was sucked into absorbing reagent at flow rate of $0.5\text{dm}^3/\text{minute}$ for 30 minutes. The procedure

was repeated nine times to obtain ten samples of NO_2 . Similarly, SO_2 was sampled in the same way, but 50 ml of TCM solution was used instead of TEA solution.

For sampling NO , the ambient air was first allowed to pass through 50 ml of 0.1M acidified potassium dichromate solution to oxidize NO to NO_2 before it was sucked into 50 ml of TEA 20% solution. After active sampling, samples were analyzed within two hours in the JKUAT GK-Chemistry laboratory.



Plate 8: A photograph of active sampling of ambient NO_2

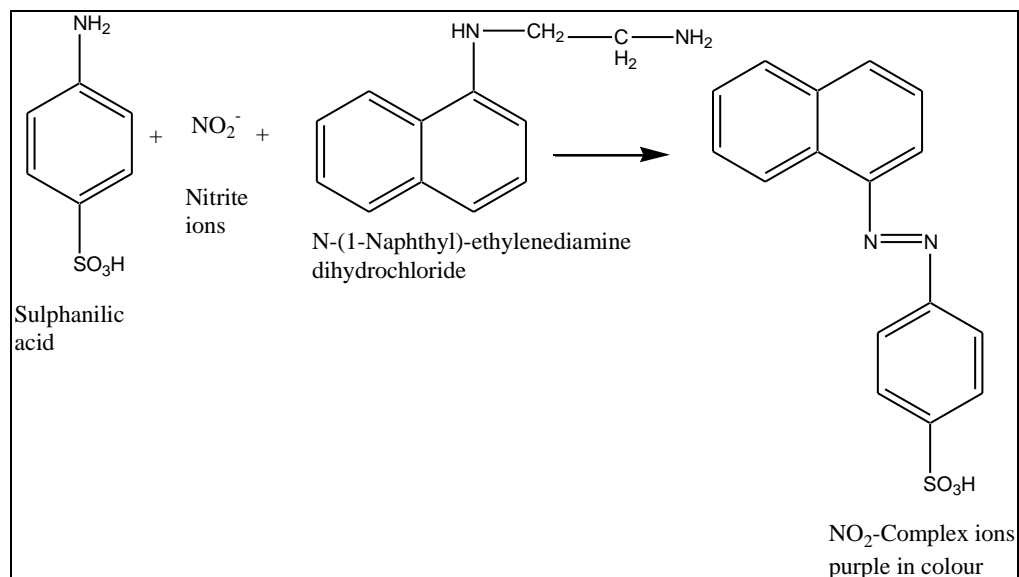
3.6.0 Analysis of samples

At the site, when samplers were exposed to ambient air, NO_2/SO_2 in ambient air diffuses towards the absorbing pad at the rate dependant upon Fick's Law of

diffusion. The amount of NO_2 / SO_2 measured is a function of its concentration in the ambient air and length of time the sampler is left open. Since diffusion is temperature-dependant, the samplers have a rather limited temperature range 10^0 to 32^0 (Khopkar, 1995). This did not affect the results because temperature range of Nairobi city temperature is within this range.

3.6.1 Saltzman reaction

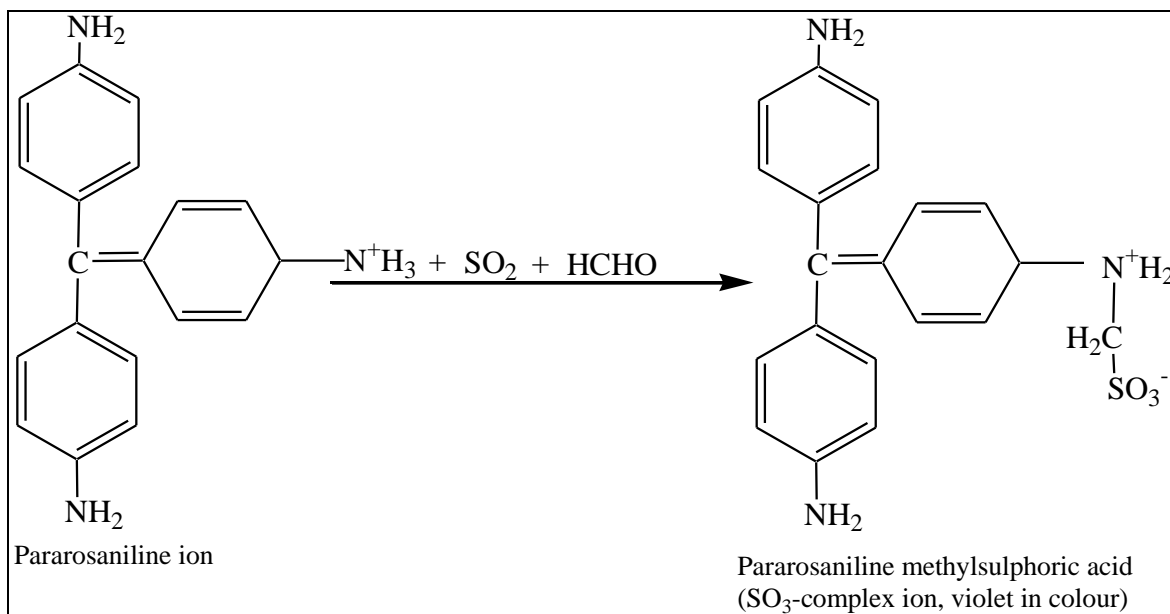
In the analysis of NO_2 , nitrogen (IV) oxide (trapped by TEA absorbing pad per sampler) reacts with N-(1-Naphthyl)-ethylenediamine dihydrochloride solution in sulphanic acid medium to form a coloured NO_2 -complex ions as shown in Scheme 3. The amount of nitrite ions trapped by absorbing pad per sampler within twenty four hours is directly proportional to the colour intensity of NO_2 -complex ions and is equivalent to the level of NO_2 in ambient air (Khopkar, 1995).



Scheme 3: A schematic diagram of the reaction of nitrite ions with N-(1-Naphthyl)-ethylenediamine dihydrochloride solution in sulphanilic acid medium

3.6.2 Pararosaniline reaction

Similarly for SO₂ analysis, when SO₂ trapped by TCM absorbing reagent reacts with pararosaniline in formaldehyde medium, coloured SO₂-complex ion is formed according to Scheme 4. The amount of sulphite ions trapped by absorbing pad per sampler within twenty four hours from troposphere is directly proportional to colour intensity of pararosaniline methylsulphoric acid and is equivalent to the amount of SO₂ in troposphere (Khopkar, 1995).



Scheme 4: A schematic diagram of the reaction sulphite ions with pararosaniline in formaldehyde medium

3.6.3 Determination of maximum wavelength of nitrite and sulphite solutions

In order to make meaningful measurements and to be confident in the quality of the data obtained, it was made sure that the instrument was operating at maximum wavelength per analyte. To achieve this, UV-VIS spectrophotometer was scanned with 1.0 µg/ml nitrite solution and 0.4 µg/ml sulphite solution separate from 500nm to 600nm wavelength and deionized water was used as a reference (blank solution) in each case. It was found out that, the maximum absorbance of nitrite solution and sulphite solution occurred at 541nm wavelength and 548nm wavelength, respectively.

3.6.4 Preparation of NO₂-calibration curve

Six solutions with varying concentration 0 µg/ml (blank), 1 µg/ml, 2 µg/ml, 3 µg/ml, 4 µg/ml and 5 µg/ml were prepared from standard nitrite solution. 2.0 ml each of these solutions was transferred into separate test tube, 1.0 ml acetone solution was transferred into each of these test tube and left to stand for 10 minutes before adding 2.0 ml of NO₂-colouring reagent solution in each test tube.



Plate 9: A photograph of test tubes in a test tube rack containing standard nitrite solutions and NO₂-colouring reagent

These test tubes were then submerged in cold water bath (10.0 °C) for 15 minutes to promote colouring processing. After 15 minutes, a purple colour had formed and the intensity was proportional to the amount of nitrite ions present in each test tube as shown in Plate 9.

Absorbance of each solution was determined at 541 nm and the absorbance of the blank was used as reference. The calibration curve of standard nitrite solution was obtained by plotting absorbance measured against the concentrations of nitrite solution and was to determine the mass of nitrite ions per sampler.

3.6.5 NO₂-Samples Analysis

The concentration of NO₂ in ambient air per site was calculated from the average mass of nitrite ions trapped per absorbing pad measured spectrophotometrically. The absorbing pads from exposed samplers plus blank samplers were placed into different test tubes in a test tube rack each with 2.0 ml of deionized water. 1.0 ml of acetone solution was transferred into each test tube and left to stand for 10 minutes. Then, 2.0 ml of NO₂-colouring reagent solution was added into each test tube and submerged in cold water at 10.0 °C for 15 minutes to promote purple colour formation.

The absorbance of each solution was measured at 541 nm and with the absorbance of sample and the calibration curve; the mass of NO₂ per air sample was calculated.

3.6.6 NO-Samples Analysis

The amount of NO was calculated from the difference between the amount of NO₂ in exposed samplers with acidified potassium dichromate solution and exposed samplers without acidified potassium dichromate solution.

3.6.7 Preparation of calibration curve of sulphite ions

Six solutions with varying concentration 0.0 $\mu\text{g/ml}$ (blank) 0.4, $\mu\text{g/ml}$, 0.8 $\mu\text{g/ml}$, 1.2 $\mu\text{g/ml}$, 1.6 $\mu\text{g/ml}$ and 2.0 $\mu\text{g/ml}$ (SO_2) were prepared from working sulphite-TCM solution. 10.0 ml each of these solutions and 1.0 ml of 0.6% sulphamic acid (destroys SO_2 interferences such as NO_2 and O_3) were transferred into separate 100ml conical flasks.



Plate 10: A photograph of conical flasks with a mixture of Sulphite-TCM solutions and SO_2 -colouring reagent

After 10 minutes, 2.0 ml of 0.2% formaldehyde solution and 5.0 ml of PRA solution (0.2% pararosaniline) were added into each conical flask simultaneously while stirring and left to stand for 30 minutes to allow fully formation of deep purple colour as shown in plate 10. The absorbance of each standard solution was

measured at 548 nm and the absorbance of the blank was used as reference. The calibration curve of standard sulphite solution was obtained by plotting absorbance measured against the concentrations of standard sulphite solutions and was used to determine the mass of sulphite ions per sampler.

3.6.8 SO₂-Samples Analysis

The concentration of SO₂ in ambient air was calculated from the amount of sulphite ions trapped per absorbing pad measured spectrophotometrically. Absorbing pads from exposed samplers plus blank samplers were placed into different 100ml conical flasks. 10.0 ml of 0.4M TCM solution and 1.0 ml of 0.6% sulphamic acid were added into each flask and left to stand for ten minutes. After that, 2.0 ml of 0.2% formaldehyde solution and 5.0 ml of PRA solution were added simultaneously while stirring and left to stand for 30 minutes to allow for fully colour formation. Then, the absorbance of each sample solution was measured at 548 nm and mass of SO₂ trapped per absorbing pad was calculated by using SO₂-calibration curve.

3.7.0 Calculations

3.7.1 Calculation of passive sampling

Since the dimension of passive sampler (7.5 cm (ℓ) and 1.0 cm (i.d)) is constant and the sampling duration was twenty four hours, an average mass of NO₂ or SO₂ trapped per sampler is expressed as shown in equation (33)

$$M = (y \pm a) / b \text{ (from the calibration curve)} \quad (33)$$

Where

M = Average mass of NO₂ or SO₂ which is equivalent to nitrite /sulphite ions per sampler

y = Absorbance of the sample

a = y-intercept of the calibration curve

b = Slope of the calibration curve

But from equation (32), concentration of NO₂ / SO₂ in ambient air calculated as shown in equations (34) and (35) (Chacha and Frenzel, (2005);

$$\begin{aligned} [\text{NO}_2 / \text{SO}_2] &= \frac{M \times \ell}{D \times A \times t} \\ &= \frac{\left(\frac{y \pm a}{b}\right) \mu\text{g} \times 7.5 \text{ cm} \times 10^6}{D \times 3.14 (0.5)^2 \text{ cm}^2 \times 24 \times 3600 \text{ s}} \end{aligned} \quad (34)$$

$$= \frac{1.105 \times 10^2 \times \left(\frac{y \pm a}{b}\right)}{D} \mu\text{g}/\text{m}^3 \quad (35)$$

But, $D_{\text{NO}_2} = 0.154 \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{SO}_2} = 0.127 \text{ cm}^2 \text{ s}^{-1}$

For example, one of NO₂- sample had an absorbance of 0.011; the concentration of NO₂ in ambient air according to this result is as follows;

According to equation (34),

$$\begin{aligned}
 [\text{NO}_2] &= \frac{\left(\frac{y \pm a}{b}\right) \mu\text{g} \times 7.5 \text{ cm} \times 10^6}{D \times \pi \times (0.5)^2 \text{ cm}^2 \times 24 \times 3600 \text{ s}} \\
 &= \frac{1.1052 \times 10^2 \times \left(\frac{y \pm a}{b}\right)}{D} \mu\text{g}/\text{m}^3
 \end{aligned}$$

But, according to calibration curve of nitrite ions, the value of $(y \pm a)/b$ is

$$(0.011 + 0.007)/0.102 \text{ and } D_{\text{NO}_2} = 0.154 \text{ cm}^2 \text{ s}^{-1}$$

$$\begin{aligned}
 [\text{NO}_2] &= \frac{0.018 \times 1.1052 \times 10^2}{0.154 \times 0.102} \mu\text{g}/\text{m}^3 \\
 &= 126.64629488 \mu\text{g}/\text{m}^3 \\
 &\approx 127 \mu\text{g}/\text{m}^3
 \end{aligned}$$

This means that the concentration of NO_2 in ambient air is $127 \mu\text{g}/\text{m}^3$. Hence, all concentrations of air samples of NO_2 sampled were calculated as shown in the above example. Similarly, the concentrations of SO_2 per sampler were calculated in the same way, but the calibration curve of sulphite ions and diffusion coefficient of sulphite ($D_{\text{SO}_2} = 0.127 \text{ cm}^2 \text{ s}^{-1}$) were used instead of those of nitrite ions.

3.7.2 Calculation of active sampling

The concentration of air pollutant (NO₂/SO₂) in ambient air was calculated according to equation (36)

$$[\text{NO}_2/\text{SO}_2] = (A - A_0) \times B_x \times 10^3 / V_{\text{std}} \times V_b / V_a \text{ } \mu\text{g}/\text{M}^3 \quad (36)$$

Where

A_0 = Absorbance of the blank solution

A = Absorbance of the sample solution

B_x = Reciprocal of the slope of the calibration equation

V_a = Volume of absorbing reagent used the experiment (ml)

V_b = Total volume of the solution being analysed (ml)

V_{std} = Air volume sampled (dm³)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1.0 Determination of maximum wavelength of nitrite and sulphite solutions

It is important for any instrument to be accurate and precise in chemical analysis. UV-Vis spectrophotometer was scanned with nitrite-complex and sulphite-complex solutions respectively from 480 nm to 600nm wavelength. It was determined that nitrite-complex ions and sulphite-complex ions had highest absorbance at 541nm and 548nm, respectively as shown in figures 3 and 4. Thus, throughout the study, all measurements of nitrite ions and sulphite ions were taken at 541 nm and 548 nm wavelengths, respectively.

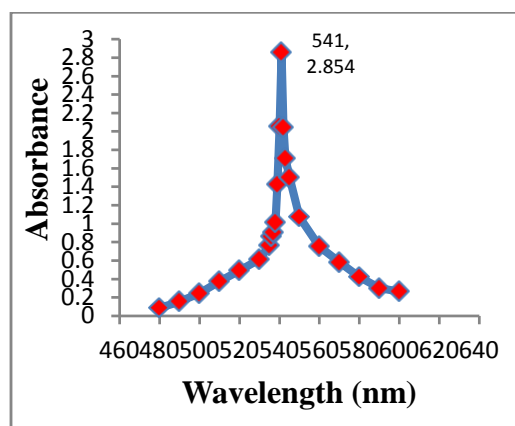


Fig. 3: Nitrite-complex spectrum

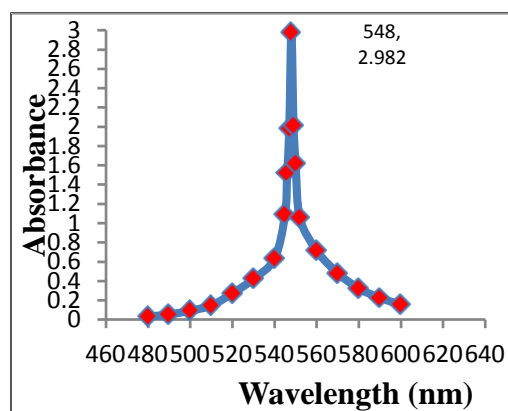


Fig. 4: Sulphite-complex spectrum

4.1.1 Calibration curves of standard Nitrite and Sulphite solutions

The calibration curves of standard nitrite and sulphite solutions were obtained by plotting absorbance of standard solutions in each case against their concentrations

as shown in figures 5 and 6. The figures 5 and 6 show that, there is a linear relationship that exists between absorbance and concentration of standard solutions in each case whereby the value of correlation coefficient (r) in each case is almost a unity. Thus, the law of Beer-Lambert was obeyed. These calibration curves were used in calculating the amount of nitrite and sulphite ions air samples throughout the study, respectively.

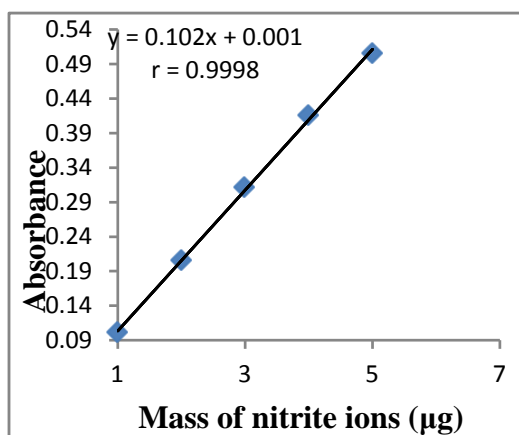


Fig. 5: The calibration curve of standard nitrite solution

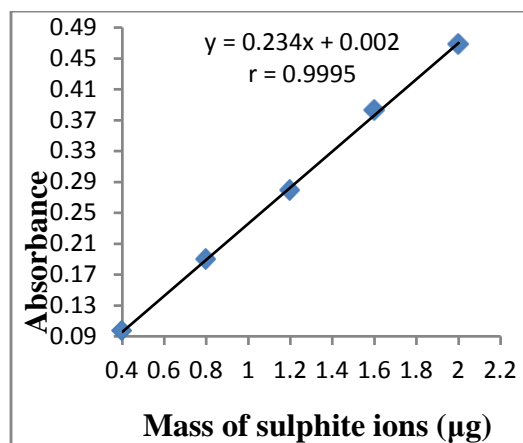


Fig. 6: The calibration curve of standard sulphite solution

4.1.2 Interferences in sample analysis

The principal interferences in NO_2 analysis are O_3 and SO_2 and in the study, acetone solution was used to destroy these interferences before analyzing NO_2 in the air samples. Similarly, sulphamic acid was used in SO_2 analysis to destroy any oxide of nitrogen and ozone which are the main interferences in SO_2 determination.

4.2.0 Levels of NO and NO₂ in ambient air at twelve sites within Nairobi city

4.2.1 Nitrogen (II) oxide (NO)

The mean concentration of NO in ambient air at twelve sites within Nairobi city as determined by passive sampling during the study carried out between November-2006 to September-2007 are given in Table 2. Air samples were sampled ten times per season per site and mean and standard error mean were calculated and recorded.

Table 2: 24-hour Concentration level of NO in ambient air at twelve sites

Site	Wet season (n =10) µg/m ³	Dry season (n =10) µg/m ³
KNH's gate (KNH Road side)	44.64 ± 2.16	79.98 ± 1.91
Dagorett Corner Ngong' Road side)	72.57 ± 2.99	90.06 ± 3.32
Bus Stage (Jogoo road)	75.00 ± 2.94	104.50 ± 4.99
Co-op. Bank (Haille Sellasie road side)	84.62 ± 2.21	111.35 ± 4.30
Savora Paraftric (Kenyatta Road side)	77.38 ± 2.65	114.73 ± 4.99
Globe cinema Roundabout	89.46 ± 2.36	162.20 ± 6.47
City Kabanas (Nairobi-Mombasa road side)	88.44 ± 3.70	124.67 ± 5.55
Tetra pak Comp. (Industrial area)	61.49 ± 2.92	86.77 ± 3.01
Pangani (Nairobi-Thika road side)	75.21 ± 2.56	107.33 ± 2.83
NYS's gate (Nairobi-Thika road side)	67.56 ± 2.48	81.33 ± 4.08
Githurai (Nairobi-Thika road side)	58.65 ± 3.65	80.52 ± 2.51
Control site (Dandora med. center's gate)	24.97 ± 1.02	25.35 ± 1.07

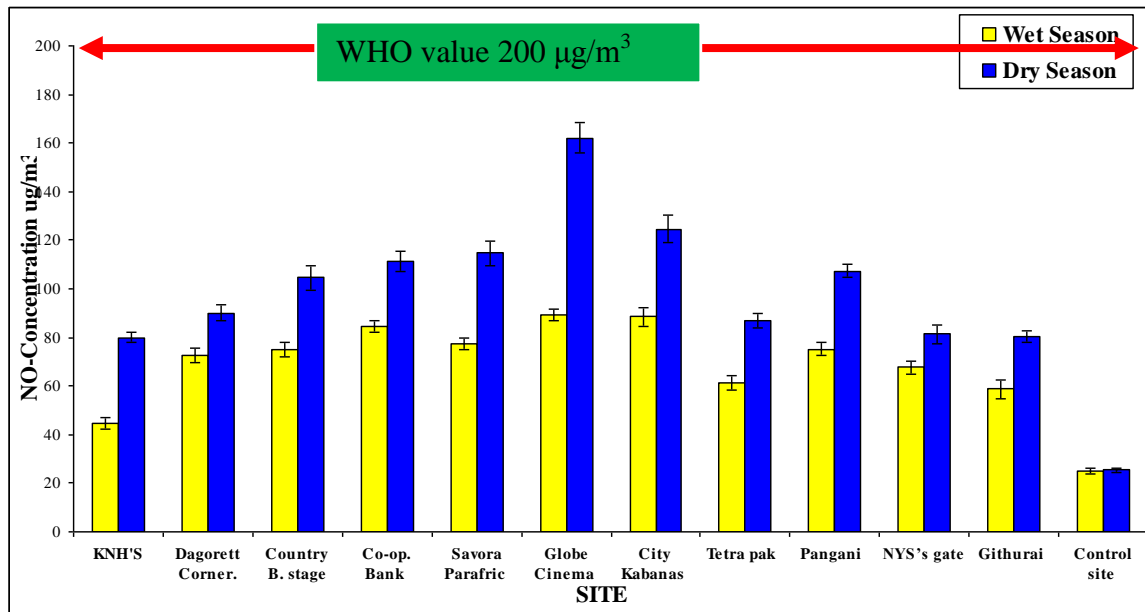


Fig. 7: Variation of NO-concentration in ambient air at the twelve sites within Nairobi City determined between November 2006 and September 2007

The results in table 2 and figure 7, show that the highest concentration of NO during the wet season was recorded at Globe Cinema roundabout site with $89.46 \pm 2.36 \mu\text{g}/\text{m}^3$ followed by City Kabanas site along Nairobi-Mombasa road with $88.44 \pm 3.70 \mu\text{g}/\text{m}^3$ and the lowest concentration was recorded at the control site with $24.97 \pm 1.02 \mu\text{g}/\text{m}^3$. However, during the dry season, the highest concentration of NO was recorded at City Kabanas site with $162.20 \pm 6.47 \mu\text{g}/\text{m}^3$ followed by Globe cinema site with $124.67 \pm 5.55 \mu\text{g}/\text{m}^3$ and the lowest concentration was recorded at the Control site with $25.35 \pm 1.07 \mu\text{g}/\text{m}^3$.

The high concentrations of NO recorded at the City Kabanas site and Globe cinema roundabout site during both seasons may be attributed to high traffic density and factories within the vicinity. This observation was also noted by Bjarne *et al* (2005). Their findings show that NO is produced along with NO₂ by the oxidation of nitrogen compounds in vehicle engines at high temperatures.

High levels of NO and NO₂ is emitted along the highway with high traffic. May be that is why in the figure 7, the NO concentration gradually decreases from the city center towards outskirts of Nairobi city as traffic density decreases.

Generally, NO concentration in the Nairobi city was found to range from 44.64 $\mu\text{g}/\text{m}^3$ to 162.20 $\mu\text{g}/\text{m}^3$ which was below WHO value of 200 $\mu\text{g}/\text{m}^3$. This range is comparable to what was reported by Odhiambo, *et al* (1997) which ranged from 94.0 $\mu\text{g}/\text{m}^3$ to 174.8 $\mu\text{g}/\text{m}^3$.

4.2.2: Nitrogen (IV) oxide (NO₂)

Table 3 shows mean concentration level of NO₂ in ambient air at twelve sites within Nairobi city as determined by use of passive sampling during the study carried out between November-2006 to September-2007.

Table 3: 24-Hour NO₂-Concentration in ambient air at twelve sites within Nairobi city

Site	Wet season µg/m ³ (n =10)	Dry season µg/m ³ (n =10)
KNH's gate (KNH Road side)	93.58 ± 1.37	131.19 ± 4.39
Dagorett Corner Ngong' Road side)	101.36 ± 2.96	154.60 ± 4.70
Bus Stage (Jogoo road)	110.27 ± 2.37	170.80 ± 3.90
Co-op. Bank (Haille Sellasie road side)	127.80 ± 3.74	190.10 ± 2.64
Savora Parafric (Kenyatta Road side)	135.90 ± 3.62	197.40 ± 5.97
Globe cinema Roundabout	133.90 ± 4.53	216.00 ± 5.00
City Kabanans (Nairobi-Mombasa road side)	156.40 ± 3.36	231.70 ± 3.79
Tetra pak Comp. (Industrial area)	137.60 ± 3.91	186.90 ± 5.66
Pangani (Nairobi-Thika road side)	123.30 ± 3.53	160.20 ± 2.25
NYS's gate (Nairobi-Thika road side)	113.32 ± 4.10	124.80 ± 4.56
Githurai (Nairobi-Thika road side)	92.11 ± 3.09	108.54 ± 2.98
Control site (Dandora med. center's gate)	37.15 ± 1.14	47.84 ± 2.66

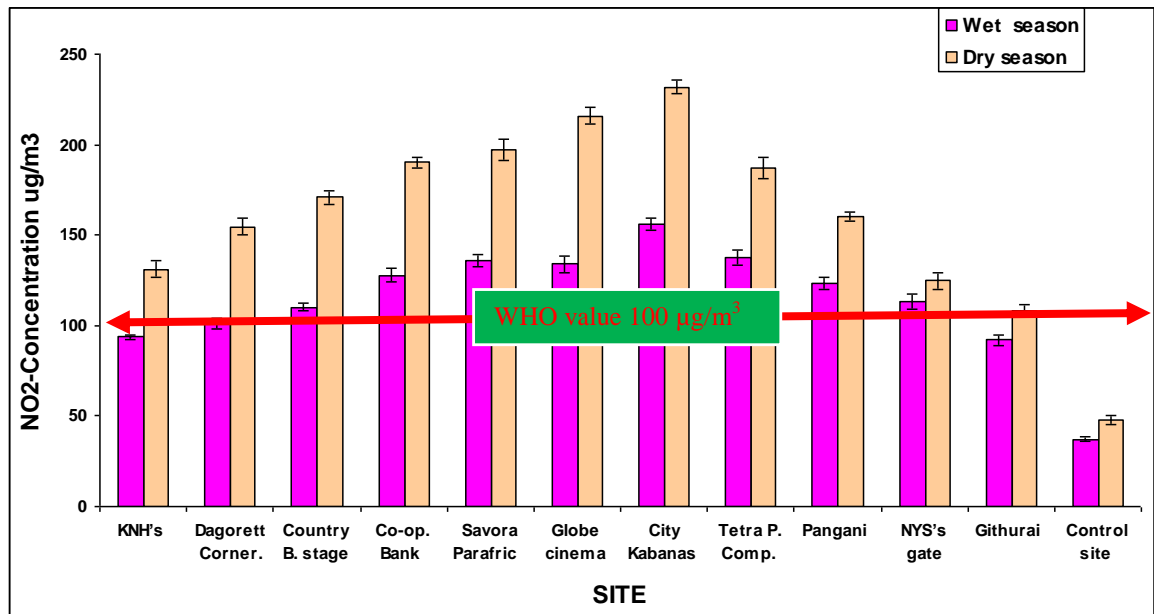


Fig. 8: Variation of NO₂-concentration in ambient air at the twelve sites within Nairobi City determined between November 2006 and September 2007

In the table 3, the highest NO₂-concentration was recorded at the City Kabanass site during the wet season with $156.40 \pm 3.36 \mu\text{g}/\text{m}^3$ followed by Tetra Pak Company's gate site (in industrial area) with $137.60 \pm 3.91 \mu\text{g}/\text{m}^3$ and Control site with lowest concentration of $37.15 \pm 1.14 \mu\text{g}/\text{m}^3$. While during the dry season, the highest mean concentration was recorded at City Kabanass site with a mean of $231.70 \pm 3.79 \mu\text{g}/\text{m}^3$ followed by Globe cinema roundabout site with a mean of $216.00 \pm 5.00 \mu\text{g}/\text{m}^3$ and control site with lowest mean concentration of $47.84 \pm 2.66 \mu\text{g}/\text{m}^3$. The high concentration of NO₂ recorded at the City Kabanass site during both wet and dry seasons may be due to the presence of high traffic density and factories within the vicinity which emit high levels of NO₂.

Generally, values of this study were much higher compared to what was reported by Odhiambo, *et al* (1997). The mean concentration of the study ranged from $37.15 \pm 1.14 \mu\text{g}/\text{m}^3$ to $231.379 \mu\text{g}/\text{m}^3$ while mean concentration reported by Odhiambo, *et al* (1997) ranged from 8.3 to $69.6 \mu\text{g}/\text{m}^3$ (see appendix X). This could be attributed to the few vehicles during that time compared to these days, their sampling sites were within the city center unlike in this study and their values were expressed as weekly mean concentrations not as 24-hour mean concentrations.

In figure 8, NO_2 concentration gradually decreases from the city center towards its outskirts. This is probably due to decrease in number of motor vehicles towards the outskirts of the city. However, all the values recorded at the twelve sites during dry season were above the 2005 WHO air quality guideline value of $100 \mu\text{g}/\text{m}^3$, but this was higher than what was recorded at Control site. While during the wet season, only values recorded at Kenyatta national hospital site, Githurai site and Control site were below the WHO air quality guideline value.

The NO_2 -mean value of Nairobi city was found to be $136.78 \pm 9.72 \mu\text{g}/\text{m}^3$ which is above the WHO air quality guideline value. These results were much below the values reported by Sami, *et al* (2003) (www.rsc.org/Jem.html), their findings show that the 8-hour mean concentration of NO_2 at four busiest roundabout of Lahore city, Pakistan, ranged from 2632-3064 $\mu\text{g}/\text{m}^3$.

On the other hand, the study results are comparable to values reported by Msafiri (2004) who carried out a research work at eight bus stations in Dar es Salaam, Tanzania ranged from 88 to 297 $\mu\text{g}/\text{m}^3$ (see appendix X). Furthermore, these results imply that Nairobi city is less polluted with NO_2 than Cairo city since in 2002, a research work was carried out in Cairo city, Egypt and showed that, annual average concentrations ranged between 2500 and 8300 $\mu\text{g}/\text{m}^3$.

In the streets of Cairo the average concentrations were between 7500 and 8300 $\mu\text{g}/\text{m}^3$ and the 24-hour average limit value of 150 $\mu\text{g}/\text{m}^3$ was exceeded during one to five days in the streets of Cairo (Gihan, 2004). Also these results were much higher than what was reported by Chacha and Frenzel (2005), who used passive samplers in determination of mean concentration of NO_2 in ambient air within Technical University of Berlin, Germany. They found out that 24-hour mean concentration of NO_2 in ambient air was 2.7 $\mu\text{g}/\text{m}^3$.

4.3 Level of SO₂ in the troposphere of Nairobi city

Level of SO₂ recorded at twelve sampling sites in Nairobi city is shown in the table 4 below. Air samples were sampled ten times per season per site and mean and standard error mean were calculated and recorded as in table 4.

Table 4: 24-Hour Concentration of SO₂ in ambient at the twelve sites

Site	Wet season µg/m ³ (n =10)	Dry season µg/m ³ (n =10)
KNH's gate (KNH Road side)	85.66 ± 2.81	99.31 ± 2.63
Dagorett Corner Ngong' Road side)	100.53 ± 0.68	121.10 ± 3.69
Bus Stage (Jogoo road)	106.20 ± 1.31	144.00 ± 1.48
Co-op. Bank (Haille Sellasie road side)	116.10 ± 2.66	189.90 ±4.21
Savora Parafric (Kenyatta Road side)	120.30 ± 2.82	195.50 ±2.92
Globe cinema Roundabout	135.40 ± 1.40	215.90 ±2.95
City Kabanas (Nairobi-Mombasa road side)	138.60 ± 2.76	224.10 ±1.16
Tetra pak Comp. (Industrial area)	116.50 ± 1.80	187.40 ±0.08
Pangani (Nairobi-Thika road side)	110.21 ± 4.27	195.30 ±3.36
NYS's gate (Nairobi-Thika road side)	106.90 ± 1.01	115.70 ±1.61
Githurai (Nairobi-Thika road side)	78.57 ± 1.16	92.62 ± 0.39
Control site (Dandora med. center's gate)	32.33 ± 1.51	35.69 ±2.20

From table 4 and figure 9, the highest SO₂ concentration was recorded at City Kabanass site during the wet season with a mean of 138.60 ± 2.76µg/m³ and Control site had the lowest concentration of 32.33 ± 1.51µg/m³. While during the dry season, the highest mean concentration of SO₂ was recorded at City Kabanass site with a mean concentration of 224.10 ± 1.16µg/m³ and Control site had the lowest concentration with a mean of 35.6978 ± 2.20µg/m³.

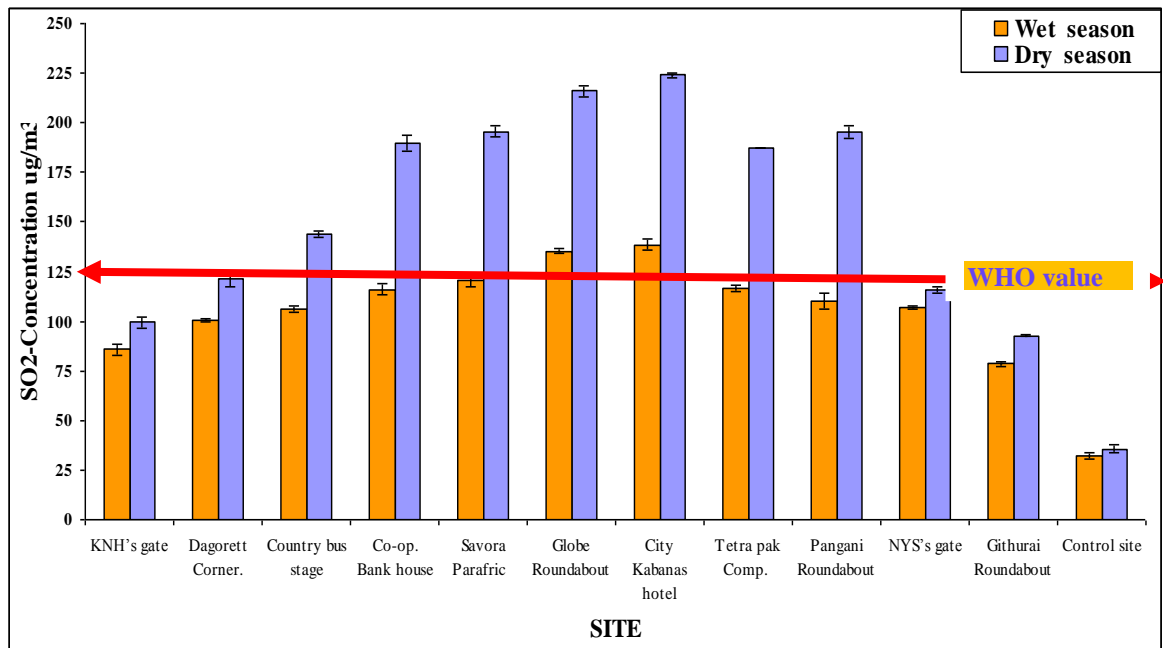


Fig. 9: Variation of SO₂-concentration in ambient air at the twelve sites within Nairobi City determined between November 2006 and September 2007

This high concentration of SO₂ at the City Kabanass site during both seasons is probably attributed to high number of motor vehicles (mostly diesel engine vehicles) along Nairobi-Mombasa road and several factories within the vicinity. In

the figure 9, the SO₂ concentration level in Nairobi city troposphere gradually decreases from the city center towards its outskirts except along Nairobi-Mombasa road. This could be due to decrease in number of motor vehicles and factories (using sulphur-containing diesel) from the city center towards the outskirts. This agrees with what was reported by Sami, *et al.*, (2003) and Osuntogun, *et al.*, (2004) (www.rsc.org/Jem.html). They point out that, SO₂ concentration along highways was in correlation with the number of motor vehicles. The SO₂ in all sampling sites was low during the wet season than the dry season this could be due to precipitation of SO₂ in the troposphere resulting the formation of acid droplet or acids rain.

In this study, the results ranged from $32.33 \pm 1.51 \mu\text{g}/\text{m}^3$ to $224.10 \pm 1.16 \mu\text{g}/\text{m}^3$ with a mean of $127.66 \pm 10.45 \mu\text{g}/\text{m}^3$. This is much lower than what was reported by Sami *et al* (2003) who carried out a study on measurements of SO₂ at four busiest roundabouts of Lahore city, Pakistan. Their findings showed that the 8-hour mean concentrations of SO₂ ranged from 5070 to 6760 $\mu\text{g}/\text{m}^3$ and were proportional to traffic density. Also these results are much lower than what was reported by Osuntogun, *et al* (2004) (www.rsc.org/Jem.html). They found that, the 8-hour mean concentrations ranged form 1,508 to 2,990 $\mu\text{g}/\text{m}^3$.

In our study the result showed that the level of SO₂ in the Nairobi city troposphere is within the range to that of the Dakar city, Senegal which ranged between 100 to

334 $\mu\text{g}/\text{m}^3$ (Bjarne, *et al.*, 2005). Nairobi city is less polluted with SO_2 compared to Kitwe city, Zambia because according to Environmental Council of Zambia, the 24-hour mean concentrations of SO_2 in parts of Kitwe city between in 1996 and 2000 ranged from 119 to 1207 $\mu\text{g}/\text{m}^3$ (Lemmy, 2004).

4.4 Comparison of concentrations of NO , NO_2 and SO_2 at ten sites

The level variations of NO , NO_2 and SO_2 in ambient air at twelve sites within Nairobi city are shown in the figure 10.

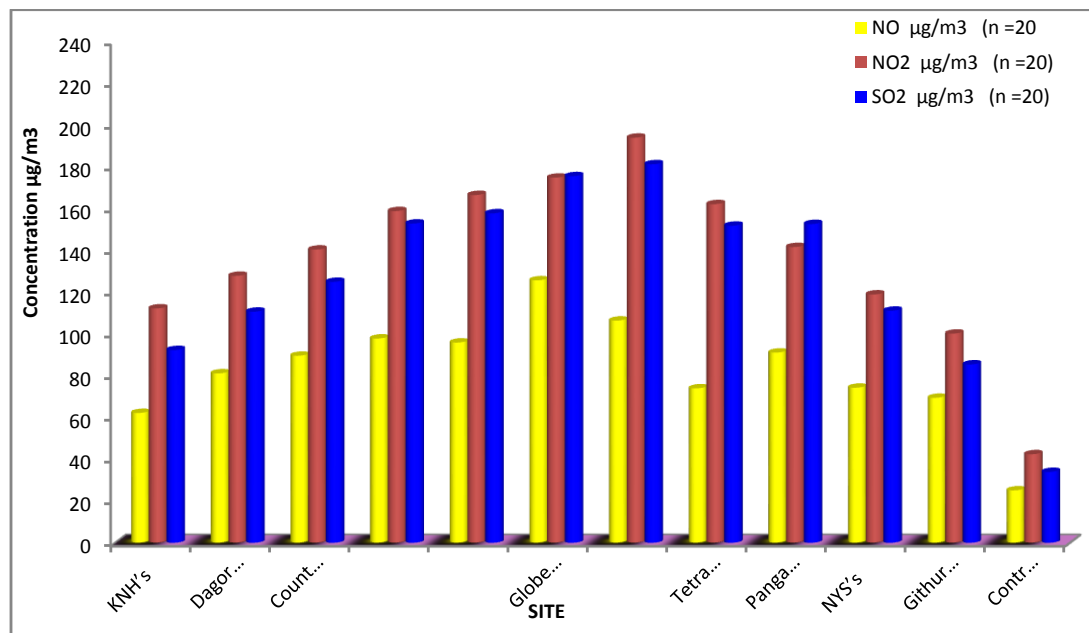


Fig. 10: Bar graphs of 24-hour mean concentrations of NO , NO_2 and SO_2 in ambient air at twelve sites between November-2006 to September-2007

In the figure **10**, it is clear that concentration of each air pollutant recorded at all sites during the dry season is much higher than the one recorded during the wet season. During the wet season there is high water content in the troposphere and part of the amount of these air pollutants dissolved in water vapour and gets washed to the ground surface. This observation is in line with the work of Gerboles *et al* (2005). In their research work, they found out that high water content in the atmosphere reduces amounts of most of air pollutants in the atmosphere.

The highest mean concentration of NO was recorded at Globe cinema roundabout site while the highest mean concentrations of NO₂ and SO₂ were recorded at City Kabanas site along Nairobi-Mombasa road and the lowest concentrations of NO, NO₂ and SO₂ was recorded at Control site. The high levels of NO at Globe Cinema roundabout site could be due to high traffic density, presence of high buildings that act as air current barriers resulting in trapping the air pollutants emitted within the site and since wind normally blow from east to west direction of the city, there is likely hood of emissions from other parts of the city being blown to Globe Cinema roundabout site. Also at Globe cinema roundabout the movement of vehicles is slow at peak hours due to congestion.

The high levels of NO, NO₂ and SO₂ at City Kabanas site along Nairobi-Mombasa road may be due to the presences of high traffic density especially heavy transportation tracks. This observation is in line with what was reported in Sami *et*

al (2003) ([www.rsc, Org/Jem.html](http://www.rsc.org/Jem.html)) research work. Their findings show that concentrations of NO_x and SO_2 in the troposphere along highways are proportional to traffic density. Also level of SO_2 at City Kabanas site along Nairobi-Mombasa road was found to be highest during the wet and dry seasons. This could be due to the presence of high number of diesel-engine tracks on Nairobi-Mombasa road always compared to any other site diesel is known to be sulphur containing fuel (Matsuo, 1981).

Ambient NO_2 -concentration recorded at the twelve sites was found to be higher compared to that of NO and SO_2 except at Globe Cinema roundabout and Pangani roundabout sites where SO_2 -concentrations were higher. This shows that, emission of NO_2 in the city is either higher compared to that of NO and SO_2 or the life-span of NO_2 in the troposphere is longer than that of NO and SO_2 gases. The lowest concentrations of NO , NO_2 and SO_2 were recorded at control site for both the wet and the dry seasons. This is perhaps due to less NO_x and SO_2 emissions in the area and it is free from the city emissions since it is 15 km east of the Nairobi city where wind normally blow from.

NO -mean value at all sites was recorded lowest because NO is unstable (short life-span) in the troposphere, it is easily oxidized to NO_2 by both ambient ozone and oxygen. Among the selected sites, the mean values of all the air pollutants were

highest at Globe cinema roundabout and at City kabanas. This is attributed by high number of motor vehicles road and factories within the vicinity.

Finally, there is need to safeguard the quality of air in the Nairobi environment. Because clean air is a public good; indeed no other resource exhibits the same degree of 'publicness'; Land can be parceled and fenced; Water can be bottled; Scenery can be hidden; One can even isolate himself from noise; But man has no choice but to breathe the air around him whether polluted or not.

4.5 Comparison between the results of active sampling and passive sampling methods

In order to check the conformity of passive sampling, active sampling method was used as reference method. Table 5 shows the results of active sampling and passive sampling methods which were obtained during the preliminary study at co-operative bank house, Haille Sellasie road side in the city centre on the month of October 2006.

Table 5: Mean concentrations of NO, NO₂ and SO₂ in ambient air at co-operative bank house, Haille Sellasie road side in the city centre

Season	Passive sampling ($\mu\text{g}/\text{m}^3$)			Active sampling ($\mu\text{g}/\text{m}^3$)		
Wet	NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
	85	127	122	84	125	121
	96	111	118	91	116	116
	91	104	139	88	109	135
	85	138	142	80	136	139
	87	136	125	86	134	120
	83	134	117	79	134	116
	95	123	113	92	121	110
	96	135	128	94	136	123
	85	147	117	84	146	114
	81	122	100	77	121	99
Dry	115	188	165	113	186	170
	111	195	186	110	191	189
	124	203	209	109	198	203
	134	201	201	129	198	194
	117	179	218	113	173	210
	121	203	199	119	199	197
	117	187	185	112	186	178
	124	189	219	122	186	213
	110	196	187	102	198	185
	116	185	184	113	186	180

The results of passive sampling were plotted against the results of active sampling method as shown in figures 11, 12 and 13. There was good agreement between the results of passive and active sampling methods per air pollutant with coefficient of correlations of 0.9815, 0.9966 and 0.9968 for NO, NO₂ and SO₂ respectively.

No much different between the results of active sampling method and of passive sampling method. This is agrees with the work of Parrah and Linda, (1988). From their calibration experiments, passive samplers had strong correlation to active method with the value of $r = 0.9539$ for ambient NO₂ for a 24-hour exposure period.

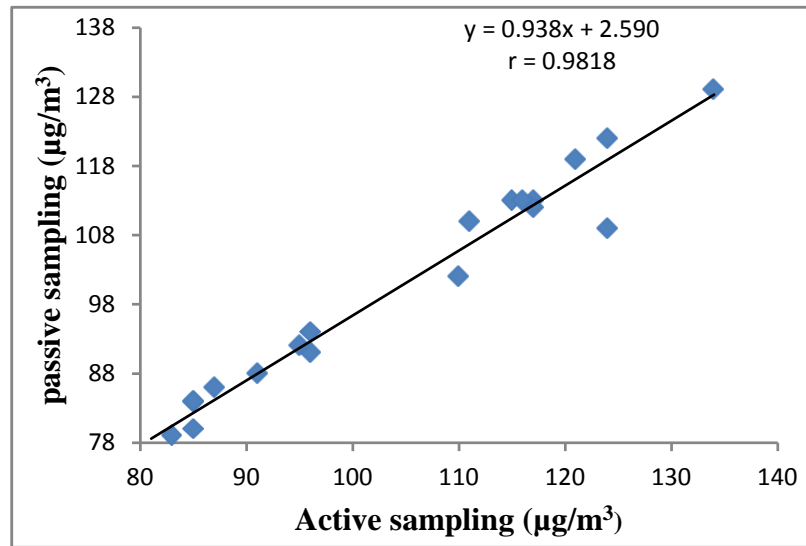


Fig. 11: A graph of NO showing the relationship between the results of active method and passive method

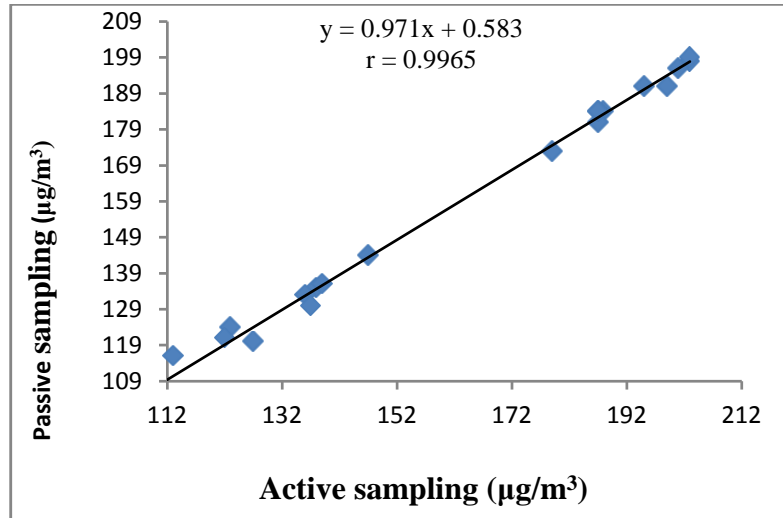


Fig. 12: A graph of NO_2 showing the relationship between the results of active method and passive method

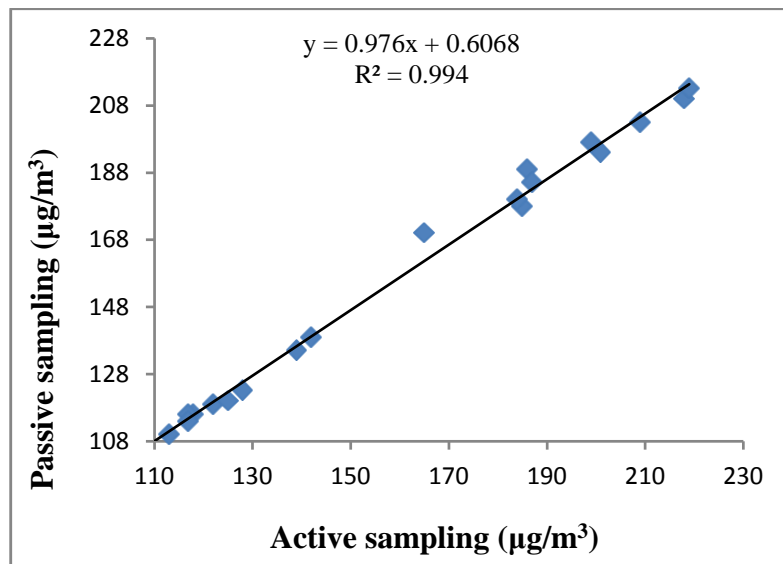


Fig. 13: A graph of SO_2 , showing the relationship between the results of active method and passive method

The results in table 5 were also statistically compared as shown in the table 6. There was no significant difference between the two kinds of results at 95% confidence interval. Values of t-test for all gases were within required paired difference range; $t_{NO} = -3.7810$, $t_{NO_2} = -6.2700$ and $t_{SO_2} = -7.0040$ are within the range -7.1015 to -2.0785, -6.7129 to -3.3821 and -7.5013 to -4.0804 respectively. This indicates that passive sampling method is a reliable technique for determining levels of NO, NO₂ and SO₂ in the troposphere.

Table 6: Statistical paired methods tests

Pollutant	Correction (r)	Paired Differences					t	Sig. (2-tailed)
		mean	Std. deviation	Std. error mean	95% Confidence Interval of the difference			
					lower	upper		
NO	0.9819	-4.5900	5.9476	1.2141	-7.1015	-2.0785	-3.7810	0.0010
NO ₂	0.9966	-5.0485	3.9440	0.8051	-6.7129	-3.3821	-6.2700	0.0000
SO ₂	0.9968	-5.7908	4.0506	0.8268	-7.5013	-4.0804	-7.0040	0.0000

This finding agrees with the research work of Annika, *et al* (1999) (www.rsc.org/Jem.html). They validated passive samplers for NO₂, both in laboratory and outdoor test using TEA as absorbing medium. They found out that the sensitivity and capacity of the method make it suitable for 24-hour duration in polluted environments and its precision varied within 3.5 to 23% depending of the concentration of air pollutant and the accuracy varied from 91 to 100%.

4.6 Comparison between the results of TEA, TCM and activated charcoal

One of the achievement of this study was the discovery of activated charcoal as absorbing agent of NO, NO₂ and SO₂ in the ambient air. Table 6 shows results obtained by use of TEA, TCM and activated charcoal (absorbing reagents) during the preliminary study at co-operative bank house, Haille Sellasie road side in the city centre on the month of October 2006.

Table 7: Concentrations of NO, NO₂ and SO₂ in ambient air obtained by use of TEA, TCM and activated charcoal as absorbing reagents

Season	Absorbing agent ($\mu\text{g} / \text{m}^3$)					
	TEA		TCM	Activated charcoal		
	NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	85	127	122	84	118	113
	96	111	118	98	97	109
	91	104	139	93	86	128
	85	138	142	85	123	136
	87	136	125	93	117	119
	83	134	117	81	129	111
	95	123	113	98	117	100
	96	135	128	98	127	116
	85	147	117	89	138	108
	81	122	100	83	110	90
Dry	115	188	165	112	170	143
	111	195	186	104	181	169
	124	203	209	120	183	206
	134	201	201	131	183	195
	117	179	218	114	166	205
	121	203	199	124	195	181
	117	187	185	219	174	183
	124	189	219	127	193	210
	110	196	187	105	204	172
	116	185	184	119	177	177

To check suitability of activated charcoal as absorbent, the results of activated charcoal were plotted against the results of TEA and TCM, respectively, as shown in figures 14, 15 and 16. There was a good agreement between the results of TEA, TCM and activated charcoal per air pollutant with coefficient of correlations of 0.9788 for NO, 0.9798 for NO₂ and 0.9920 for SO₂.

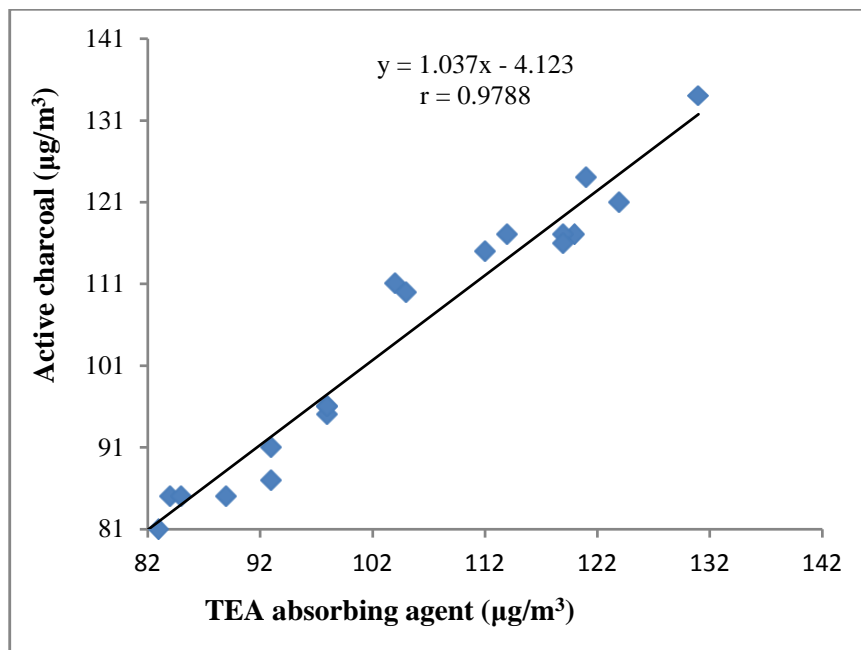


Fig. 14: A graph of NO showing the relationship between the results of TEA and activated charcoal

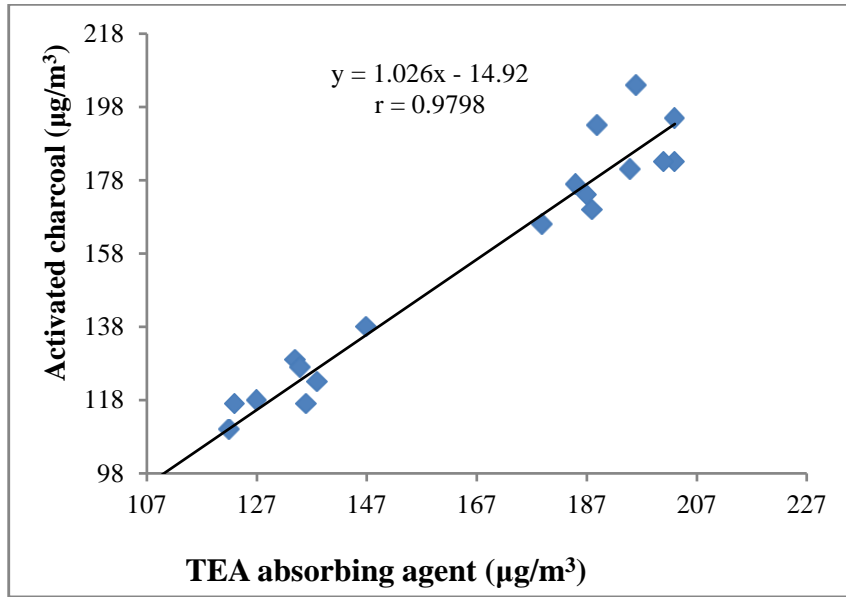


Fig. 15: A graph of NO₂ showing the relationship between the results of TEA and activated charcoal

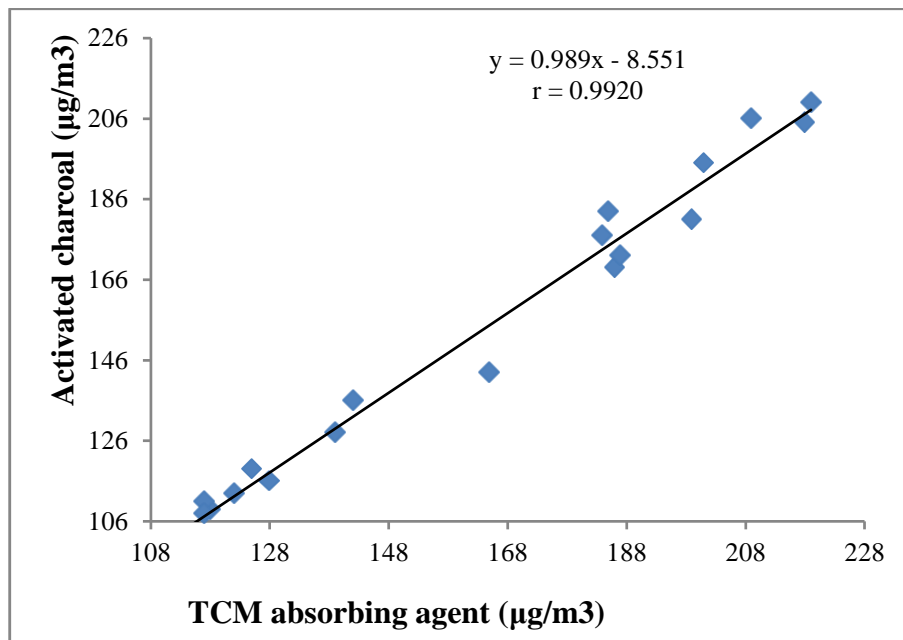


Fig. 16: A graph of SO₂ showing the relationship between the results of TCM and activated charcoal

The results of TEA, TCM and activated charcoal were further statistically compared as shown in the table 6. There is no significant difference (at 95% confidence interval) between these results. Values of t for all gases were within the required paired difference range; that is $t_{NO} = 0.4390$ is within the range -2.3631 to 3.6356, $t_{NO_2} = -0.8420$ is within the range -14.1385 to 5.9602 and $t_{SO_2} = 1.0820$ is within the range -1.4822 to 4.7305.

Table 8: Paired results tests of the results of TEA, TCM and activated charcoal

Comparison of two types of results		Paired Differences						t	Degree of freedom	Sig. 2-tailed
		r	Mean	Std Dev.	Std Error mean	95% Confidence interval				
						Lower	Upper			
NO Pair	TEA and Activated charcoal	0.9787	0.6362	7.1029	1.4499	-2.3631	3.6356	0.4390	23	0.6650
NO ₂ Pair	TEA and Activated charcoal	0.9795	-4.0892	23.7988	4.8579	-14.138	5.9602	-0.8420	23	0.4090
SO ₂ Pair	TCM and Activated charcoal	0.9917	1.6242	7.3564	1.5016	-1.4822	4.7305	1.0820	23	0.2910

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

There was a good agreement between the results obtained by passive sampling method and values obtained by active sampling method. This confirmed that passive sampling is reliable method in sampling NO_x and SO_2 from the troposphere. The detection limit of the method was $7\mu\text{g}/\text{m}^3$ and $4\mu\text{g}/\text{m}^3$ and precision was $4\mu\text{g}/\text{m}^3$ and $3\mu\text{g}/\text{m}^3$ for NO_2 and SO_2 , respectively for a 24-hour sampling.

The research work results show that the level of NO in the Nairobi troposphere was found to be $82.87 \pm 3.19\mu\text{g}/\text{m}^3$ which is below the WHO air quality value of $200\mu\text{g}/\text{m}^3$ and that of NO_2 was found to be $136.78 \pm 9.72\mu\text{g}/\text{m}^3$ which is above the WHO air quality guideline value of $100\mu\text{g}/\text{m}^3$. Thus, level of NO_x was $219.65 \pm 12.91\mu\text{g}/\text{m}^3$ (amount of NO and NO_2) in ambient air. While level of SO_2 was found to be $127.668 \pm 10.45\mu\text{g}/\text{m}^3$ which is within the WHO value of $125\mu\text{g}/\text{m}^3$. This indicates that Nairobi city is polluted especially with NO_2 gas.

The levels of NO , NO_2 and SO_2 in ambient air was found to decrease gradually from the city center towards its outskirts except along Nairobi-Mombasa road. This may be due to gradual decrease in number of motor vehicles and factories as one

move from the city center to the outskirts of Nairobi city. The high levels of NO, NO₂ and SO₂ measured in the city centre and along Nairobi-Mombasa road seemed to be a pointer to the fact that vehicular emission is the main contributor to these gases in Nairobi city.

Finally, one of the achievement of this study was the innovation of activated charcoal as an absorbing agent of NO, NO₂ and SO₂. There was a good agreement between the results of activated charcoal, TEA and TCM per air pollutant. Activated charcoal has ability to absorb ambient NO, NO₂ and SO₂, the way TEA and TCM do and hence it can be used in sampling ambient NO_x and SO₂.

5.2 RECOMMENDATIONS

This research work has shown that there is need to safeguard the quality of air in the Nairobi environment. Therefore, City council, NEMA and other relevant bodies should establish national emission standards and related measures for both commercial and personal vehicles, factories and reinforcement.

The certification of vehicles and factories should only apply to those that meet emission standards, assembly line testing to be done after certain period of time and emission restrictions on imported vehicles. It is recommended that biodiesel should be use produced commercially to replace the current fuel which causes air pollution. Biodiesel has various benefits; reduction of greenhouse emissions and energy security poverty alleviation.

There is need to set up air quality monitoring centers within Nairobi city by use of passive sampling method (less expensive) to be carrying out daily monitoring of ambient NO_x and SO_2 in Nairobi city. This will result more data on air pollution that can be used by city council and NEEMA for effective planning and management of air pollution in the city. It is also, advisable that levels of other air pollutants such as ozone (O_3), volatile organic compounds (VOCs), oxides of carbon (CO and CO_2) and polycyclic aromatic hydrocarbons (PAHs) to be determined in the city.

Finally, further research work should be done on activated charcoal to increase its application to other air pollutants.

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APPENDICES

Appendix I: Concentrations of NO, NO₂ and SO₂ in ambient air determined at Dagorett corner and Kenyatta National Hospital's gate within Nairobi city, Kenya between November 2006 and September 2007

Season	Expt	Dagorett corner			KNH's gate		
		NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	1	83.20	102.00	99.40	49.00	95.40	75.00
	2	78.20	105.00	103.00	38.50	76.50	85.00
	3	81.60	113.00	99.40	38.50	102.00	78.00
	4	55.00	113.00	104.00	44.90	111.00	75.00
	5	65.30	108.00	97.30	57.50	102.00	85.30
	6	75.70	97.10	101.00	44.90	114.00	81.80
	7	78.30	88.20	99.40	51.20	76.50	88.70
	8	74.00	97.10	99.40	38.50	76.50	98.10
	9	71.40	88.20	103.00	38.50	86.50	88.70
	10	63.00	102.00	99.40	44.90	95.40	101.00
Dry	1	102.00	165.00	121.00	83.60	140.00	91.90
	2	90.00	177.00	114.00	74.90	129.00	88.50
	3	90.00	165.00	111.00	83.60	140.00	85.10
	4	66.90	143.00	136.00	92.30	118.90	108.00
	5	75.40	152.00	143.00	101.00	122.00	105.00
	6	83.90	161.00	128.00	101.00	103.00	98.30
	7	71.80	132.00	111.00	83.60	142.00	105.00
	8	90.00	165.00	125.00	94.00	142.00	98.30
	9	84.00	143.00	111.00	81.10	132.00	105.00
	10	78.50	143.00	111.00	83.20	143.00	108.00

Appendix II: Concentrations of NO, NO₂ and SO₂ in ambient air determined at Co-operative Bank house and at Country bus stage within Nairobi city, Kenya between November 2006 and September 2007

Season	Expt	Co-op. Bank house			Country bus stage		
		NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	1	83.60	125.00	122.00	88.30	109.00	109.00
	2	92.30	116.00	113.00	68.30	96.70	105.00
	3	83.60	109.00	126.00	61.60	118.00	109.00
	4	83.60	136.00	129.00	73.50	113.00	105.00
	5	83.60	134.00	118.00	85.50	102.00	100.00
	6	74.90	134.00	113.00	73.50	113.00	114.00
	7	92.30	121.00	111.00	85.50	113.00	105.00
	8	93.80	136.00	118.00	73.50	109.00	101.00
	9	83.60	146.00	111.00	66.80	121.00	105.00
	10	74.90	121.00	100.00	73.50	108.00	109.00
Dry	1	113.00	186.00	165.00	109.00	172.00	139.00
	2	110.00	191.00	184.00	84.00	161.00	145.00
	3	109.00	198.00	209.00	112.00	171.00	142.00
	4	135.00	198.00	188.00	122.00	174.00	153.00
	5	113.00	173.00	200.00	84.00	161.00	149.00
	6	84.50	199.00	192.00	122.00	187.00	146.00
	7	112.00	186.00	184.00	109.00	179.00	139.00
	8	122.00	186.00	209.00	110.00	169.00	146.00
	9	102.00	198.00	184.00	84.00	147.00	139.00
	10	113.00	186.00	184.00	109.00	187.00	142.00

Appendix III: Concentrations of NO, NO₂ and SO₂ in ambient air determined at Savora Parafric hotel and at Global cinema roundabout within Nairobi city, Kenya between November 2006 and September 2007

Season	Expt	Savora Parafric hotel			Global roundabout		
		NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	1	89.80	138.00	111.00	90.00	153.00	143.00
	2	74.00	122.00	104.00	97.60	136.00	138.00
	3	66.00	114.00	111.00	90.00	147.00	140.00
	4	79.00	143.00	126.00	90.00	124.00	131.00
	5	88.00	152.00	122.00	89.80	136.00	139.00
	6	70.00	133.00	126.00	78.30	113.00	135.00
	7	78.30	138.00	123.00	89.80	113.00	131.00
	8	74.90	143.00	123.00	89.80	136.00	131.00
	9	83.80	138.00	134.00	78.30	134.00	131.00
	10	70.00	138.00	123.00	101.00	147.00	135.00
Dry	1	110.00	214.00	208.00	146.00	228.00	224.00
	2	92.30	221.00	184.00	135.00	246.00	227.00
	3	107.00	228.00	196.00	145.00	231.00	217.00
	4	126.00	183.00	200.00	108.00	194.00	215.00
	5	146.00	210.00	193.00	137.00	213.00	211.00
	6	119.00	192.00	207.00	108.00	204.00	221.00
	7	107.00	183.00	184.00	108.00	213.00	196.00
	8	126.00	177.00	203.00	127.00	204.00	224.00
	9	107.00	183.00	184.00	108.00	223.00	207.00
	10	107.00	183.00	196.00	108.00	204.00	217.00

Appendix IV: Concentrations of NO, NO₂ and SO₂ in ambient air determined at City Kabanas hotel and Tetra Pak Comp.'s gate within Nairobi city, Kenya between November 2006 and September 2007

Season	Expt	City Kabanas hotel			Tetra Pak Comp.'s gate		
		NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	1	94.90	159.00	159.00	51.20	143.00	117.00
	2	93.80	155.00	155.00	60.90	151.00	125.00
	3	91.80	153.00	153.00	49.00	143.00	119.00
	4	93.10	162.00	162.00	70.60	123.00	107.00
	5	59.70	153.00	153.00	65.30	130.00	119.00
	6	83.20	153.00	153.00	70.60	118.00	113.00
	7	94.90	161.00	161.00	65.30	142.00	123.00
	8	94.90	153.00	153.00	65.30	130.00	115.00
	9	83.20	162.00	162.00	68.30	143.00	109.00
	10	94.90	153.00	153.00	48.40	153.00	118.00
Dry	1	165.00	235.00	231.00	97.90	184.00	189.00
	2	187.00	244.00	227.00	86.70	171.00	189.00
	3	165.00	247.00	224.00	86.70	188.00	193.00
	4	141.00	221.00	224.00	97.90	211.00	177.00
	5	130.00	209.00	221.00	86.90	203.00	185.00
	6	141.00	232.00	218.00	75.60	198.00	177.00
	7	165.00	244.00	227.00	86.90	189.00	197.00
	8	187.00	232.00	224.00	75.60	184.00	189.00
	9	165.00	232.00	224.00	97.90	194.00	193.00
	10	176.00	221.00	221.00	75.60	147.00	185.00

Appendix V: Concentrations of NO, NO₂ and SO₂ in ambient air determined at Pangani roundabout and at National Youth Service headquarter's gate within Nairobi city, Kenya between November 2006 and September 2007

Season	Expt	Pangani roundabout			At NYS's gate		
		NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	1	70.60	142.00	98.10	68.30	115.00	113.00
	2	80.40	118.00	105.00	78.30	104.00	110.00
	3	80.40	107.00	101.00	68.30	115.00	106.00
	4	79.10	118.00	111.00	80.40	128.00	106.00
	5	68.10	112.00	100.00	61.50	92.20	106.00
	6	68.10	134.00	105.00	68.30	104.00	103.00
	7	68.10	123.00	103.00	60.20	128.00	106.00
	8	90.10	123.00	118.00	65.20	104.00	103.00
	9	79.10	133.00	118.00	68.30	115.00	110.00
	10	68.10	123.00	143.00	56.60	128.00	106.00
Dry	1	101.00	162.00	193.00	89.80	101.00	114.00
	2	119.00	171.00	205.00	89.80	138.00	110.00
	3	101.00	162.00	203.00	99.30	109.00	117.00
	4	110.00	153.00	196.00	70.90	128.00	119.00
	5	92.30	153.00	205.00	90.10	109.00	121.00
	6	101.00	162.00	177.00	61.30	119.00	125.00
	7	110.00	153.00	196.00	80.20	128.00	117.00
	8	119.00	171.00	205.00	70.90	138.00	110.00
	9	110.00	153.00	177.00	90.10	140.00	114.00
	10	101.00	162.00	196.00	70.90	138.00	110.00

Appendix VI: Concentrations of NO, NO₂ and SO₂ in ambient air determined at Pangani roundabout and at Githurai roundabout and at Dandora medical center's gate within Nairobi city, Kenya between November 2006 and September 2007

Season	Expt	At Githurai roundabout			At Dandora		
		NO	NO ₂	SO ₂	NO	NO ₂	SO ₂
Wet	1	44.00	82.60	80.80	22.20	42.50	41.90
	2	55.60	74.90	75.30	25.10	33.70	32.40
	3	44.00	88.20	78.70	21.30	36.10	29.40
	4	56.60	89.80	79.80	27.20	36.70	31.40
	5	66.80	101.00	81.40	31.90	34.50	36.90
	6	52.00	89.80	74.50	24.40	41.20	25.00
	7	78.30	101.00	81.40	27.10	31.90	34.90
	8	66.80	89.80	74.50	24.40	36.70	31.50
	9	55.60	101.00	74.50	23.20	36.70	27.50
	10	66.80	103.00	84.80	26.70	41.50	32.40
Dry	1	74.80	111.00	85.10	25.10	40.60	49.40
	2	83.90	102.00	92.10	22.20	53.10	38.90
	3	65.80	111.00	95.60	21.90	56.40	31.50
	4	84.40	103.00	88.00	27.10	51.90	41.90
	5	75.30	112.00	95.00	22.30	50.90	25.50
	6	84.40	93.40	88.00	27.10	56.00	28.50
	7	77.40	111.00	92.10	32.00	56.00	35.40
	8	84.40	102.00	95.60	26.10	40.90	38.90
	9	81.40	129.00	95.60	22.20	38.60	31.90
	10	93.40	111.00	99.10	23.70	34.00	35.00

Appendix VII: The average yearly ambient air quality 24-hour SO₂ levels in parts of Kitwe city, Zambia

Year	Fire Brigade µg/m ³	Central Shaft µg/m ³	Nkana Hospital µg/m ³	Wusakile Hospital µg/m ³
<i>Zambian Guideline</i>	125	125	125	125
1996	233	808	133	119
1997	675	1,207	177	316
1998	233	991	138	141
1999	381	865	175	155
2000	756	1,025	185	192

Source: Modified from Mopani Copper Mines Plc's Environmental Impact Statement-August 2002.

Appendix VIII: Assessment of Ozone, Nitrogen Oxides, Air Particulate matter (PM10) and Trace Elements Level in the Ambient Air of Nairobi City by George Odhiambo in 1997

Sample	Pollutant						Vehicles
	O ₃	NO	NO ₂	*PM ₁₀	*Fine	*Coarse	
FW1	0.072	0.050	0.010	66.7	23.8	42.9	6301
FW2	0.078	0.056	0.018	165.5	57.9	107.6	8240
FW3	0.081	0.059	0.007	179.8	63.8	116	13218
FW4	0.075	0.066	0.006	259.1	74.1	185	10810
MW2	0.080	0.077	0.037	413.2	196.8	216.4	15204
MW3	0.062	0.053	0.012	162.0	50.9	111.1	8204
MW4	0.071	0.061	0.010	142.4	68.3	74.1	8120
MW5	0.068	0.091	0.014	444.4	206.0	238.4	18042
AW1	0.006	0.093	0.013	243.1	217.7	25.5	18824
AW3	0.049	0.075	0.012	395.8	155.1	240.7	13682
AW4	0.022	0.073	0.013	157.4	138.9	18.5	13214

* indicates concentrations that are in $\mu\text{g m}^{-3}$; the others are in ppm. In the sample column the first letter indicates the month of sampling, the rest indicate the week of sampling

Appendix IX: World Health Organization Ambient Air Quality Guidelines

Pollutant	Guideline Value	Averaging Time
Ozone	100 $\mu\text{g}/\text{m}^3$	8 hours
Nitrogen dioxide	200 $\mu\text{g}/\text{m}^3$	1 hour
	100 $\mu\text{g}/\text{m}^3$	24 hours
	40 $\mu\text{g}/\text{m}^3$	Annual
Sulfur dioxide	500 $\mu\text{g}/\text{m}^3$	10 min
	125 $\mu\text{g}/\text{m}^3$	Annual
	50 $\mu\text{g}/\text{m}^3$	24 hours

Appendix X: Average pollutant concentrations at the sampled bus stations in Dar es Salaam.

Bus Station	Average Pollutant Concentration ($\mu\text{g}/\text{m}^3$)		
	SO ₂	NO ₂	PM
Mwenge	1,297	208	1,211
Ubungo	1,740	239	1,143
Posta	1,410	297	794
Mnazi Mmoja	1,331	184	782
Kariakoo Market	1,829	119	592
Uhuru	2,483	257	892
Tandika	128	88	648
Buguruni	1,797	228	1,008

Source: Msafiri (2003)

Appendix XI: Typical ranges of long-term average (annual) concentrations of SO₂ measured by passive samplers at 11 selected sites in Cairo, Egypt, 2002.

