A Study of the Chemical Quality of Ambient Air at Selected Intersections in the Durban Metropolis.

by

Shalini Singh

Submitted in partial fulfilment of the requirements for the degree of

Master of Technology

in Department of Chemical Engineering and Quality Assurance

Faculty of Science, Engineering and Built Environment

Durban Institute of Technology

January 2003

DECLARATION OF CANDIDATE

I, Shalini Singh declare that unless otherwise indicated, this dissertation is my own work and that it has not been submitted for any degree at another Tertiary Institution.

S. Singh

January 2003

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to the following people and organisations for their assistance and contribution during the course of this project :

- The Department of Quality Assurance for awarding me a scholarship for this project.
- The Ethekweni Water Services for the opportunity to study whilst still in their employ.
- The Ethekweni Water Services for the use of their Laboratory and historical data.
- My supervisor, Professor K.G Moodley, for his valuable guidance, untiring support, constructive criticism, proof reading, technical and editorial assistance throughout my studies.
- My co-supervisor, Mr. S. Govender, for his guidance, editorial assistance and support during the preparation of this project and manuscript.
- Mr. D. Singh, for his assistance with the statistical aspects of the thesis.
- My Mentor, Mr. D.H Goodes, for his guidance and continued support throughout the project.
- Mr. R. Kallicharan for his help and guidance in the Mechanical Engineering aspects of this project.
- Mr. R. Bissett for his continued support and guidance throughout the project.
- My colleague Mr. E. Isreal for his assistance during the collection of samples.
- To Mr.A Vissers, Mr. N. Gobrie, Ms. S Jackson and Ms. S.Singh for the help in compiling this report.
- Finally, to my family and friends for their patience, understanding and support in all my ventures and God for making all things possible.

Abstract

Motor vehicles are considered a major source of air pollution in urban environments. Nitrogen dioxide (NO_2) and nitric oxide (NO) which are collectively referred to as oxides of nitrogen (NOx) are formed at high temperatures during combustion processes in the engines of motor vehicles and are emitted via the exhaust into the atmosphere. Nitrogen dioxide is regarded as an irritant of the respiratory system.

The impact of traffic related emissions on air quality is frequently under-estimated. Often traffic emissions seem to attract attention only when pollution levels are so high that visibility becomes a problem. In the Durban Metro, limited information related to traffic impacts on air quality is available. This is because the Metro uses only one active sampler to monitor nitrogen dioxide at a site in the South Durban Industrial Basin. This is due to the high cost of the equipment, space and security requirements.

A Durban Metro survey showed NO_2 concentrations to be highest in urban areas closest to the kerbside. It also recommended further traffic related monitoring in urban areas. Hence, particulate emissions from the vehicle exhausts were assessed. In the present study passive sampling was used to determine concentrations of NO_2 and dust sweepings were used to determine concentration of Pb at selected traffic intersections and busy roadways, leading out of the city. An 8th site was used to compare passive and active sampling. The average traffic count data from the Durban Metro Traffic Department was used as one of the criteria for the selection of sites. Other criteria used were buildings and structures around the intersection and levels of traffic congestion. Nitrogen dioxide in ambient air was trapped onto a pre-coated filter which was conditioned in the laboratory. Colorimetry was used to determine the concentrations of NO_2 as nitrites. Dust sweepings were acid digested and analysed for lead using Inductively Coupled Plasma (ICP).

The preliminary study used 14- day sampling periods but this resulted in over-saturation of the filters. Hence subsequent sampling periods were reduced to7 days.

The duration of the sample collection for the entire study was from 28 November 2000 to 4 December 2001 to accommodate seasonal variations.

The study focused on:

- compliance of NO_2 concentrations to DEAT air quality guideline values
- reliability of the passive sampling compared to active sampling
- seasonal variation of NO_2 concentrations
- the effect of distance from the kerbside on the concentration of NO_2
- comparing lead concentrations to US-EPA standards

The study found that relative to active sampling, passive sampling was a cost effective, reliable method for estimating NO_2 concentrations. Furthermore, NO_2 levels at all sites were well below the DEAT guideline value for NO_2 concentrations in ambient air. Higher concentrations of NO_2 were recorded during winter months, highlighting seasonal variations. The passive sampler gave slightly lower values compared to the active analyser.

The concentration of nitrogen dioxide decreased with distance from the kerbside. On several occasions the concentration of Pb exceeded the US-EPA standard. Furthermore the concentration of Pb was dependent on the number of municipal sweepings.

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 - LITERATURE SURVEY

2.4.3 Studies using Passive Samplers

CHAPTER 3 - METHODOLOGY

CHAPTER 4 - RESULTS AND DISCUSSION

BIBLIOGRAPHY

APPENDIX

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Cal. Factor : Calibration Factor

DEAT : Department of Environmental Affairs and Tourism.

DMC : Durban Metro Caravan

EDS : Edwin Swales

NACA : National Association for Clean Air.

%RH : Relative Humidity

SCL : Sea Cow Lake

SPJ : Spaghetti Juction

r : Regression ie. a model of the relationship between the expected value of a random variable and the values of one or more possibly related variables.

US-EPA : United States Environmental Protection Agency

VE : Victoria Embankment

VOC : Volatile organic compound.

WAR : Warwick

GLOSSARY

Air pollutant : Is a substance which when emitted to atmosphere to the time that it is removed from atmosphere causes harm to man, material and environment.

Air Guideline : Is the maximum pollutant concentration that is recommended in the "interest of public health"

Air Standard : Is the maximum concentration that a pollutant can exceed a certain number of times for a prescribed period. This is legislated and organisations contravening can be prosecuted.

Carburetor : Device used to provide a mixture of air to vapour fuel in the internal combustion engine.

Compression / Compression Pressure : Fuels are preferred to have a high limiting compression pressure without detonation to achieve more power.

Combustion : The production of heat and light energy through a chemical process, usually oxidation.

Crankshaft : It is a part of the engine that converts reciprocating motion of the pistons into rotary motion.

Detonation : Is a result of rapid pre -flame reactions within highly stressed gases.

Dust : Any solid particulate matter over 1 micron in size.

Dust Fallout : Fall out of the air, collected in an open mouthed container that is measured and analysed.

Dust lead concentration (μg/g) : Measures how much lead (Pb) is present in a given quantity of dust.

Dust lead loading ($\mu g/m^2$) : Is a function of both concentration of lead (Pb) in dust and the measure of how much lead (Pb) is in the given quantity of dust.

Emission Inventory : A group of air pollutants that is emitted into a given atmosphere in amounts per day, by type of source.

Engine : A machine that produces mechanical energy.

Environmental Management System : That part of overall management system that includes organisational structure, planning activities, responsibilities, practices, procedures, processes and resources for developing, implementing, achieving, reviewing and maintaining the environmental policy.

Environmental Objective : An overall goal, arising from the environmental policy, that an organisation sets and that is quantified where applicable.

Environmental Impact : Any change to environment, whether adverse or beneficial, wholly or partially resulting from an organisation's activities, products or services.

Hot spot : Areas of potential exceedances of guideline values.

Hydrocarbon : Compounds containing various combinations of carbon and hydrogen

Internal Combustion Engine : An engine in which both the heat energy and the ensuing mechanical energy are produced inside the engine.

Inversion Layer : Layer of cool air is trapped by a layer of warm air above it. The warm air prevents the cool air from rising and dispersing, thereby trapping the cool air and it's pollutants.

Julian Day : A number that represent the day and month of the year calculated in chronological order.

Knock : It occurs when the gas during the compression stroke is burnt by compression instead of a spark from the spark plug, before optimum ignition point is reached.

Ozone : It is an air pollutant that is produced as a result of photochemical processes. It is a pungent, toxic and colourless gas.

Particulate : A particle of solid or liquid matter in air between 0.01 - 10 micron in diameter.

Photo- multiplier Tube : It is a device which converts the light energy to an electrical signal. The resulting current is amplified and is displayed or recorded.

Piston : It is a part made from cast iron or aluminum alloy that is able to withstand high temperatures and pressure so that it can be transferred to the crankshaft.

Photochemical Process : The chemical changes brought about by the radiant energy of the sun acting upon various polluting substances. The products are known as photochemical smog.

Pollution Episodes : Occur when the concentration of polluting substances interferes with the well being of people over a given period.

Relative Humidity % : It is the ratio between the partial pressure of water vapour and water vapour saturation pressure.

Sensitivity : When the concentration of a particular element of solution absorbs 1% of incident radiation.

Shapiro-Wilk Test : Is a test designed to detect departures from normality without requiring that the mean or variance of the hypothesised normal distribution be specified in advance.

Smog : The irritating haze resulting from the sun's effect on certain pollutants in the air, mainly emitted from the motor vehicle exhaust. Also a mixture of fog and smoke.

Topography : The configuration of surface, including its relief and position of its natural and man made features.

1.1 Aim

There are a number of pollutant gases in the atmosphere originating from variety of sources. Some of these pollutant gases are NO_X from motor vehicles, SO_2 from smelters, HCl from chemical industries, HF from aluminium plants and H_2S from smelting operations[1]. There is a perception by the general public that industries are the major source of air pollution. This may be so in highly industrialised areas. However recent studies[2, 3] indicate that motor vehicle emissions contribute significantly to the pollution of the atmosphere. The objective of this study will be to highlight the need to focus on air pollution control from industries as well as from motor vehicle emissions. The latter will be achieved by assessing the impact of the motor vehicle emissions on the quality of air at selected traffic intersections in the Durban Metropolis. Furthermore the quality of the data obtained by using a specific type of passive sampler will be assessed. It is envisaged that this study will also reinforce the importance of environmental management in the government of an industralised metropolis.

In pursuance of these aims this study will evaluate motor vehicle- related pollution by:

- measuring the concentration of nitrogen dioxide as an indicator of gaseous pollution at selected major traffic intersections and along busy roadways in the Durban Metropolis.

- comparing the above values to guidelines stipulated by the Department of Environmental Affairs and Tourism (DEAT).

- measuring the concentration of particulate lead.

- comparing lead concentrations to the US-EPA standards.

- investigating the effect of distance from the kerb on the concentration of gaseous pollutants.

1.2 Objectives

- To assess the cost effectiveness and reliability of the passive sampling technique in comparison with the active sampling technique when measuring the concentration of nitrogen dioxide as an indicator of gaseous pollution.
- To identify suitable sites for the location of samplers in future monitoring.
- To identify areas where emphasis for future traffic related investigations should be undertaken in view of the potential to exceed guideline values.
- To assess the importance of implementing an effective Environmental Management System within an organisation

1.3 Salient aspects pertinent to this study

To provide a background to the aims and objectives of this study a brief discussion of the following aspects of the project is given.

1.3.1 Air Pollutants and Air Quality

The composition of ambient air in a pristine atmosphere should be of 78% nitrogen, 21% oxygen, 0.03% carbon dioxide and traces of other gases and water vapour[4]. This composition may however differ from area to area due to the impact of pollution. In urban areas[5] motor vehicles are considered a major contributor to air pollution. Pollutants in the atmosphere may be present in the form of gases or particulates[6]. In addition to NOx motor vehicles are responsible for the emission of other pollutants such as carbon monoxide (CO), hydrocarbons and particulate matter. Particulate matter are known[5] to contain lead (Pb) species as one of the toxic components. Particulates may however be present as liquid droplets or solid particles[7]. Both gases and particulate pollutants may be primary, secondary and precursor[6], depending on their emission source. Some of these pollutants are emitted directly into the atmosphere while others are emitted as precursors. The latter are the source of secondary pollutants due to a variety of chemical reactions[5]. Primary pollutants are those that are emitted directly into the atmosphere from a known source and remain unchanged eg. nitric oxide. Secondary pollutants are formed as a result of chemical reactions between primary pollutants and the atmosphere eg. nitrogen dioxide, sulphur dioxide and ozone. Precursors are formed when substances emitted into the atmosphere undergo changes to form pollutants eg. nitrogen oxides.

1.3.1.1 Gaseous Pollutants

All oxides of nitrogen[8] are collectively referred to as NOx. A principal oxide of nitrogen is nitric oxide(NO). Nitric oxide is derived from the oxidation of nitrogen (N_2) in the air within the engine of the motor vehicle as well as that present in petrol[9]. NO_2 is one of the oxides of nitrogen formed at high temperatures during the combustion process[9].

$$2NO + O_2 \rightarrow 2\,NO_2$$

Some pertinent oxo-components of nitrogen are nitrites, nitrates, N-nitroso compounds and peroxyacyl nitrates[9].

Nitrogen dioxide, considered the most dangerous oxide of nitrogen[4] is a reddish brown gas with a pungent odour[9]. It has been reported to damage metals, archival and artistic materials[9]. Several reports have indicated NO_2 as one of the components responsible for producing brown haze, that affects visibility in ambient air in certain areas[9]. Nitrogen dioxide is an irritant and may contribute to respiratory problems[9]. It also forms particulate nitrate salts. Nitrogen dioxide is corrosive and highly oxidising. It's low partial pressure prevents condensation[9]. Nitrogen dioxide is a known toxic substance and is harmful to human health[10].

Both NO and NO_2 are more prominent in polluted atmospheres than other oxides of nitrogen[9]. Hence this project will concentrate on nitrogen dioxide.

1.3.1.2 Particulate Pollutants

There are a number of metal species in the atmosphere originating from a variety of sources. The toxicity of these metal species depend on the chemical composition of compounds and the concentrations in which they are present in the atmosphere. Some of these metal species[7] are lead, beryllium, arsenic, silver and tin.

Lead species are present in particulates emitted from the motor vehicle exhaust. The source of lead is from compounds which are added to petrol. The particulates in which the lead are found are formed in the cooling exhaust gases of motor vehicles. The particulates may be emitted directly into the atmosphere or may be deposited on the walls of the exhaust where they accumulate until they are emitted. The levels of the lead emitted will depend on the engine design, engine age, driving pattern and weather conditions. Larger particulates are deposited closer to the source while smaller particulates travel longer distances[11].

"Criteria pollutant" is a term given to pollutants which are commonly known to be harmful to human health[6]. These pollutants are SO_2, $NO_{X,}$ CO, particulate matter (PM) such as lead. Their toxicity depends on the concentration of the pollutant and the length of exposure.

The harmful effects of pollutants on the environment depend on their source, physical form and toxicity. The sources of air pollution[6] can be anthropogenic or natural. Anthropogenic sources are man made and originate from transportation, stationary source fuel combustion, various industrial processes, solid waste disposal and forest fires. Natural sources originate from lightning, biological processes in soil and releases from the ocean.

Although air quality is a vital factor for promoting a healthy life yet little cognisance is taken of the effect of our activities on the environment. Short term demands such as the need for increased housing, expanding industrial infrastructure and transport takes precedence over air quality. These activities when not adequately managed, lead to a range of environmental problems like degradation of air quality, increased atmospheric pollution and damage of buildings and vegetation. An article in the Sunday Times (1 March 1998) highlighted poor air quality of some urbanised and industrialised areas like Gauteng and the Vaal Triangle in South Africa where the pollution levels matched some of the world's most polluted cities like Bangkok, Beijing, Mexico City and Sao Paulo. The article went on to stress the risk of communities living and working in such areas where the level exceeds the guidelines laid down by The World Health Organisation (WHO) and United States Environmental Protection Agency (US-EPA).

1.3.2 Legislation Governing Air Quality

The National Environmental Management Act[12] no.107 of 1998 states clearly that ".....everyone has the right to an environment that is not harmful to his or her health or well being". The Act goes further to state: "... everyone has a right to have the environment protected, for the benefit of present and future generations, through reasonable legislative and other measures that prevent pollution and ecological degradation, promote conservation and secure sustainable development and use of natural resources while promoting justifiable economic and social development...."

The Air Pollution Prevention Act[13] of 1965 regulates the control of noxious and offensive gases emitted from industries, the control of smoke and wind borne dust pollution and pollution from diesel vehicles. It should be noted that the latter is only regulated in selected cities in the country , while the former is controlled by a permit system. The implementation of the Act is monitored by the Chief Air Pollution Control Officer under the Department of Environmental Affairs and Tourism (DEAT). There are several government initiatives on a national scale which are driving the need for the manufacture and use of cleaner fuels. The above Act together with a policy on Integrated Environmental Management are being re-assessed[14] by a task group of air quality professionals.

The Environmental Management System[15] (EMS) ISO 14001 defines the environment as "a surrounding in which an organisation operates". This incorporates the air, water, flora, fauna, humans and their interrelations. The interaction between humans and their interrelations with the environment are bound to impact either positively or negatively on the surrounding. The implementation of an effective EMS represents a crucial tool to manage an organisation's impacts on the environment. However it must be implemented, monitored, evaluated and maintained at all levels for any potential impacts that an organisation may have on the environment. The effect of disregarding environmental management has resulted in massive clean up and relocation at costs to many organisations[4].

1.3.3 Air Quality Management

Prolonged exposure to relatively high doses of polluted air is hazardous to the health of people living under such conditions. In order for communities and industries to co-exist harmoniously all the role players must come together and be made aware of the mixture of pollutants in the atmosphere, their levels and their emitters. This can form the basis for discussion on air pollution control and ensure accountability for pollution incidents in the long term. However air quality is a complex issue. Evaluation of pollution levels should be aimed at providing clear and enforceable guidelines for industrial emissions. This should result in the:

- creation of a conducive environment for people working in or living close to such industries.

- development of a management system to minimise the levels of air pollutants. This plan must include monitoring of air quality, maintaining of emission inventories, town planning and pollution models.

An air quality management strategy must focus on emission inventories, regulatory control, modelling, monitoring and town planning. A strategy which integrates the above initiatives would represent a basic input to the air quality control plans and development of an abatement policy. Emission inventories would help to determine the design of the monitoring system, enable regulatory control and can be used for modelling which estimates human exposure. The monitoring program serves as a means to quantify the air pollution. Town planning is considered because abatement strategies have to be designed based on development of an area and air pollution levels specific to that area.

The air quality management strategy must facilitate collection of historical trends, compliance, evaluations, verification and control strategies. These inputs[16] can be achieved by:

- Defining the indicators to be monitored
- Defining the study area
- Designing a monitoring system
- Procuring, installing equipment and measuring indicators
- Assessing reliability of procedures
- Evaluating results
- Reporting results
- Focusing on future planning for controlling potential incidents.

The course of installing any management strategy with a view to improvement is a journey that never ends[17]. Continuous improvement[18] strategies arise from focusing on each process in a system. This can be seen in the diagram below.

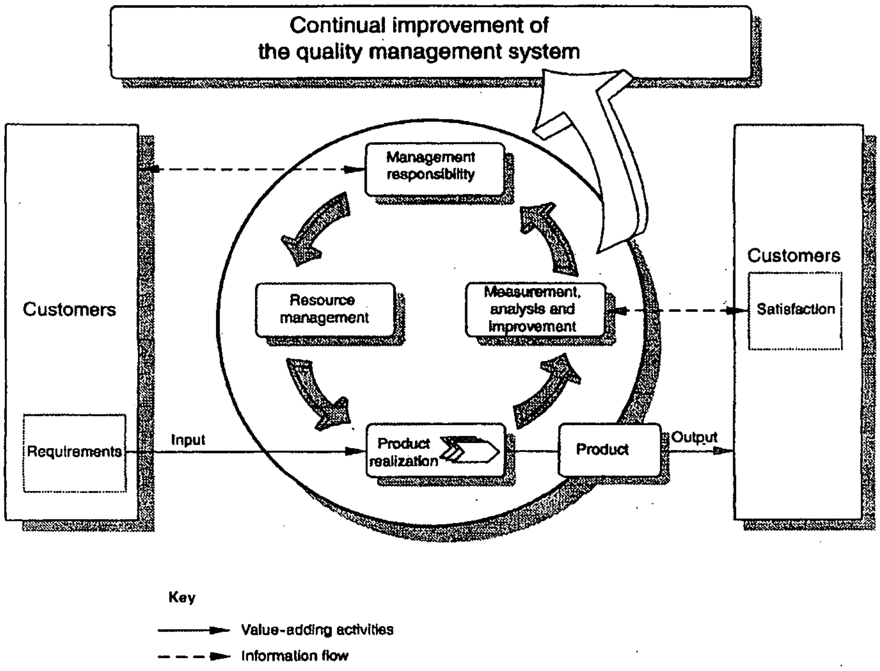


Figure1: Process Model[18]

The steps shown above need to complement each other to ensure an effective system which meets the requirements of both authorities and stakeholders. This process approach helps detect activities prior to them going out of control. According to Harrington[19], 1987 most of the companies who have implemented a process approach have reported improvement. Companies who failed[19] did so because of mismanagement.

Quality gurus Philip Crosby[17] and Joseph Juran[20] emphasise steps for quality planning and improvement in management strategies.

The common steps from both their teachings stress the need for :

- identifying and understanding customer needs
- establishing a unit of measure
- establishing a mechanism of measurement
- establishing a method of evaluation
- optimising the method to measure defined indicators effectively
- proving the reliability of the method

Furthermore quality control must be used when designing any management system. The following questions needed to be answered:

- was the method completed properly?
- did the method work for your samples?
- were the facilities adequate and instruments properly calibrated?

The flow below shows the steps used in designing an air quality management system for this study.

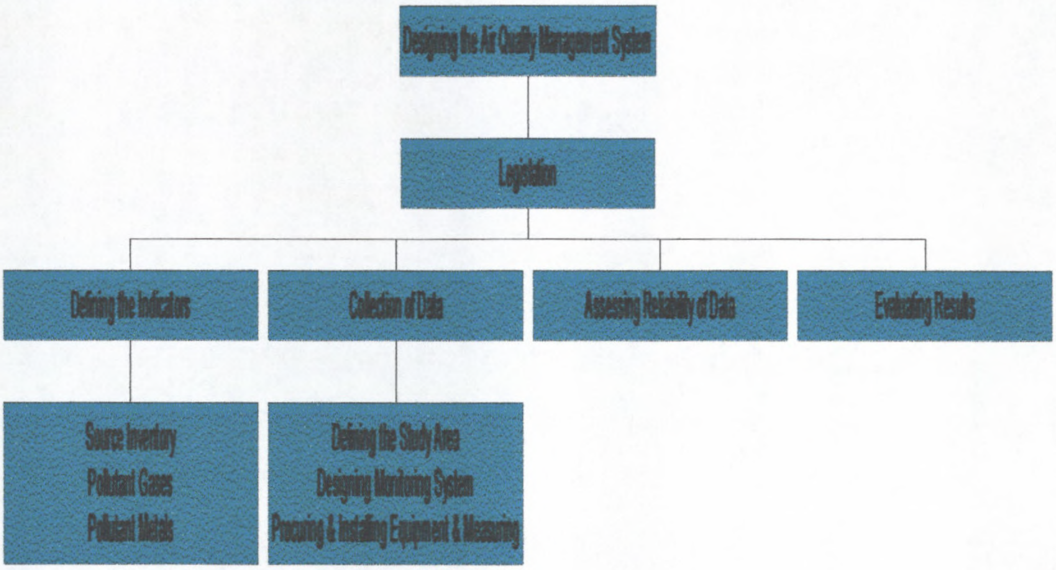


Figure 2: Design of a Simple Air Quality Management System.

Chapter 2 Review of the Literature

This chapter will discuss the background to this study, motor vehicle engines and their emissions, selected pollution episodes, techniques of air sampling and studies involving passive sampling.

2.1 Background to the Study

An inventory of emissions by motor vehicles in the Durban Metro commissioned by the Ethekweni Municipality. This study provided a Metro wide air pollution source emissions inventory[2] for the Unicity which revealed the following distribution for sources of NOx : 74.7% from motor vehicle emission, 20.6% from industrial processes and 4.7% from other mobile sources.

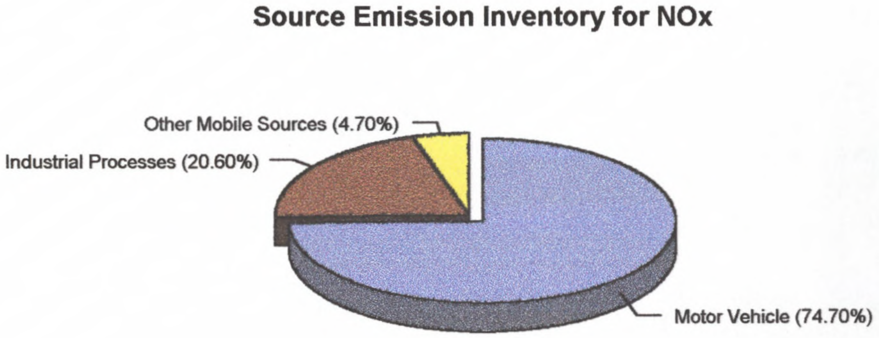


Figure 3: Source Emission Inventory for Oxides of Nitrogen

Another study[21] was commissioned by the Ethekweni Municipality to measure NO_2 concentrations at 119 selected sites. The emissions inventory resulting from this project showed that motor vehicle emissions were the major source of NOx in the atmosphere. It was also found that the highest NO_2 concentrations were recorded at sites closest to the roads[21] in urban areas.

2.2 Engines and their Emissions

In 1862 Beau- de- Rochas developed[22] the internal combustion engine. He laid down specific rules to ensure maximum efficiency of the engine. The first successful petrol engine was invented by Charles.E Duryea in 1892.

2.2.1 Composition of Petrol

When crude oil is refined it produces hydrocarbon varying in nature from gases to waxes. Petrol is made up of a mixture[23] of alkanes and cycloalkanes.

To meet the demand for high performance by motorists, the quality of petrol is maintained at a superior level by strategies used to boost the octane rating. The octane rating determines how far the petrol can be compressed during the combustion process before it ignites from compression instead of igniting from the spark plug. Ignition from the spark plug represents optimum ignition. Thus ignition by compression only, causes the engine to knock. Knocking is an undesirable condition because it can cause damage to the engine. Therefore, petrol with high antiknock qualities are desired. This has and is still being addressed in many countries by the addition[22] of tetraethyl lead-$Pb(C_2H_5)_4$.

Motorists in South Africa currently have a choice of using leaded or unleaded petrol. The South African Bureau of Standards (SABS) and stakeholders are responsible for the development of specifications in respect of production and marketing petrol in South Africa[23]. The specification of leaded petrol is set by SABS 299. It states that " the maximum lead content in leaded[23] petrol may not exceed 0.4gPb/l ". The specification of unleaded petrol is set by SABS 1598. It states that " the maximum lead content in unleaded[23] petrol may not exceed 0.013gPb/l".

2.2.2 The Formation of Pollutants from Internal Combustion Process.

This section will discuss the formation of nitrogen dioxide, other gaseous pollutants and lead particles during the internal combustion process. It will also describe the formation of nitrogen dioxide in the atmosphere.

2.2.2.1 The formation of Nitrogen dioxide

A motor vehicle obtains its power from an internal combustion process[24] within the engine. In this process petrol or diesel is ignited[25] in the compression step; the other steps by which an engine operates, being suction, expansion and exhaustion. Prior to the compression stroke, air and petrol are mixed to desired combinations by a carburetor or by a fuel injection system. During the combustion process which involves high temperatures, nitrogen (N_2) in the air of the engine chamber is oxidised to form small amounts of NO. The quantities of NO formed depend on the air to petrol ratio during combustion, the N_2 content of the petrol and the air[9].

The combustion of N_2 from the air in the engine cylinder is described [9] by the Zeldovitch mechanism - (1946).

$O_2 + M \rightarrow 2O + M$ M represents nitrogen found in petrol.

$N_2 + O \rightarrow NO + N$ N_2 represents nitrogen from the air in cylinder.

$N + O_2 \rightarrow NO + O$

Some NO is oxidised to NO_2 before reaching the tailpipe of the exhaust and small volumes of NO are also released with exhaust gas and oxidised[9] in the atmosphere to NO_2. The gases produced in the engine[7] are emitted to the atmosphere via the exhaust. During accelerating and cruising, the engine demands higher revolutions of the crankshaft per minute to maintain speed. This is achieved by increasing the air to petrol ratio and the airflow into the engine. Therefore, NO concentrations are much higher during cruise and acceleration as opposed to deceleration and idling[7].

2.2.2.2 Nitrogen dioxide in the Atmosphere

Smog is a common feature present in polluted environments[7]. It is an irritant resulting from a mixture of fog and smoke[7]. The levels of smog in the atmosphere depend on the extent of inter- reactions among sunlight, hydrocarbons and NO_2 in the air. Hydrocarbons and NOx pollutants are chiefly formed in and are emitted by the motor vehicle exhaust[7].

When there is an accumulation of the primary pollutant NO in the atmosphere, especially during calm mornings, the concentrations of secondary pollutants like O_3 and NO_2 are very small due to the absence of sunlight. As the sun rises and the conditions become hotter, NO_2 is generated. The NO concentration is depleted and the concentration of NO_2 in the atmosphere increases and peaks[10]. Sunlight dissociates NO_2 to form NO and atomic oxygen (O). Oxygen reacts with diatomic oxygen to form O_3, a photochemical pollutant. The concentration of O_3 peaks at midday[1] when ambient temperatures are normally highest.

During this period the NO_2 concentrations are depleted by the following mechanism:

$$NO_2 + hv \rightarrow NO + O$$

$$O + O \rightarrow O_3$$

As the afternoon traffic volumes increases, the NO concentration increases. NO reacts with diatomic oxygen to form NO_3 radical. The NO_3 radical is short lived and reacts with diatomic oxygen to regenerate NO_2[1] as shown by the reactions below:

$$NO + O_2 \rightarrow NO_3^*$$

$$NO_3 + O_2^* \rightarrow NO_2 + O_3$$

According[1] to Cradle and Johnstone NO_2 can also be formed by the following mechanism.

$$NO + O_3 \rightarrow NO_2 + O_2$$

2.2.2.3 The Formation of Other Gases.

The other gaseous components[7] of the exhaust compartment are carbon dioxide, water vapour, hydrogen, unburned and partially oxidised hydrocarbons and sulphur dioxide (SO_2) as well as un-reacted nitrogen and oxygen. The SO_2 is derived from the reaction between sulphur in the crude petroleum and the oxygen in the air during the combustion process. Carbon monoxide is present in the exhaust as a result of incomplete combustion in the chamber.

2.2.2.4The Formation of Particulates

Lead particulates are formed when the petrol is burnt[7]. The diameter of lead particulates range from 0.01 to 5.00 μ. Small quantities of these particulates may adhere to the walls of the exhaust. When these exceed a critical mass they fall off or are blown out of the tailpipe of the exhaust. Larger quantities of lead are emitted via the exhaust at varying times and speeds of the motor vehicle. Lead particulates[7] have been shown to contain PbCl.Br, α and β $NH_4Cl.Br$, 2 $NH_4Cl.PbCl.Br$ and $3Pb_3(PO_4)_2.PbCl.Br$.

2.3 Selected cases of Pollution involving Nitrogen Dioxide and Lead

This section highlights events from different parts of the world, where pollution incidents from anthropogenic sources have impacted on the lives of people living nearby.

2.3.1 Selected episodes of pollution involving Nitrogen Dioxide (NO_2)

In 1943 a new environmental feature was encountered in Los Angeles. It was referred to as a 'new type of pollution'. The feature became known as 'smog'[1]. Los Angeles is an area that has congested surroundings and high traffic volumes[1]. This led to the accumulation of pollutants in the air. By1944 people started to become aware of the presence of 'smog'. This 'smog' produced a 'blue haze' that affected visibility and persisted during what was termed 'smog' episodes. Reduction in visibility during the 'smog episodes' could have had possible hazardous effects during driving. In addition, during 'smog episodes' people complained of sore throats, runny nose and eyes and headaches[1]. Air pollution personnel suspected 'smog episodes' to be SO_2 related and instructed industry to reduce SO_2 emissions; however the 'smog' persisted[1]. Later investigations showed that petrol vapour, with NO_2 and other reagents in the presence of sunlight was the major contributor to the 'smog'[1]. In an effort to prevent this occurrence, scientists and air pollution personnel subsequently restricted the amount of vapour emissions escaping from petrol storage tanks from refineries[1].

Cities in Western Europe often experience high NO_2 concentrations especially during winter. In December 1991, in London, hourly NO_2 concentrations of 423 ppb were reported[26]. The current NO_2 guideline for an hourly average stipulated by DEAT for South Africa is 200 ppb.

Hutchinson and Clewley[27] collected data from various sources of air pollution during studies in the West Midlands of the United Kingdom. They concluded that road traffic was the main source of atmospheric air pollutants. They found for instance that almost all (over 96%) of CO, benzene and buta-1,3-diene comes from traffic emissions. In the case of NOx road traffic emissions account for about 85 % of this pollutant.

Laboratory tests on asthmatics showed altered responses in their airways when they were exposed to NO_2 concentrations between 0.11 and 0.20 ppm for one hour[28]. There is no evidence linking mortality with high NO_2 'smog' days[28]. However, eye irritations, sore throats and impaired respiratory function have been reported during ‘high smog’ days[28].

In the presence of moisture NO_2 forms a nitric acid (HNO_3) solution as indicated by the following equation.

$$2\,NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Air laden with HNO_3 can irritate the lungs and can corrode metal surfaces due to its acidic properties[9].

It is believed that NO_2 in the presence of excess O_3 and moisture reacts as follows to form nitric acid[9].

$$2\,NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

2.3.2 Selected episodes of Pollution involving Lead (Pb)

Lead poisoning via water and air pollution has been well documented. The first anecdotal account of lead as a poison dates back to the fall of the Roman Empire. Lead was assumed to be leached out from water pipes used by the Roman aristocracy[29]. Since then there have been claims that lead is responsible for some types of neuropsychological impairment[30].

Inhaled lead is more readily absorbed by the body than lead that may be ingested[31]. Lead particles 1 μm in diameter or less are able to reach the alveoli of the lungs and are transported into the bloodstream. Irritability, nervous paralysis, anemia, miscarriage, mental retardation, cerebral palsy and atrophy of the nervous system have been reported in cases of lead poisoning[28].

Increased lead loadings in blood levels of humans have also been associated with cardio-vascular problems and poor circulation of red blood cells[10]. Surveys in California have associated lead poisoning with coughing, sinus trouble, headaches, throat complaints, stomach complaints, shortness of breath, nose complaints, hay fever, allergies, eye complaints, chest pains, bronchitis and asthma[10]. Investigations later traced some of these complaints to particular lead pollution incidents[10]. Lead is a known toxic substance and is harmful to human health[10].

Lead is the most common heavy metal in the atmosphere. Although small quantities of lead are emitted from industries the emissions from the motor vehicle exhaust is considered the major source[28].

An epidemiological and environmental study in the cities of Los Angeles, Cincinnati and Philadelphia revealed blood lead levels of populations in urban areas to be higher than blood lead levels of populations in rural areas. This report also stated that men had higher blood lead levels than women. No reasons were given for the latter observation. Studies in one of the cities showed people living in the centre of the city reported higher blood lead levels than people living upwind from the center of the city. The study concluded that the blood lead levels are proportional to the lead in the atmosphere and exposure to the pollutant[10].

A study in Los Angeles showed people living within 76.2m away from the freeway had higher blood lead levels than those living further away from the freeway[10].

2.4 Air Sampling and Analysis of Samples.

Air can be sampled actively, using suction pumps and passively by using diffusion tubes. The principles of operation of passive and active samplers and analysis methods available are described below:

2.4.1 Types of Passive Samplers

Passive sampling has been widely used throughout the world to measure ambient and indoor air quality. There are different types of passive samplers. The most commonly used samplers are the Palmes Tube and the Yanagisawa Sampler

2.4.1.1 The Ogawa Passive Sampler

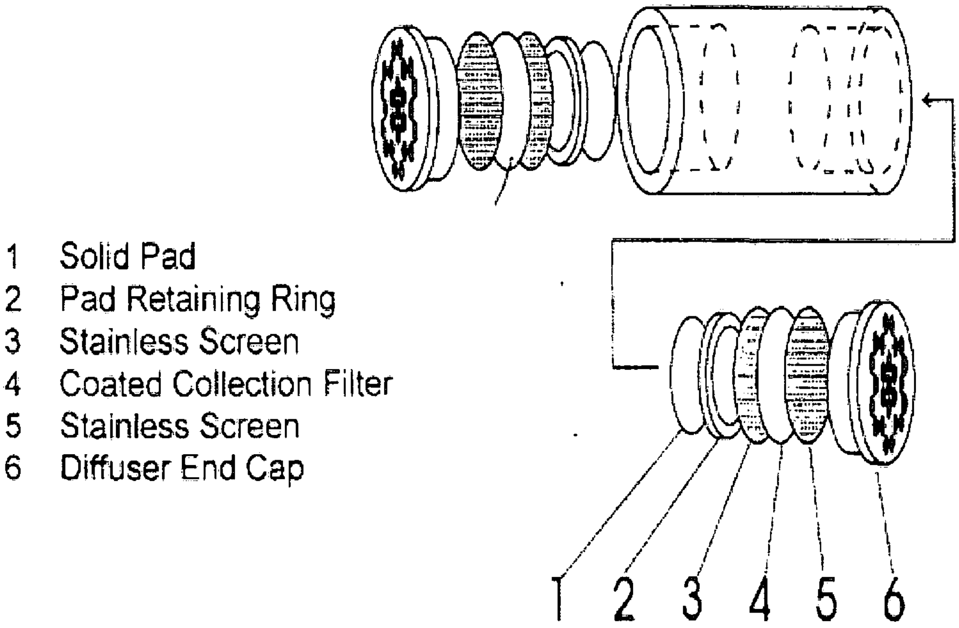


Figure 4: Components of the Ogawa Passive Sampler

The Ogawa sampler[32] consists of 2 chambers. Each chamber consists of a solid pad, pad retaining ring, stainless steel screen , coated collection filter, another stainless steel screen and a diffuser cap. The assembly of components within the chamber must follow the sequence above starting with the solid pad and moving outward.

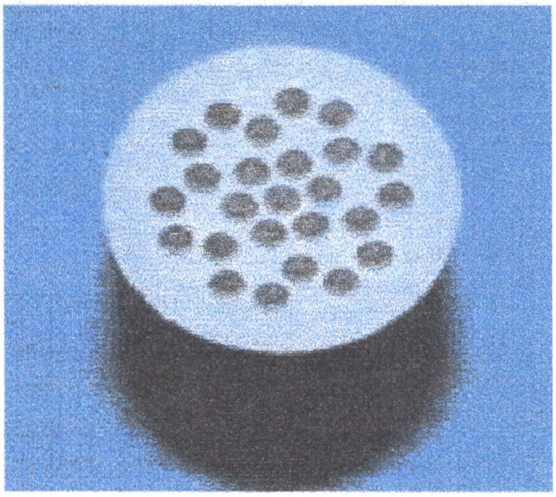


Figure 5: Illustration of Diffuser Cap in Ogawa Passive Sampler

Nitrogen dioxide from ambient air is absorbed onto the exposed filter through a diffuser cap with holes of known path length and cross sectional area onto a filter impregnated with triethanolamine (TEA). The path length and cross sectional area are used to determine the conversion coefficient which is required in the calculation of the concentration of NO_2. The NO_2 on the filter is converted into NO_2^-. Glasius[18] *et al* investigated this conversion and reported the mechanism as follows:

$$\mathbf{2\,NO_2 + N\,(CH_2\,CH_2\,OH)_3 + 2OH^- \rightarrow 2\,NO_2^- + {}^-O - {}^+N\,(CH_2\,CH_2\,OH)_3 + H_2O}$$

The reaction occurs in a ratio of 1:1 from NO_2 to NO_2^-. Exposed filters are extracted with distilled water for NO_2^-. It was also stated that hydroxyl ions are possibly formed from the dissociation of TEA in purified water. They also reported that this mechanism was supported by Palmes and Johnstone, 1987. The sample solutions are treated with sulphanilamide, 1-napthylene-diamine-dihydrochloride (NEDA) and the absorbance read spectrophotometrically at 545nm.

Detection is based on the principle[33] of diazotisation and coupling. The diazotisation product is formed by the reaction between sulphanilamide and the nitrite radical. When diazotisation is complete, the product is coupled with N - (1 - Naphthyl)- ethylenediamine dihydrocloride. This coupling leads to a product with a reddish pink colour. The mechanism[34] is shown below.

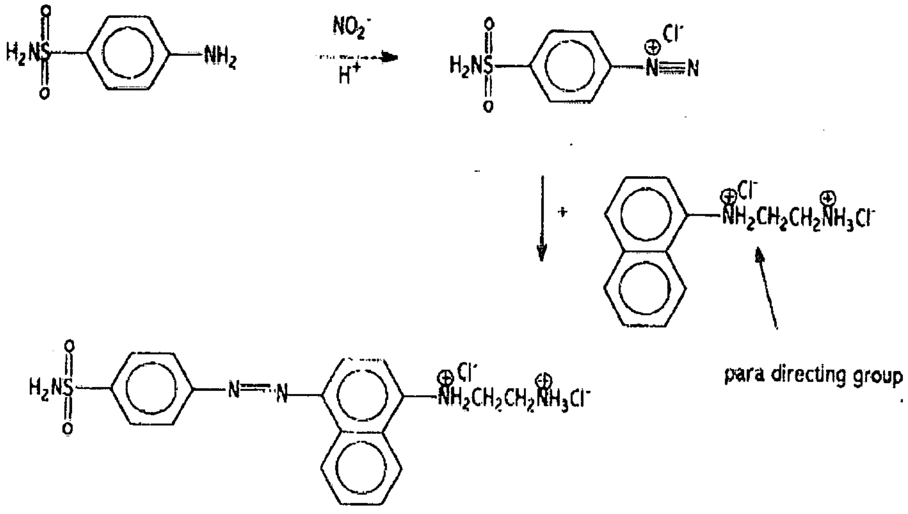


Figure 6: Diazotisation and Coupling for Concentration of Nitrite

Although the Ogawa passive sampler is not as widely used as the Palmes and Yanagisawa passive samplers the supplier has claimed that there is:

- a direct relationship between NO_2 collected and the collecting speed[32] as shown in Fig. 7.
- a linear relationship between collecting coefficient[32] of NO_2 and relative humidity and temperature[32] as indicated in Figs. 8 and 9 respectively.

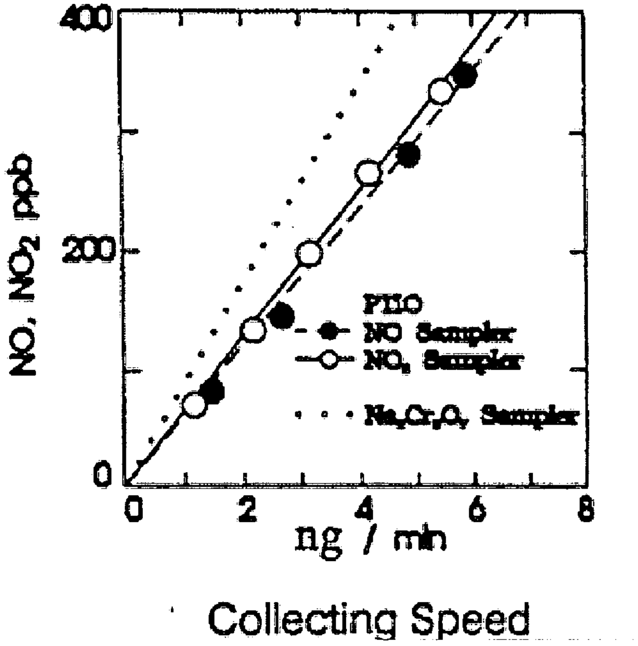


Figure 7: Concentration exposure and Collection Rate

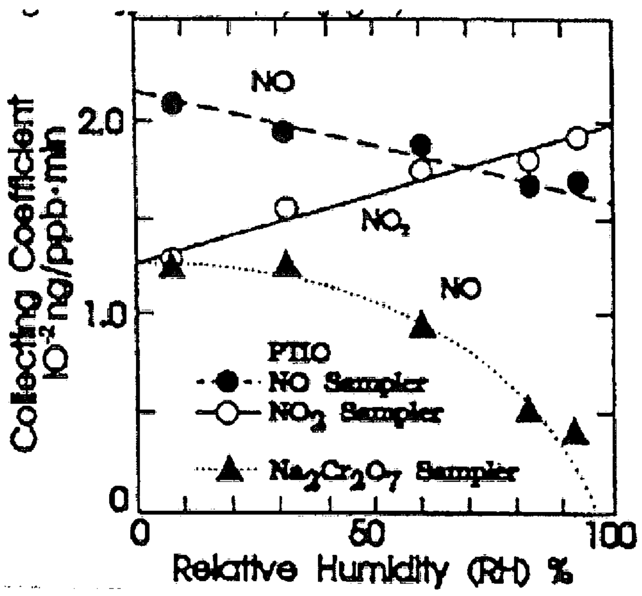


Figure 8: Relation of Relative Humidity and Collecting Coefficient

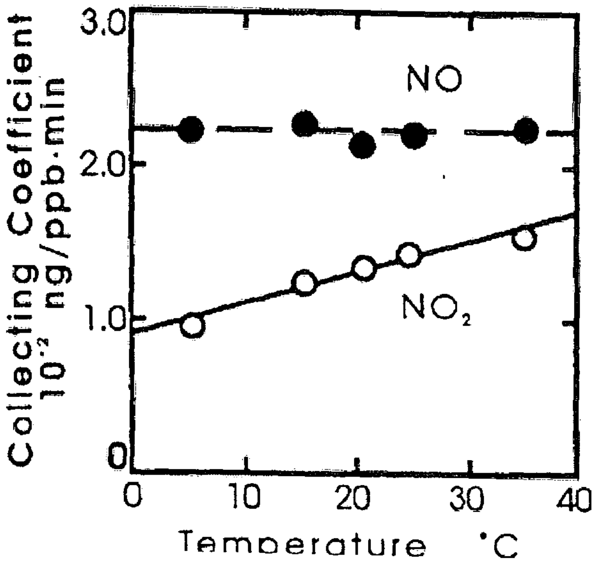


Figure 9: Relation of Temperature and Collecting Coefficient

2.4.1.2 The Palmes Tube Passive Sampler

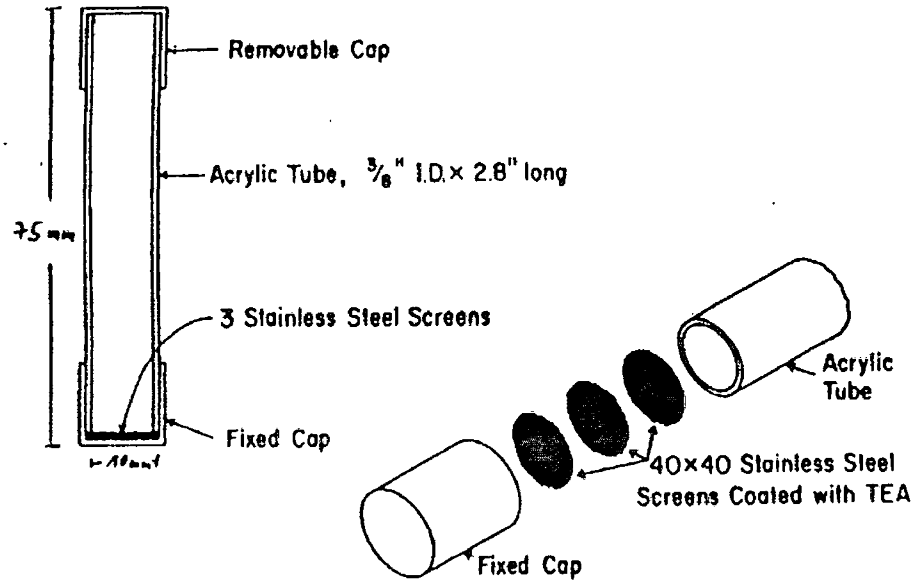


Figure10: Palmes Type Passive Sampler

The Palmes tube has been widely used to evaluate NO_2 concentrations in work place and personal exposure monitoring. This tube was developed[36] in 1976 by E D Palmes. The sampler consists of a hollow acrylic tube 71 mm in length and 11mm in diameter. Three stainless steel meshes are enclosed by caps on either side of the hollow cylinder. The meshes are preconditioned with 33% triethanolamine (TEA) in ethanol and dried before use. Samplers are covered with stainless steel bowls to prevent the entry of moisture and to minimise the effects of wind turbulence since the Palmes Tube has been known[9] to be sensitive to wind speed, Peroxyacetylnitrate (PAN) and nitrous acid (HNO_2). Peroxyacetylnitrate and nitrous acid are formed when NO and NO_2 are oxidised by chemical reactions in ambient air. Nitrous acid is sensitive to sunlight and is unstable during the day forming OH radicals. In the absence of sunlight, nitrous acid accumulates in air[7]. Ambient air diffuses through the cylinder and is trapped onto the pre-conditioned impregnated steel meshes. Nitrites are extracted directly by adding sulphanilamide and N-(1-Naphthyl)-ethylenediaminedihydrochloride (NEDA) solution into the tube. The nitrite concentration[9] is determined spectrophotometrically at 540 nm.

Detection limits of 0.03 ppm for a 1hour exposure have been reported when the samples were analysed using ICP[9].

2.4.1.3 The Yanagisawa Passive Sampler

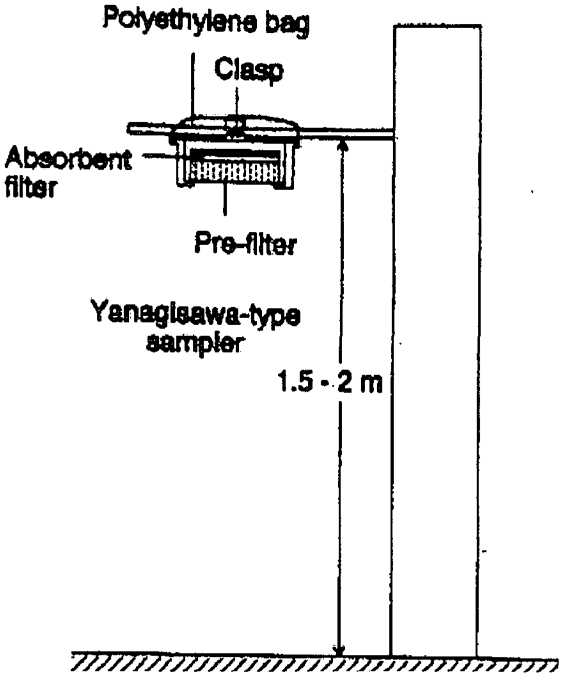


Figure 11: Yanagisawa Type Passive Sampler

The Yanagisawa passive sampler was developed in 1982 by Yanagisawa and Nishimura[9].This sampler consists of a badge and a filter impregnated with triethanolamine (TEA). The badge is composed of layers of hydrophobic teflon-type filter material made from chromium trioxide (CrO_3) and a triethanolamine (TEA) cellulose fiber filter. The five layers of filter type material serve as the interface between the coated filter and ambient air and oxidises NO to NO_2. The NO_2 accumulates by diffusion onto the TEA surface. A polyethylene bag is placed above to prevent the entry of moisture into the sampler[37]. After exposure nitrite ions are extracted with sulphanilic acid, phosphoric acid and N- (1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). The extracted solution was evaluated spectrophotometrically at 540 nm. Detection limits of 0.07 ppm for a 1hour exposure have been reported [9].

2.4.1.4 The use of flow injection for analysis of solutions from passive sampling.

This method of analysis determines the concentration of nitrite by using a simple, sensitive flow injection mechanism[35]. The nitrite sample solution is injected into a carrier solution containing EDTA and ammonium buffer. It is passed through an in-line copperised cadmium reduction column. This is illustrated in the schematic diagram below.

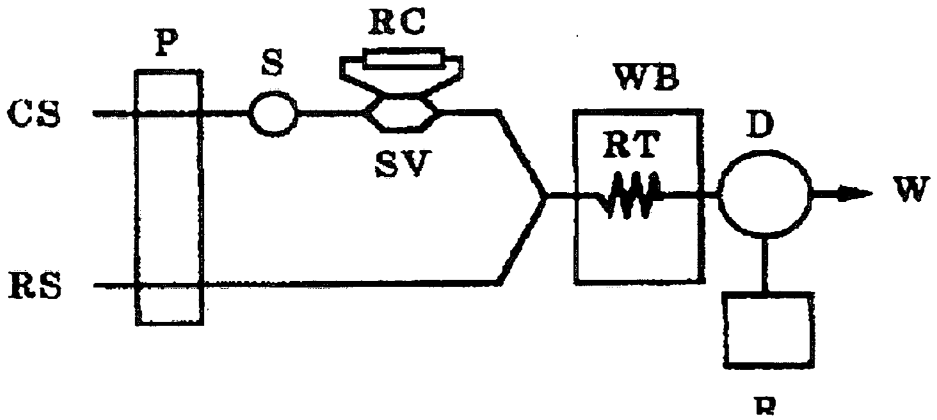


Figure: 12 Flow Injection System

Key:

RS - reagent solution	P - double plunger micro pump
S - sample injector	RC - Cd/ Cu reduction column
SV - column switching valve	CS - carrier gas
D - spectrophotometric detector	W- waste
R - recorder RT - reaction tubing	

The nitrite concentration is determined spectrophotometrically by diazotization/ coupling reaction. This method is able to anlayse 40 samplers per hour and is very sensitive with a detection limit of 5×10^{-8} M. Although the flow injection method of analyses determines the nitrite concentration of samples faster than the method used during this study, nitrites from ambient air still have to be sampled on the pre-coated filters. Hence, this method should therefore be confined to water samples.

2.4.2 Types of Active Samplers cum analysers

There are two types of active samplers. They both use suction to draw in air from the environment. One type of active sampler is designed to collect the particulates in air samples whereas the other type of samples the gaseous part only. The latter are connected to an in-line analysis system. These are briefly described below:

2.4.2.1Greiss - Saltzman Sampler cum anlysers

For the Greiss-Saltzman method[32] sampling involves the use of a pump to draw air through a fritted bubbler type apparatus for a sampling period not exceeding 30 minutes. The air is bubbled into a Greiss- Saltzman solution which is made up of sulphanilic acid, N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA) and acetic acid. The colour forms within 15 minutes and is read at a wavelength of 550nm within one hour of developing.

Although SO_2 and PAN cause interferences, their concentrations in ambient air are too low to cause errors in results. This method is suitable to measure concentrations from 20 ppb to 800ppb over 30 minute sampling period. Diluted sodium nitrite solutions are run as standards and are used during calibrations. Saltzman also reported[32] that 0.72 moles of nitrite was equal to one mole of NO_2.

This method to analyse concentration of nitrogen oxide is not preferred when compared to passive sampling as the former restricts selection of sampling sites in terms of power supply and security.

With some modification, the Saltzman method can also be used to continuously monitor concentration of NO_2. For this method, ambient air is sampled continuously through a gas- liquid set up into a contact solution which collects the NO_2. These solutions are the same as those mentioned above. The basis of detection is also by the principle of diazotisation and coupling. The colour develops and is read continuously on a spectrophotometer. Ozone causes significant interferences, hence this method is not recommended by the US-EPA. The detection limit is 10 ppb. The system can be calibrated by using nitrite standards or NO_2 gas standards, which is the preferred method.

2.4.2.2 The Chemiluminescent Sampler cum Analyser

Since this is the type being used as part of this study, it will be described in detail in section 3.3.1.

2.4.3 Studies using Passive Samplers

This section will deal with studies which compared the passive sampling and active sampling with regard to reliability. It will also discuss the efficacy of samplers in the long term under varying conditions of use.

2.4.3.1 Studies using Palmes Tubes Samplers

The study[38] by Dhammapala et al, 1995 compared passive sampling using Palmes tubes and active sampling involving chemiluminescent analysers. An active analyser was placed at an Eskom monitoring site in Mpumalanga Province. The active sampler was calibrated before and after sampling. At the same time passive samplers were used to determine the NO_2 concentration at the same site.

The duration of this study was 15 days. The passive samplers were exposed for 2, 7 and 15 day sampling periods. The samples collected over 2 days were stored until the 15 day samples were collected and were analysed together. The results of this study are shown in the table 1.

Table 1: Results between active and passive sampling at Eskom Site.

Exposure Period	**Eskom Passive Sampler 1**	**Eskom Passive Sampler 2**	**Ave. Passive at Eskom**	**Eskom Active Analyser**
2	7.6	6.9	7.25	9.6
7	5.1	6.2	5.65	5.4
15	5.8	7.0	6.4	3.8

The above study concluded that the use of the passive sampler is viable. From results it is apparent that they also found storage of samples after collection and prior to analysis did not affect the results markedly.

A study[39] by Hangartner and Burri, 1987 used Palmes passive samplers and did the following:

- Compared data obtained with that from parallel active samplers and found good agreement between the two types of samplers.
- Determined detection limits of NO_2 to be 0.022ppb at 99.99% confidence level.
- Ascertained that addition of values for periods sampled for a whole year gave an annual average comparable with that for active samplers.
- Investigated the effect of storing passive samplers for 4 months after exposure but prior to analyzing and found that the results were not significantly different from data for samplers analysed immediately after exposure.
- Varied the temperature and collected samples (4°C, 22°C and 37°C) and found no effect.
- Noted that changes from wind speeds from 0.5m/s to 4m/s had no effect on the results.

In contrast[40] Moriske and Schondube, 1998 compared Palmes passive sampling to chemiluminescent active sampling under various conditions. Tests were conducted in a closed chamber. NO_2 was dosed into the chamber via a permanent diffusion tube. The first condition tested both the sampling techniques at different temperatures ranging from -10°C to +30°C. Results showed that when temperatures were below 0°C, the passive sampler read between 47.3% to 83% of the active analyser. When temperatures were above 10°C, the passive sampler read 51.9 to 115.7 % of the active analyser. The best agreement between passive and active sampling was reported during temperatures between 23 °C to 30°C when the passive sampling read between 76.8% to 115.7 % of the active analyser.

During the second condition Moriske and Schondube[40] investigated the effects of humidity on passive and active sampling. They tested relative humidites which ranged from 0% to 95 %. The best agreement between both sampling techniques was reported when relative humidities were higher than 30%.

The third condition investigated by Moriske and Schondube[40] was wind speed. They tested both sampling techniques under various wind speeds between 0.05 m/s to 2 m/s. Good agreement between passive and active sampling was reported during above speeds with 98.4 % to 118% agreement between both techniques.

Stuart, Smith[41] et al, 1999 reported that passive sampling to active sampling at 17 sites with similar characteristics in the United Kingdom. Sampling for 2 and 4 week periods produced good correlation as illustrated in the table below.

Table 2: Comparison between different sampling periods.

Exposure Type	Regression equation	Correlation Coefficient (r)
2 week normal	$y = 1.09\ (\pm 0.020)x$	0.99
4 week normal	$y = 1.08\ (\pm 0.062)x$	0.97

y = diffusion tube result   x = analyser result $P = 0.05$

The comparison between passive and active sampling for all exposures showed no difference with a 99.8 % confidence level.

A study[36] by Hansen, Kruse and Lohse, 2001 at three sites in Western Greenland investigated NO_2 concentrations during the period 1 July 1998 to 1 October 2000. Palmes Tubes were located at sites that were typically of an"urban environment". Another was located at a site typical of a "rural environment" and the last was located at a site that was typically a mixture of both types of climates. A fourth site was chosen at a distance of 25 km from the site located in the "urban environment", where there was minimal contribution from any pollutants. Samplers were mounted on traffic poles at a height of 3m above ground level. The tubes were exposed for four weeks and conditioned and measured spectrophotometrically.

The results revealed that NO_2 concentrations were higher in areas where motor traffic concentrations were higher. However lower concentrations of NO_2 were evident at sites away from main roads and highways. All sites demonstrated a seasonal variation with higher values in winter. This is understandable if we note car drivers are obliged to leave their engines idling for many hours of the day so as not to cold start engines in the afternoon. This coupled with the calm conditions facilitated accumulation of increased concentrations of NO_2 in the atmosphere.

2.4.3.2 A Study using the Yanagisawa Passive Sampler

The effects of acid rain on the cedar and pine forests of Hiei Mountains in Kyoto City, Japan was investigated[37] using the Yanagisawa passive sampler by Yamada *et al.* Thirteen sites ranging from the base of the mountain to the summit were selected for this study. Samplers were mounted[37] at a height of approximately 1.5 to 2.0 m above ground level. Field exposure testing was at 2 separate sites. Five pairs of passive samplers were mounted adjacent to the inlet manifold of a active (continuous) analyser at each site. The results from the passive sampler were compared [37] to the active analyser and produced the following linear relationship $y = 0.88x + 1.08$ ($r=0.984$).

Passive samplers were exposed for 30 and 45 days. The relative standard deviations produced for the exposure was 1.4% and 5 % respectively. The study noted that " the results from the passive sampler were almost consistent with the active sampler for a 45 day sampling period hence the sampler was suitable for long term exposure". However no actual results were reported to substantiate this statement in the report.

The efficiency of absorption under different temperatures was investigated[37]. The ratio of passive sampling to active sampling from August to November were between 0.87-1.10 for temperature ranging from 10-30 ^{0}C. The ratio of passive sampling to active sampling from December to February were between 0.73-0.86 for temperature ranging from 4-8 ^{0}C.

There was no change in absorption efficiencies with temperatures ranging from 10 ^{0}C to 30 ^{0}C. However sampler efficiencies were reported to decrease by 10% at temperatures below 10 ^{0}C.

Their results revealed changes in NO_2 concentrations as the day progressed. Higher NO_2 concentrations were obtained between 8h00 to 11h00 and from 18h00 to 22h00. These contributions were related to the emissions from motor vehicles, industry and changing wind patterns in nearby areas[37]. These researchers also found that there was a seasonal variation with winter maximums and summer minimums. The higher results were related to influences by temperature inversion layers at an altitude of 300m from the base of the Mountains while the lower summer values were attributed to the breakdown of NO_2 by OH radicals and sunlight. The NO_2 decreased by half from the base of the mountains to the summit of the mountain[37].

2.4.4 Studies of Lead in Particulates

Briggs and Ellerbeck, 1988 studied[42] the concentration of air borne dust along a roadway in an urban environment. Samplers were placed within 10 m from the roadway. This study concluded that the exposure diminishes as the distance from the kerb side increases.

Studies[11] by Vleggaar et al, 1980 determined that smaller particle sizes travel a longer way in the atmoshpere, while larger particles are deposited a few metres away from the roadside. They further showed that lead content of the dust were derived from petrol additives and obtained higher concentrations of lead at urban or highly congested sites when compared to industrial sites[11]. Their studies also showed a marked seasonal variation[11] with winter maximums and summer minimums, due to more frequent temperature inversions and poor dispersion due to calmer conditions[11].

A study [43] by Von Schirnding, Y, Fuggle, 1984 investigated dust lead levels at 'hotspots' in the Woodstock area of Cape Town. The duration of the study was from May 1983 to June 1984. Sites were selected in urban residential areas with heavy motor vehicle traffic. Dust samples were collected along pavements. Samples were digested in HNO_3 and evaluated on a Perken Elmer AA spectrophotometer at a wavelength of 283 nm. Results revealed highest lead concentration at sites with heaviest traffic volumes. Therefore leaded petrol was possibly the main contributor to high lead levels. Other factors such as the speed of motor vehicles, topography, industrial sources and meteorological factors also contributed to these levels. Hence the planning of residential areas, schools, recreational facilities and informal vendors next to the pavement of streets needs to be controlled and regulated so as to minimise human exposure from emissions near the roadside.

Nriagu , Blankson and Ocran , 1995 reported[44] Algeria, Egypt, Nigeria and South Africa contributed the highest lead emissions in the continent. They also reported that the lead content in petrol in African[44] countries was reported as the highest in the world.

In 1993 legislation set the limit of lead content of petrol in South Africa as 0.4 g/l in contrast to the to the lead content of petrol in the European countries and United States/Canada which were 0.15 g/l and 0.026 g/l respectively, for the same period[44]. South Africa is responsible for 53% of the lead emissions in Africa.

Although the average numbers of vehicles on African roads are less than countries overseas, the age and mechanical condition of vehicles impact severely on the concentration of pollutants in the atmosphere. Studies at bus terminals in Nigeria, indicated very high concentrations of volatile organic compounds such as benzene and CO. Lead levels at bus terminals were not measured but irregular driving patterns and congested streets coupled with the age and mechanical condition of these vehicles will most likely contribute to high levels of lead[44]. Their studies showed Dust fallout lead concentrations in urban dusts as high as 7000 µg/g in Lagos, > 5000 µg/g in Cairo, 4000 µg/g in Nairobi and >1000 µg/g in Tripoli.

In 1995, Nriagu , Blankson and Ocran , undertook studies[44] in Cairo. They found considerable correlation between traffic densities and lead levels in breast milk and lead absorption in infants and children. It showed further that children with sickle cell disease and children with reduced iron intake are more susceptible to toxic lead poisoning. Since both these features are common to Africa, these researchers recommended that more focus should be awarded to controlling emissions and exposure to lead sources[44].

Studies in Cape Town on young newspaper street vendors in urban districts showed considerably higher blood lead levels when compared to young street vendors in sub-urban districts[44]. Investigations between students from rural areas and students in urban areas revealed that blood lead concentrations of the urban students were far higher than the blood lead levels of rural students. In some cases these values were doubled for the urban students. Other studies of blood lead levels between students with schools along busy streets and students with schools away from busy streets showed blood lead levels to be significantly higher in students at schools near busy streets[44].

Studies[45] by Nriagu and Liggans , in1998 found that the main source of urban airborne lead is from leaded petrol. Their study showed interesting information about sources of lead fall out rates at three primary schools in Durban South Industrial Basin. The schools were selected to represent three racial groups living in the area. The schools were located in Bluff, Austerville and Merebank. Duration of sample collection period was from May 1977 to September 1997. This study used dust wipe samples to evaluate levels of dust lead loading ($\mu g/m^2$), dust lead concentration ($\mu g/g$) and flux / lead deposition rates ($\mu g/m^2$). The dust wipe samples were taken over an area of 0.0929 m^2 inside and outside the classroom.

Dust fallout rates were measured on a specially designed table which was at a height of 1m above ground level. Dust was collected over a 2 day period covering an area of 0.0929 m^2. The table was placed outside the classroom. Samples for tests were collected and sent to the University of Michigan for analysis. Samples were digested and analysed using the graphite furnace atomic absorption method.

The dust lead loadings of the schools near the freeway was expected to be the highest, however this was not the case. The school closest to the freeway was Merebank. It had the lowest dust lead loading. The school on the Bluff had the highest value of all three schools. It was therefore concluded in this particular case that factors other than the motor vehicles contributed to the lead levels in this area. Investigations revealed that the schools on the Bluff were painted with lead paints on the exterior only and was painted more frequently than the school in Austerville and Merebank. The total contribution of lead at the school in the Bluff was therefore likely derived from leaded paint and distributed by the wind, rain and the by wear and tear from student usage.

Lead fallout rates were however very different. Merebank had the highest result with Bluff having the lowest result. This was more consistent with other studies[45].

Mathee, Rollin and Levin[3], 2002 investigated the exposure to lead amongst first grade children in schools in Woodstock, Hout Bay and Mitchells Plain in Cape Town. The objective of their study was to determine whether the blood lead levels of children decreased after the introduction of unleaded petrol in that City. Their study consisted of socio-demographic surveys, collection of blood samples, ambient air monitoring at the schools. The study showed significant reduction in blood lead levels in children from 1991 when preliminary studies were conducted to the present. They concluded that the reduction in blood lead levels were attributed mainly to the introduction of unleaded fuel.

Chapter 3 METHODOLOGY

This section will describe the selection of sampling sites, the setting up of samplers used for collecting pollutants, sample collection and storage until analysis. It will also describe the preparation of chemicals and the methods of analysis for determination of concentrations of nitrogen dioxide and of lead. Pre-liminary work investigating the effectiveness of the prescribed method for the evaluation of nitrogen dioxide, the repeatability and reliability of passive sampling compared to active sampling will also be discussed.

3.1 Selection of Sampling Sites

The Metro study[21] of the concentration of nitrogen dioxide in the Metropolis recommended a more detailed evaluation using passive sampling techniques for nitrogen dioxide and particulate monitoring for lead at major traffic intersections. To select the latter, the average number of vehicles at Durban's main intersections per hour was extracted from the Durban Metro Traffic Department statistics (refer to Appendix B for specific traffic counts). Those intersections showing the highest traffic volume and with significantly greater congestion were selected as sampling sites. The map below shows the sampling sites which were selected.

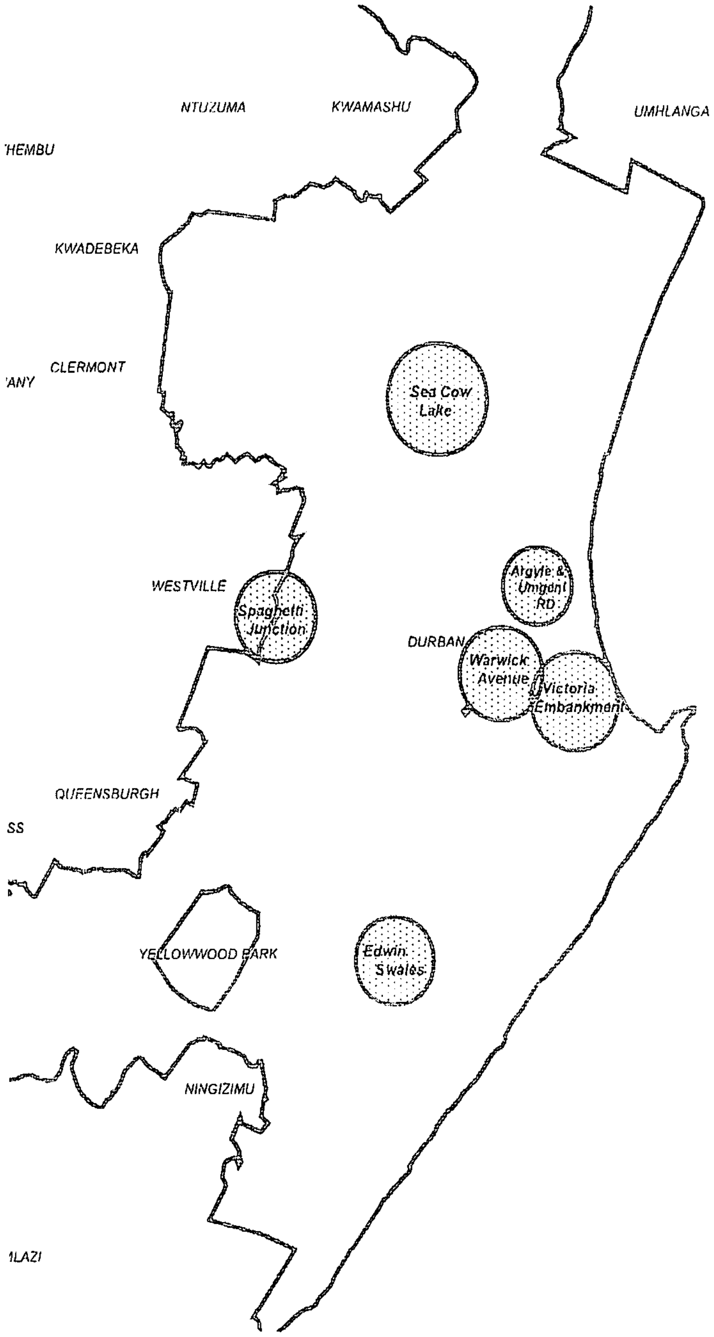


Figure 13: The Map of the Sampling Sites selected in the Durban Metropolis

3.1.1 Selection of Sampling Sites at Traffic Intersections and Motor-ways leading out of the City

3.1.1.1 Traffic Intersections within the City

- Intersection of Warwick Avenue and Cannongate Road- Eastbound - (hereafter referred to as Warwick Ave)
- Intersection of Sea Cow Lake Road and North Coast Road - Eastbound - (hereafter referred to as Sea Cow Lake)
- Intersection of Argyle Road and Stamford Road Intersection - Westbound (hereafter referred to as Argyle)
- Intersection of Edwin Swales Road and South Coast Road - Westbound (hereafter referred to as Edwin Swales)
- Intersection of Victoria Embankment and Gardiner Street - Southbound (hereafter referred to as Victoria Embankment)

The position of each sampler on the traffic light pole at each intersection is illustrated from Figure 14 to Figure 18.

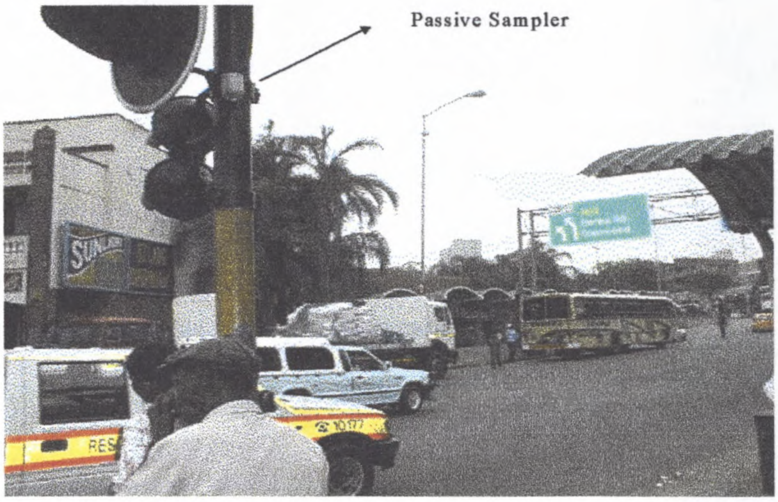


Figure 14: Warwick Intersection

Figure 15: Sea Cow Lake Intersection

Figure 16: Argyle Intersection

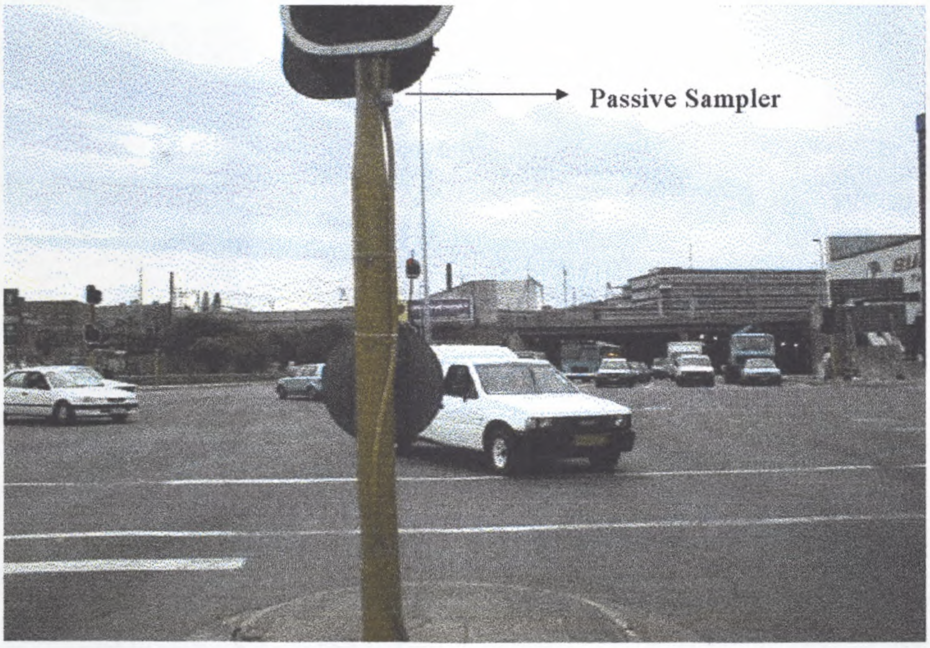


Figure 17: Edwin Swales Intersection

Figure18: Victoria Embankment Intersection

3.1.1.2 Sites on Motor- ways leading out of the City

- Three level interchange - Eastbound, inbound lane at Spaghetti Junction approximately 0.5 km before the 'Sherwood / Mayville' off ramp - (hereafter referred to as Spaghetti Junction)
- King's Park Pool area.

The position of each sampler is illustrated in the figures19 and 20 below.

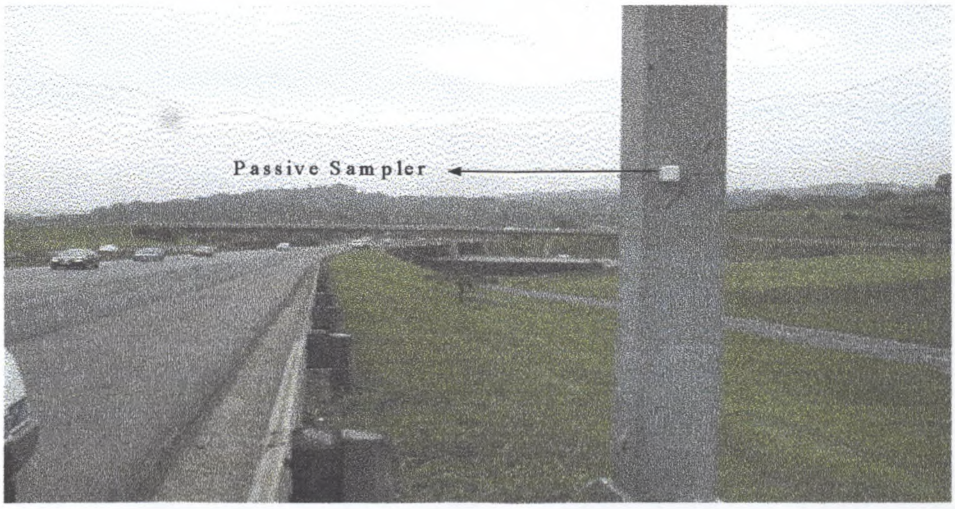


Figure 19: Roadway at Spaghetti Junction

Figure 20: King's Park Swimming Pool

3.1.1.3 Selection of Sites for Parallel Active and Passive Sampling

- Wentworth Reservoir in Boston Road
- Durban Metro Caravan at Settler's Primary School in Merebank

The position of the sampler at Settler's Primary School is illustrated in the Figure 21.

Figure 21: Durban Metro Caravan at Settler's School

3.2 Setting up of Samplers

3.2.1For Passive Sampling at Traffic Intersections and Motor-ways leading out of the City

Passive samplers were secured to electricity and traffic light poles at a height[21] approximately 3 ± 0.7 metres above the ground at all intersections and at a height[21] approximately 3 ± 0.2 metres along the fence poles at the King's Park Pool site.

The distance at which the samplers were mounted from the edge of the pavement were governed by the location of traffic poles and the height of cabling on the traffic poles.

The Kings Park Swimming Pool was selected to investigate the effect of distance on pollutant level from kerbside. This site was selected because it provided a large sampling area which was convenient for placing samplers. NMR Avenue provided the busy roadway / motor-way that represented the first sampling point called the 'Kerb' site. The King's Park Pool field behind the parking area provided the three subsequent sampling points to represent distance inland from the kerbside. The subsequent sampling sites were referred to as 'Fence 1', 'Fence 2' and 'Fence 3'.

Table 3 and Table 4 shows the sites where passive sampling was done at traffic intersections and motor-ways leading out of City.

Table 3: Sites where Passive Sampling was done at Traffic Intersections

Sampling Site	Distance from Edge of Pavement (m)	Height of Sampler above ground (m)
Victoria Embankment	0.6	3.3
Edwin Swales	0.8	3.7
Argyle	0.6	3.4
Warwick	0.7	3.4
Sea Cow Lake	0.5	3.7
Spaghetti Junction	2.3	2.9

Table 4: Sites where Passive Sampling was done at Motor-ways leading out of City.

Sampling Site	Distance from Edge of Pavement (m)	Height of Sampler above ground (m)
Kerb @ King's Park Pool	7	2.8
Fence 1 @ King's Park Pool	40	3.1
Fence 2 @ King's Park Pool	72	3.1
Fence 3 @ King's Park Pool	141	3.1

3.2.2Parallel Active and Passive Sampling at Wentworth Reservoir and at Settler's School

Passive samplers were mounted adjacent to the inlet manifolds of the analysers at both sites. Active analysers were housed within a hut at the Wentworth Site and within a Caravan at Settlers School. The distances at which the samplers were mounted from the edge of the pavement were governed by location of the hut at Wentworth Reservoir and the Caravan at Settlers School. The height at which the samplers were mounted on the roof depended on the position of the inlet manifold on the Durban Metro Caravan and the hut at the Wentworth Weather Station. Table 5 below shows the sites where both passive and active sampling was done. Figure 22 illustrates the housing of the analyser within the Durban Metro caravan at Settler's School.

Table 5: Sites where both Parallel Active and Passive Sampling were done.

Sampling Site	Distance from Edge of Pavement (m)	Height of Sampler above ground (m)
Wentworth Reservoir	90	4
Settler's Mobile Station	25	4

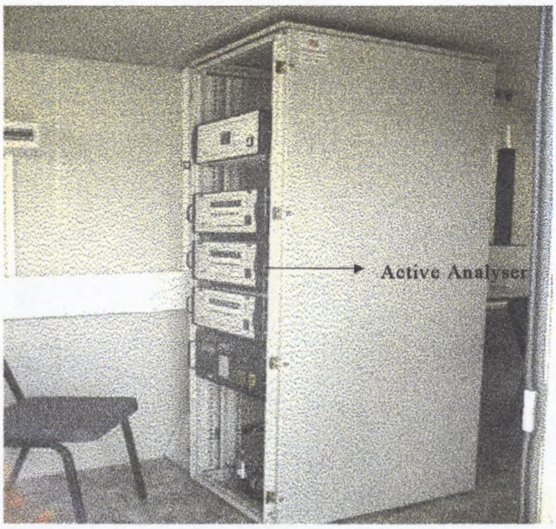


Figure 22: Active Analyser housed within the Durban Metro Caravan at Settler's School.

3.3 Sample Collection

Two sampling techniques were chosen for collecting nitrogen dioxide (NO_2). The two techniques were active sampling using on- line chemiluminescence active analysers and passive sampling using coated filters.

The method of "sweeping the pavement" was chosen for collecting dust to determine the lead (Pb) concentration at selected sites.

3.3.1 Active Sampling

Active sampling involved the use of a chemiluminescence analyser which continuously monitors airborne species.

Figure 23: Front view of Chemiluminescence Analyser

Active sampling involving on- line analysers was used to monitor NO_2. The analyser was stationed in the Durban Metro Caravan which was located at Settler's Primary School in the South Durban Basin. On-line active analysers for NO_2 analysis are expensive. The use of this instrument restricts site selection because it requires relatively large space, power sources and security.

3.3.1.1Operation of the Chemiluminescence Analyser

A chemiluminescence analyser was used to continuously measure nitrogen dioxide concentrations. This active analyser does not detect the nitrogen dioxide concentration directly. Detection of nitrogen dioxide is based on the reaction of NO with ozone (0_3).

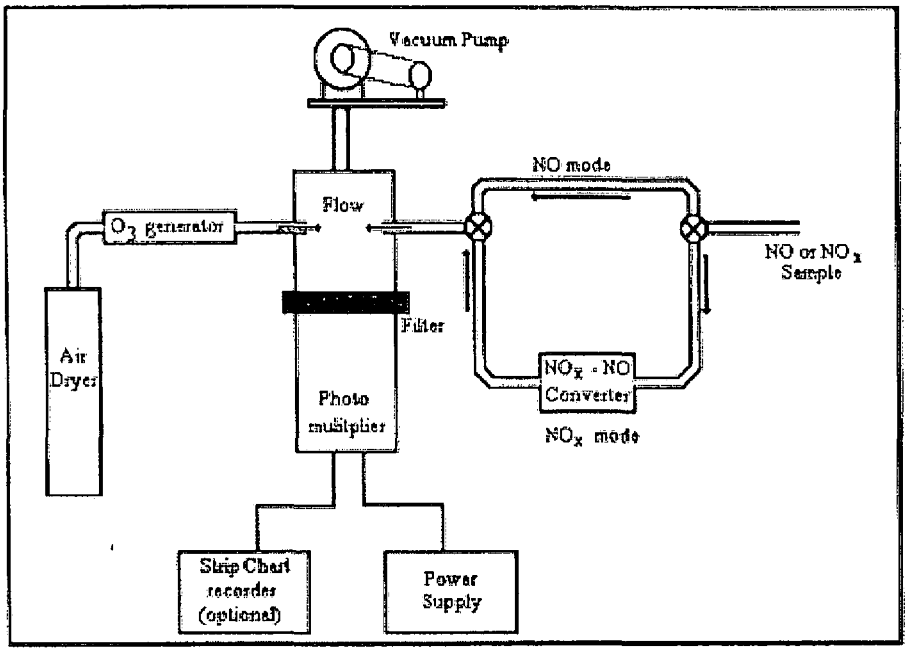


Figure 24: Schematic diagram of Chemiluminescence Analyser[47]

The principle of the operation of the anlyser is given below:

As shown in Figure 24, an ambient stream of air is sampled via a pump system into a vessel. The vessel contains infrared reflective walls and a photo multiplier tube. Ozone is added to the ambient air sample stream containing NO. The result of the reaction of NO with 0_3 is an excited NO_2 radical.

$$NO + 0_3 \rightarrow NO_2^* + 0_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

The output is measured by the photo multiplier tube. This output is proportional to the concentration of NO in the air sampled. This ambient air sample stream is divided in two. One stream comprising of ambient NO_2 is passed through a heated molybdenum strip and any remaining NO_2 is converted to NO. Another measurement is made to determine the concentration of $NO_{X.}$ The difference between the concentration of the NO_X and NO concentration determines the NO_2 concentration. The NO_2 concentration is calculated and displayed by a computer.

$$3\,NO_2 + Mo \xrightarrow{315\,^{\circ}C} 3NO + Mo\,O_3$$

Analysers are need to be "serviced" weekly and quarterly. The weekly check consists of various visual checks for leaks, LED displays, filter changes, a span and zero check. Apart from leaks, no adjustments are made during the weekly checks. Weekly checks were done by departmental employees who have had appropriate training from the suppliers of the analysers. The quarterly checks are in depth multipoint calibrations. Adjustments may be made during quarterly checks. Quarterly checks were conducted by personnel from certified laboratories.

During a "span" check, ambient air is passed over charcoal scrubbers to form zero air (represents a system response when no pollutants are present). Zero air is passed over a NO_2 permeation tube. The NO_2 permeation tube is able to emit known concentrations of pure NO_2 at specified temperatures. A known concentration of NO_2 permeates from the tube into the sample stream. All flows and temperature are constant during the span check. The output from this tube should be the same as the amount of NO_2 permeated from the tube into the air stream. This value is recorded. Zero air is passed through the NO_2 permeation tube to verify the baseline readings. The multipoint calibration uses standard gases that have been approved by certification bodies. The standard gas is passed through a calibrated system that dilutes the gas to pre-determined concentrations. These concentrations form the points of the multipoint calibration. The output from these concentrations should be the same as the concentrations of the gases diluted initially. Adjustments to the analyser may be made. All deviations must be recorded[9]. Appendix: A contains the calibration records for analyser stationed in The Durban Metro Caravan.

3.3.2 Passive Sampling

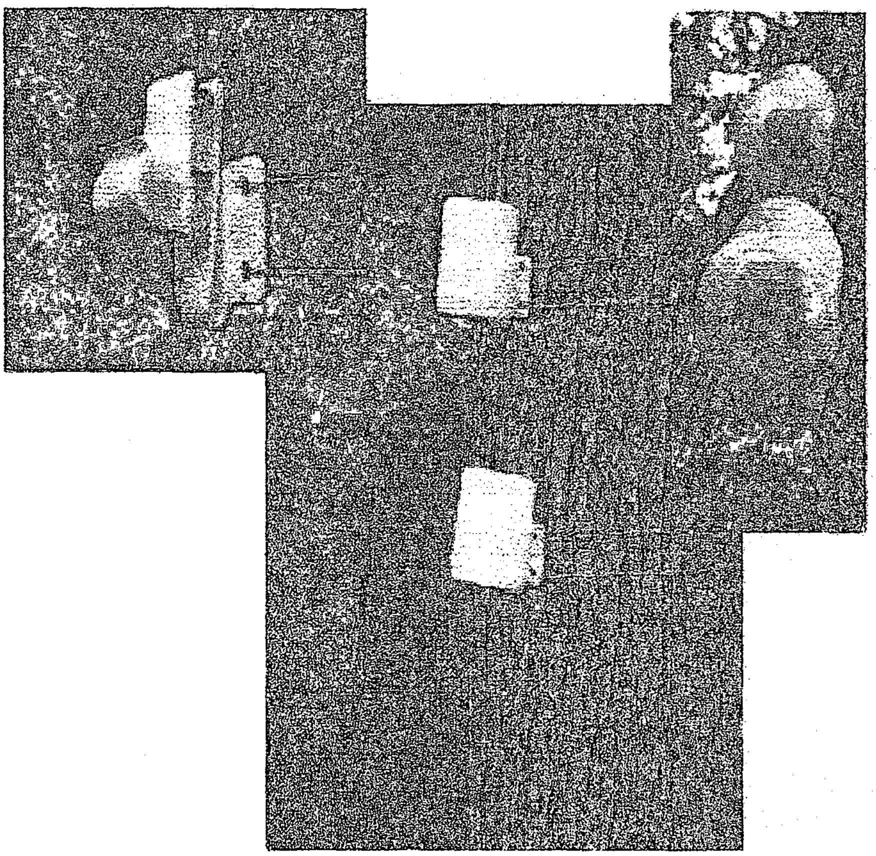


Figure 25: Ogawa Passive Sampler illustrating Shelter Set up

Passive sampling was recommended[21] as a cost effective method to evaluate the concentrations of NO_2 over an extended period and to cover a wider sampling area. The technique does not require a source of electrical energy or a highly secured and sufficiently large site. This sampler uses the principle of passive diffusion to quantify the concentration of NO_2 in ambient air. The principle of operation of the Ogawa passive sampler which was used during this study was discussed in Chapter 2 under section 2.4.1.1.

3.3.3 Dust Sweepings

Collection of dust fallout using receptacles is a common method for sampling particulate emissions from vehicle exhausts. However, during the preliminary study, sampling vessels were frequently removed or damaged. We were therefore obliged to resort to take dust sweepings off the pavements at selected intersections as an alternative method to collect particulates[43]. High volume samplers which are commonly used for the collection of particulates are expensive. Only two such samplers were available. This meant that the number of sites selected would have been restricted to two. Furthermore, operation of these instruments restricts site selection because it requires a source of power and security.

Figure 26: Sampling Point at Selected Intersection for Dust Sweepings

3.4 Storage

3.4.1 Passive Samplers and it's components

The components of the sampler were washed and dried after each use. The stainless steel rings were boiled in purified water on medium heat for 10 minutes and then dried. All components were handled with gloves during washing steps and with forceps during assembly stage. Loaded samplers were placed in re-sealable plastic bags and then sealed in air tight opaque containers. The latter were stored in the refrigerator until the time they were taken to be used.

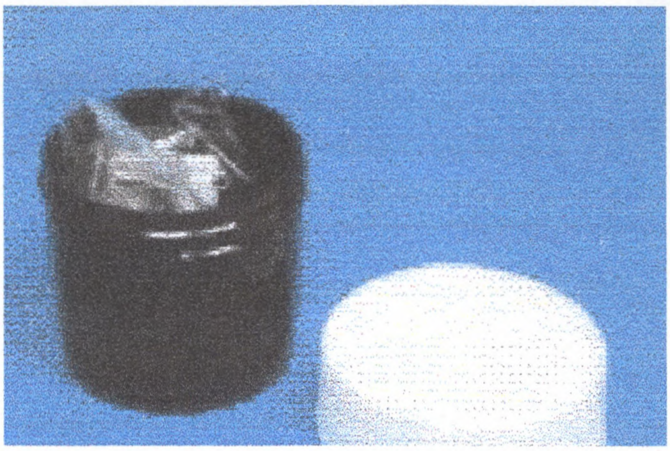


Figure 27: Transport container for sampler in clip housed in plastic bag

The claims of the supplier regarding the shelf lives of the filters are given in the table below. These recommended time frames should always be adhered to for optimum results.

Table 6: Shelf life of Passive filters under various conditions as given by the supplier.

	Refrigerated Storage Method	Frozen Storage Method
Sealed in glass vial pouch	90 days	1 year
Re-sealed in vial, after opening	90 days	
Loaded sampler in bag placed in vial with lid	90 days	
Exposed loaded sampler, in bag placed with the lid.	14 days	
Extracted solution in water, in sealed vial.	90 days	

3.4.2 Dust Sweepings

Dust sweepings were collected in clean sample bottles and stored air tight until they were ready for analysis.

3.5 Preparation of Solutions and Reagents

It should be noted that the term "purified water" used hereafter refers to deionised water which was obtained via filtration through a Modular Water System and a conductivity of $0.1\mu Scm^1$.

3.5.1 Materials and Reagents

3.5.1.1 Materials and Reagents to determine the Concentration of NO_2.

Solutions of sulphanilamide and NEDA were mixed[32] in the proportion of 10:1 to give the colouring agent. The latter was added to the solution obtained by extracting the nitrite from the passive filter using purified water. The sulphanilamide and NEDA solutions were prepared as follows:

Sulphanilamide (8g, Univar grade - Saarchem, batch no. 39954) was weighed into a 50 ml beaker. Concentrated phosphoric acid (20 ml, BDH, AR grade, batch no.1015141 and purified water, 70 ml) were added to dissolve the sulphanilamide. The resulting solution was made to 100ml volume with purified water.

(1- Naphthyl)- ethylene dihydrochloride (0.56g, Sigma grade, batch no. 129H 0883) was weighed into a 50 ml beaker. Purified water was used to dissolve the (1-Naphthyl)- ethylene dihydrochloride. The resulting solution was made to 100ml with purified water.

3.5.1.2 Materials and Reagents to determine the Concentration of Pb.

The following materials were used[43] in the determination of Pb concentration in dust sweepings.

Nitric acid (55%. Unilab Saarchem, batch no: 1016890) and Whatman filter paper 320 with medium retention and flow rate.

3.5.2 Standards

3.5.2.1 Preparation of standards to determine the Concentration of NO_2.

Sodium nitrite (5g, Riedel-de-Haen Ag Seelze- Hannover AR grade, batch no.4E 00311) was dried for 4 hours in an oven at 105 °C. Sodium nitrite (1.5g) weighed in a 50ml beaker and dissolved with purified water was made up to 1000ml with purified water[32].

$$\text{g } NO_2^- \text{ in 1 litre stock} = \frac{(1.5\text{g Na } NO_2^-) \times (46\ NO_2^-)}{69\text{ Na } NO_2^-}$$

$$= 1\text{g of } NO_2^- \text{ in 1 l}$$

$$= 1000\ \mu\text{g in 1000ml}$$

$$= 1\ 000\ \mu\text{g / ml.}$$

Working standards were prepared as follows:

The nitrite standard stock solution (10 ml) was diluted to 1000 ml with purified water to produce 10 mg / l NO_2^-. Standards were prepared by serial dilution with purified water. 2, 4, 6, 8 and 10 ml aliquots of above solution were diluted to 100 ml to make 5 working standard solutions. In addition an absorbance reading was measured using a purified water sample as a blank. The absorbance of these solutions were read on the spectrophotometer and stored in it's memory. Subsequent values of nitrite were read off the calibration curve in memory. The calibration curve was checked weekly by using a solution of known concentration. A typical result is shown in Table 7 below:

Table 7: Absorbance vs Nitrite of a known Concentration

Absorbance (ABS)	Nitrite concentration (mg/l)
0.003	0.000
0.205	0.200
0.408	0.400
0.608	0.600
0.798	0.800
0.995	1.000

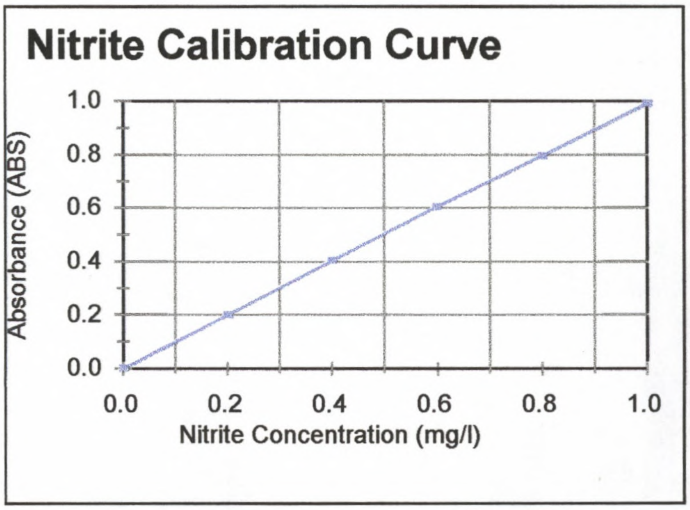


Figure 28: Curve for Nitrite for a known Concentration

3.5.2.2 Preparation of standards to determine the Concentration of Pb.

The lead standard stock solution was prepared from a Merck titrosol and diluted to 1000ml with purified water to produce 1000ppm. Standards were prepared by serial dilution with purified water. 50, 100 and 200 ml aliquots of above solution were diluted to 1000 ml to make 3 working standard solutions. These solutions represented a 3 point calibration for the ICP that was used for measuring the concentration of lead. A similar calibration check was run with every batch of samples analysed. When results for test samples were above 200 ppm, they were diluted to concentrations which yielded results within the working solutions. In this case, the dilution factor from this solution was used to calculate the results for concentration of lead for the sample. In addition an absorbance reading was measured using a purified water sample as a blank.

3.5.3 Test Solutions and Analysis

3.5.3.1 Preparation of test solutions to determine the Concentration of NO_2.

The typical procedure for treating an exposed filter is given below:

After exposure the filters from the sampler were analysed[32] in the laboratory as follows: Purified water (8ml) using a 10 ml graduated pipette was placed into a clean, labelled vial. The filter was removed from the sampler assembly using forceps and placed into a vial.

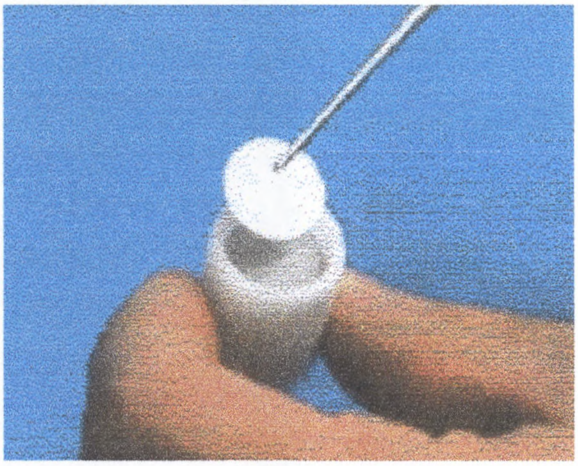


Figure 29: Insertion and removal of collection filter is performed using tweezers.

The vial was sealed, shaken and left to acclimatize to room temperature for half an hour. Thereafter the vial was transferred into the refrigerator to cool for a further half an hour. After this period the colour reagent (2 ml) was added to the vial and refrigerated for a further half hour. The vial was removed from the refrigerator after conditioning and allowed to stand at room temperature for 20 minutes.

3.5.3.2 Analysis of test solutions to determine the Concentration of NO_2.

The concentration of the conditioned sample was determined[48] as follows:

The coloured solution from the vial was poured into a cuvette. The latter was placed into the holder of a Cary 1/3 spectrophotometer (shown in figure 30) and the absorbance of the solution at 545nm was read and recorded. It is noted that prior to measurement the instrument was set for zero absorbance with purified water. Thereafter a blank determination was done. This value was subtracted from the readings obtained.

Figure 30: The Cary 1/3 Spectrophotometer used to determine Nitrogen dioxide concentration.

3.5.3.3 Preparation of test solutions to determine the Concentration of Pb.

Dust sweepings were taken to the laboratory and dried in an oven at approximately 105 ^{0} C for 3 hours. 5 g of dust sweepings was weighed into the porcelain petri-dish. The dust sweeping samples were digested with concentrated HNO_3 (10 ml) in a steam bath for 1½ hours. Digested samples were cooled, filtered with Whatman no.320 and brought to 100 ml mark in a volumetric flask with purified water [43].

3.5.3.4 Analysis of test solutions to determine the Concentration of Pb.

The filtrate was analysed to determine the concentration of Pb using the ICP[24]. The principle of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was developed in the 1960's. It provided a quick, sensitive and efficient method to determine concentration of dissolved metals[24].

3.6 Preliminary Study for the determination of Concentration of Nitrogen Dioxide

An investigation was conducted to determine whether the filters contained nitrite prior to exposure. In addition the pre-liminary work attempted to determine the reproducibility and reliability of results.

3.6.1 Determination of the Concentration of Nitrogen dioxide on filters prior to exposure

Ten filters were analysed to determine the concentration of nitrite on the filters before they were exposed. These filters were removed from the storage bottle, prepared for analysis and the concentration of nitrogen dioxide was determined. The method used for the determination of concentration of nitrogen dioxide was recommended by the supplier of the Ogawa Sampler and is shown in Appendix C.

Filter Number1 from Table 1 was used as an example to show the manual calculation involved for the determination of concentration of nitrogen dioxide in ppb. Corel Quattro-Pro was used to analyse subsequent data. The effects of temperature and relative humidity on the absorption of nitrogen dioxide onto the filters had to be accounted. Hence the conversion coefficient ($\propto$) had to be computed. Table 4 of Appendix C provided by the suppliers of Ogawa filters gave a combination of temperature and relative humidity from which a conversion coefficient could be read off directly, however for temperature = 17 ^{0}C and relative humidity % = 60 at which this investigation was carried out, was not included, therefore a further table, also provided by the supplier of the Ogawa filter was used to select the vapour pressure coefficient [P] before proceeding with the computation for ($\propto$). [P] at 17 ^{0}C = 1.0615 was read directly off table 5 in Appendix C. The equation[32] below was used to compute ($\propto$) for NO_2.

$$\text{Conversion Coefficient } (\propto) = \frac{10\,000}{(0.677 \times [P] \times \{RH]) + (2.009 \times [T]) + 89.8}$$

The value for the constants (0.677; 2.009 and 89.8) were provided by the supplier of the Ogawa passive filters.

The value of laboratory data are :

[RH] = 60 %

[T] = 17 ^{0}C

Sample volume = 8 ml

Sampling period = 10080 min

Slope of curve = Calibration factor = Concentration / Absorbance

= 0.9968

Insertion of these values into the above equation gives:

$$\text{Conversion Coefficient } \propto \; = \frac{10\ 000}{(0.677 * [1.0615]*[60] + (2.009 * [17]) + 89.8}$$

$$= 59.85$$

$$\text{Concentration } NO_2\ (\mu g/ml) = \frac{\text{Absorbance}}{\text{Calibration factor}}$$

$$= \frac{0.014}{\text{Calibration factor}}$$

$$= \frac{0.014}{0.99968}$$

$$= 0.014$$

$$\text{Mass } NO_2\ (ng) = 0.014 * \text{sample volume} * 1000$$

$$= 0.014 * 8 * 1000$$

$$= 112.04$$

$$\text{Concentration } NO_2\ (ppb) = \frac{\propto NO_2 * \text{Mass } NO_2\ (ng)}{\text{Time (min)}}$$

$$= \frac{59.85 * 112.04}{10080}$$

$$= 0.67$$

Table 8: Concentration of Nitrogen dioxide on filter

Filter Number	Absorbance	Concentration NO_2 (ppb)
1	0.014	0.670
2	0.020	0.955
3	0.027	1.290
4	0.015	0.717
5	0.021	1.003
6	0.021	1.003
7	0.050	2.389*
8	0.018	0.860
9	0.026	1.242
10	0.018	0.860

*Possible outlier

The Statistical Package for Social Science (SPSS) was used to analyse the data statistically. Using the data from table 8 the Dixon test was performed to identify possible outliers in the results and to determine if the value 2.389 could be removed from the data. Subsequently, 2.389 was identified as an outlier. When the value 2.389 was removed from the data, no outliers were identified This is illustrated graphically in Figure 31 with the outlier value included and Figure 32 when the outlier value was removed from the data.

Further, a Shapiro-Wilk test for normality indicated that the distribution was not normal (0.003), with the value 2.389 included in the data, this can be seen in Table 9. However, when the value 2.389 was removed from the data the distribution was normal (0.566). $P > 0.05$ at a 95 % level of confidence is the norm for the acceptance that the distribution is normal. This is illustrated graphically in Figure 32 which shows the points about the line and Table 10 respectively.

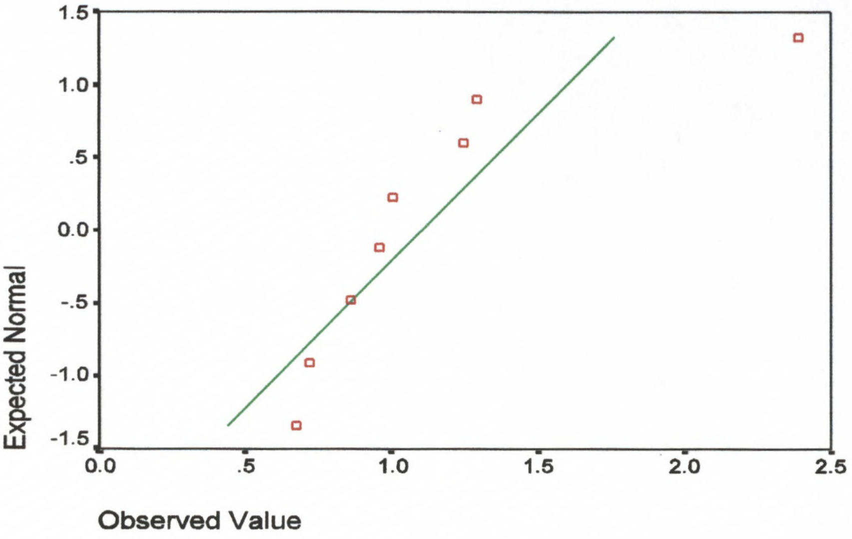


Figure 31: Q-Q Plot to illustrate outliers in data set.

Table 9: Test for Normality

Shapiro- Wilk		
Statistic	df	Significance
0.739	10	0.003

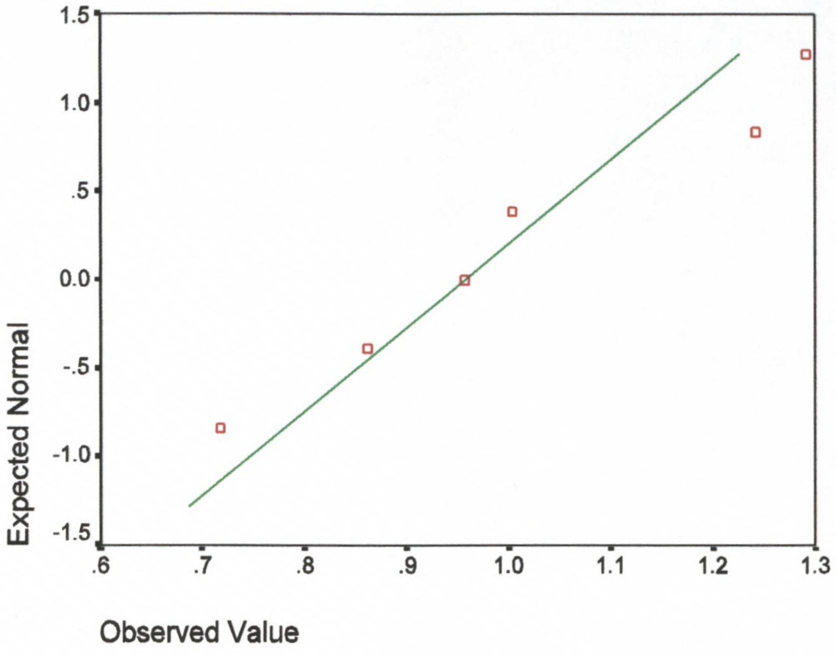


Figure 32: Q-Q Plot to illustrate no outliers in data set.

Table 10: Test for Normality

Shapiro- Wilk		
Statistic	df	Significance
0.938	9	0.566

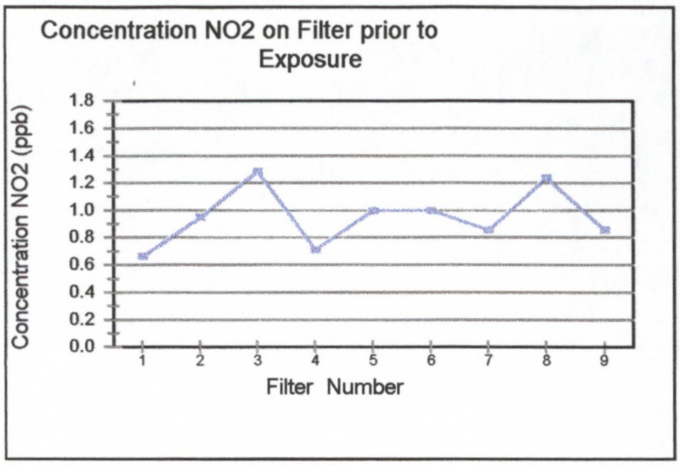


Figure 33: Concentration Nitrogen dioxide (ppb) prior to exposure

With the value 2.389 removed form the data the trend above shows no outlying results. Therefore the results revealed that negligible amounts of nitrite were on the filter prior to exposure.

3.6.2 To investigate the suitability of the prescribed method to remove all the nitrogen dioxide trapped onto the filter

This preliminary investigation was conducted to determine whether the prescribed method of washing effectively extracted all nitrite trapped onto the filter paper.

Filter samples for three sites shown in Table 11 were subjected to the same extraction procedure outlined in section 3.1.2.2 and analysed for nitrite. Thereafter the same filter paper was placed into a clean vial and the procedure repeated. The second solution was analysed for nitrite. The results of the first and second solution are shown in Table 11.

Table 11: Extraction of Nitrogen dioxide trapped onto the filter paper.

Sampling Site	**1st washing NO_2 (ppb)**	**2nd washing NO_2 (ppb)**	**Final NO_2 (ppb) (sum of 1st wash & 2nd wash)**
VE	23.13	0.22	23.35
SPJ	20.01	0.00	20.01
EDS	31.93	0.34	32.27
ARG	20.67	0.34	21.01
WAR	36.35	0.43	36.78
SCL	17.16	0.17	17.33
WWR	10.9	0.34	11.24
MOB	8.13	0.21	8.34

Ho: Nitrite present if there is no difference in means

[σ^2 (first wash) = σ^2 (second wash)]

Ha: If there is a difference, then no nitrite present after second wash.

The Statistical Package for Social Science (SPSS) was used to analyse the data statistically. The means from the data in Table 12 were used in a Hypothesis test to ascertain whether the prescribed method of analysis was adequate to extract all NO_2

trapped onto the filter. A Kendall's W test was performed to determine the significance in the number of washings to the filters.

Table 12: Concentration NO_2 (ppb) first wash vs Concentration NO_2 (ppb) second wash on the Ogawa filter.

	Concentration NO_2 (ppb) First Wash	Concentration NO_2 (ppb) Second Wash
Mean	21.83	0.32
Variance	96.28	0.00863

At a 95 % confidence level, the p value = 0.00050. $P > 0.05$ at 95 % level of confidence is a standard norm for the acceptance of the null hypothesis. This implies that the null hypothesis is rejected and there is very strong evidence to accept Ha ie.no nitrite present after second wash. This showed that the prescribed method of analysis was adequate to extract all NO_2 trapped onto the filter.

3.6.3 To investigate the Reproducibility of results on the filters at the same site.

Nine samplers were placed into a closed cupboard on the fourth floor of a central business district building. Eight samplers with one filter each, were exposed and the ninth sampler which represented the blank was unexposed. Sampling under these conditions was used to investigate the repeatability between passive samplers. The cupboard was opened twice for short intervals during the sampling period to verify the sampling set up.

The highest nitrogen dioxide concentration obtained was 3.47 ppb and the lowest was 2.95 ppb. Eight results produced a nitrogen dioxide concentration of approximately 3 ppb. The average concentration for this study was 3.19 ppb. This is shown in the Table 13.

Table 13: The Reproducibility of results on the filters at the same site.

Filter Number	Absorbance	Concentration NO_2 (ppb)
1	0.0924	3.22
2	0.0859	2.95
3	0.0907	3.15
4	0.0917	3.19
5	0.0917	3.19
6	0.0945	3.31
7	0.0984	3.47
8	0.0889	3.07
9 (blank)	0.0154	
Average concentration NO_2 (ppb)		3.19

These results show that the Ogawa passive sampling technique provides reproducible results between filters sampled under the same conditions. Hence, the number of filters used to sample at a specific site can be reduced, thus reducing running costs of monitoring.

3.6.4 Pre-liminary study to investigate the suitability of the sampling period

A pre-liminary study to determine the ideal sampling period was done at the following sites: Warwick, Argyle, Victoria Embankment, Edwin Swales, Sea Cow Lake, Spaghetti Junction, Wentworth Reservoir and the King's Park Pool sites.

Two samplers were mounted at each site and each sampler contained two filters. One blank filter was mounted at Wentworth Reservoir for each sampling period. This site was selected in order to compare results between the passive sampler and an active analyser stationed here. The results yielded good repeatability between duplicates. Refer to Appendix D and E for detailed results. The table below represents the results of a comparison between a 14 day and 7 day sampling period.

Table 14: Comparison between 14 day and 7 day sampling period

Site	Absorbance NO_2 14 day sampling period	Absorbance NO_2 7 day sampling period
VE	1.52	0.48
SPJ	1.17	0.43
EDS	1.63	0.65
ARG	1.07	0.39
WAR	2.00	0.74
SCL	1.07	0.33
WWR	0.45	0.17
Kerb	0.88	0.36
F1	0.94	0.29
F2	0.99	0.27
F3	1.35	0.30

Consequently, the resulting final uv/ vis absorbance reading for the 14 day sampling period exceeded the range required by the Beer Lambert Law of light absorption[46].

The high NO_2 concentration during the 14 day sampling period can be attributed to the duration of exposure leading to saturation of the filter. Hence it was decided that reducing the sampling period from 14 days to 7 days would improve the accuracy of absorbance readings without compromising the analytical result. Subsequent sampling periods were therefore reduced to 7 day periods using one sampler with duplicate filters at each sampling site.

3.6.5 To investigate the Correlation between results from Passive and Active Sampling

Three passive samplers with duplicate filters were mounted adjacent to the inlet manifold of the active analyser at Settler's School. Sampling under these conditions were used to investigate the reliability of passive sampling when compared to the active sampling.

The table below shows the results for passive sampling over a seven day collection period.

Table 15: Results for Passive Sampling at Settler's School

Filter number	Passive Sampling on Individual Filters NO_2 concentration (ppb)
1	5.79
	5.74
2	5.94
	6.09
3	5.63
	5.75
Ave.NO_2 (x_p)	5.82

An average result of active sampling for the same sampling period as the passive sampling is shown above for nitrogen dioxide concentration (ppb)= x_a = 6.01 ppb. The Statistical Package for Social Science (SPSS) was used to analyse the data statistically. A one sample t-test was applied to ascertain whether the difference between the means obtained by passive sampling or active sampling were significant or not at a 95 % confidence level. The null hypothesis adopted stated that the means of the results given between the two methods of sampling are the equal.

Ho: No difference between active and passive sampling.

Ha: There is a difference between active and passive sampling

At a 95 % level of confidence the p value = 0.05. Hence, this implies the null hypothesis is accepted ie. the Ogawa passive sampler can be used as a cost effective and reliable alternative to the active on-line analyser. Appendix K shows the calculations for the p value above.

Dispersion of pollution depends on several factors such as weather conditions, positioning of industrial sites and land and building contours. Naturally where there is congestion and where driving patterns are of a stop/start/accelerating nature pollution of the atmosphere would be greater than in areas where traffic flows freely[49]. This section will compare the results of active and passive sampling and discuss the results for nitrogen dioxide and lead at selected intersections and motor ways leading out of the city and consider the influence of rainfall on these pollutants.

4.1 Comparison of results for nitrogen dioxide from Active and Passive Sampling

There were only two sites at which this was possible, namely, Settler's School and Wentworth Reservoir.

4.1.1 Settler's School

The analyser at this site was operational from 12 December 200 to 4 December 2001

It was found that active sampling gave higher values for the concentration of nitrogen dioxide than passive sampling for most of the sampling period with two exceptions for the period 8 May to 15 May 2001. The average concentration of nitrogen dioxide was found to be 32 ppb by passive sampling and 22 ppb by active sampling. It appears that the lower results of the active analyser during the period 8 May to 15 May 2001 were due to the fact that the equipment needed calibration. After the quarterly multipoint calibration was done on 21 May 2001 the results from the active sampler were again higher than that for the passive sampler. For the period 5 June to 12 June 2001 the concentration of nitrogen dioxide was 22 ppb by passive sampling to 21 ppb active sampling. The latter results were only marginally lower than for passive sampling and did not warrant concern. Although no deviations were reported by the Technician conducting the calibrations for the active analyser, the results obtained in

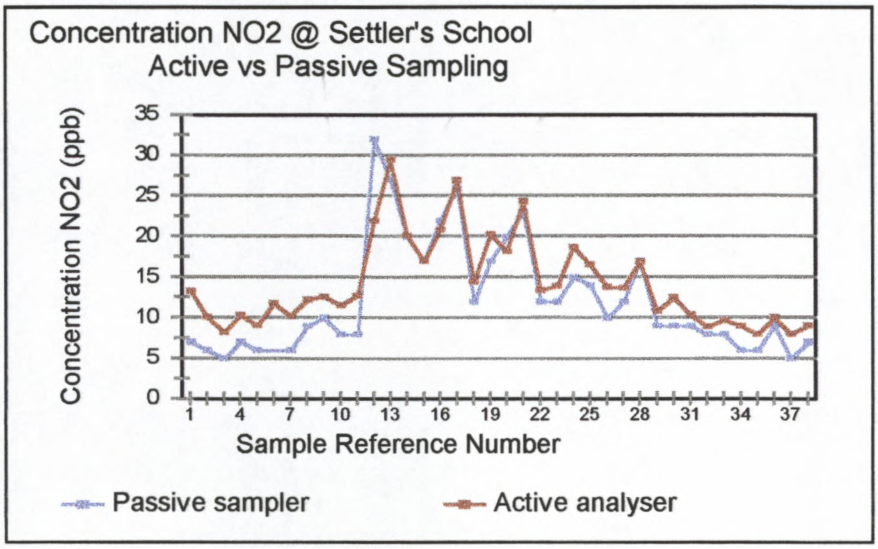


Figure 34: Comparison between Active and Passive Sampling at Settler's School

The average concentrations of nitrogen dioxide obtained by active and passive sampling at Settler's School for the duration of the project are shown in the Table 16 below. This gives a ratio of 1.14 for the results of active to passive sampling.

The Statistical Package for Social Science (SPSS) was used to analyse the data statistically. The means from the data in Table 16 were used in a Hypothesis test to ascertain the comparison between active and passive sampling at Settler's School for the duration of the study. The null hypothesis adopted states that there is no difference between the means of the results given between active and passive sampling for the determination concentration of nitrogen dioxide.

Ho: No difference between the means of active and passive sampling.

Ha: There is a difference between the means of active and passive sampling.

Table 16: Comparison between Active and Passive Sampling at Settler's School.

Table 16: Comparison between Active and Passive Sampling at Settler's School.

	Concentration NO_2 (ppb) Average Passive sampling	Concentration NO_2 (ppb) Average Active sampling
Mean	12.32	14.13

At a 95 % confidence level, the p value = 0.101. This implies that there is little or no evidence that there is a difference between the means of active and passive sampling. Hence, the null hypothesis is accepted. Further, a test for normality indicated that the distribution was normal.

4.1.2 Wentworth Reservoir

The analyser was operational for period 15 May to 26 June 2001 only. During this sampling period, the analyser recorded lower results than the passive sampler 4 out of 6 times.

Table 17: Comparison between the Active Sampling and Passive Sampling at Wentworth Reservoir.

Average Passive Sampling Concentration NO_2 (ppb)	Average Active Sampling Concentration NO_2 (ppb)
20.33	18.53

The ratio of the average concentration of nitrogen dioxide of active to passive sampling at Wentworth Reservoir was 0.91. Upon investigation it was found that the analyser required repairs and was removed from the site. Due to lack of funding no active analyser was replaced at this site. In this case the results of the passive sampler provided a reliable indication that the active analyser was not functioning optimally. The observations at this site affirms our recommendation that the calibration of the active samplers should be checked at shorter intervals.

4.2 Concentration of Pollutants at other Sampling Sites

The results for sampling at traffic intersections and motor-ways leading out of City are discussed in terms of duration of collection of pollutants at different sites and the effect of distance from the kerbside on the levels of pollutants found.

Passives samplers were replaced and collected every seven days with the exception when sampling days coincided with public holidays. During the latter, sampling periods were replaced with eight day and six day intervals. One sampling period during Christmas represented a twenty eight day period because of the lack of personnel during the holiday since it was recommended that two persons always sample for security reasons. The above six day, eight day and twenty eight day results are excluded from data discussed in this project. Dust samples as sweepings were collected every seven days at the same times as the samplers were replaced.

4.2.1 Concentrations of nitrogen dioxide at various sites

The results for concentration of nitrogen dioxide and the investigation of the influence of rainfall and seasonal variations on these values will be discussed in this section.

4.2.1.1 Concentrations of nitrogen dioxide at all sampling sites

Samples were collected over the period from 12 December 2000 to 12 December 2001. Thirty eight samples in total, each collected over seven day intervals were retrieved for the duration of the sampling period. This period represented winter and summer months so that seasonal variations were monitored. Relative humidity %, ambient temperature and rainfall values were obtained from the Durban Metro Caravan. These parameters were however obtained from the weather office at the Airport when results were not available from the above source during breakdowns and maintenance. These periods are shown in the weekly summaries in Appendix E.

The variation in the average level of nitrogen dioxide (from highest value to lowest value) for the different sites was found to be in order : Warwick, Edwin Swales, Victoria Embankment, Spaghetti Junction, Agyle and Sea Cow Lake. Although Warwick represented the site with the highest nitrogen dioxide concentration, all the sites show similar trends for the duration of the project, these are shown in Figure 35 to 40.

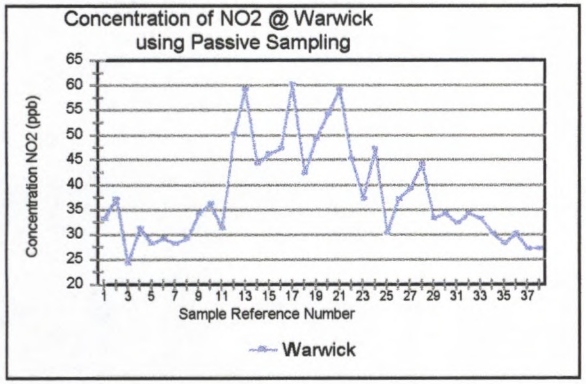


Figure 35: Concentration of NO_2 at Warwick Avenue

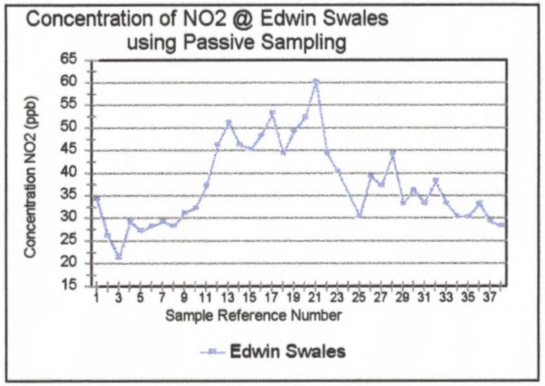


Figure 36: Concentration of NO_2 at Edwin Swales

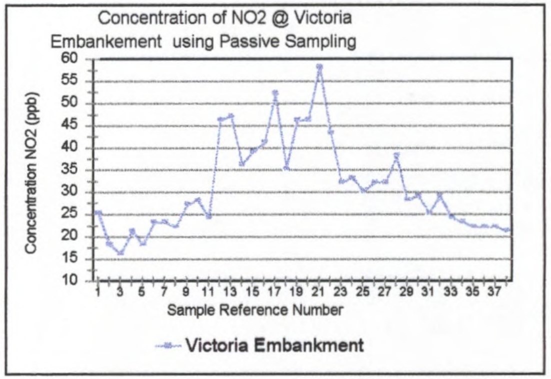


Figure 37: Concentration of NO_2 at Victoria Embankment

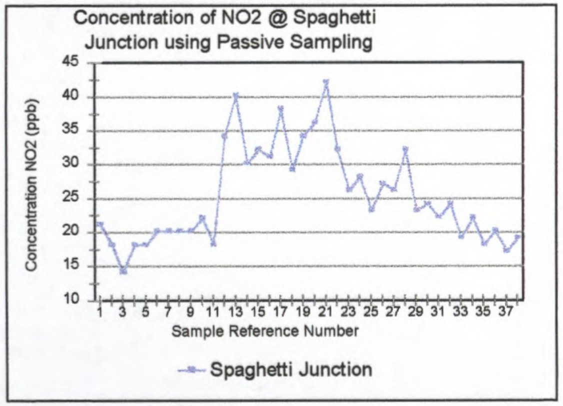


Figure 38: Concentration of NO_2 at Spaghetti Junction

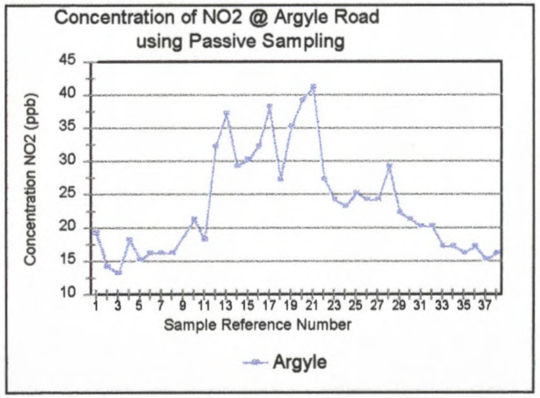


Figure 39: Concentration of NO_2 at Argyle Road

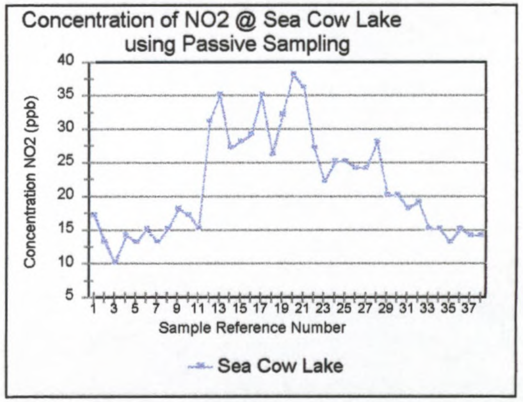


Figure 40: Concentration of NO_2 at Sea Cow Lake

In all cases it is observed that there is an increase in the concentration of nitrogen dioxide in the period approximately May to July 2001 and a decrease in period approximately November 2000 to February 2001. Furthermore the concentration of nitrogen dioxide at Warwick Avenue, Edwin Swales and Victoria Embankment ranged from ± 16 to 60 ppb whereas at all other sites it ranged from ± 10 to 42 ppb.

The sites at Edwin Swales, Victoria Embankment, Spaghetti Junction, Argyle and Sea Cow Lake recorded their highest concentration of nitrogen dioxide during sampling period 10 July to 17 July 2001.This period coincided with the school holiday.

4.2.1.2 The Influence of Rainfall on concentration of nitrogen dioxide

Levels of rainfall representing all sites were recorded for the duration of the project. The influence of rainfall on the concentration of nitrogen dioxide at Warwick Avenue is shown in Table 18. This table represents the sampling periods and the corresponding concentration of nitrogen dioxide obtained with various levels of rainfall.

Table 18: Concentration of nitrogen dioxide and the rainfall associated with the level of gaseous pollutant at Warwick Avenue.

Sampling Period	Rainfall (mm)	Concentration NO_2 (ppb)
15/05/01-22/05/01	0.0	59.0
10/07/01- 17/07/01	0.0	59.0
12/06/01-19/06/01	0.2	60.0
27/11/01- 04/12/02	10.2	27.0
06/02/01- 13/02/01	24.0	24.0

As can be seen, a distinct relationship exists between the concentration of nitrogen dioxide and rainfall. The highest concentrations of nitrogen dioxide recorded coincided with sampling periods which recorded relatively no or low volumes of rainfall. Conversely, lowest concentrations of nitrogen dioxide recorded coincided with high volumes of rainfall.

The Statistical Package for Social Science (SPSS) was used to analyse the data from Table18 statistically. It is observed that as the rainfall increases the concentration of nitrogen dioxide decreases. This trend can be confirmed by a very strong negative relationship and a -0.91 correlation coefficient. Appendix I shows the calculation for the value of the correlation coefficient. Hence there is negative correlation between the concentration of nitrogen dioxide and rainfall ie. the higher the rainfall the lower the concentration of nitrogen dioxide.

4.2.1.3 The Influence of Distance from kerbside on the concentration of nitrogen dioxide.

This section will discuss the effect of distance from the kerbside on the concentration of nitrogen dioxide to assess the environmental impact along a roadway with high traffic volumes. Table 19 shows the effect of distance from the kerbside to annual average concentration of nitrogen dioxide along a busy roadway leading out of the City.

Table 19: The effect of distance from the kerbside on the concentration of nitrogen dioxide.

Site	Distance from edge of pavement (m)	Annual Ave. NO_2 (ppb)
Kerb	7.0	20.7
Fence 1	40.0	19.1
Fence 2	72.0	17.9
Fence 3	141.0	18.2

From the table above no exceedances of the annual average guideline value were recorded at any of these sampling sites during the project.

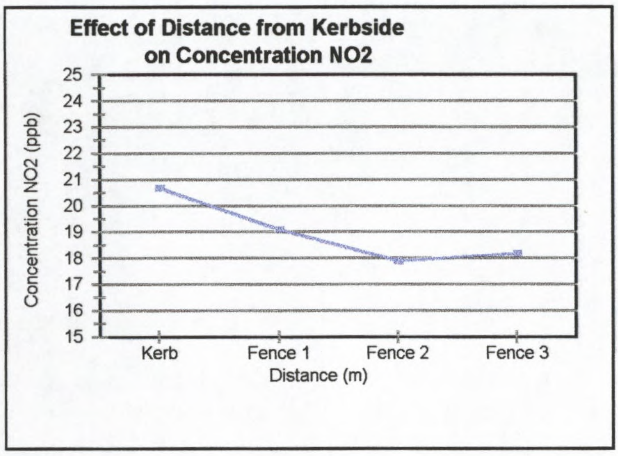


Figure 41: The effect of distance from kebside on concentration of nitrogen dioxide at King's Park Pool Site

The Statistical Package for Social Science (SPSS) was used to analyse the data from Table 19 statistically. Figure 41 illustrates the effect of distance from kerbside on the concentration nitrogen dioxide. Graphically it is observed that there is a negative correlation at all four sites implying that the concentration of nitrogen dioxide decreases with distance from the kerbside. This trend can be confirmed by the r value of -0.78. Appendix H shows the calculation for the r value.

The 'Kerb' recorded the highest concentrations of nitrogen dioxide followed by 'Fence 1' which recorded the second highest concentration. The concentrations of nitrogen dioxide stabilised from 'Fence 2' to 'Fence 3' which represented sites inland from the kerbside.

Although the kerbside emissions for the concentration of nitrogen dioxide are higher inland than from the 'Kerb', the contributions from the traffic along Walter Gilbert Road could have contributed to the results obtained for 'Fence3'.

4.2.1.4 The Influence of Seasons on the concentration of nitrogen dioxide

A comparison of the results from figures 35 to 40, indicates that there is a common trend in the concentrations of nitrogen dioxide at sampling sites over specific sampling periods. The highest concentrations of nitrogen dioxide were recorded from May to the end of July 2001. The latter quarter typically represents the onset of winter. In addition the inversion layer which occurs predominantly in winter traps pollutants in ambient air. It has also been known that the calm winter conditions tend to favour the accumulation of pollutants which result in their higher levels being recorded. The combination of the inversion layer, the traffic generated by the tourists during the holidays and other meteorological factors like calm, stable conditions could have contributed to the higher concentrations of nitrogen dioxide experienced during this sampling period. Conversely, lower concentrations of nitrogen dioxide were recorded from November 2000 to February 2001. The latter quarter typically represents summer months. The winds and rainfall of the summer months could possibly be responsible for the dispersion of pollutants over this sampling period and hence their lower results. A seasonal pattern is therefore evident.

4.2.2 Concentration of lead at various sites

The results for sampling at traffic intersections and motor-ways leading out of City are discussed in terms of duration of collection of pollutants at different sites.

4.2.2.1 Concentration of lead at all sampling sites

Samples were collected over a period from 12 December 2000 to 27 November 2001. Thirty eight samples in total, each collected over seven day intervals were retrieved for the duration of the sampling period. This period represented winter and summer months so that seasonal variations were monitored. Rainfall values were obtained from the Durban Metro Caravan at Settler's School. This parameter was however obtained from the weather office at the Airport when results were not available from this source during breakdowns and maintenance. These periods are shown in the weekly summaries in Appendix F.

The variation in the average level of lead (from highest value to lowest value) for the different sites was found to be in order : Spaghetti Junction, Argyle Road, Victoria Embankment, Warwick Avenue, Sea Cow Lake Road and Edwin Swales Drive.

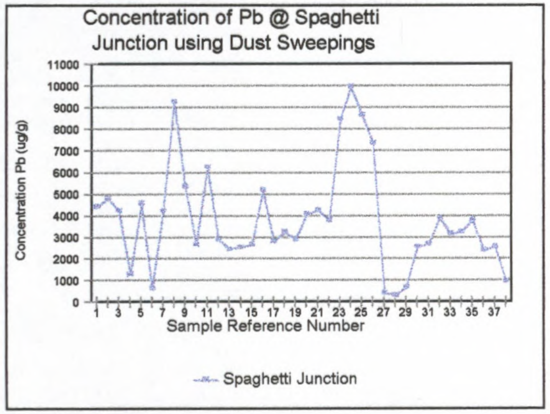


Figure 42: Concentration Lead at Spaghetti Junction

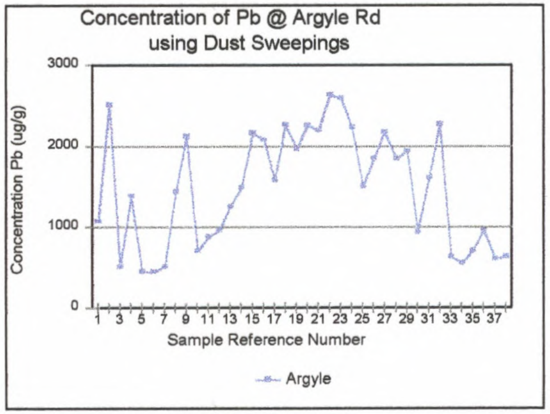


Figure 43: Concentration Lead at Argyle Rd

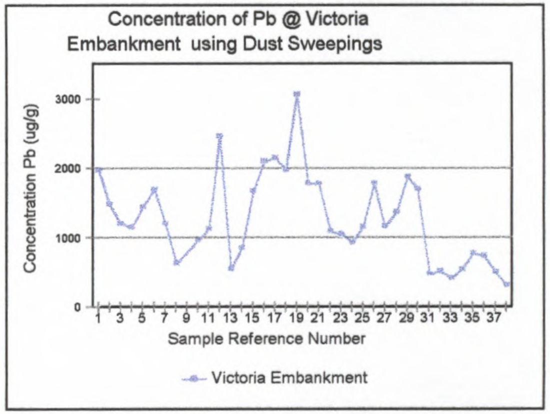


Figure 44: Concentration Lead at Victoria Embankment

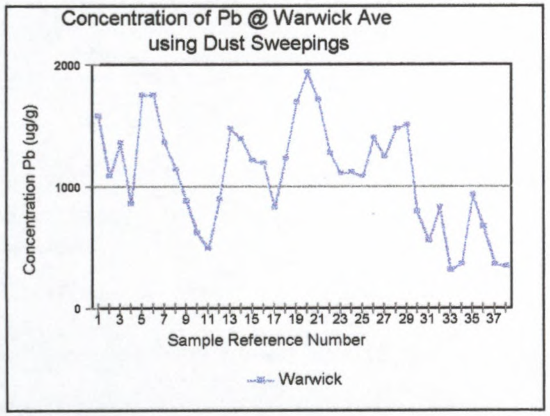


Figure 45: Concentration Lead at Warwick Ave.

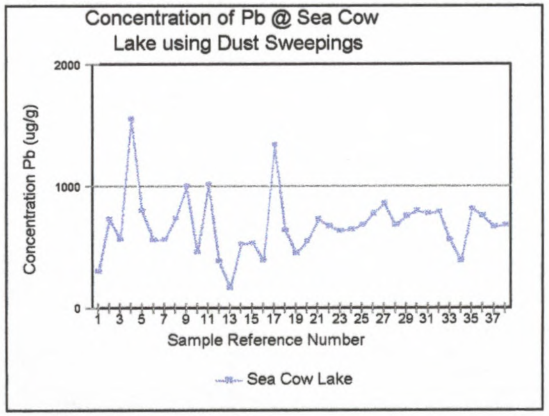


Figure 46: Concentration Lead at Sea Cow Lake Rd.

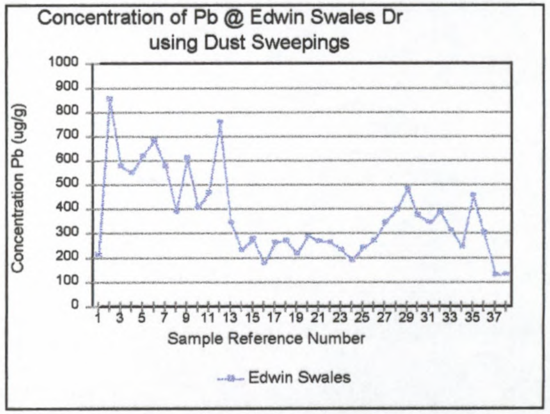


Figure 47: Concentration Lead at Edwin Swales Dr.

At most sites it is observed that there is an increase in concentration of lead in the period approximately June and July 2001. There was however no evidence that the high concentrations of lead coincided with school holidays as was the case with concentration of nitrogen dioxide. It was also evident that there was no set pattern when the concentrations of lead were low.

The table below represents the relationship between the average concentration of lead, vehicle counts and the influence of the number of municipal road sweepings undertaken at each site.

Table 20: Concentration of Lead (μg/g), vehicle count and municipal road sweeping at selected intersections and busy roadway.

Site Ranking (highest to lowest)	Site	No. of Road sweepings per week.	Ave. Concentration Pb (μg/g)	Ave. vehicle per hr
1	SPJ	0	3770	12322
2	ARG	3	1458	5233
3	VE	7	1267	4603
4	WAR	7	1090	-
5	SCL	7	672	3844
6	ED	7	308	5479

Although sampling site selection was based on the volume of traffic per hour, using the statistics supplied by the Traffic Department, Warwick Avenue was the only sampling site not included in the latter. Hence the criteria for selection of this site was solely on geographical location and observed vehicular quality in the area.

Table 20 shows that the average concentrations of lead from dust sweepings was possibly influenced by the volume of traffic per hour and the vehicle entrainment on the surface of the road at each sampling site. There is also evidence from the table above that fluctuations in the results recorded at the sampling sites are possibly influenced by the frequency of municipal road sweeping. Results for concentration of lead would possibly be much higher than observed results, if the sites were not swept as frequently as they were.

4.2.2.2 The Influence of Rainfall on concentration of Lead

Levels of rainfall were recorded for the duration of the project. The influence of rainfall on the concentration of lead at Spaghetti Junction is presented in the table below, it represents the sampling periods and the corresponding concentration of lead and average wind speed obtained with various levels of rainfall.

Table 21: Concentration of Lead and the rainfall associated with the level of pollutant at Spaghetti Junction.

Sampling Period	Rainfall (mm)	Average wind speed (m/s)	Concentration Pb (μg/g)
27/02/01- 06/03/01	0	1.94	577
07/08/01-14/08/01	0	2.00	8601
21/08/01- 28/08/01	0.3	1.97	359
28/08/01- 04/09/01	2.3	2.00	255
20/03/01- 27/03/01	10	1.90	5304
16/10/01- 23/10/01	38.8	2.05	3105

The Statistical Package for Social Science (SPSS) was used to analyse the data from Table 21 statistically. Although the highest concentrations of lead recorded coincided with the sampling period which recorded no rainfall, the table above shows a little relationship between the concentration of lead and rainfall. It is observed that there is a small correlation between the two variables. This can be confirmed by a 0.07 correlation coefficient. Appendix J shows the calculation for the value for the correlation coefficient. In addition it is observed that at a constant wind speed, in this case approximately 2 m/s, has no effect the concentration of lead.

4.3 Concentration of Nitrogen dioxide at all Sampling Sites in relation to Guideline Values

The seven day sampling period results were equated to an annual average so that comparisons to DEAT guideline values would be appropriate. The annual average of concentration of nitrogen dioxide in ambient air is 50 ppb as stipulated by DEAT.

The table below shows no exceedences of the guideline value during the sampling period.

Table 22: The relationship between concentration of nitrogen dioxide (ppb) and guideline value at selected intersections and busy roadway.

Site Ranking (highest to lowest)	Sampling Site	Annual Average NO_2 (ppb)	Average vehicle per hour
1	WAR	38	-
2	ED	37	5479
3	VE	31	4603
4	SPJ	25	12322
5	ARG	23	5233
6	SCL	21	3844
7	WWR	13	-
8	Settler's (passive)	12	-
9	Settler's (active)	14	-

The table above shows that the sampling site which had the highest traffic volume per hour did not record the highest concentration of nitrogen dioxide. It is also illustrated graphically in Figure 48 below. This is evident at Spaghetti Junction where the highest traffic volume per hour did not influence the concentration of nitrogen dioxide . Although the morning and evening traffic at this sampling site is of a stop/start nature which typically increases motor vehicle emissions, the meteorological factors, surroundings, elevation and winds of the site possibly cleanse or disperse pollutants in the air.

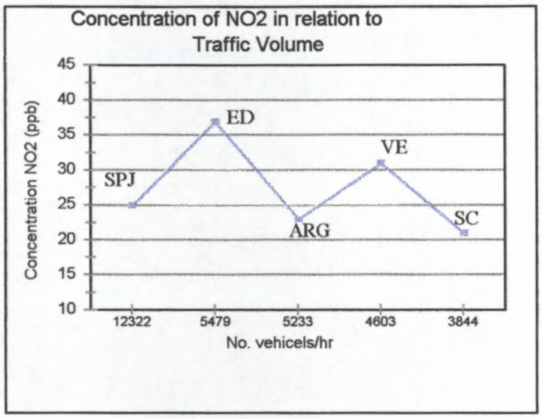


Figure 48: Concentration Nitrogen dioxide at all sampling sites in relation to traffic volume.

On the other hand the site at Edwin Swales, which recorded lower traffic volumes per hour than Spaghetti Junction, is surrounded by a number of tall buildings and structures. These buildings and tall structures tend to trap the pollutants and cause congestions that contribute to higher concentrations of nitrogen dioxide. The same reasoning can be assigned to the concentrations of nitrogen dioxide at Victoria Embankment where the winds from the harbour possibly help to cleanse the site.

The figure below illustrates that the 7 day sampling periods earlier in the study yielded higher concentrations of nitrogen dioxide than for the corresponding sampling periods later. An example of this can be seen from the sampling site at Warwick where sample

reference no.1 (Dec'00) = 33 ppb and sample reference no.38 (Dec' 01) = 27 ppb. Hence, the year 2000 could have had higher concentrations of nitrogen dioxide than the year 2001. This could possibly be due to an increase in the number of newer model motor vehicles, motor vehicles in better mechanical condition and more consistent driving patterns at the intersections. The detailed concentrations of nitrogen dioxide are shown in Appendix: I.

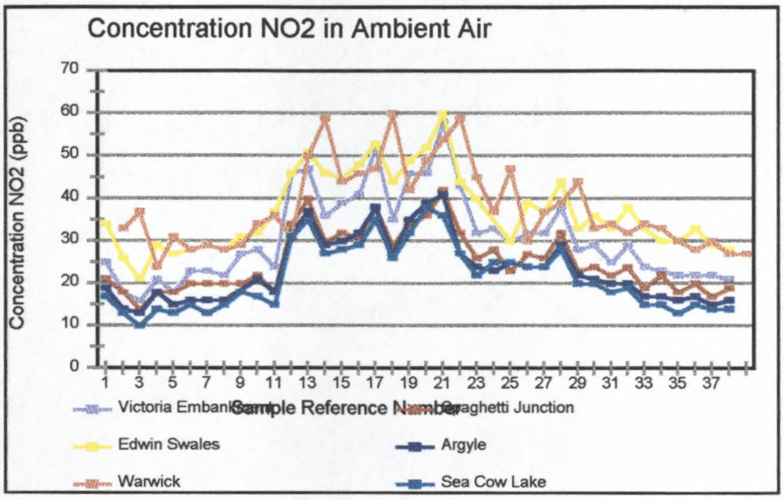


Figure 49: Concentration of Nitrogen dioxide at all sampling sites in relation to Guideline values.

4.4 Concentration of Lead at all Sampling Sites in relation to Guideline Values

The standard recommended by US-EPA for concentration lead in dust is 500 ug/g[43]. In view of the absence of local standards and guideline values, inter-site comparisons were used to determine the sites with the highest concentration of lead during this project. However comparisons to the US-EPA standard were applied as a reference as they were used in past studies.

All sites recorded concentrations of lead higher than the 500 ug/g standard recommended by the US-EPA on numerous occasions. This is shown on table 20 in section 4.2.2.1. The detailed concentrations of lead in dust sweepings are shown in Appendix F.

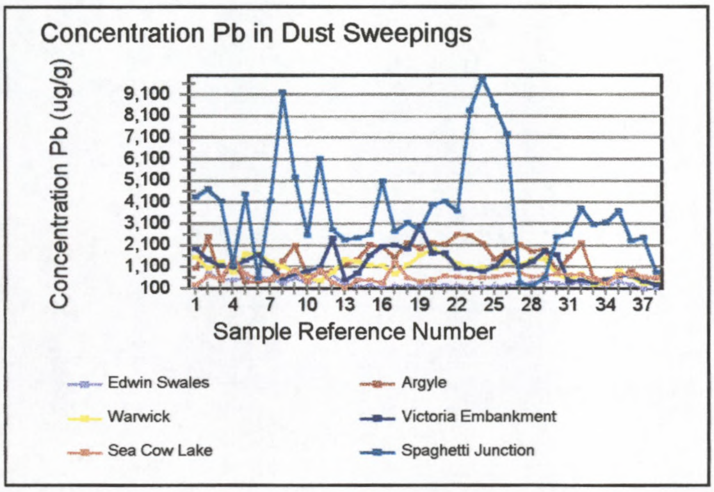


Figure 50: Comparison of Concentration of Lead at all the sampling sites.

Among other objectives this study intended to highlight the need for government officials to focus on the impacts of motor vehicle emissions on the quality of ambient air in the metropolis. To this end the study designed a simple air quality management strategy by defining the study area, assigning the indicators of pollution, acquiring the equipment and devising a method of evaluating the quality of the data produced.

Two methods of sampling ambient air were used to determine the concentration of gaseous pollutant. One method used active sampling which was sophisticated and complex. The other method involved passive sampling which was simpler and less sophisticated and, most importantly, very cost effective.

Pre-liminary work involving the Ogawa sampler showed that the method used for extraction of nitrogen dioxide from filters was efficient. There was good correlation between results obtained by passive and active sampling (as described in section 3.6.2). In this study Ogawa passive sampling filters gave reproducible results (as described in section 3.6.3). They were found to be a cost effective and a feasible method to evaluate the quality of ambient air in the metropolis. As noted in section 2.1 only two studies[2, 21] used Ogawa filters. These did not report on the efficiency and reproducibility of these filters. However studies[38, 39, 41] involving other passive sampling devices have compared the efficiency and reproducibility of passive and active samplers. Specifically research by Hangartner and Burri[39] , Stuart et al[41] and Dhammapala et al[38] showed that there was good correlation between Palmes tubes (passive sampler) and an active sampler. Similarly Yamada et al[37] showed that there was good correlation between the Yanagisawa passive sampler and an active sampler.

Analysis of the results at all sites showed an influence of the seasons on the concentration of gaseous pollutant. High concentrations of gaseous pollutants were recorded over winter months. Although the values did not exceed the annual average guideline value, the potential to exceed them is likely during this season. It is worthy of note that other researchers also reported similar findings. Hansen et al[36] and

Yamada et al[37] using Palmes tubes and Yanagisawa passive samplers, respectively, found that the levels of pollutants varied with seasons.

Short term exposure to levels of nitrogen dioxide exceeding the guidelines value have been known[9] to be harmful to human health. Therefore the impacts at more congested sites, which are used by a variety of light and heavy vehicles, needed to be assessed. The results for Warwick Avenue and Edwin Swales Drive, which represent typically congested sites were found to have higher concentrations of nitrogen dioxide than other sites like Victoria Embankment and Sea Cow Lake where dispersion of pollutants by winds are more likely.

As anticipated our results (details given in section 4.2.13) show that concentrations of pollutant generally decrease with distance from kerbside. These results corroborate the findings of Hansen et al[36].

Determination of lead by the method of sweeping dust off the pavement was an economical method to determine the concentration of lead emission. There are several the advantages of this sampling method compared to sampling with the expensive high volume samplers, namely, no electricity required, no field calibration required, no specialised training required, constant sampling period, easy to prepare sample, larger sampling area, long term monitoring, low cost, low interference from other pollutants and maintenance free.

In view of the fact that our results show dependence on the level of congestion of the sampling site it is recommended that further studies should be undertaken to investigate this aspect. Subsequent to this study, two traffic related sampling sites were selected for future monitoring. These sites are at the pumpstation in Riverside Road and at the Clinic in Cato Manor.

On the basis of results for the sampling done at varying distances from the kerbside it is recommended that monitoring equipment be located close to the source so that the impact of the motor vehicle emissions on vendors, pedestrians and residents along the kerbside of roadways can be evaluated Also further investigations should be done in areas where there are buildings which prevent the dispersion of the pollutants to longer distances from the kerbside.

In view of possible exceedences in concentrations of nitrogen dioxide from passive samplers and lead from dust sweepings, strict environmental management strategies[15] are urged to prevent the need for the future use of expensive fire fighting mechanisms, to control pollution incidents, that were required in other developed countries. Also clear guidelines and standards which are enforceable must be set as a foundation for control. A pro-active air quality management system must then be implemented with the latter as a foundation. The implementation of air quality management systems would help reduce potential liability and risk of exceeding the DEAT guideline and recommended US-EPA standard values. This would prevent pollution, the consequent site clean up procedures and negative health impacts. Such pro- active management also makes better business sense by providing better economic rewards and enhancing the image of the regulatory organisation responsible for it's management.

The following are recommendations to the Departments responsible for the protection of the environment.

- identify areas that requires air quality management
- devise a plan of action and make it known to all stakeholders
- estimate the levels of emission to be permitted in the future
- impose constraints on development to protect fragile environments

There are various ways in which these can be achieved. However, emission inventory, modelling, monitoring and evaluation of results form an integral basis for achieving and maintaining an efficient environmental management system.

Any air quality management system must be initiated using an emission inventory which must provide an invaluable tool to forecast sources of pollution within a geographical area. It can include emissions from major sources like big industries and the sum of smaller, informal industrial sources. Fragile ecosystems must be identified and hence development strategies steered to less sensitive locations. Emission inventories are also able to identify communities that are of greatest risk to pollution sources. The combination of emission inventory with modelling is able to determine short term ground level exposure and thus facilitate the compilation of air quality trends. This would form the basis for planning abatement policies.

Ambient air quality monitoring will form the basis for determining the kind of control required in specific areas. Monitoring must be able to provide accurate, reliable and useful measurements. Monitoring must use simple methodologies which are cost effective. Availability of resources must be realistic. An effective management and training program must be initiated. These must be audited and recorded for future reference and traceability. Sampling periods must be chosen so that the results could be compared to standard or guideline values. Site selection must be appropriate to the indicators under investigation. It must also consider access to the site, security, vandalism, meteorology, sources of potential turbulence and public safety.

Quality control and quality assurance procedures must be introduced so that data integrity is maintained throughout the system.

1. Barker, K., et al (1961). **Air Pollution**: World Health Organisation, Switzerland, pp 22-24, 99-103, 149-151.

2. Hurt, Q., (1997). **Durban Metro Emissions Inventory**: Ecoserv Environmental Consultants, RSA, p 6.

3. Mathee, A., Rollin, H., Levin, J., (2002). **Blood Lead Levels in school children following the introduction of Unleaded petrol in South Africa.** In proceedings of Conference of National Association for Clean Air, RSA, pp 1-2.

4. Liptrot, G.F., (1983). **Modern Inorganic Chemistry** : Bell and Hyman, London, pp 219, 247,255, 285.

5. Wood, M., (1990). **The Impact of Different Transportation Options on the Air Quality in the Johannesburg Metropolitan Area**: M.Wood Environmental Management Consultant, RSA, p 2.

6. Scorgie, Y., et al, (2001). **Air Quality Management and Pollution Control in South Africa.** Division of Continuing Extra- Mural Education, RSA, pp 1, 3, 5,16.

7. Faith, W.L., (1959). **Air Pollution Control**: Air Pollution Foundation, USA, pp 1-2, 16, 23, 167, 193-194, 202-203.

8. Mtinkheni, M., et al, (1998). **Air Quality Indicators in the South Durban Area, An Analysis based on Sulphur dioxide, Nitrogen dioxide and Carbon Monoxide**: CSIR, RSA, pp 3-4

9. United States Environmental Protection Agency, (1993). **Air Quality Criteria For Oxides of Nitrogen**, Volume 1 of 111: United States Environmental Protection Agency, USA, pp1-14 to 1-19, 3-5 to 3-19, 4-4, 5-18, 6-2, 6-8 to 6-9.

10. Stern,C., (1968). **Air pollution and It's Effects** : Academic Press Incorporated, N.Carolina, pp165, 600-602, 604-605.

11. Vleggar, C.M., et al (1980). **Trace Elements in Airborne Particulates in South Africa**: Atomic Energy Board, RSA, pp1-2..

12. **National Environmental Management Act**, Report No. 107, (1998): GPO, RSA, pp 401, 407, 429.

13. **Atmospheric Pollution Prevention Act,** Report No. 45, (1965):GPO, RSA, p 1.

14. Held, G., et al (1995). **Air Pollution and Its impacts on the South African Highveld**: Environmental Scientific Association, pp 1-57.

15. Stables, D.J., (2001), **Quality Management Systems**: Technikon South Africa, RSA, p 392.

16. Norwegian Institute for Research, (2001). **An Air Quality Management Plan for South Durban** :Norwegian Institute for Research, Norway, pp 2, 3, 6, 10.

17. Crosby, P., (1984). **Quality Without Tears** :Mc Graw- Hill, New York, pp 1-11.

18. Tricker, R., Lucas, B.S., (2001). **ISO 9001:2001:In Brief**: Butterworth-Heinemann, Oxford, pp 63-67.

19. South African Bureau of Standards, (2000). **SABS ISO 9002:2000 Guidelines - Quality Management Systems**: SABS, RSA, p 10.

20. Juran,J., (1992). **Juran on Quality by Design**: The Free Press, USA, pp 1-27.

21. Hurt, Q., (2000). **Durban Metro Air Quality Survey** :Ecoserv Environmental Consultants, RSA, pp 21- 22.

22. Giri, N.K, (1996). **Automobile Mechanics** : Khanna, India, pp 10, 16, 57.

23. 6/6/2001: An Mbendi Profile: **South Africa, Oil and Gas Industry**: Marketing and Distribution. Mbendi's E Mail Energy News.
http://mbendi.co.za/indy/oilg/ogds/af/sa/p0015.htm pp 2, 3.

24. Van Staden, C.P., (1987). **Motor Trade Theory N1**:Lexicon, RSA, pp 72-95.

25. Lall, (2002).**Durban Solid Waste** (DSW), pers.comm.
telephone nos. 3024826, 4683272, 3055759 and 5641586, 2002.

26. Derwent, R.G., (1973). **Transformation of Air Pollutants in Commoner,** B.,(Ed.), Air Pollution: Harcourt Brace Jovanovich, Denmark, p 140.

27. Hutchinson, D., Clewley, L., (1996). **West Midlands Emissions Inventory. Air Quality Management,** Hester, R., Harrison R.,(Ed.), The Royal Society of Chemistry, UK, pp 19-39.

28. Strauss, W., Mainwaring S.J., (1984). **Air Pollution-The Effects**: Edward Arnold, USA, pp 3-6, 39-50.

29. 1/11/1997: **Lead, Flouride, the Roman Empire and Decline of Academic Achievement in US**: Dan Montogomery, pp 1,2.
www.sonic.net/kryptox/environ/lead/romans.htm

30. Energy Research Institute, (1997). **Cape Town Brown Haze Study** .Report no. GEN 182: Energy Research Institute, RSA, p 15.

31. Brodine, V., Harcourt, B., (1973). **Environmental Issues Series in Commoner. Air Pollution**: Harcourt Brace Jovanovich B.,(Ed.), UK, pp.136, 139-145, 141-142.

32. Ogawa & Company, USA,Inc, (1997).Report no. 128, **NO, NO_2 ,NOx and SO_2 Using the Ogawa Sampler**: Ogawa & Company, USA, Inc., pp 1-20.

33. Morrison, R, Boyd, R, (1987). **Organic Chemistry (5th Ed)**: Allyn and Bacon Inc., pp 960-973.

34. Gengan, R., (2002). **Durban Institute of Techology**, per. Comm.
telephone no. 3085443, 2002.

35. Higuchi, K., Motomizu, S., (1999). **Flow Injection Spectrophotometric Determination of Nitrite and Nitrate in Biological Samples**, J, Analytical Services, pp 129-134.

36. Hansen, S.T, Kruse, M., Lohse.C., (2001). **Monitoring of Nitrogen Dioxide (NO_2) Greenland**. J. Environmental Monitoring. J, Environmental Monitoring, pp 3, 139-145.

37. Yamada, E., Kimura, M., Tomozawa, K., Fuse, Y., (1999). **Simple Analysis of Atmospheric NO_2, SO_2 and O_3 in Mountains by using Passive Samplers**. J, Environmental Science and Technology, vol.33, pp 4141- 4145.

38. Dhammapala, R.S., Pienaar, J.J., Lachmann, G., Ayers, G.P., Gillitte, R.W., (1995). **Monitoring Air Quality in Southern Africa using Diffusive Samplers**., In proceedings of National Association for Clean Air Conference: National Association for Clean Air, RSA, p 6.

39. Hangartner, M., Burri, P., (1987). **Passive Sampling of Nitrogen dioxide and Sulphur dioxide in Ambient Air in Berlin**. An Alternative Approach to Workplace Monitoring, A, Brown RH, Saunders KJ,(Ed.), Royal Society of Chemistry, London, pp 387-391.

40. Moriske et al (1998). **Use of Passive sampling for measuring Nitrogen Dioxide in Developing and Developed Countries**: In proceedings of the 11th World Clean Air and Environmental Congress Vol 1: National Association for Clean Air, RSA, pp 7B-4.

41. Stuart. J., et al (1999). **Validation of Nitrogen Dioxide Diffusion Tube Methodology**: Stanger Science and Environment, UK, pp 1-5.

42. Vleggaar. G., et al, (1988). **Trace Elements in the Atmosphere**. Report EMA-I/88/12: CSIR, RSA, pp 1-2.

43. Von Schirnding. J., et al, (1984). **Atmospheric, Soil and Dust Lead Levels in the Woodstock Area, Cape Town**: University of Cape Town, RSA, pp 1-5.

44. Nriagu, J., Blankson, M., Ocran, K.,(1995). **Childhood Lead Poisoning in Africa: A growing public health problem**. J, Science of the Total Environment, pp 181, 93-100.

45. Nriagu, J., Liggans, G., (1998). **Lead Poisoning of children in Afica, IV: Exposure to dust lead in primary schools in south-central Durban, South Africa**. J, Science of the Total Environment, pp117-126, 221.

46. Skoog, D., West, D., (1980). **Fundamentals of Analytical Chemistry**: Saunders College, USA, pp 489-495.

47. Teledyne Advanced Pollution Instrumentation Inc., (2001). **Continuous Analyser Training Manual**: Teledyne Advanced Pollution Instrumentation Inc., RSA, pp 20- 27.

48. American Public Health Association, (1998). **Standard Methods for the Examination of Water and Wastewater**: American Public Health Association, USA, pp 3000, 3-37.

49. Johnson, C.T., Sandford, J., Flemming, D., Thomas,A, (1998). **Interface between Research, Regulation and Implementation of Transportation demand measures in USA**, In proceedings of the 11th World Clean Air and Environmental Congress Vol 1: National Association for Clean Air, RSA, pp 2-F1.

Appendix A-1

Calibration certificates and data for active analyser at Settler's School for 30 October 2000.

TECHNOLOGY SERVICES INTERNATIONAL
(a Division of ESKOM ENTERPRISES)

GAS ANALYSER CALIBRATION LABORATORY

CERTIFICATE OF CALIBRATION

Date of issue	**: 30 October 2000**
Certificate number	**: TSI 02/2000**

Head of Laboratory :

Page 1 of 2 pages.

The values in this certificate are correct at the time of calibration. Subsequently the accuracy will depend on such factors as the care executed in handling and use of the device, and the frequency of use. Re-calibration should be performed after the period so chosen to ensure that the instrument's accuracy remains within the desired limits.

This certificate is a correct record of the measurements made.

Appendix A -1 continued

ADVANCE POLLUTION INSTRUMENTS (API) 200A NO_X ANALYSER SN: 1570

INITIAL ZERO AND SPAN CHECK

The zero response was checked using zero air, returning a response of 20.0ppb on the NO channel and –4.5ppb on the NO_2 channel. The span response was checked at 858.0ppb generated by dilution of the standard gas via the TSI calibrator, with the analyser NO_2 converter in-line. This returned a response of 590.0ppb (31.2% low) on the NO channel, 14.0ppb on the NO_2 and 604.0ppb on the NO_X channel.

DYNAMIC CALIBRATION

Further zero and span checks were carried out to enable the analyser NO response to be corrected to the audit concentration of 858.0ppb, with the analyser NO_2 converter out-of-line. Following this, three intermediate response checks were done to check the analyser linearity. The final calibration results are shown below:-

Audit Concentration	Analyser response			NO Deviation (ppb)
	NO	NO_2	NO_X	
0	0	1	1	<1
288.4	280	1	281	<9
345.8	339	1	340	<7
431.7	427	1	428	<5
858.0	858	1	859	<1

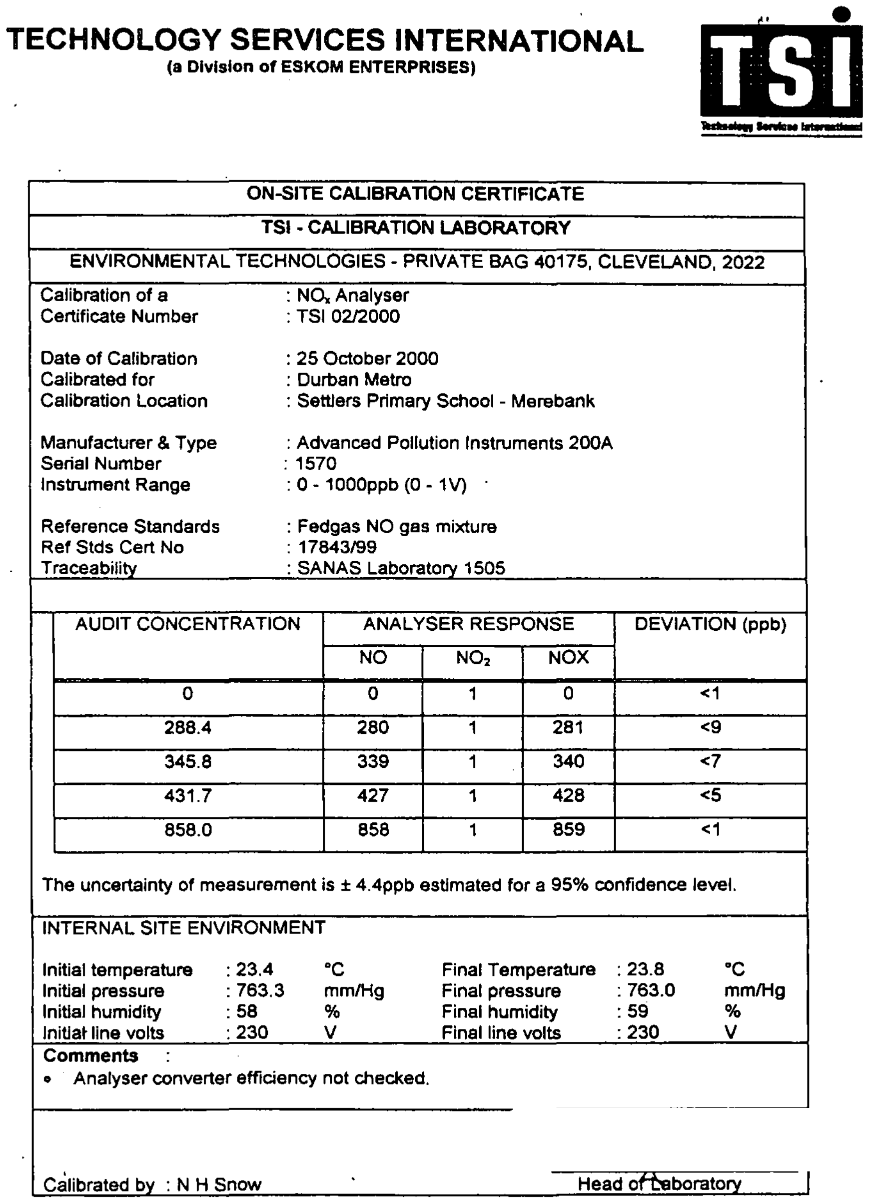
The NO_2 converter efficiency was not checked.

A calibration certificate (TSI 02/2000) for this analyser is enclosed, together with the regression analysis carried out on the results.

INSTRUMENT STATUS

System Function	Limits	Units	Initial Value	Final Value
Operating Range	-	ppb	0 - 500	0 - 1000
Output Range	-	V	0 - 1	0 - 1
Gas Pressure	25 - 35	in Hg	28.7	28.9
Sample Flow	0.65 ±0.065	Lpm	0.5	0.5
Ozone Flow	±80	cc/min	77	77
A Zero	-	mV	15.6	20.9
PMT Signal	0 - 5000	mV	19.2	27.5
PMT Temperature	7 ±1	°C	7.7	7.5
HVPS	400 - 900	mV	685	720
DCPS	2500 ±200	mV	2604	2611
Converter temp	-	°C	314.2	315.0
R/Cell Temperature	50 ±1	°C	49.8	50.5
R/Cell pressure	-	in Hg	5.3	5.3
NO_X slope	1 ±0.2	-	1.012	1.049
NO_X offset	-	-	-0.8	-0.8
NO slope	1 ±0.2	-	1.010	1.059
NO offset	-	-	-2.0	-2.0
IZS Temperature	50 ±1	°C	50.0	50.1
Test Voltage	-	mV	3.8	7.0

Appendix A -1 continued



TECHNOLOGY SERVICES INTERNATIONAL

(a Division of ESKOM ENTERPRISES)

ON-SITE CALIBRATION CERTIFICATE

TSI - CALIBRATION LABORATORY

ENVIRONMENTAL TECHNOLOGIES - PRIVATE BAG 40175, CLEVELAND, 2022

Calibration of a	: NO_x Analyser
Certificate Number	: TSI 02/2000
Date of Calibration	: 25 October 2000
Calibrated for	: Durban Metro
Calibration Location	: Settlers Primary School - Merebank
Manufacturer & Type	: Advanced Pollution Instruments 200A
Serial Number	: 1570
Instrument Range	: 0 - 1000ppb (0 - 1V)
Reference Standards	: Fedgas NO gas mixture
Ref Stds Cert No	: 17843/99
Traceability	: SANAS Laboratory 1505

AUDIT CONCENTRATION	ANALYSER RESPONSE			DEVIATION (ppb)
	NO	NO_2	NOX	
0	0	1	0	<1
288.4	280	1	281	<9
345.8	339	1	340	<7
431.7	427	1	428	<5
858.0	858	1	859	<1

The uncertainty of measurement is ± 4.4ppb estimated for a 95% confidence level.

INTERNAL SITE ENVIRONMENT

Initial temperature	: 23.4	°C	Final Temperature	: 23.8	°C
Initial pressure	: 763.3	mm/Hg	Final pressure	: 763.0	mm/Hg
Initial humidity	: 58	%	Final humidity	: 59	%
Initial line volts	: 230	V	Final line volts	: 230	V

Comments :

- Analyser converter efficiency not checked.

Calibrated by : N H Snow

Head of Laboratory

Appendix A -1 continued

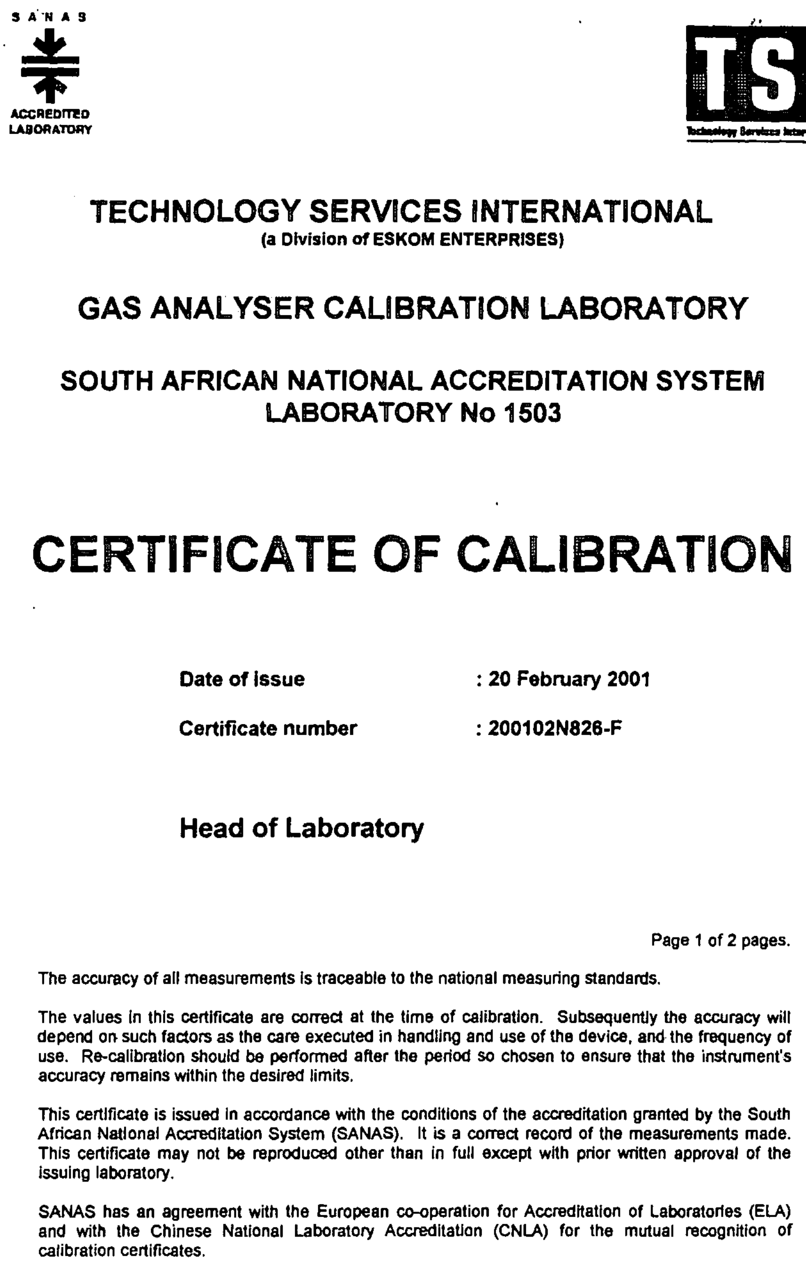
```
Regression Analysis - Linear model: Y = a+bX
-----------------------------------------------------------------------------
Dependent variable: DWWM1000.Noxrespons  Independent variable: DWWM1000.Noxaud
-----------------------------------------------------------------------------
                                Standard             T              Prob.
Parameter         Estimate        Error            Value            Level
-----------------------------------------------------------------------------
Intercept          4.87971        3.32037         1.46963           .23800
Slope             0.997637     7.04135E-3         141.683           .00000
-----------------------------------------------------------------------------

                           Analysis of Variance
-----------------------------------------------------------------------------
Source             Sum of Squares     Df  Mean Square    F-Ratio  Prob. Level
Model                   384945.32      1    384945.32    20074.0       .00000
Error                   57.528925      3    19.176308
-----------------------------------------------------------------------------
Total (Corr.)           385002.85      4

Correlation Coefficient = 0.999925          R-squared =  99.99 percent
Stnd. Error of Est. = 4.37908
```

Appendix A-2

Calibration certificates and data for active analyser at Settler's School for 20 February 2001.



TECHNOLOGY SERVICES INTERNATIONAL
(a Division of ESKOM ENTERPRISES)

GAS ANALYSER CALIBRATION LABORATORY

SOUTH AFRICAN NATIONAL ACCREDITATION SYSTEM
LABORATORY No 1503

CERTIFICATE OF CALIBRATION

Date of issue : 20 February 2001

Certificate number : 200102N826-F

Head of Laboratory

Page 1 of 2 pages.

The accuracy of all measurements is traceable to the national measuring standards.

The values in this certificate are correct at the time of calibration. Subsequently the accuracy will depend on such factors as the care executed in handling and use of the device, and the frequency of use. Re-calibration should be performed after the period so chosen to ensure that the instrument's accuracy remains within the desired limits.

This certificate is issued in accordance with the conditions of the accreditation granted by the South African National Accreditation System (SANAS). It is a correct record of the measurements made. This certificate may not be reproduced other than in full except with prior written approval of the issuing laboratory.

SANAS has an agreement with the European co-operation for Accreditation of Laboratories (ELA) and with the Chinese National Laboratory Accreditation (CNLA) for the mutual recognition of calibration certificates.

Appendix A-2 continued

ADVANCE POLLUTION INSTRUMENTS (API) 200A NO_X ANALYSER SN: 1570

INITIAL ZERO AND SPAN CHECK

The zero response was checked using zero air, returning a response of 0.4ppb on the NO channel and 1.0ppb on the NO_2 channel. The span response was checked at 858.0ppb generated by dilution of the standard gas via the TSI calibrator, with the analyser NO_2 converter in-line. This returned a response of 1065.0ppb (24.1% high) on the NO channel, 10.0ppb on the NO_2 and 1075.0ppb on the NO_X channel.

DYNAMIC CALIBRATION

Further zero and span checks were carried out to enable the analyser NO response to be corrected to the audit concentration of 858.0ppb, with the analyser NO_2 converter out-of-line. Following this, three intermediate response checks were done to check the analyser linearity. The final calibration results are shown below:-

Audit Concentration	**Analyser response**			**NO Deviation (ppb)**
	NO	NO_2	NO_X	
0	2	1	3	<3
288.4	288	1	289	<1
345.8	348	1	349	<4
431.7	434	1	435	<4
858.0	858	1	859	<1

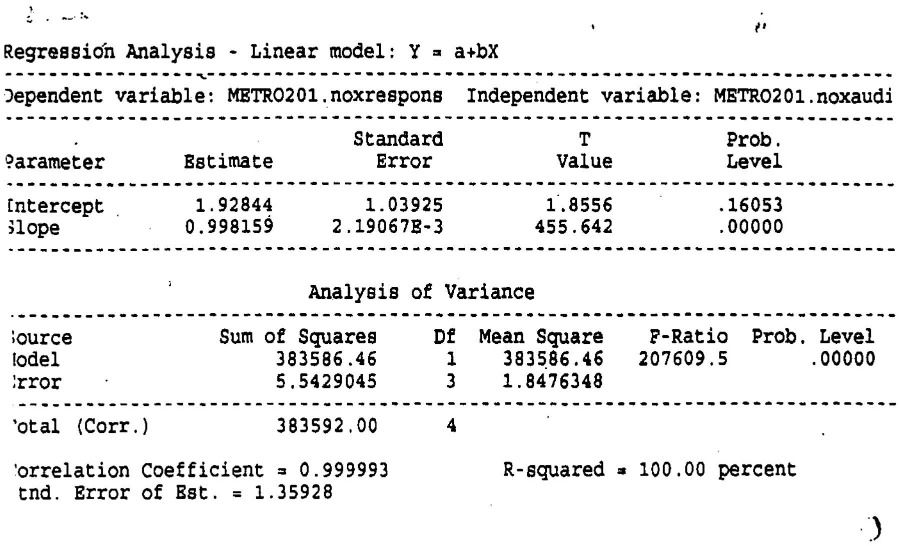
The NO_2 converter efficiency was checked and found to be 97.9%, which falls within the manufactures specifications..

A calibration certificate (200102N826-F) for this analyser is enclosed, together with the regression analysis carried out on the results.

INSTRUMENT STATUS

System Function	**Limits**	**Units**	**Initial Value**	**Final Value**
Operating Range	-	ppb	0 - 1000	0 - 1000
Output Range	-	V	0 - 1	0 - 1
Gas Pressure	25 - 35	in Hg	28.9	29.1
Sample Flow	0.65 ±0.065	Lpm	0.49	0.49
Ozone Flow	±80	cc/min	77	78
A Zero	-	mV	16.2	14.9
PMT Signal	0 - 5000	mV	19.2	22.5
PMT Temperature	7 ±1	°C	7.3	7.4
HVPS	400 - 900	mV	720	720
DCPS	2500 ±200	mV	2606	2605
Converter temp	-	°C	315.2	315.7
R/Cell Temperature	50 ±1	°C	50.4	50.0
R/Cell pressure	-	in Hg	7.8	7.8
NO_X slope	1 ±0.2	-	1.049	0.846
NO_X offset	-	-	-0.8	-0.8
NO slope	1 ±0.2	-	1.059	0.844
NO offset	-	-	-2.0	-2.0
IZS Temperature	50 ±1	°C	50.1	50.1
Test Voltage	-	mV	7.0	4.4

Appendix A-2 continued



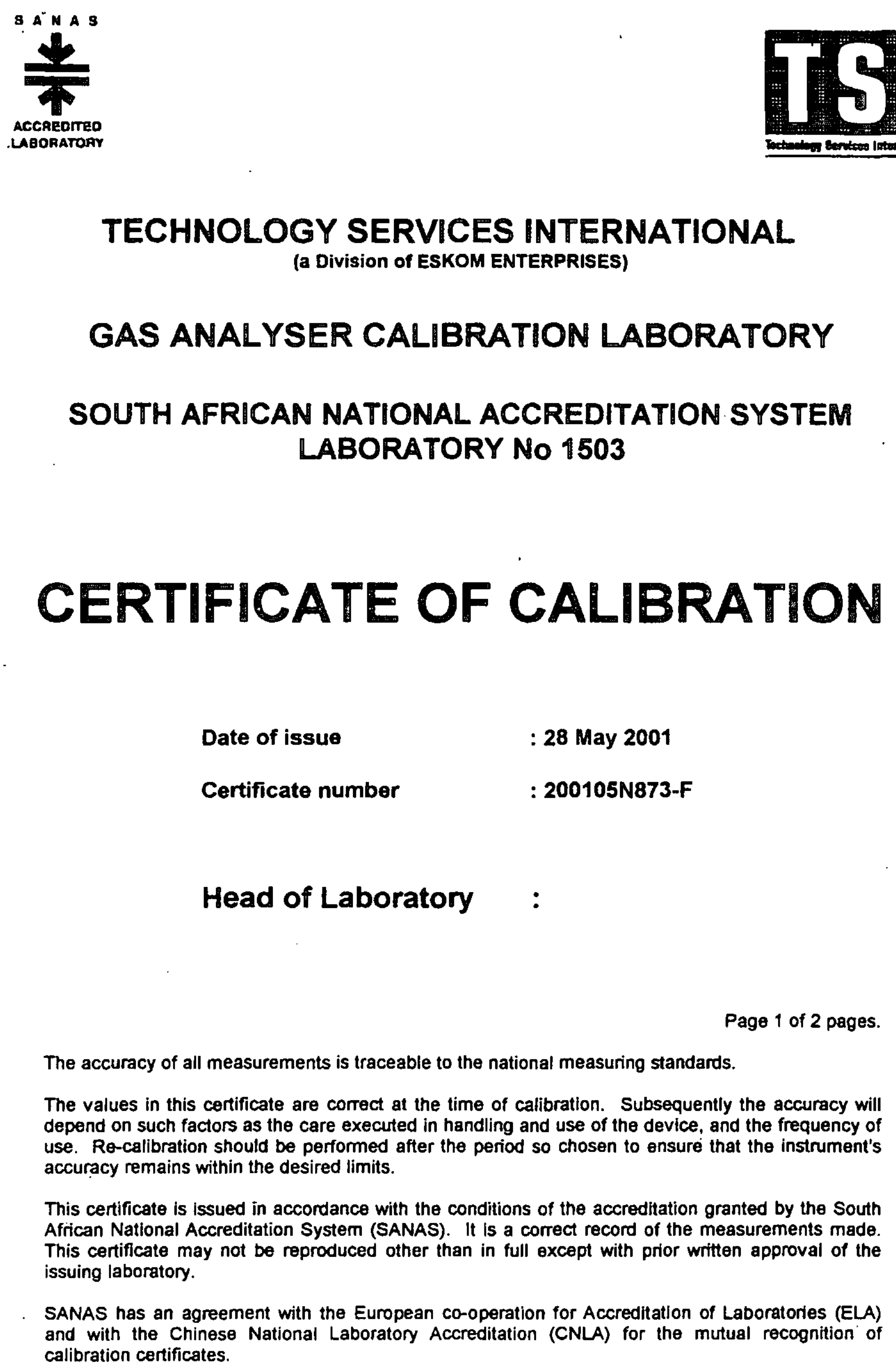
```
Regression Analysis - Linear model: Y = a+bX
------------------------------------------------------------------------------
ependent variable: METRO201.noxrespons  Independent variable: METRO201.noxaudi
------------------------------------------------------------------------------
                               Standard             T               Prob.
arameter         Estimate        Error            Value             Level
------------------------------------------------------------------------------
ntercept          1.92844        1.03925          1.8556            .16053
lope              0.998159     2.19067E-3        455.642            .00000
------------------------------------------------------------------------------

                               Analysis of Variance
------------------------------------------------------------------------------
ource                  Sum of Squares    Df  Mean Square    F-Ratio  Prob. Level
odel                        383586.46     1    383586.46   207609.5       .00000
rror                        5.5429045     3    1.8476348
------------------------------------------------------------------------------
otal (Corr.)                383592.00     4

orrelation Coefficient = 0.999993           R-squared = 100.00 percent
tnd. Error of Est. = 1.35928
```

Appendix A-3

Calibration certificates and data for active analyser at Settler's School for 28 May 2001.



SANAS
ACCREDITED
LABORATORY

TSI
Technology Services International

TECHNOLOGY SERVICES INTERNATIONAL

(a Division of ESKOM ENTERPRISES)

GAS ANALYSER CALIBRATION LABORATORY

SOUTH AFRICAN NATIONAL ACCREDITATION SYSTEM LABORATORY No 1503

CERTIFICATE OF CALIBRATION

Date of issue : 28 May 2001

Certificate number : 200105N873-F

Head of Laboratory :

Page 1 of 2 pages.

The accuracy of all measurements is traceable to the national measuring standards.

The values in this certificate are correct at the time of calibration. Subsequently the accuracy will depend on such factors as the care executed in handling and use of the device, and the frequency of use. Re-calibration should be performed after the period so chosen to ensure that the instrument's accuracy remains within the desired limits.

This certificate is issued in accordance with the conditions of the accreditation granted by the South African National Accreditation System (SANAS). It is a correct record of the measurements made. This certificate may not be reproduced other than in full except with prior written approval of the issuing laboratory.

SANAS has an agreement with the European co-operation for Accreditation of Laboratories (ELA) and with the Chinese National Laboratory Accreditation (CNLA) for the mutual recognition of calibration certificates.

Appendix A-3 continued

ADVANCE POLLUTION INSTRUMENTS (API) 200A NO_X ANALYSER SN: 1570

INITIAL ZERO AND SPAN CHECK

The zero response was checked using zero air, returning a response of -0.5ppb on the NO channel and 2.0ppb on the NO_2 channel. The span response was checked at 858.0ppb generated by dilution of the standard gas via the TSI calibrator, with the analyser NO_2 converter in-line. This returned a response of 918.0ppb (7.0% high) on the NO channel, 10.0ppb on the NO_2 and 928.0ppb on the NO_X channel.

DYNAMIC CALIBRATION

Further zero and span checks were carried out to enable the analyser NO response to be corrected to the audit concentration of 858.0ppb, with the analyser NO_2 converter out-of-line. Following this, three intermediate response checks were done to check the analyser linearity. The final calibration results are shown below:-

Audit Concentration	Analyser response			NO Deviation (ppb)
	NO	NO_2	NO_X	
0	1	1	2	<2
345.8	342	1	343	<4
431.7	430	1	431	<2
574.4	572	1	573	<3
858.0	858	1	859	<1

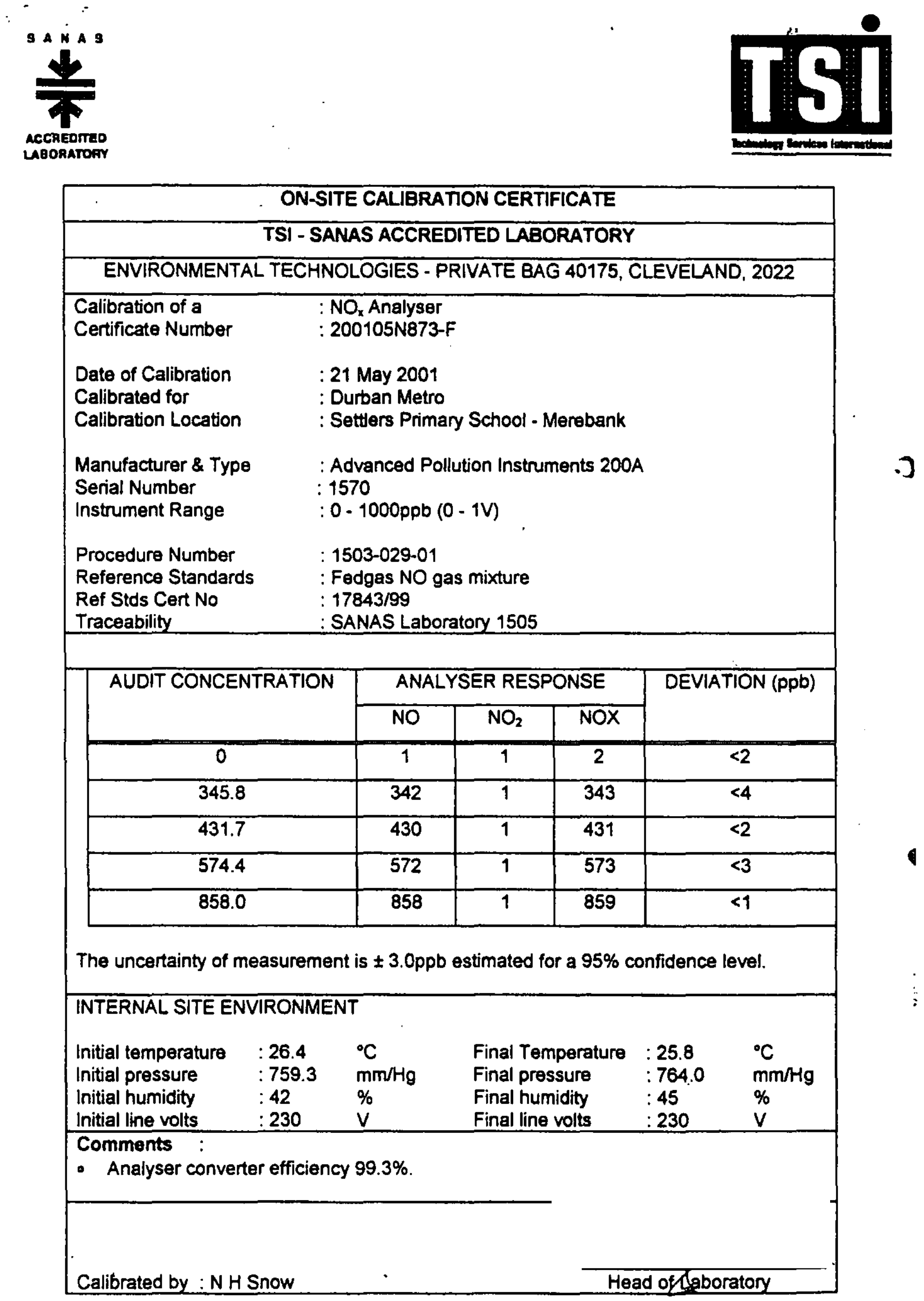
The NO_2 converter efficiency was checked and found to be 99.3%, which falls within the manufactures specifications..

A calibration certificate (200105N873-F) for this analyser is enclosed, together with the regression analysis carried out on the results.

INSTRUMENT STATUS

System Function	Limits	Units	Initial Value	Final Value
Operating Range	-	ppb	0 - 1000	0 - 1000
Output Range	-	V	0 - 1	0 - 1
Gas Pressure	25 - 35	in Hg	28.4	29.0
Sample Flow	0.65 ±0.065	Lpm	0.49	0.49
Ozone Flow	±80	cc/min	77	78
A Zero	-	mV	17.6	17.3
PMT Signal	0 - 5000	mV	25.4	20.0
PMT Temperature	7 ±1	°C	7.3	7.3
HVPS	400 - 900	mV	708	708
DCPS	2500 ±200	mV	2610	2610
Converter temp	-	°C	315.4	314.6
R/Cell Temperature	50 ±1	°C	50.1	50.1
R/Cell pressure	-	in Hg	10.3	10.5
NO_X slope	1 ±0.2	-	0.916	0.865
NO_X offset	-	-	-0.8	0.5
NO slope	1 ±0.2	-	0.918	0.878
NO offset	-	-	-0.5	-2.3
IZS Temperature	50 ±1	°C	50.3	50.2
Test Voltage	-	mV	5.5	4.9

Appendix A-3 continued



SANAS
ACCREDITED
LABORATORY

TSI
Technology Services International

ON-SITE CALIBRATION CERTIFICATE

TSI - SANAS ACCREDITED LABORATORY

ENVIRONMENTAL TECHNOLOGIES - PRIVATE BAG 40175, CLEVELAND, 2022

Calibration of a : NO_x Analyser
Certificate Number : 200105N873-F

Date of Calibration : 21 May 2001
Calibrated for : Durban Metro
Calibration Location : Settlers Primary School - Merebank

Manufacturer & Type : Advanced Pollution Instruments 200A
Serial Number : 1570
Instrument Range : 0 - 1000ppb (0 - 1V)

Procedure Number : 1503-029-01
Reference Standards : Fedgas NO gas mixture
Ref Stds Cert No : 17843/99
Traceability : SANAS Laboratory 1505

AUDIT CONCENTRATION	ANALYSER RESPONSE			DEVIATION (ppb)
	NO	NO_2	NOX	
0	1	1	2	<2
345.8	342	1	343	<4
431.7	430	1	431	<2
574.4	572	1	573	<3
858.0	858	1	859	<1

The uncertainty of measurement is ± 3.0ppb estimated for a 95% confidence level.

INTERNAL SITE ENVIRONMENT

Initial temperature	: 26.4	°C	Final Temperature	: 25.8	°C
Initial pressure	: 759.3	mm/Hg	Final pressure	: 764.0	mm/Hg
Initial humidity	: 42	%	Final humidity	: 45	%
Initial line volts	: 230	V	Final line volts	: 230	V

Comments :

- Analyser converter efficiency 99.3%.

Calibrated by : N H Snow

Head of Laboratory

Appendix A-3 continued

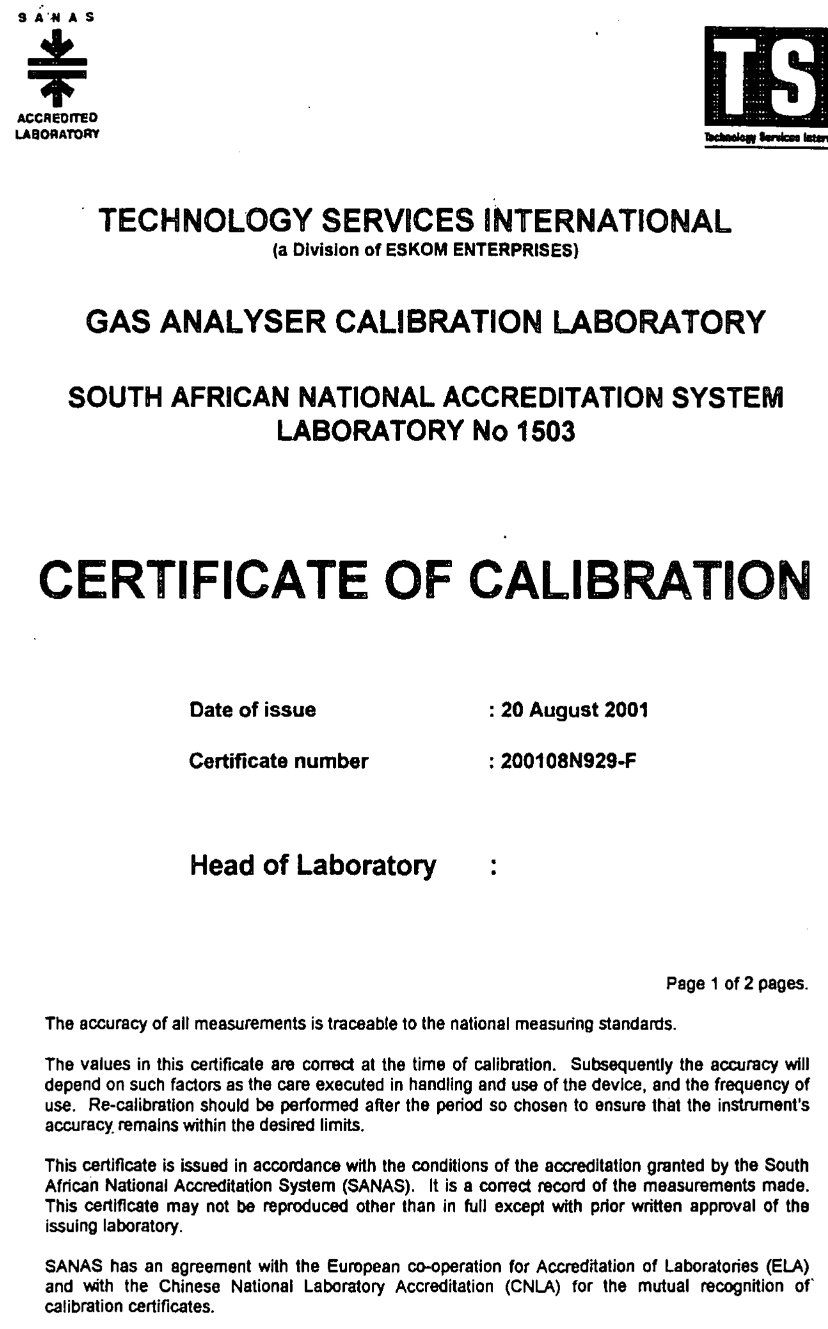
```
Regression Analysis - Linear model: Y = a+bX
-----------------------------------------------------------------------------
Dependent variable: METRO501.noxrespons  Independent variable: METRO501.noxau
-----------------------------------------------------------------------------
                                Standard            T              Prob.
Parameter        Estimate         Error           Value            Level
-----------------------------------------------------------------------------
Intercept        -1.65284        1.56591        -1.05552          .36868
Slope             1.00016     2.98928E-3         334.583          .00000
-----------------------------------------------------------------------------

                           Analysis of Variance
-----------------------------------------------------------------------------
Source              Sum of Squares     Df  Mean Square    F-Ratio  Prob. Level
Model                    395440.60      1    395440.60   111946.1       .00000
Error                    10.597262      3     3.532421
-----------------------------------------------------------------------------
Total (Corr.)            395451.20      4

Correlation Coefficient = 0.999987          R-squared = 100.00 percent
Stnd. Error of Est. = 1.87947
```

Appendix A-4

Calibration certificates and data for active analyser at Settler's School for 20 August 2001.



S A N A S
ACCREDITED
LABORATORY

TSI
Technology Services International

TECHNOLOGY SERVICES INTERNATIONAL
(a Division of ESKOM ENTERPRISES)

GAS ANALYSER CALIBRATION LABORATORY

SOUTH AFRICAN NATIONAL ACCREDITATION SYSTEM
LABORATORY No 1503

CERTIFICATE OF CALIBRATION

Date of issue : 20 August 2001

Certificate number : 200108N929-F

Head of Laboratory :

Page 1 of 2 pages.

The accuracy of all measurements is traceable to the national measuring standards.

The values in this certificate are correct at the time of calibration. Subsequently the accuracy will depend on such factors as the care executed in handling and use of the device, and the frequency of use. Re-calibration should be performed after the period so chosen to ensure that the instrument's accuracy remains within the desired limits.

This certificate is issued in accordance with the conditions of the accreditation granted by the South African National Accreditation System (SANAS). It is a correct record of the measurements made. This certificate may not be reproduced other than in full except with prior written approval of the issuing laboratory.

SANAS has an agreement with the European co-operation for Accreditation of Laboratories (ELA) and with the Chinese National Laboratory Accreditation (CNLA) for the mutual recognition of calibration certificates.

Appendix A-4 continued

ADVANCE POLLUTION INSTRUMENTS (API) 200A NO_X ANALYSER SN: 1570

INITIAL ZERO AND SPAN CHECK

The zero response was checked using zero air, returning a response of 0.6ppb on the NO channel and -0.4ppb on the NO_2 channel. The span response was checked at 858.0ppb generated by dilution of the standard gas via the TSI calibrator, with the analyser NO_2 converter in-line. This returned a response of 831.0ppb (2.9% low) on the NO channel, 1.6ppb on the NO_2 and 832.60ppb on the NO_X channel.

↓ +2

DYNAMIC CALIBRATION

Further zero and span checks were carried out to enable the analyser NO response to be corrected to the audit concentration of 858.0ppb, with the analyser NO_2 converter out-of-line. Following this, three intermediate response checks were done to check the analyser linearity. The final calibration results are shown below:-

Audit Concentration	Analyser response			NO Deviation (ppb)
	NO	NO_2	NO_X	
0	1	1	2	<2
345.8	343	0	343	<3
431.7	430	0	430	<2
574.4	574	0	574	<1
858.0	858	0	858	<1

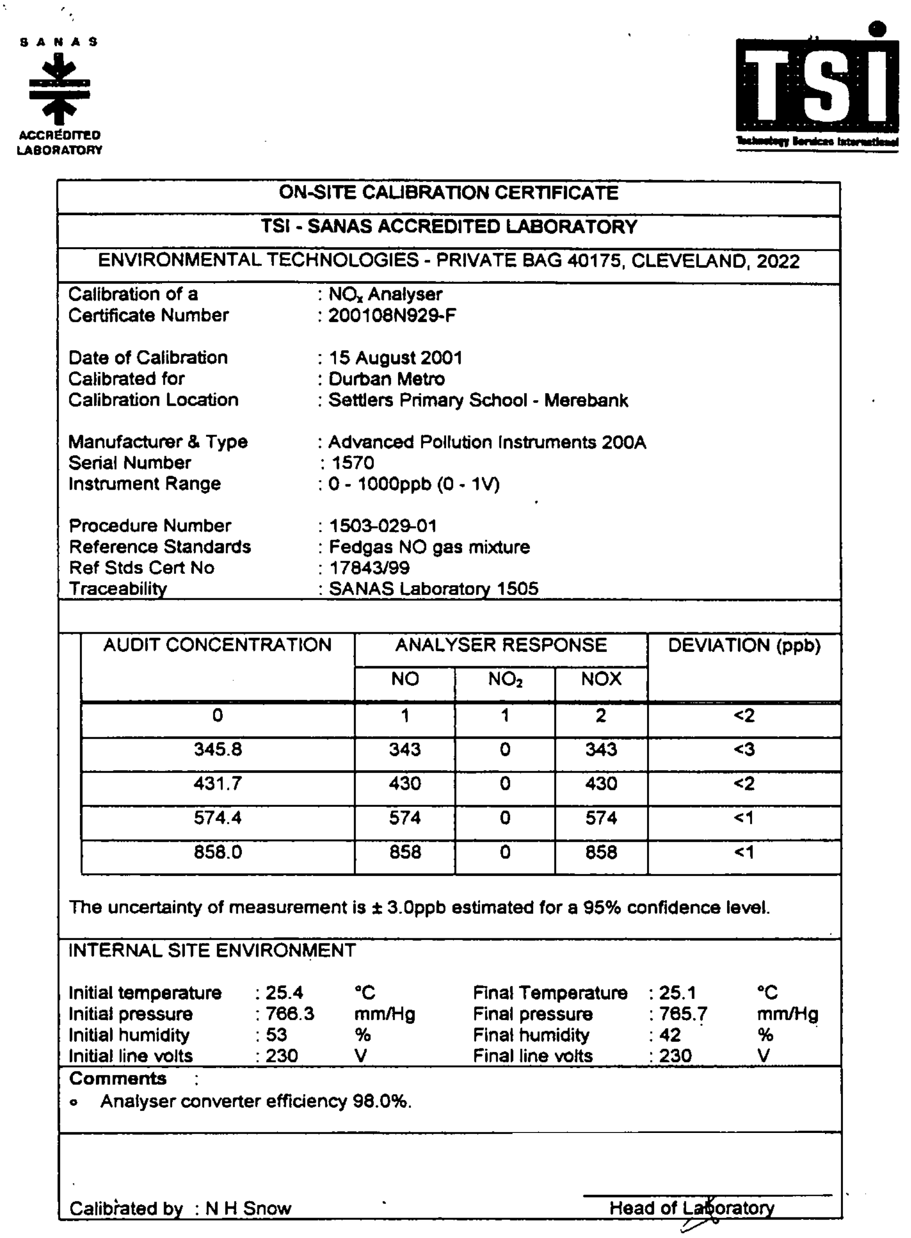
The NO_2 converter efficiency was checked and found to be 98.0%, which falls within the manufactures specifications..

A calibration certificate (200108N929-F) for this analyser is enclosed, together with the regression analysis carried out on the results.

INSTRUMENT STATUS

System Function	Limits	Units	Initial Value	Final Value
Operating Range	-	ppb	0 - 1000	0 - 1000
Output Range	-	V	0 - 1	0 - 1
Gas Pressure	25 - 35	in Hg	28.4	28.4
Sample Flow	0.65 ±0.065	Lpm	0.49	0.49
Ozone Flow	±80	cc/min	77	78
A Zero	-	mV	17.6	25.4
PMT Signal	0 - 5000	mV	25.4	32.1
PMT Temperature	7 ±1	°C	7.3	7.4
HVPS	400 - 900	mV	708	708
DCPS	2500 ±200	mV	2610	2605
Converter temp	-	°C	315.4	315.2
R/Cell Temperature	50 ±1	°C	50.1	50.2
R/Cell pressure	-	in Hg	10.3	12.1
NO_X slope	1 ±0.2	-	0.865	0.894
NO_X offset	-	-	0.5	0.5
NO slope	1 ±0.2	-	0.878	0.902
NO offset	-	-	-2.3	-2.3
IZS Temperature	50 ±1	°C	50.3	50.0
Test Voltage	-	mV	4.9	6.4

Appendix A-4 continued



SANAS ACCREDITED LABORATORY

TSI Technology Services International

ON-SITE CALIBRATION CERTIFICATE

TSI - SANAS ACCREDITED LABORATORY

ENVIRONMENTAL TECHNOLOGIES - PRIVATE BAG 40175, CLEVELAND, 2022

Calibration of a : NO_x Analyser
Certificate Number : 200108N929-F

Date of Calibration : 15 August 2001
Calibrated for : Durban Metro
Calibration Location : Settlers Primary School - Merebank

Manufacturer & Type : Advanced Pollution Instruments 200A
Serial Number : 1570
Instrument Range : 0 - 1000ppb (0 - 1V)

Procedure Number : 1503-029-01
Reference Standards : Fedgas NO gas mixture
Ref Stds Cert No : 17843/99
Traceability : SANAS Laboratory 1505

AUDIT CONCENTRATION	ANALYSER RESPONSE			DEVIATION (ppb)
	NO	NO_2	NOX	
0	1	1	2	<2
345.8	343	0	343	<3
431.7	430	0	430	<2
574.4	574	0	574	<1
858.0	858	0	858	<1

The uncertainty of measurement is ± 3.0ppb estimated for a 95% confidence level.

INTERNAL SITE ENVIRONMENT

Initial temperature	: 25.4	°C	Final Temperature	: 25.1	°C
Initial pressure	: 766.3	mm/Hg	Final pressure	: 765.7	mm/Hg
Initial humidity	: 53	%	Final humidity	: 42	%
Initial line volts	: 230	V	Final line volts	: 230	V

Comments :

- Analyser converter efficiency 98.0%.

Calibrated by : N H Snow

Head of Laboratory

Appendix A-4 continued

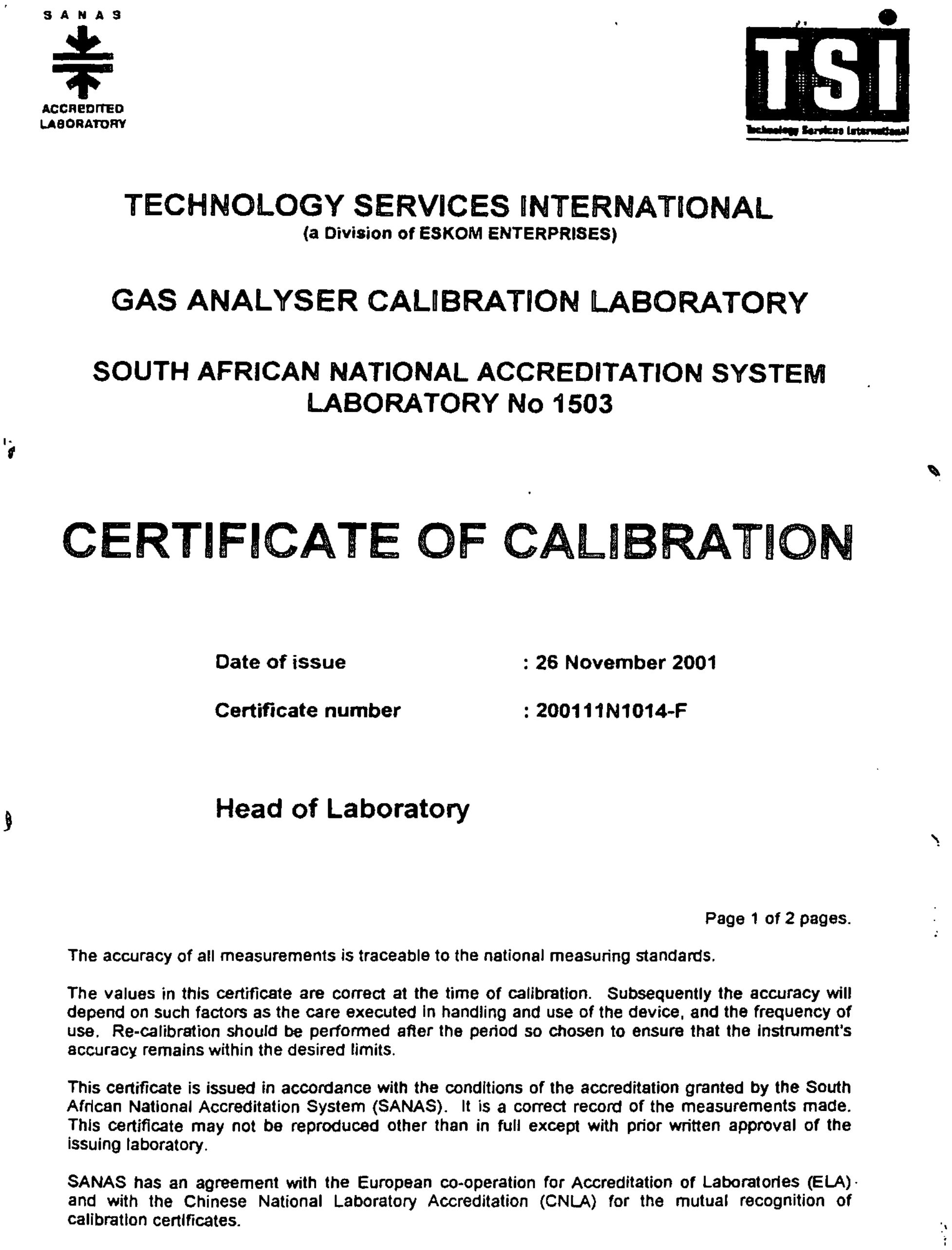
```
egression Analysis - Linear model: Y = a+bX
--------------------------------------------------------------------------------
ependent variable: DBN0801.cnoxrespon   Independent variable: DBN0801.cnoxaudit
--------------------------------------------------------------------------------
                                 Standard             T              Prob.
arameter         Estimate           Error            Value            Level
--------------------------------------------------------------------------------
ntercept         -0.82492         1.32169        -0.624142          .57678
lope             0.999921      2.52307E-3          396.311          .00000
--------------------------------------------------------------------------------

                            Analysis of Variance
--------------------------------------------------------------------------------
ource              Sum of Squares     Df  Mean Square    F-Ratio  Prob. Level
odel                    395247.54      1    395247.54   157062.2       .00000
rror                    7.5495097      3    2.5165032
--------------------------------------------------------------------------------
otal (Corr.)            395255.09      4

orrelation Coefficient = 0.99999          R-squared = 100.00 percent
nd. Error of Est. = 1.58635
```

Appendix A-5

Calibration certificates and data for active analyser at Settler's School for 26 November 2001.



SANAS
ACCREDITED
LABORATORY

TSI
Technology Services International

TECHNOLOGY SERVICES INTERNATIONAL
(a Division of ESKOM ENTERPRISES)

GAS ANALYSER CALIBRATION LABORATORY

SOUTH AFRICAN NATIONAL ACCREDITATION SYSTEM LABORATORY No 1503

CERTIFICATE OF CALIBRATION

Date of issue	: 26 November 2001
Certificate number	: 200111N1014-F

Head of Laboratory

Page 1 of 2 pages.

The accuracy of all measurements is traceable to the national measuring standards.

The values in this certificate are correct at the time of calibration. Subsequently the accuracy will depend on such factors as the care executed in handling and use of the device, and the frequency of use. Re-calibration should be performed after the period so chosen to ensure that the instrument's accuracy remains within the desired limits.

This certificate is issued in accordance with the conditions of the accreditation granted by the South African National Accreditation System (SANAS). It is a correct record of the measurements made. This certificate may not be reproduced other than in full except with prior written approval of the issuing laboratory.

SANAS has an agreement with the European co-operation for Accreditation of Laboratories (ELA) and with the Chinese National Laboratory Accreditation (CNLA) for the mutual recognition of calibration certificates.

Appendix A-5 continued

ADVANCE POLLUTION INSTRUMENTS (API) 200A NO$_X$ ANALYSER SN: 1570

INITIAL ZERO AND SPAN CHECK

The zero response was checked using zero air, returning a response of 0.6ppb on the NO channel and -0.5ppb on the NO$_2$ channel. The span response was checked at 858.0ppb generated by dilution of the standard gas via the TSI calibrator, with the analyser NO$_2$ converter in-line. This returned a response of 843.0ppb (1.7% low) on the NO channel, 6.0ppb on the NO$_2$ and 849.0ppb on the NO$_X$ channel.

DYNAMIC CALIBRATION

Further zero and span checks were carried out to enable the analyser NO response to be corrected to the audit concentration of 858.0ppb, with the analyser NO$_2$ converter out-of-line. Following this, three intermediate response checks were done to check the analyser linearity. The final calibration results are shown below:-

Audit Concentration	Analyser response			NO Deviation (ppb)
	NO	NO$_2$	NO$_X$	
0	0.7	0.3	1.0	<1
345.8	341	0	341	<5
431.7	427	0	427	<5
574.4	570	0	570	<5
858.0	858	0	858	<1

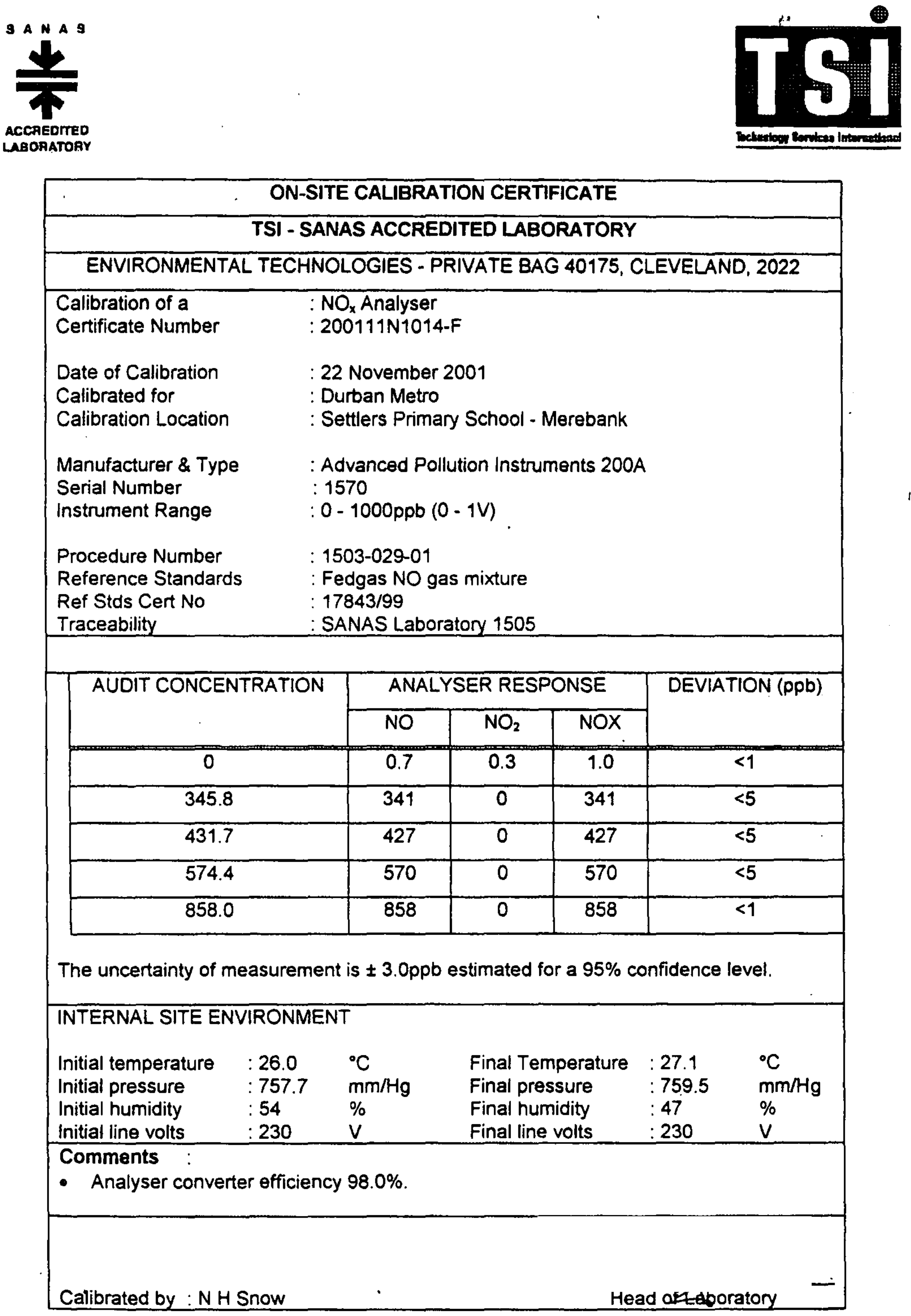
The NO$_2$ converter efficiency was checked and found to be 98.0%, which falls within the manufactures specifications..

A calibration certificate (200111N1014-F) for this analyser is enclosed, together with the regression analysis carried out on the results.

INSTRUMENT STATUS

System Function	Limits	Units	Initial Value	Final Value
Operating Range	-	ppb	0 - 1000	0 - 1000
Output Range	-	V	0 - 1	0 - 1
Gas Pressure	25 - 35	in Hg	28.4	28.3
Sample Flow	0.65 ±0.065	Lpm	0.49	0.48
Ozone Flow	±80	cc/min	77	77
A Zero	-	mV	36.2	36.0
PMT Signal	0 - 5000	mV	41.9	43.2
PMT Temperature	7 ±1	°C	7.2	7.2
HVPS	400 - 900	mV	708	708
DCPS	2500 ±200	mV	2604	2605
Converter temp	-	°C	314.1	315.4
R/Cell Temperature	50 ±1	°C	50.3	50.1
R/Cell pressure	-	in Hg	13.2	13.1
NO$_X$ slope	1 ±0.2	-	0.894	0.912
NO$_X$ offset	-	-	0.5	0.5
NO slope	1 ±0.2	-	0.902	0.992
NO offset	-	-	-2.3	-2.3
IZS Temperature	50 ±1	°C	50.0	50.1
Test Voltage	-	mV	8.0	8.7

Appendix A-5 continued



SANAS ACCREDITED LABORATORY

TSI Technology Services International

ON-SITE CALIBRATION CERTIFICATE

TSI - SANAS ACCREDITED LABORATORY

ENVIRONMENTAL TECHNOLOGIES - PRIVATE BAG 40175, CLEVELAND, 2022

Calibration of a	: NO_x Analyser
Certificate Number	: 200111N1014-F
Date of Calibration	: 22 November 2001
Calibrated for	: Durban Metro
Calibration Location	: Settlers Primary School - Merebank
Manufacturer & Type	: Advanced Pollution Instruments 200A
Serial Number	: 1570
Instrument Range	: 0 - 1000ppb (0 - 1V)
Procedure Number	: 1503-029-01
Reference Standards	: Fedgas NO gas mixture
Ref Stds Cert No	: 17843/99
Traceability	: SANAS Laboratory 1505

AUDIT CONCENTRATION	ANALYSER RESPONSE			DEVIATION (ppb)
	NO	NO_2	NOX	
0	0.7	0.3	1.0	<1
345.8	341	0	341	<5
431.7	427	0	427	<5
574.4	570	0	570	<5
858.0	858	0	858	<1

The uncertainty of measurement is ± 3.0ppb estimated for a 95% confidence level.

INTERNAL SITE ENVIRONMENT

Initial temperature	: 26.0	°C	Final Temperature	: 27.1	°C
Initial pressure	: 757.7	mm/Hg	Final pressure	: 759.5	mm/Hg
Initial humidity	: 54	%	Final humidity	: 47	%
Initial line volts	: 230	V	Final line volts	: 230	V

Comments :

- Analyser converter efficiency 98.0%.

Calibrated by : N H Snow

Head of Laboratory

Appendix A-5 continued

ADVANCE POLLUTION INSTRUMENTS (API) 200A NO_X ANALYSER SN: 1570

INITIAL ZERO AND SPAN CHECK

The zero response was checked using zero air, returning a response of 0.6ppb on the NO channel and -0.5ppb on the NO_2 channel. The span response was checked at 858.0ppb generated by dilution of the standard gas via the TSI calibrator, with the analyser NO_2 converter in-line. This returned a response of 843.0ppb (1.7% low) on the NO channel, 6.0ppb on the NO_2 and 849.0ppb on the NO_X channel.

DYNAMIC CALIBRATION

Further zero and span checks were carried out to enable the analyser NO response to be corrected to the audit concentration of 858.0ppb, with the analyser NO_2 converter out-of-line. Following this, three intermediate response checks were done to check the analyser linearity. The final calibration results are shown below:-

Audit Concentration	Analyser response			NO Deviation (ppb)
	NO	NO_2	NO_X	
0	0.7	0.3	1.0	<1
345.8	341	0	341	<5
431.7	427	0	427	<5
574.4	570	0	570	<5
858.0	858	0	858	<1

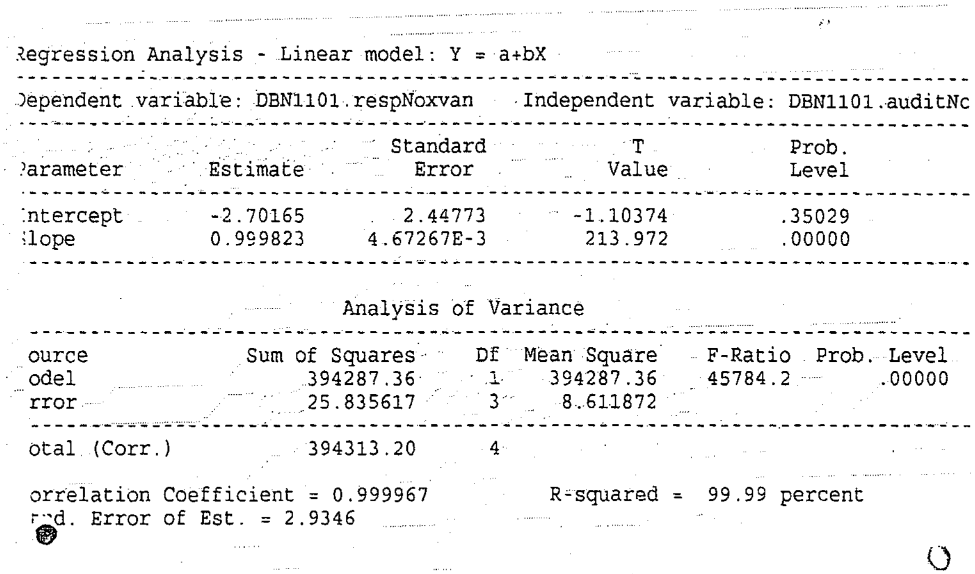
The NO_2 converter efficiency was checked and found to be 98.0%, which falls within the manufactures specifications..

A calibration certificate (200111N1014-F) for this analyser is enclosed, together with the regression analysis carried out on the results.

INSTRUMENT STATUS

System Function	Limits	Units	Initial Value	Final Value
Operating Range	-	ppb	0 - 1000	0 - 1000
Output Range	-	V	0 - 1	0 - 1
Gas Pressure	25 - 35	in Hg	28.4	28.3
Sample Flow	0.65 ±0.065	Lpm	0.49	0.48
Ozone Flow	±80	cc/min	77	77
A Zero	-	mV	36.2	36.0
PMT Signal	0 - 5000	mV	41.9	43.2
PMT Temperature	7 ±1	°C	7.2	7.2
HVPS	400 - 900	mV	708	708
DCPS	2500 ±200	mV	2604	2605
Converter temp	-	°C	314.1	315.4
R/Cell Temperature	50 ±1	°C	50.3	50.1
R/Cell pressure	-	in Hg	13.2	13.1
NO_X slope	1 ±0.2	-	0.894	0.912
NO_X offset	-	-	0.5	0.5
NO slope	1 ±0.2	-	0.902	0.992
NO offset	-	-	-2.3	-2.3
IZS Temperature	50 ±1	°C	50.0	50.1
Test Voltage	-	mV	8.0	8.7

Appendix A-5 continued



```
egression Analysis - Linear model: Y = a+bX
-----------------------------------------------------------------------------
ependent variable: DBN1101.respNoxvan    Independent variable: DBN1101.auditNc
-----------------------------------------------------------------------------
                              Standard             T               Prob.
arameter       Estimate         Error             Value            Level
-----------------------------------------------------------------------------
ntercept       -2.70165        2.44773          -1.10374           .35029
lope           0.999823      4.67267E-3          213.972           .00000
-----------------------------------------------------------------------------

                            Analysis of Variance
-----------------------------------------------------------------------------
ource                 Sum of Squares     Df  Mean Square    F-Ratio  Prob. Level
odel                       394287.36      1    394287.36    45784.2      .00000
rror                       25.835617      3     8.611872
-----------------------------------------------------------------------------
otal (Corr.)               394313.20      4

orrelation Coefficient = 0.999967          R-squared =  99.99 percent
d. Error of Est. = 2.9346
```

Appendix B

Traffic Counts per hour

ID_CODE	INTERSECTION		Ave per hr
24	(E) OUTER RING ROAD	HIGGINSON HIGHWAY	3328
504	RUSSELL STREET	WEST STREET	3390
377	N.M.R. AVENUE	GOBLE ROAD	3391
23	(E) OUTER RING ROAD	EDWIN SWALES V.C. DR	3414
244	GREY STREET	ALICE STREET	3449
547	SOUTHERN FREEWAY OFF RAMP	EDWIN SWALES V.C. DR	3455
612	UMGENI ROAD	OLD FORT ROAD	3474
11	N2	AT JOYNER ROAD	3478
26	**(E) OUTER RING ROAD**	**MR93**	**3492**
31	(W) OUTER RING ROAD	R610	3539
562	STANGER STREET	VICTORIA EMBANKMENT	3607
191	FIELD STREET	LEOPOLD STREET	3635
32	(W) OUTER RING ROAD	HIGGINSON HIGHWAY	3672
520	SOLDIERS' WAY	ORDNANCE ROAD	3674
39	ALBERT STREET	ALICE STREET	3687
35	(W) OUTER RING ROAD	MR93	3716
713	(E) R613	OLD MAIN ROAD	3735
401	NORTH COAST ROAD	SEA COW LAKE ROAD	3844
109	BROAD STREET	SMITH STREET	4028
593	UMBILO ROAD	EDWIN SWALES V.C. DR	4029
77	BELLAIR ROAD	EDWIN SWALES V.C. DR	4075
34	(W) OUTER RING ROAD	MR448	4202
400	NORTH COAST ROAD	RIVERSIDE ROAD	4230
27	(E) OUTER RING ROAD	UMGENI ROAD	4239
549	SOUTHERN FREEWAY OFF RAMP	VICTORIA EMBANKMENT	4252
608	UMGENI ROAD	GOBLE ROAD	4348
189	FENTON ROAD	VICTORIA EMBANKMENT	4592
253	GREY STREET	WEST STREET	4593
230	GARDINER STREET	VICTORIA EMBANKMENT	4603
477	RECREATION ROAD	EDWIN SWALES V.C. DR	4610
502	RUSSELL STREET	VICTORIA EMBANKMENT	4764
605	**UMGENI ROAD**	**ARGYLE ROAD**	**4896**
52	ALIWAL STREET	VICTORIA EMBANKMENT	5000
197	FIELD STREET	VICTORIA EMBANKMENT	5188
410	NORTHERN FREEWAY	ARGYLE ROAD	5233
527	**SOUTH COAST ROAD**	**EDWIN SWALES V.C. DR**	**5479**
112	BROAD STREET	VICTORIA EMBANKMENT	6164
429	**OUTER RING ROAD**	**WESTERN FREEWAY**	**12322**

ID_CODE INTERSECTION Ave per hr

Appendix C-1

Method prescribed for the determination nitrogen dioxide as by the Ogawa passive Sampler manufacturer.

Analytical Method for NO2

While preparing the reagents always use reagent grade chemicals, or highest grade available.
For the analysis of NO2 you will need the following reagents:

Sulfanilamide Solution

The sulfanilamide solution is prepared by dissolving 80 g of reagent grade sulfanilamide in a mixture of 200 ml concentrated phosphoric acid and 700 ml water. This solution is then diluted with water to make a total of 1000 ml.

NEDA Solution

The NEDA solution is prepared by dissolving 0.56 g N-(1-Naphthyl)-ethylenediamine dihydrochloride into 100 ml water. Store in a refrigerator.

Color Producing Reagent

Prepare color-producing reagent immediately before use. Mix the sulfanilamide solution and the NEDA solution in a 10:1 ratio. (10 parts Sulfanilamide solution to 1 part NEDA solution).

Nitrite Standard Stock Solution

Dry Sodium Nitrite, for over 4 hours, at a temperature of 105-110 °C. Dissolve 1.5 g of this dried Sodium Nitrite in 1-liter water. A 1 ml sample of this solution contains 1000μg of Nitrite.

Nitrite Working Standard Solution

Dilute the Nitrite standard stock solution by 100 times with water. Then, 0, 2, 4,6,8, and 10 ml samples are each diluted with water to make 100 ml solutions. This produces working standard solutions of 0 - 1.0 μg nitrite/ml.

Analytical Operation

Samples

After exposure to the test environment, the stainless screens and cellulose fiber filter are put into a 25 ml glass vial, containing 8ml water, and then shake immediately. Use separate glass vials for NO2 and NOx elements. Vials should be stoppered, per accepted laboratory practice.

Over the next 30 minutes, occasional shaking of the vials is recommended.

At the end of the first 30 minute period, vials are cooled to 2-6 °C, and 2 ml of color producing reagent are added. Shake quickly, after adding the color-producing reagent, and continue to keep vials cool for an additional 30 minutes.

Vials are then allowed to equilibrate at room temperature, for about 20 minutes, and the amount of colored derivative is determined with a spectrophotometer at a wavelength of 545 nm.

Unexposed elements are put through the same procedure to obtain a blank value determination.

Standard Solutions

From the previously prepared nitrite working standard solutions, (those containing 0 - 1.0 µg nitrite/ml), mix 8 ml of each of the nitrite working standards with 2 ml of color reagent, shaking immediately, to prepare a standard curve. Chill standard solution, like samples, before adding color reagent.

Supplement

It is strongly recommended that separate pipettes be used for nitrite standard stock solution from those used for preparing nitrite working standard solutions.

When the exposed NOx element is placed in a vial with 8 ml of water, nitrite ion is produced. When 2 ml of the color producing reagent is added, and the reaction is allowed to take place at 2-6 °C, the amount of colored derivative produced is proportional to the amount of original nitrite. If the reaction takes place at warmer temperatures the amount of color derivative produced is not consistent.

It is recommended to use at least 3 blanks for each lot analyzed.

Procedures that help secure accurate analysis results include:

1. Screens and/or filter pads should be added to vials already containing a solution, never into a dry vial.

2. Vials must be shaken immediately after adding color reagent.

3. Cooling must be done according to the protocol.

Appendix C-2

Calculation of Concentration for NO2

In order to do the calculation you need to do the following steps:

1. Preparing the Standard Curve
2. Calculation of Concentration Data

Preparing the Standard Curve

In this procedure we will establish the Slope of the standard curve. You will need access to a spectrometer or a colorimeter and you will measure the absorbance of 6 standard samples.

1. Refer to Table 2 on the following page. The first two columns refer to values related to the concentration of the standard NO_2 solution. The next three columns refer to values related to the absorbance. The last column refers to the calculation of the Slope of the standard curve. Begin at the top left and proceed by filling in values in the different cells. Those cells which have been "*grayed out*" do not require a numerical value. When you finally enter a value at the bottom right cell you have completed the computation procedure.
2. Make sure that you have access to six standard samples. Make sure that the standard samples are of 0, 0.1, 0.2, 0.4, 0.6 and 0.8 µg/ml NO_2 solutions.
3. The first column requires the concentration of the standard sample (x). Enter the values if they do not exist on the table.
4. The second column requires the calculation of x^2. Enter the values if they do not exist on the table
5. Compute Σx^2 (sum of all x^2) and enter the value in cell (8).
6. Using your colorimeter or spectrometer to measure the absorbance (y) of each sample. Enter the corresponding values in cell (2) through (7).
7. Cell (2) represents the blank absorbance y_0 (i.e. absorbance when the concentration is 0.0 µg/ml). Using this value calculate ($y - y_0$) and enter the net absorbance A for the various standard samples.
8. The next row represents the product between the concentration and the absorbance. Fill in the values of $x(y - y_o)$.
9. Compute $\Sigma x(y-y_0)$ and enter the sum in cell (9).
10. Compute the Slope by calculating $\frac{\Sigma x(y-y_0)}{\Sigma x^2}$ (cell (9) divided by (8) and enter the value in cell G

Appendix C-2 continued

Concentration of Standard NO_2 Solution (μg/ml)		Absorbance			Slope
x	x^2	y	$y - y_0$	$x(y - y_0)$	$\frac{\Sigma x(y-y_0)}{\Sigma x^2}$
(1)	(1) x (1)		A	(1) x A	(9) / (8)
0	0	(2)			
0.1	0.01	(3)	(3) - (2)		
0.2	0.04	(4)	(4) – (2)		
0.4	0.16	(5)	(5) – (2)		
0.6	0.36	(6)	(6) – (2)		
0.8	0.64	(7)	(7) – (2)		
	Σx^2			$\Sigma x(y-y_0)$	(9) / (8)
(8)	1.21			(9)	G

Table 2: Preparing the Standard Curve for NO, NO2 and NOx

CALCULATION OF CONCENTRATION DATA

After the Slope for the standard curve has been prepared, you will calculate the concentration. You will need access to a spectrometer or a colorimeter and you will measure the absorbance of the sample that you have collected. Here are the steps:

1. Refer to Table 3 on the following page. Each calculation has to be repeated several times depending upon the samples which you have.
2. Enter the location (descriptive term) for each site.
3. Enter the exposure time associated with each site. Enter values in row (3)

NO_2 Calculation

Using your spectrometer or colorimeter measure the absorbance for the sample associated with each site. Enter the values in row (9).

Measure the absorbance associated with a blank sample (0 μg/ml). Enter the values in row (2).

Calculate the absorbance for each sample. Enter the values in row (10) by taking the difference between rows (9) and (2).

Calculate the solution concentration in row (11). This is done by taking the absorbance in row (10) and dividing it by G – the Slope of the standard curve. Note, G was computed previously using Table 2.

Calculate the collected weight in ng and enter the value in row (12). This value is obtained by taking a product of the solution concentration (11) and the abstract amount (usually 8 ml) and a factor of 1000 (for converting from PPM to PPB).

Next calculate the concentration in row (13). This value is obtained by multiplying the concentration conversion coefficient α_{NO2} by the collected weight (12) and dividing by the exposure time (3). At 20°C and 70% relative humidity $\alpha_{NO2} = 56$. For other values of temperature and relative humidity please refer to the following section for calculation of α_{NO2}.

Compound	Blank Absorbance	Slope of the Standard Curve	Temperate °C	Rel. Humidity %	Concentration Conversion Coefficient $\propto NO_2$
NO_2	(2)	G =	20	70	56

$\propto NO_2 = 56$ when Temperate °C = 20 and Rel. Humidity % = 70. For other combinations of temperature and relative humidity please refer to the discussion provided in the following section.

Specification		Sample
Sample Number		
Sample Location		
Sample Time (min) (3)	(3)	
Sample Absorbance (9)	(9)	
Absorbance (10)	(9)-(2)	
Solution Concentration (μg/ml) (11)	(10)/G	
Collected Weight (ng) (12)	(11) x 8 x 1000	
Concentration (ppb) (13)	$\propto NO_2$ x (12)/(3)	

Table 3 from Ogawa procedure.

Appendix C-3

Calculation of Concentration Conversion Coefficients for NO and NO_2

Typical values of α_{NO2} are provided in Table 4.

For a combination of temperature and relative humidity which does not exist in Table 4 you can calculate α_{NO2} using the following formulas:

[T] = Ambient temperature in degree Centigrade
[RH] = Relative humidityin %

P_N = 17.535 (water vapor pressure in mm Hg at 20 degC)

P_T = Vapor pressure of water at the ambient temperature [T]
(see Table 5 for typical values)

$$[P]=\left\{\frac{2P_N}{P_T+P_N}\right\}^{2/3}$$

(see Table 5 for typical values)

$$\alpha_{NO_2}=\frac{10000}{(0.677x[P]x[RH])+(2.009x[T])+89.8}$$

Example Calculation for α_{NO} and α_{NO2}

Let us calculate α_{NO2} at 9 °C and 60% Relative Humidity.

Looking at Table 4 we have $\alpha_{NO2} = 64$.

Let us now use the formulas provided earlier:

$$[T] = 9$$
$$[RH] = 60$$
$$P_N = 17.535$$
$$P_T = 8.609 \text{ (see Table 5)}$$
$$[P] = \left\{\frac{2P_N}{P_T + P_N}\right\}^{2/3}$$
$$= \left\{\frac{2\text{x}17.535}{8.609+17.535}\right\}^{2/3}$$
$$= 1.216 \text{ (see Table 5)}$$

$$\alpha_{NO_2} = \frac{10000}{(0.677\text{x}[P]\text{x}[RH]) + (2.009\text{x}[T]) + 89.8}$$
$$= \frac{10000}{(0.677\text{x}1.216\text{x}60) + (2.009\text{x}9) + 89.8}$$
$$= 63.58$$

Appendix C-4

Table 4 shows the conversion coefficient as a function of temperature and relative humidity.

Temperature (°C)	Relative Humidity(%)	α_{NO2}	α_{NO}
-10	50	84	61
-9	50	83	61
-8	50	81	61
-7	50	80	61
-6	50	79	61
-5	50	78	61
-4	50	77	61
-3	50	76	60
-2	50	75	60
-1	50	74	60
0	50	74	60
1	60	68	64
2	60	68	63
3	60	67	63
4	60	66	63
5	60	66	63
6	60	65	62
7	60	65	62
8	60	64	62
9	60	64	61
10	60	63	61
11	60	63	61
12	60	62	60
13	60	62	60
14	60	61	60
15	70	58	63
16	70	58	62
17	70	57	62
18	70	57	61
19	70	57	61
20	70	56	60

Table 4: α_{NO} and α_{NO2} as a function of temperature and relative humidity

... Table continued on next page

Appendix C-5

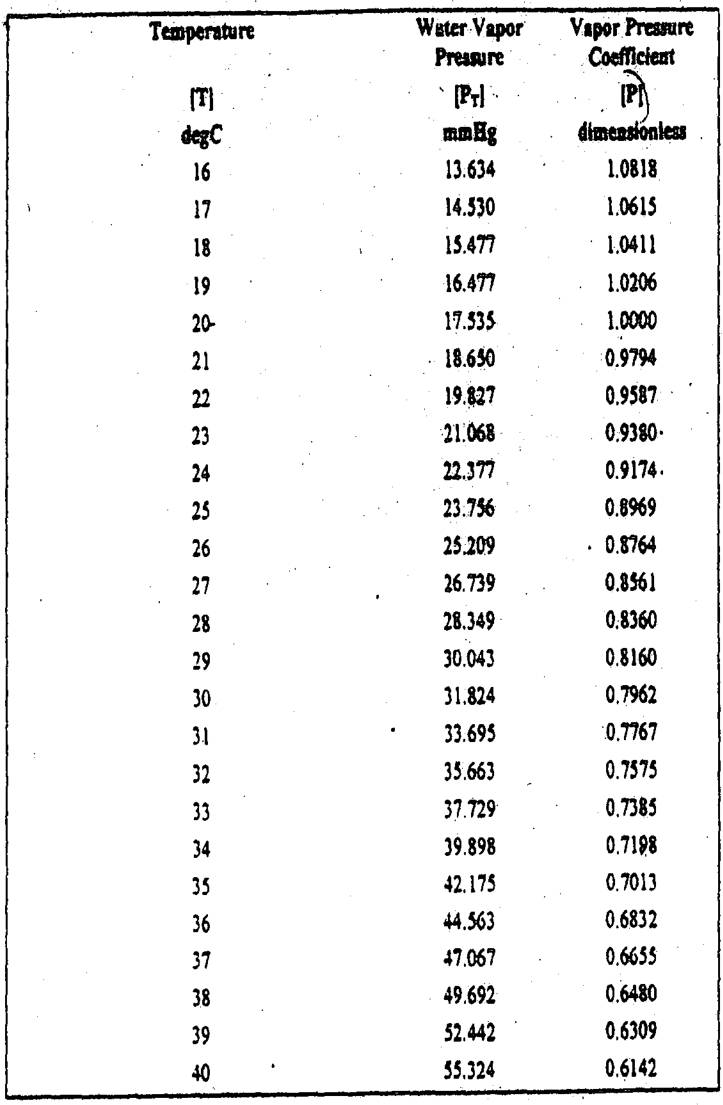
Table 5 shows water vapour coefficients as a function of temperature.

Temperature [T] degC	Water Vapor Pressure $[P_T]$ mmHg	Vapor Pressure Coefficient [P] dimensionless
-10	2.149	1.4697
-9	2.326	1.4609
-8	2.514	1.4518
-7	2.715	1.4421
-6	2.931	1.4320
-5	3.163	1.4213
-4	3.410	1.4101
-3	3.673	1.3984
-2	3.956	1.3861
-1	4.258	1.3732
0	4.579	1.3599
1	4.926	1.3459
2	5.294	1.3314
3	5.685	1.3164
4	6.101	1.3009
5	6.543	1.2849
6	7.013	1.2685
7	7.513	1.2515
8	8.045	1.2341
9	8.609	1.2163
10	9.209	1.1980
11	9.844	1.1794
12	10.518	1.1605
13	11.231	1.1412
14	11.987	1.1217
15	12.788	1.1018

Table 5: Water Vapor Coefficients as a function of Temperature

... Table continued on next page

Appendix C-5 continued



Temperature [T] degC	Water Vapor Pressure [P_T] mmHg	Vapor Pressure Coefficient [P] dimensionless
16	13.634	1.0818
17	14.530	1.0615
18	15.477	1.0411
19	16.477	1.0206
20	17.535	1.0000
21	18.650	0.9794
22	19.827	0.9587
23	21.068	0.9380
24	22.377	0.9174
25	23.756	0.8969
26	25.209	0.8764
27	26.739	0.8561
28	28.349	0.8360
29	30.043	0.8160
30	31.824	0.7962
31	33.695	0.7767
32	35.663	0.7575
33	37.729	0.7385
34	39.898	0.7198
35	42.175	0.7013
36	44.563	0.6832
37	47.067	0.6655
38	49.692	0.6480
39	52.442	0.6309
40	55.324	0.6142

Table 5: Water Vapor Coefficients as a function of Temperature

Appendix D

Nitrogen dioxide (ppb) results for 14 day pre-liminary study

No. Days Sampled	14 days	14 days	14 days	14 days
Sampling Period	5/9-19/9/00	19/9-3/10	3/10-17/10	17/10-31/10
Survey No.	Survey No.	Survey No.	Survey No.	Survey No.
	1	2	3	4
Victoria Embank.	31	29	35	77
Spaghetti Jun.	27	26	28	45
Edwin Swales	43	37	31	67
Argyle Rd	24	23	26	44
Warwick Ave	46	41	49	79
Sea Cow Lake	28	22	19	51
Wentworth Res.	11	11	8	20
Mobile- Settlers				
Kerb	21	17	20	39
Fence 1	22	16	22	43
Fence 2	sampler fell off	21	20	46
Fence 3	32	27	33	54

Appendix E

Nitrogen dioxide (ppb) results for 7 day study

Sampling Period	Surv No.	VE	SPJ	EDS	ARG	WAR	SCL	WWR	Sett (pass)	Sett (act)	Kerb	F 1	F 2	F3
12/12-19/12/00	1	25.0	21.0	34.0	19.0	33.0	17.0	9.0	7.0	13.3	19.0	15.0	14.0	16.0
30/1-6/2/01	2	18.0	18.0	26.0	14.0	37.0	13.0	6.0	6.0	10.1	13.0	12.0	11.0	10.0
6/2-13/2/01	3	16.0	14.0	21.0	13.0	24.0	10.0	4.0	5.0	8.3	13.0	8.0	9.0	9.0
13/2-20/2/01	4	21.0	18.0	29.0	18.0	31.0	14.0	8.0	7.0	10.3	13.0	12.0	11.0	13.0
20/2-27/2/01	5	18.0	18.0	27.0	15.0	28.0	13.0	6.0	6.0	9.1	13.0	11.0	11.0	12.0
27/2-6/3/01	6	23.0	20.0	28.0	16.0	29.0	15.0	0	0	11.8	0	0	0	0
6/3-13/3/01	7	23.0	20.0	29.0	16.0	28.0	13.0	7.0	6.0	10.2	14.0	14.0	13.0	13.0
13/3-20/3/01	8	22.0	20.0	28.0	16.0	29.0	15.0	9.0	9.0	12.2	15.0	13.0	12.0	13.0
20/3-27/3/01	9	27.0	20.0	31.0		34.0	18.0	11.0	10.0	12.6	18.0	19.0	15.0	15.0
27/3-3/4/01	10	28.0	22.0	32.0	21.0	36.0	17.0	11.0	8.0	11.5	19.0	15.0	16.0	15.0
3/4-10/4/01	11	24.0	18.0	37.0	18.0	31.0	15.0	8.0	8.0	12.7	16.0	16.0	14.0	14.0
8/5-15/5/01	12	46.0	34.0	46.0	32.0	50.0	31.0	19.0	32.0	22.0	25.0	21.0	23.0	24.0
15/5-22/5/01	13	47.0	40.0	51.0	37.0	59.0	35.0	25.0	27.0	29.5	32.0	31.0	30.0	30.0
22/5-29/5/01	14	36.0	30.0	46.0	29.0	44.0	27.0	19.0	20.0	20.2	27.0	24.0	23.0	23.0
29/5-5/6/01	15	39.0	32.0	45.0	30.0	46.0	28.0	17.0	17.0	17.0	25.0	23.0	24.0	22.0
5/6-12/6/01	16	41.0	31.0	48.0	32.0	47.0	29.0	22.0	22.0	20.9	26.0	26.0	24.0	26.0
12/6-19/6/01	17	52.0	38.0	53.0	38.0	60.0	35.0	23.0	26.0	26.9	32.0	31.0	30.0	29.0
19/6-26/6/01	18	35.0	29.0	44.0	27.0	42.0	26.0	16.0	12.0	14.4	24.0	22.0	21.0	22.0
26/6-3/7/01	19	46.0	34.0	49.0	35.0	49.0	32.0	22.0	17.0	20.3	29.0	29.0	26.0	27.0
3/7-10/7/01	20	46.0	36.0	52.0	39.0	54.0	38.0	22.0	20.0	18.2	30.0	24.0	32.0	30.0
10/7-17/7/01	21	58.0	42.0	60.0	41.0	59.0	36.0	28.0	23.0	24.3	36.0	38.0	34.0	33.0
17/7-24/7/01	22	43.0	32.0	44.0	27.0	45.0	27.0	18.0	12.0	13.4	23.0	26.0	21.0	21.0
24/7-31/7/01	23	32.0	26.0	40.0	24.0	37.0	22.0	12.0	12.0	13.9	24.0	21.0	19.0	20.0
31/7-7/8/01	24	33.0	28.0		23.0	47.0	25.0	19.0	15.0	18.7	24.0	21.0	18.0	21.0
7/8-14/8/01	25	30.0	23.0	30.0	25.0	30.0	25.0	15.0	14.0	16.5	22.0	22.0	18.0	19.0
14/8-21/8/01	26	32.0	27.0	39.0	24.0	37.0	24.0	13.0	10.0	13.8	22.0	24.0	19.0	20.0
21/8-28/8/01	27	32.0	26.0	37.0	24.0	39.0	24.0	11.0	12.0	13.7	21.0	18.0	18.0	17.0
28/8-4/9/01	28	38.0	32.0	44.0	29.0	44.0	28.0	18.0	17.0	16.9	25.0	25.0	23.0	22.0
4/9-11/9/01	29	28.0	23.0	33.0	22.0	33.0	20.0	11.0	9.0	10.8	20.0	17.0	16.0	17.0
11/9-18/9/01	30	29.0	24.0	36.0	21.0	34.0	20.0	13.0	9.0	12.5	21.0	19.0	17.0	17.0
9/10-16/10/01	31	25.0	22.0	33.0	20.0	32.0	18.0	10.0	9.0	10.3	19.0	18.0	15.0	16.0
16/10-23/10/01	32	29.0	24.0	38.0	20.0	34.0	19.0	9.0	8.0	8.9	18.0	15.0	14.0	14.0
23/10-30/10/01	33	24.0	19.0	33.0	17.0	33.0	15.0	6.0	8.0	9.7	14.0	12.0	11.0	11.0
30/10-6/11/01	34	23.0	22.0	30.0	17.0	30.0	15.0	8.0	6.0	9.0	15.0	13.0	12.0	13.0
6/11-13/11/01	35	22.0	18.0	30.0	16.0	28.0	13.0	8.0	6.0	8.0	15.0	13.0	12.0	12.0
13/11-20/11/01	36	22.0	20.0	33.0	17.0	30.0	15.0	9.0	9.0	10.0	14.0	12.0	12.0	12.0
20/11-27/11/01	37	22.0	17.0	29.0	15.0	27.0	14.0	7.0	5.0	8.0	14.0	12.0	12.0	12.0

Appendix E continued.

27/11-4/12/01	38	21.0	19.0	28.0	16.0	27.0	14.0	9.0	7.0	9.0	15.0	13.0	11.0	12.0
AnnuAve.		31.0	58.0	37.1	23.3	37.8	21.5	13.2	12.3	14.0	20.7	19.1	17.9	18.2
Max.conc		58.0	42.0	60.0	41.0	60.0	38.0	28.0	32.0	29.0	36.0	38.0	34.0	33.0
Minconc		16.0	14.0	21.0	13.0	24.0	10.0	4.0	5.0	8.0	13.0	8.0	9.0	9.0

Key: 0 = no result (no filters available for analysis)

Appendix F

Lead (ug/g) results for 7 day sampling period

Sampling Period	Survey No.	EDS	ARG	WAR	VE	SCL	SPJ
12/12-19/12/00	1	209	1,056	1,565	1,956	294	4,369
30/1-6/2	2	848	2,499	1,077	1,460	720	4,736
6/2-13/2	3	571	491	1,345	1,178	555	4,173
13/2-20/2	4	546	1,373	851	1,127	1,543	1,216
20/2-27/2	5	615	431	1,738	1,423	789	4,509
27/2-6/3	6	681	435	1,740	1,674	547	577
6/3-13/3	7	571	491	1,345	1,178	555	4,173
13/3-20/3	8	385	1,423	1,130	605	728	9,209
20/3-27/3	9	606	2,108	870		990	5,304
27/3-3/4	10	401	690	608	948	448	2,587
3/4-10/4	11	463	865	478	1,113	1,003	6,175
8/5-15/5	12	753	954	887	2,443	375	2,839
15/5-22/5	13	339	1,238	1,464	521	157	2,382
22/5-29/5	14	227	1,474	1,378	829	517	2,478
29/5-5/6	15	273	2,144	1,204	1,651	523	2,595
5/6-12/6	16	171	2,064	1,182	2,082	384	5,122
12/6-19/6	17	259	1,562	815	2,130	1,330	2,755
19/6-26/6	18	264	2,252	1,223	1,950	627	3,183
26/6-3/7	19	212	1,952	1,683	3,044	441	2,833
3/7-10/7	20	284	2,245	1,928	1,760	539	4,021
10/7-17/7	21	264	2,180	1,703	1,756	719	4,183
17/7-24/7	22	259	2,622	1,261	1,069	663	3,715
24/7-31/7	23	229	2,579	1,098	1,029	624	8,392
31/7-7/8	24	186	2,219	1,107	913	635	9,903
7/8-14/8	25	237	1,484	1,072	1,140	670	8,601
14/8-21/8	26	267	1,834	1,393	1,765	767	7,294
21/8-28/8	27	340	2,160	1,234	1,135	850	359
28/8-4/9	28	393	1,829	1,465	1,352	670	255
4/9-11/9	29	478	1,921	1,495	1,859	745	620
11/9-18/9	30	369	920	781	1,680	789	2,504
2/10-9/10	31	339	1,593	546	455	767	2,636
9/10-16/10	32	386	2,253	817	496	778	3,845
16/10-23/10	33	308	612	304	396	548	3,105
23/10-30/10	34	239	538	354	525	378	3,190
30/10-6/11	35	450	691	922	758	805	3,734
6/11-13/11	36	296	944	661	713	746	2,331
13/11-20/11	37	125	587	349	478	655	2,483
20/11-27/11/01	38	127	612	337	290	669	887
Ave ug/g		368	1458	1090	1267	672	3770
Max.Conc		3105	2622	1928	3044	1543	9903
Min. Conc		125	431	304	290	157	255

Appendix G

Exclusion of Data:

1. For Passive Sampling.

Site/Sites	**Period**	**Reason**
Fence 2	5/9-19/9/00	Sampler missing
Warwick	3/10 - 17/10/00	Sampler missing
King's Park Pool, WWR, DMC	27/2-6/3/01	Shortage filters, dely from Japan
Argyle	20/3 - 27/3/01	Sampler missing
Victoria Embankment	18/9-26/9/01	Sampler missing
Sea Cow Lake	2/10-9/10/01	Traffic pole run over in accident

2. For Dust Sweepings

Site/Sites	**Period**	**Reason**
Spaghetti Junction	28/11-6/12/00	Sample lost- broken dish

Appendix G continued

3. For Active sampling by Durban Metro Caravan situated at Settler's School.

Julian Day	Duration Excluded	Parameter Excluded	Reason for Data Exclusion
(2000) 261-261	11.20-11.40	NO_2	**Routine QC check**
37601	12.20- 12.55	NO_2	Routine QC check
275-275	13.35-13.55	NO_2	Routine QC check
278-278	0.50 -2.20	NO_2	Power failure
278-278	18.30-21.30	NO_2	Power failure
282-282	14.10-14.35	NO_2	Routine QC check
292-292	13.45-14.05	NO_2	Routine QC check
303-303	12.15-12.35	NO_2	Routine QC check
300-300	11.36	NO_2	Channel set up incorrectly
307-307	15.45-16.03	NO_2	Routine QC check
313-313	11.27-11.45	NO_2	Routine QC check
326-326	10.30-11.03	NO_2	Routine QC check
343-343	15.33-16.00	NO_2	Routine QC check
347-347	15.30-15.54	NO_2	Routine QC check
2-4 (2001)	10.57-22.10	All data	Changing logger program used weather office data
8-8	12.45-13.10	NO_2	Routine QC check
15-15	12.15-12.40	NO_2	Routine QC check
25-25	14.35-14.55	NO_2	Routine QC check
30-30	12.50-13.05	NO_2	Routine QC check
39-39	13.15-16.50	NO_2	Calibration check
40-40	10.15-10.35	NO_2	Routine QC check
43-43	12.15-12.30	NO_2	Routine QC check
52-52	10.20-10.25	NO_2	Routine QC check
57-57	10.35-10.50	NO_2	Routine QC check

Appendix G continued

Julian Day	**Duration Excluded**	**Parameter Excluded**	**Reason for Data Exclusion**
64-64	10.25-10.55	NO_2	Routine QC check
70-70	12.00-12.15	NO_2	Routine QC check
79-79	10.35-11.15	NO_2	Routine QC check
85-85	9.10-10.10	NO_2	Routine QC check
92-92	14.10-14.35	NO_2	Routine QC check
96-97	21.45-14.50	Humidity	Datalogger channel lost
99-99	12.10-12.30	NO_2	Routine QC check
107-107	10.45-11.15	NO_2	Routine QC check
108-108	9.11-11.25	NO_2	Routine QC check
114-114	13.35-14.00	NO_2	Routine QC check
116-116	15.05-21.20	All	Data not collected on time
124-124	7.45-8.40	All	Data logger program setup problems
127-127	13.10-13.30	NO_2	Routine QC check
134-134	14.30-14.45	NO_2	Routine QC check
123-135	9.20-12.40	Ambient temperature	Sensor failed
142-142	11.30-12.20	NO_2	Calibration check
149-149	12.25-12.45	NO_2	Routine QC check
156-156	14.45-15.20	NO_2	Routine QC check
163-163	13.20-13.50	NO_2	Routine QC check
169-169	12.15-12.40	NO_2	Routine QC check
177-177	12.20-12.40	NO_2	Routine QC check
183-183	11.30-12.05	NO_2	Routine QC check

Appendix G continued

Julian Day	Duration Excluded	Parameter Excluded	Reason for Data Exclusion
193-193	16.45-17.05	NO_2	Routine QC check
198-198	14.00-14.30	NO_2	Routine QC check
205-205	13.55-14.15	NO_2	Routine QC check
212-212	12.25-12.40	NO_2	Routine QC check
219-219	12.10-12.35	NO_2	Routine QC check
227-227	13.10-13.45	NO_2	Dynamic QC calibrations
233-233	11.55-12.45	NO_2	Routine QC check
241-241	14.00-14.25	NO_2	Routine QC check
249-249	13.55-14.15	NO_2	Routine QC check
257-257	13.15-13.50	NO_2	Routine QC check
257-257	3.15-4.40	NO_2	Power failure

Appendix H

Regression Data for Figure 41

Regression Output:

Constant	20.06682
Std error of Y Est	0.962291
R^2	0.615325
R	-0.78
No. of observations	4
Degrees of freedom	2
X Coefficients(s)	-0.01737
Std. error of Coefficient	0.009714
Regression equation is	$Y = 20 - 0.17x$

Appendix I

Regression Data for Table 18

Regression Output:

Constant	56.84938
Std error of Y Est	8.852955
R^2	0.829472
R	-0.91
No. of observations	5
Degrees of freedom	3
X Coefficients(s)	-1.60602
Std. error of Coefficient	0.420423
Regression equation is	$Y = 56.85 - 1.61x$

Appendix J

Statistical data for the level of rainfall on the concentration of lead

Regression Output:

Constant	2899.7
Std error of Y Est	3767.6
R^2	0.005
R	0.07
No. of observations	6
Degrees of freedom	4
X Coefficients(s)	15.6
Std. error of Coefficient	110.12
Regression equation is	$Y = 2899.7 + 15.6\ x$

Appendix K

T test to for Correlation of Active vs Passive

t = -2.660

test value = 6

df = 5

Significance (2 tailed) = 0.045

Mean difference = -0.1782

95% Confidence Interval of the difference (lower) = -0.3503

95% Confidence Interval of the difference (upper) = -0.0060

Appendix K

The Influence of wind speed on concentration of Lead

Sampling Period	Average wind speed (m/s)	Maximum wind speed (m/s)
27/02/01 -06/03/01	1.94	5.78
20/03/01- 27/03/01	2.00	8.70
07/08/01 - 14/08/01	1.97	6.26
21/08/01 - 28/08/01	2.00	6.23
28/08/01 - 04/09/01	1.90	5.50
16/10/01 - 23/10/01	2.05	7.32
Average	**1.98**	**6.63**