The Behaviour of Particulate Matter and Carbon Dioxide Concentrations in Harare

By

WILBES MBIYA

Supervisors

Dr. D. Nyanganyura
((University of Zimbabwe)

Professor. Dr F. Meixner
(Max Plank Institute for chemistry and
Biogeochemistry Department in Germany)

Mr B. Chipindu
(University of Zimbabwe)

A thesis submitted in partial fulfilment for the degree of Master of Science in Agricultural Meteorology

UNIVERSITY OF ZIMBABWE

FACULT OF SCIENCE **PHYSICS DEPARTMENT**

JUNE 2007

DEDICATION

A special dedication goes to my parents Mr. and Mrs. Mbiya and my sisters (Primrose, Linda and Judith) for their support and encouragement over the years and to my loving God who gave me strength.

‘GLORY BE TO GOD’

Abstract

As African countries industrialize, the emission of various pollutants is likely to increase. Air pollution can have adverse impacts on human and animal health and ecosystems. There has been very limited air pollution monitoring activities in Southern Africa. This paper presents results of a study of the temporal behaviour of particulate matter ($PM_{2.5}$), total dust precipitation (TDP) and carbon dioxide (CO_2), determination of the effects of meteorological parameters on the concentrations of the $PM_{2.5}$ and CO_2 and the spatial distribution of TDP as well as trace elements in residential areas of Harare, Zimbabwe. The ($PM_{2.5}$) concentrations were determined as scattering coefficients using a nephelometer and CO_2 measurements were carried out using an infra-red gas analyser. The TDP were collected using plastic pots and samples were analysed for the trace elements (iron, lead and nickel) using an atomic absorption spectrometer. CO_2 mixing ratios and $PM_{2.5}$ concentration followed a similar diurnal trend, with maximum peaks observed at around 2300 and troughs around midday. High wind speeds were associated with low concentrations of both CO_2 and $PM_{2.5}$ and low wind speeds with high concentrations of both CO_2 and $PM_{2.5}$. Wind from the city centre and the industrial areas advected towards the sampling site. The concentration of ($PM_{2.5}$) decreased significantly during rainfall. CO_2 mixing ratios were not greatly affected by rainfall. The southern residential areas of Harare which are close to the dumping sites, busy highways, busy bus terminus and industrial areas recorded significant amounts of the trace elements and TDP than the northern residential areas which are far away from the main sources of pollution. The northern residential areas are upwind of the main sources of air pollution whilst the southern residential areas are located downwind of the main air stream of Harare and are highly polluted.

Acknowledgements

My deepest appreciation goes to Dr D. Nyanganyura and Prof F. Meixner who helped me throughout the course of this project, Dr D. Nyanganyura has been there when I needed him most. I also cherish the assistance which I received from my colleague Anywhere. I would like to thank Max Plank Institute for Chemistry and Biogeochemistry Department in Germany for loaning the nephelometer to Physics department. Without the understanding of Prof F. Meixner and his institute my project could not have been successful.

I would also like to thank all the MAGM staff members for their support. My gratitude also goes to Mr. Dube, Mr. Chinzou, K. Sithole and other staff members of Chemistry Department for assisting and allowing me to use their equipment. Also to my Agricultural meteorology colleagues thanks for the encouragement.

Last but not least I would like to thank my parents and sisters for their support both financially and morally. To my best friend Patience Marimo, I thank you for being my source of strength and inspiration throughout this project.

Thank you all and may the good Lord continue to bless you.

Table of contents

List of Figures

List of tables

List of acronyms

AWS Automatic Weather Station

CH_4 Methane gas

CO_2 Carbon dioxide

DOY day of year

Fe Chemical symbol for iron

IR Infra-red

Ni Chemical symbol for nickel

NOx Mixture of nitrogen oxides

O_3 Ozone

PAHs Polycyclic aromatic hydrocarbons

Pb Chemical symbol for lead

PM Particulate Matter. Any material, except pure water, that exists in the solid or liquid state in the atmosphere.

PM_{10} An air pollutant consisting of small particles with an aerodynamic diameter of less than or equal to 10 μm

$PM_{2.5}$ An air pollutant consisting of small particles with an aerodynamic diameter of less than or equal to 2.5 μm

PPB Parts Per Billion

PPM Parts Per Million

RH relative humidity

SADC Southern Africa Development Community

SO_2 Sulphur dioxide

TDP Total Dust Precipitation

TSP Total Suspended Particulates

VOC Volatile organic compounds

CHAPTER 1 INTRODUCION

The levels of air pollution are generally high in urban areas because of many industrial and domestic activities that produce pollutants. Some examples of anthropogenic sources of atmospheric particulates are traffic, coal combustion processes, waste incineration, cement and fertilizer production, and use of domestic fuels such as wood. Man's activities can alter the natural geochemical cycle as the pollutants end up being deposited into the terrestrial and aquatic environment at rates comparable to natural processes (Andren, 1977). Air pollution monitoring is of importance in providing public information and in measuring the effectiveness of pollution control policies (Harrison, 1994). Dust analysis is an effective method of establishing the levels of pollution because dust is easy to sample and its composition can be used as a finger print for a source; for example traffic emissions (Mao, 1996).

1.1 Why study air pollution in Harare?

Harare is the capital city of Zimbabwe and according to the last census of 2002, Harare and Chitungwiza together had a population of 2.5 million people. Harare, as compared to other cities in Zimbabwe, has a large and expanding industrial base and the largest fleet of vehicles in Zimbabwe. In 2002, Harare had an estimated 1.2 million registered vehicles which were approximately two thirds of Zimbabwe's total vehicle population. Some of the vehicles in Harare are rather old and most of them do not have catalytic converters

Another contributing factor of air pollution in Harare comes from the use of old and outdated technology in the manufacturing industry. In Harare most companies cannot replace this old equipment because of unavailability of foreign currency to procure new equipment. Most of the industries that emit pollutants in Harare either do not have pollution abatement equipment to control emissions into the atmosphere or they do not invest in the equipment because the penalties for polluting are not high enough to act as deterrance.

The health impact of toxic pollutants emitted into the atmosphere of Harare and other urban areas elsewhere in the world has gained greater attention from the governments and scientific community in the last two decades. Knowledge of the identities, ambient concentrations and impacts of these pollutants is of prime concern to environmentalists since it is well known that high pollution levels in the air may cause pollution effects on plants and exposed population (Mujuru, 2004).

1.2 Justification/motivation

As a result of rapid urbanization and industrialization, numerous environmental problems have emerged, ranging from local to global scale. To cope with these problems, we need to monitor and understand environmental changes in air pollution, especially in urban areas where most people live and, probably, the largest environmental changes have taken place (Changnon, 1981; Cotton and Pielke, 1995).

The city of Harare Health Department monitors total suspended particulates (TSP). Current research on air pollution in Zimbabwe does not incorporate the effects of meteorological parameters on ambient aerosol concentrations. Much work has only been done to quantify the pollutants on monthly and annual basis without looking specifically at the diurnal variations and variations under different weather conditions. This may have been due to unavailability of equipment and lack of funds to sponsor such projects.

1.3 Objectives of research

The main objectives of this research are

- To study the temporal behaviour of particulate matter ($PM_{2.5}$) and carbon dioxide in Harare;
- To determine the effects of meteorological parameters on the diurnal concentrations of $PM_{2.5}$ and carbon dioxide, and
- To determine the spatial distribution of total dust precipitation including trace elements in residential areas of Harare.

1.4 Target area

The areas chosen (University of Zimbabwe and the surrounding areas) lie in Harare, the capital city of Zimbabwe, which has got a high vehicle fleet and heavily built industrial sites compared to other cities or towns in the country. University of Zimbabwe was chosen to represent a lowly polluted area of the city since most of the time the wind is north easterly and in that direction there are no industrial sites which means the air is not highly polluted.

1.5 Expected benefits

The major benefits anticipated from this investigation are

- To raise understanding of the diurnal behaviour of particulate matter, as well as determine the effects of precipitation and humidity on concentrations of particulate matter in the atmosphere,
- To contribute to and increase the current knowledge of the general pollution levels in Harare.

In line with the objectives of the project, the results will be used in preparation of near to long term measures or policies. These measures should include how best residential stands should be located with respect to wind direction and source strength. The information to be obtained in this project will assist meteorologists on the current situation of particulate matter ($PM_{2.5}$) in Harare and its effects on microclimate.

1.6 Thesis layout

Chapter 1 gives the introduction of the study, objectives, the scope and the general character of research. Chapter 2 provides the literature review on atmospheric pollution, categories of pollutants, sources of pollutants, consequences and importance of air pollution and the relationship between air pollution and the atmosphere; Chapter 3 looks at the study area, the methods to be employed, experimental design, sampling procedures and the equipment used, and Chapter 4 gives an account on the analysis of results and discussions on the results obtained. Chapter 5 focuses on the results obtained on spatial distribution of TDP and trace elements, temporal behaviour of carbon dioxide and $PM_{2.5}$ and on the effects on meteorological parameters on carbon dioxide and $PM_{2.5,}$ and presents some recommendations.

CHAPTER 2 LITERATURE REVIEW

The thin envelope of atmosphere that surrounds the earth and on which all present forms of life depends comprises of a mixture of gases. Although it consists principally of nitrogen (N_2) and oxygen (O_2), with varying but important amounts of water vapour, the atmosphere also contains a range of trace gases that have significance far beyond their relative abundance. These trace gases include naturally occurring gases such as carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), as well as artificially produced gases such as chlorofluorocarbons (CFCs). They are significant primarily because they control processes such as photosynthesis and the greenhouse effect of the atmosphere, without which the average annual global temperature would be about $-18^{o}C$ rather than approximately $15^{o}C$ (Lindesay, 1997).

The atmosphere is not simply a mixture of gases. Every cubic centimetre of air contains up to thousands of suspended particles; most of these are only a fraction of a micrometer in diameter. The composition of atmospheric particles varies widely not only from place to place but also from particle to particle within a given parcel of air (Brasseur *et al.*, 1999).

Air is never perfectly 'clean' in the sense of containing only nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), water vapour (H_2O) and the inert gases. Even before man existed, there were many sources of the trace-constituent species, some of which would be classified as pollutants (Wayne, 2000). Air pollution is part of our environment in which we live. It adversely affects the lives of large number of people and causes considerable damage to economies, nature and property. 'Natural air pollution' is caused by volcanic eruptions, pollens, dust and terpenes from plants and forest fires. Man has accentuated the frequency and intensity of release of some of the pollutants (Wayne, 2000).

2.1. Air or atmospheric pollution

Since air is never "perfectly clean", it means that there are gases or aerosols which are emitted naturally or anthropogenically, build up in concentrations sufficiently high to cause direct or indirect damage to humans, plants, animals, other life forms, ecosystem, structures or works of art (Jacobson, 2002). These are contaminants present in the atmosphere, such as dust, fumes, mist, smoke, or vapour in such quantities and with such characteristics and durations as to be injurious to human, plant, and animal life or to properties (IMV, 1992).

2.2 Categories of pollutants

Pollutants do exist in all the three states of matter, namely solid, liquid and gaseous states. These pollutants can be classified on the basic physical form, formation and their impact to the environment or to the living organisms.

2.2.1 Basic physical form of pollutants

Pollutants can be classified according to their physical forms that are the either as solid, liquids or gases. Generally solids and liquids form a collective group known as particulate matter whilst gases have their own class.

2.2.1.1 Gases

Gases include carbon dioxide (greenhouse gas), which is one of the gases which contribute to global warming, sulphur dioxide and hydrocarbons, for example the PAHs (polyaromatic hydrocarbons) which are produced from incomplete combustion of all types of organic materials and are known to have carcinogenic and mutagenic properties (Freudenthal and Jones, 1979).

Carbon dioxide is a colourless, odourless, natural greenhouse gas that is also responsible for much of global warming that has occurred to date. It is a by-product of chemical reactions, and not an important outdoor pollutant as it does not react to form products and is not harmful to health at typical mixing ratios. Carbon dioxide gas plays an important role in the stratospheric ozone depletion, because global warming near the earth’s surface due to carbon dioxide enhanced global cooling to the stratosphere, and such cooling feeds back to the ozone layer. Mixing ratios of carbon dioxide are not regulated in any country (Jacobson, 2002).

2.2.1.2 Particulate matter

They represent a group of solid and liquid droplets that are small enough to remain suspended in the air. Collectively they are known as aerosols (Ahrens, 2000). The term particulate matter in atmosphere is commonly referred to as ‘aerosol’, although the term properly applies to multiphase mixture of solid or liquid particles dispersed in a gas (Brasseur *et a.l*, 1999).

These are tiny particles so small that they remain suspended in the air for long periods. Particulates are released by burning of wood, diesel and other fuels, by industrial plants, and by agriculture. Particulates are a subclass of pollutants. They can also be referred to as primary or secondary particulates depending on their source of origin like pollutants. Particulates are also put into two categories namely $PM_{2.5}$ (air pollutants consisting of small particles with an aerodynamic diameter of less than or equal to 2.5 µm) and PM_{10} (air pollutant consisting of small particles with an aerodynamic diameter of less than or equal to 10 µm). The $PM_{2.5}$ are fine particles with aerodynamic diameter of 2,5 µm or less whilst PM_{10} are courser particles with aerodynamic diameter of 10µm (which is equivalent to one seventh the width of a strand of human hair (APINA, 2003c).

2.2.1.2.1 Externally and internally mixed aerosols

A wide range of chemical species may be found in the atmospheric aerosols. When individual particles differ in composition from each other, the aerosol is said to be externally mixed; when individual particles have all the same composition, the aerosol is said to be internally mixed (Brasseur *et al.*, 1999).

2.2.1.2.2 Haze

Haze is a subclass of particulates and is a layer of fine dry or wet dust or salt particles dispersed through a portion of the atmosphere and is caused by fine particles that scatter and absorb light before it reaches the observer Individually they are visible but cumulatively they diminish visibility (Ahrens, 2000). As the number of fine particles increases, more light is absorbed and scattered, resulting in less clarity, colour, and visual range. Five types of fine particles contribute to haze sulphates, nitrates, organic carbon, elemental carbon, and crustal material (Ahrens, 2000).

2.2.2 Formation

A fundamental distinction between the fine and course particle fractions lies in the source mechanisms that produce them. Mechanical processes (anthropogenic and natural) produce the relatively large particles in the coarse mode; examples are sea spray, wind blown dust, fly-ash, volcanic ash, and particles from tire and break wear. The chemical composition of the coarse fraction reflects these sources; crustal elements (iron, copper, aluminium, e.t.c) and sea water species (sodium, chlorine, e.t.c) (Ahrens, 2000).

2.2.2.1 Primary pollutants

The mechanically produced particles are examples of primary emissions, that is, particles that have been emitted into the atmosphere from an identifiable source. Sea spray, soil dust raised by winds, volcanic eruptions, and cement manufacturing are typical processes with primary particle production (Georgii and Jaeschke, 1982).

2.2.2.2 Secondary pollutants

Chemical and physical reactions or transformations may occur among primary pollutants and the constituents of the unpolluted atmosphere. The atmosphere may be viewed as the reaction vessel into which are poured reactable constituents and in which are produced a tremendous array of new chemical compounds, generated by gases and vapours reacting with each other and with particles in the air. The pollutants manufactured in the air are called secondary pollutants (Boubel *et a.*, 1994). An example is sulphate, which forms downwind of an industrial source, as emitted sulphur gases are chemically converted to condensable species, which are then incorporated into particles. This process is known as gas-to-particle conversion and is the mechanism by which aerosol particles serve as sink in the chemical cycles of several important tropospheric trace gases (Wark, 1981).

2.2.2.3 Precursor pollutants

In air pollution parlance, the primary pollutants that react are termed the precursor s of the secondary pollutants. Armed with the knowledge that each secondary pollutant arises from specific primary reactants and it is possible to control secondary pollutants by controlling how much of each primary pollutant is allowed to be emitted. Examples of these substances that undergo chemical reactions such that the resultant product is a secondary pollutant are NO_x, SO_x and reactive organic gases (Georgii and Jaeschke, 1982).

2.2.3 Impact

These pollutants are classified according to their effects on the environment, health, ecosystem, vegetation, buildings and many others. The two major classes under this category are toxic pollutants and odorants (APINA, 2003b).

2.2.3.1 Toxic pollutants

These are pollutants which are hazardous to human health or the environment. These pollutants are typically carcinogens, mutagens, and teratogens like benzene, sulphur dioxide, carbon monoxide, lead etc. Gaseous pollutants which affect vegetation like ozone and sulphur dioxide are also regarded as toxic pollutants (Boubel, 1994).

2.2.3.2 Odorants

These are usually gases which produce an unfriendly or offensive smell, like ammonia it produces a pungent and choking smell and hydrogen sulphide which smells like rotten eggs. Smell is one of the chemical senses, since it appears to be physiological reaction to contact with certain specific substances. Unfortunately, the human nose is the only good measuring device known, and it is notoriously undependable (Wark, 1981).

2.3. Chemistry and chemical composition of aerosols

The solubility of metals in particulates depends on the chemical form of the element and the source. Particulates with metal levels enriched from anthropogenic sources such as smelting, refining, incineration, wear, corrosion, etc have much more soluble metals because of their more recent origins (Graedel and Weschler, 1981).

2.3.1 Aerosol particle morphology and shape

The morphologies (structures) and shapes of aerosols particles vary with composition. The older particle, the greater the number of layers and attachments the particle is likely to have. If the particle is hygroscopic it absorbs liquid water at high relative humidities and becomes spherical. If ions are present and the relative humidity decreases, solid crystals may form within the particle. Some observed aerosols are flat, others are globular, others contain layers, and still others are fibrous. Once emitted soot can coagulate or grow. Since the soot particles are porous and have a large surface area, they serve as site on which condensation occurs. Although black carbon in soot is hydrophobic, some organics in soot attract water, in which the organics attach (Jacobson, 2002).

2.3.2 Hygroscopicity

Hygroscopic aerosols accrete water at humidities above the so-called deliquescence point. When the relative humidity (RH) decrease below this point particles do not crystallize but remain in a supersaturated droplet state often to very low RH before crystallization.(Rood et al.,1989).This phenomenon is known as hysteresis and leads to 2 possibilities with respect to the size of the ambient hygroscopic particles at a RH between crystallization and deliquescence point. Atmospheric particles may be dry (present in the lower branch of the hysteresis loop) or may be present as supersaturated droplets in the so-called upper branch of the hysteresis loop, with significantly higher light scattering. The extra scattering caused but the accretion of water at a given humidity is commonly expressed in the enhancement factor *f* or *f* (RH), defined as

$$f(RH) = \frac{\sigma_{sp}}{\sigma_{spd}} \tag{2.1}$$

Where σ_{spd} is the particle scattering coefficient at a reference low relative humidity. This reference humidity was typically less than 30% in present measurements, but is often not lower than 40% in monitoring stations. Inorganic salts formed from sulphate, nitrate, chloride, sodium and ammonium ions are known to deliquesce and absorb water in moist atmosphere (Ten Brink,1996).

2.3.3 Chemical processes

Industrialization has resulted in continued injection of pollutants into the atmosphere. These include carbon monoxide, and oxides of nitrogen and sulphur. These pollutants are introduced by anthropogenic sources, geological and biological processes.

Motor vehicles and other sources release carbon monoxide into the atmosphere and the reacts as follows

$$CO + H_2O \rightarrow CO_2 + H_2$$

Carbon dioxide is one of the most well documented “greenhouse” gases (Butler, 1979).

2.3.4 Photochemistry

The pollutants introduced into the atmosphere, besides chemical reactions, also undergo photochemical reactions. These are reactions that occur due to absorption of light energy from the sun to activate molecules concerned and then the compounds enter into reactions with other compounds to yield different products (Butler, 1979).

2.4 Sources of air pollution

The sources of ambient aerosols can be classified into anthropogenic and natural sources.
Sources, which are anthropogenic in nature, include agricultural activities, industrial activities and other combustion processes. Natural sources include wind blown dust, volcanic eruptions, and pollen gains from vegetation, sea sprays and forest fires (Noller, 1981). These two classes can be further divided into other subclasses of air pollution namely the stationery and area source and mobile source.

2.4.1 Stationary and Area source

This refers to an emission source that does not move, also known as point source and these include power plants, factories etc. The term area source is used to describe many small sources of air pollution located together whose individual emissions may be below threshold of concern, but whose collective emissions can be significant. A good example of small source is of residential wood burners, but they contribute to local and regional air pollution More than 6 million tonnes of wood are consumed annually supplying mainly rural and urban low income households in Zimbabwe. These developments have resulted in high emissions of air pollutants. In 1994 the total annual sulphur dioxide (SO_2) emission from thermal power stations was 141 Gg methane (CH_4) 19.08 Gg; nitrogen oxide (NO_x) 0.21Gg and carbon monoxide (CO) 1.38Gg (APINA, 2003a).

Pollutants released to the boundary layer may be removed quite rapidly by wet or dry deposition, as a result these processes tend to degrade the air quality only near the surface. Sulphur dioxide and other reactive compounds emitted from factories often fall into this category, and contribute to local air pollution. More widespread dispersal within the troposphere can lead to regional pollution of large geographical area (Wayne, 2000).

2.4.2 Mobile source

Mobile source refers to a source that is capable of moving under its own power. These include road and non-road transportation, farm and construction equipment. Transport systems are emitting tones of reactive atmospheric gases (mainly NO_x and SO_2 and other volatile organic compounds) and other particulate species. There has been a doubling of motor vehicle fleet between 1994 and 1999 in Zimbabwe. Zimbabwe’s petrol contains about 0.6-0.8 mg Pb/l (lead per litre) making it justifiable to monitor Pb levels in major cities (APINA, 2003b).

2.4.3 Agricultural sources

Those that raise animals and grow crops can generate emissions of gases and particulate matter. For example, ammonia produced in animal houses and aerial drift of herbicides and pesticides.

2.4.4 Natural sources

Although industrialization and the use of motor vehicles are overwhelmingly the most significant contributors to the air pollution, there are important natural sources of air pollution as well. These include wild land fires, dust storms, and volcanic activities (APINA, 2003a).

2.4.5 Key sources of air pollution in Africa

Unsustainable patterns of consumption and production of energy sources by industry, transport and household sectors have, in particular, been the leading sources of key indoor and outdoor air pollutants. Air emissions are a growing nuisance from Africa’s growing industry (UNEP, 2004).

2.4.6 Key sources of air pollution in Zimbabwe

In Zimbabwe, there are three broad sources of air pollution from anthropogenic activities. These are stationary (mainly industrial sources), mobile and indoor sources. Motor vehicles, industrial activities and thermal power generation account for a large percentage of the particulate and gaseous pollutants like oxides of nitrogen and sulphur (NOx and SO_2), carbon monoxide (CO) and volatile organic compounds (VOC) (APINA, 2003c).

2.4.7 Sources of particulate matter ($PM_{2.5}$)

It was discovered that diesel exhaust particulates (DEP) are an important constituent of $PM_{2.5}$ in New York City. Despite the fact that diesel engines are more efficient, they produce 10 times more particulates per mile than conventional gasoline engines and 30 -70 times more than engines equipped with catalytic converters (Kinney, 2000).

Volcanic eruptions forest fires and disintegrating meteorites are other sources of particulates into the atmosphere. The major sources of coarse particles are wind blown dust and PM picked off unpaved roads by vehicle traffic while fine particles are produced from, industrial and residential combustion, vehicle exhausts and secondary processes which involve the reaction of gaseous pollutants in the atmosphere (Harrison, 1994).

2.5 Impacts of air pollution

Impacts of air pollution are experienced at different scales in Zimbabwe, Southern Africa and the entire world at large. The impacts are felt on crops, ecosystems, human and animal health and on exposed materials. There is growing evidence that the Earth’s radiation budget, and thus climate, is affected through radiative forcing caused by changes in the concentration and composition of aerosol particles (Lohmann and Feichter, 2005; Ramanathan *et al.*, 2001)

2.5.1 Impact of aerosols on climate change

Aerosols are known to have both negative and positive impacts on the climate change and this has resulted in more research work being done on, their effect on climate change. The urban atmosphere contains large quantities of sulphate aerosols that block out incoming solar radiation, negating any enhanced ‘greenhouse’ warming. At the ground however, the aerosols traps in longwave radiation that could normally escape from the earth's surface, causing the air aqbove the surface to remain warmer than normal, thus preventing dew formation (Bryant, 1997)

2.5.1.1 Impact of aerosols on solar radiation and temperature

The interaction of fine particles and light can also impact the Earth's radiation balance by imposing a change in the net radiative flux at a level in the atmosphere. Solar radiation is modified when passing through the atmosphere by two main processes; light scattering and light absorption. Light scattering is a redistribution of incident light in nonparallel directions, whilst light absorption consists of a conversion of the incident light into thermal energy. The attenuation of light by these processes has important climatic consequences (Harrison, 1994). Scattering efficiency is predominantly a function of particle size, morphology, and chemical composition, and mainly due to aerosol particles in the accumulation range (0.1-1μm).The light absorption by aerosols covers the whole spectrum, and is largely due to linear-graphic carbon (also called elemental, or black carbon), whose unique known source are combustion processes (IPCC, 1995).

Depending on the intrinsic properties of aerosols, especially single scattering albedo, aerosols can cause either cooling or warming of the atmosphere, in contrast to the greenhouse gases which only cause warming. Nevertheless, the "level of scientific understanding" concerning the various climatic effects of atmospheric aerosols is still very inadequate (Cotton, 1995). Aerosol particles are thought to have an overall cooling effect, estimated to be the same order of magnitude as the positive forcing of the greenhouse gases (Harrison, 1994).The response to flux change can cause variations in atmospheric and surface temperatures which affect evaporation and condensation processes, as well as atmospheric convective and circulation patterns (Russell *at al.*, 1999).

2.5.1.2 Impact of aerosols on cloud formation

The indirect effect of aerosols on climate is based on the influence of anthropogenic aerosol emissions (or formation of aerosol by gas-to-particle conversion of anthropogenic emissions) on the number concentration of cloud condensation nuclei (CCN), with a resulting impact on cloud droplet number concentration (CDNC) and sizes (NRC, 1996). The hygroscopic particles (CCN) can alter the microstructure of the cloud by changing the concentration of the cloud droplets and the size spectrum of cloud droplets. Large numbers of CCN and cloud droplets would slow down collision and coalescence growth by virtue of their smaller size and consequently small collection efficiencies and collection kernels. Slow coalescence growth should therefore lead to less rainfall, at least from smaller clouds, which do not contain large of liquid water (Cotton, 1995).

In Twomey's words "an increase in global pollution could, at the same time, make thin clouds brighter and thick clouds darker, the crossover in the behaviour occurring at a cloud thickness which depends on the ratio of absorption to the cube root of drop (nucleus) concentration. The sign of the net global effect, warming or cooling, therefore involves both the distribution of cloud-nucleating particles vis-à-vis particulate absorption" (Cotton, 1995).

2.5.2 Impact of aerosols on human health

Particulate matter alone or in combination with other pollutants constitutes a very serious health hazard. Smoke from burning solid fuels is estimated to be responsible for 1, 6 million deaths each in the world's poorest countries (*www.who.int/inf-fs/en/)*. PM_{10} results in an increased cardio-respiratory morbidity and mortality due to long term exposure. It causes exacerbation of asthma, bronchitis and other chronic obstructive pulmonary diseases (APINA, 2004).

2.5.2.1 World Health Organization (WHO) Guidelines

The 1999 WHO air quality guideline provides a basis for protecting public health from adverse effects of environmental pollutants, and for eliminating or reducing to a minimum, contaminants that are known or likely to be hazardous to human health Air quality guidelines provide guidance to governments in making risk management decisions, particularly in setting standards. Air quality guidelines values are levels of pollutants below which lifetime exposure or exposure for a given average time does not constitute a significant health risk (WHO, 2000).

Reports from some SADC countries collected by APINA show that there is still widespread use of charcoal, kerosene, animal dung, and wood fuel in the region for cooking and lighting purposes. The people are exposed to the products of combustion such as carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides (NOx), and $PM_{2.5}$ in unventilated conditions. In Zambia, 85% of all households use wood fuel and this shows the percentage of people being exposed to the products of combustion (APINA, 2003a). SO_2 and NOx interact in the atmosphere to form fine sulphate and nitrate particles that can be transported long distances by wind and inhaled deep into the lungs. Many scientific studies have linked elevation levels of these fine particles to increased illness and premature death from heart and lung disorders such as asthma and bronchitis (UNEP, 2002).

Children and infants appear to be especially sensitive to the effects of particulate matter, which may increase the incidence or severity of acute respiratory infection. There is recent evidence in the United States of America that an increased rate of sudden death syndrome may be associated with exposure to particulate matter (Woodruffe *et a.*, 1997).

2.5.3 Impact of aerosols on urban air quality

In the complex environment of an urban atmosphere, there is great variability in the number, types and sources of particles as well as in the diurnal and seasonal patterns of their emission strengths, all of which affect human exposure. As one of many sources contributing to urban air pollution in general, the combustion of fossil fuel in motor vehicles is one of the major primary emission sources of ultra fine particles in urban atmospheres, especially in the developed nations (Cyrys, *et al.*, 2003; Shi *et al.*, 1999).

Air quality is deteriorating in urban centres due to increasing motor vehicle fleet from 1994 to 1999 in the case of Zimbabwe and rapid industrialization (APINA, 2003a). Open air waste burning in waste skips is rampant in most areas in Kampala (Uganda).There are cases where industries generating paper waste and textile off cuts burn waste in the open. This practice causes urban air quality problems (APINA, 2004). Dust from untarred roads is also a pollutant. Aerosols reduce visibility in their on right; and apart from the aspect of reduced visibility, it is also evident that limited visual range is contributing cause of automobile and aircraft accidents (Wayne, 2000).

2.5.4 Impacts of particulate matter or aerosols and gaseous pollutants on vegetation and crops

The vegetation is generally regarded as an effective scavenger of atmospheric particulates and in the processes the vegetation can be negatively affected. Size and shape of particulates influence the impaction, adherence to and uptake by plants and there is evidence that particulates of aerodynamic diameter less than 1µm may enter the leaf through the stomata. The effect of particulates on the vegetation depends on

- Physical and chemical properties of pollutants,
- The structure and properties of the receptor, especially its surface and
- The various influences of environment upon deposition (Saunders, 1986).

Particulates containing fluorides appear to cause some plant damage and magnesium oxide falling on agricultural soils has resulted in poor plant growth. Ozone concentrations in the Southern Africa Development Community (SADC) region are currently comparable to the levels that caused crop yield reductions in Europe. Ozone is known to inhibit stomatal opening by directly affecting the "guard cell" that control the opening process (UNEP, 2002).

Pollutants such as sulphur dioxide, nitrogen oxides, ozone and peroxyacl nitrates (PANs), cause direct damage to leaves of crop plants and trees when they enter leaf pores (stomata). Chronic exposure of leaves and needles to air pollutants can also break down the waxy coating that helps prevent excessive water loss and damage from diseases, pests, drought and frost. In highly polluted areas crop losses of wheat, corn, soybeans, and peanuts from damage by ozone and acid deposition amount to several tones a year.

The country reports from Southern Africa region show that vegetation has been impacted at the point source of pollution. The evidence is assessed from simple observation, like in Botswana, vegetation is missing or scarce close to a smelter compared to other areas. Vegetation sensitive to SO_2 pollution is not common within a 40 km radius of the Mufulira Smelter in Zambia, whereas it is common away from the plume (APINA, 2003a)

2.5.5 Impacts of aerosols on the natural ecosystem

Plants, animals and micro-organisms living in soil are significantly impacted by soil acidification. Acidification causes a reduction in soil fertility and plant growth rates decrease as nutrients became less available. Any animal's health may suffer when the animal feeds on plants covered by toxic particulate. Cattle and sheep that have ingested vegetation on which arsenic-containing particles have settled have been victims of arsenic poisoning (NAPCA, 1969).

2.5.6 Impacts of aerosols on exposed materials

Pollutants affect historic and cultural monuments, which create an important part of country's cultural heritage**.** The degradation of inorganic materials, such as calcareous stones and bronze sculptures, is mostly associated with SO_2 and NO_2, and recently also ozone. The degradation of organic material, such as rubber tyres and paints, has traditionally been associated only with ozone in addition to the most important natural factors such as temperature and solar radiation (Tidbald and Kucera, 1996).

Sulphur dioxide and oxides of nitrogen are the primary causes of acid rain. It occurs when these gases react in the atmosphere with water, oxygen and other chemicals to form various acidic compounds. Sunlight increases the rate of most of these reactions. The result is a mild solution of sulphiric and nitric acids. These acids fall out of the atmosphere by wet (acid rain or fog) or dry (acidic gases or particles) deposition. Prevailing winds may blow the compounds causing both wet and dry deposition over hundreds of kilometres (UNEP, 2002). Ozone (O_3) is a strong oxidizing agent, and highly reactive. When the exposure concentrations are high, duration is long and activity such as physical exercise, the greater the effects (SEI, 1998).

2.6 Importance of air pollution

Atmospheric particles are important for several reasons. First, they serve to transport non-volatile material from one place to another. Second, they affect the optical properties of the earth's atmosphere. This not only makes spectacular sunset possible, but also affects the earth's climate by altering the amount of sunlight that penetrates the atmosphere. Third, aerosol particles act as the nuclei on which cloud or fog drops form. Fourth, some trace species in the atmosphere may be present in either the gaseous phase or the particle phase. The partitioning between the phases affects the atmospheric transport of these gases and particles are deposited on the earth's surface at different rates. Finally, aerosol particles have a significant effect on chemical reactions occurring in the atmosphere (Brasseur *et al.*, 1999).

2.7 Factors that affect transportation and dilution of air pollutants

These are grouped into;

- emission or source characteristics
- the nature of the pollutant material

- meteorological characteristics
- the effects of terrain and anthropogenic structures.

2.7.1 Emission or source characteristics

Air transport is the mechanism by which air pollution moves from an emission source to a receptor. A source is the location (i.e. smokestack, chimney, exhaust pipes) from which the pollutants emanates, and the receptor is where the pollutants are deposited. The atmosphere is the sole transporter of the air pollutants. If the wind carries the plume of pollution high enough in air, it may travel several hundreds of kilometres before being brought to the earth. This is known as long distance transport. If the plume is close to the ground like that from exhaust pipes it does not travel long distances, and this is known as short distance transport (Ilyas, 2006).

2.7.2 Nature of the pollutant material

Finest particles remain suspended in the air for a long period of time and they can be transported to longer distances unlike coarse particles will soon fall to the ground and they are not transported to greater distances (Ilyas, 2006).

2.7.3 Meteorological factors in the Air Quality of Harare

Zimbabwe’s climate is predominantly semi-arid, with rainy season spanning the months, November to March, whereas the dry season stretches from May to October. The continued growth in the manufacturing and transport sectors within Harare has potential implications on air pollution and air quality management. This section highlights the air pollution problem over Harare and shows the importance of meteorological factors, for example wind speed and direction, relative humidity and temperature in understanding the nature of the problem and implications for management (Stern, 1984).

Once the pollutants are emitted into the atmosphere, their subsequent fate is solely a function of the prevailing weather conditions. Most of the pollutants are emitted in enormous quantities in relatively small air sheds over urban and industrial areas. The atmosphere has a great, but not an unlimited, ability dilute and eventually remove pollutants. Without the natural removal, scavenging, diluting and dispersing processes in the troposphere, life could perhaps no longer be possible in this earth (Bach, 1972).

2.7.3.1 Wind speed

The wind speed plays a role in diluting and dispersing air pollution. Vast quantities are spewed into the air; the wind speed determines how quickly the pollutants mix with the surrounding air and of course, how far away from their source they are transported. Strong winds tend to lower concentrations of pollutants by spreading them apart as they move downstream. Moreover, stronger winds produce more turbulence air. Turbulent air produces swirling eddies that dilute pollutants by mixing them with cleaner surrounding air. When winds die down, pollutants eddies are not readily dispersed and they tend to become concentrated (Ahrens, 2000).

2.7.3.2 Wind direction

Harare lies in the region of prevailing north-easterly winds, though it also has some occasions of moderate to strong southeast trade winds. The general transportation of pollutants therefore is to the west that is towards Norton, passing through high density suburbs like, Highfields, Kambuzuma and Mufakose. This is as a result of a general easterly flow all year around, though on occasions they are transported to the northwest as a result of the south-easterlies especially in the cool season when they are most dominant. The fact that the wind swings back and forth, from the northeast to the southeast and back, always passing the easterly direction, makes easterly winds the most dominant throughout the year in Harare (Stern, 1984).

2.7.3.2.1 Downwind distance

The greater the distance travelled by the pollutants from the discharge point, the greater the air available for dilution. Since the plume starts above the ground and needs some time to reach the ground, there is no concentration which can be detected in the immediate vicinity of the stack. An increase in concentration will be observed at a distance as the plume reaches the ground. After this, the ground level concentrations will start to decrease with increasing distance from the emission source (Mujuru, 2004).

2.7.3.3 Relative humidity

The relative humidity of moist air (h) is defined as the ratio of its actual vapour pressure to the saturation vapour pressure at the same temperature, that is

$$h = \left(\frac{e}{e_s(T)} \right) \times 100 \tag{2.2}$$

Where h is the relative humidity of moist air, e is the vapour pressure and $e_s(T)$ is the saturation vapour pressure at temperature T (Monteith and Unsworth, 1990).

The saturation vapour pressure can be calculated using the following equation,

$$e_s(T) = 613.75 \times e^{\left(\frac{17.502\,T}{240.97 + T} \right)} \tag{2.3}$$

Where T is in ^{o}C and, $e_s(T)$ is in Pascal (Jones, 1994).

During the warm afternoon, the relative humidity of the air is often below the point at which water vapour begins to condense even active hygroscopic nuclei floating particles remain small (less than 10µm). These particles selectively scatter some rays from the sunlight, while allowing others to penetrate the air. The scattering effect of dry haze produces a bluish colour when viewed against dark background and yellowish tint against light-colour background (Ahrens, 2000).

As the air cools during the night relative humidity in Harare increases to about 75% or above. Condensation may begin on the most effective hygroscopic nuclei, producing wet haze. As water collects on the nuclei, their sizes increase and they became large enough to scatter light much more efficiently. When light strikes wet haze, nearly all visible waves are scattered away evenly, causing the haze layer to appear white (Ahrens, 2000). During summer months, secondary aerosol formation is favoured and new ultra fine particles may form as a result of the condensation of low-volatility products of photochemical reactions (largely organic compounds) onto stable, nanometre-size particles (Sardar *et al*., 2004).

2.7.3.4 Temperature

Higher temperatures can accelerate production and increased concentration of photochemical oxidant in the atmosphere. There is a strong relationship between ozone concentrations and temperature at temperatures above 32 ^{o}C and in Harare maximum temperatures in summer can be as high as 35 ^{o}C. Lower temperature will be associated with lower ozone concentrations whilst high temperatures will lead to higher ozone concentrations. Dry and hot summer conditions would limit ultra fine particle growth to accumulation mode during transport (Kim *et al.*, 2002).

2.7.4 The effects of terrain and anthropogenic structures

The way in which an area is built and the shape of the landscape are known to have a significant impact on the dilution, trapping and transportation of pollutants. The surface and atmospheric modifications associated with the construction and operation of cities are massive. The introduction of new surface materials, the creation of urban canopy (layer of buildings) and emission of heat, moisture and pollutants are the most important factors involved. Together they create a new set of aerodynamic, radiative, thermal and moisture surface boundary conditions and an atmosphere which is laden with aerosols and gases (Russell and Perry, 1997).

2.7.4.1 Topography

Shape of landscape plays an important role in trapping pollutants. At night, cold air tends to drain downhill, where it settles into low-lying basins and valleys. This cold air may carry pollutants downhill from the surrounding hillsides. Valleys prone to pollution are those that are completely encased by mountains and hills. The surrounding mountains tend to block the prevailing wind. Air pollution concentrations in valleys tend to be greatest during colder months. During warm months, daytime heating can warm the sides of the valley to the point that upslope valley winds carry the pollutants upwards, like a chimney (Ahrens, 2000).

2.7.4.2 Anthropogenic structures

On average, city wind speeds are lower than those recorded in the surrounding open country owing to the shelter effect of the buildings. During the day, city wind speeds are considerably lower than those of surrounding rural areas, but during the night the greater mechanical turbulence over the city means that the higher wind speeds aloft are transferred to the lower levels by turbulent mixing. Structures play an important role in the diffusion of pollution within the urban canopy (Barry and Chorley, 2003). This is important for Harare with its tall buildings in down town area.

2.8 Air pollution and the atmosphere

Some industrial processes, vehicle emissions, fires and dust are the main sources of air pollution over Harare. Aerosols reach receptors by being transported and transformed in the atmosphere. The atmosphere acts as the medium for transportation, dilution and physical and chemical transformations. The location of receptors relative to the sources as well as atmospheric influences, affect pollutant concentrations and the sensitivity of receptors to these concentrations determine the effects. The directions and wind strength, existences of inversion layers are some of the meteorological conditions which affect aerosol transport. Air pollution can be divided into three categories depending on the scales of motion and period of time affect a particular area. The different scales are macro scale (scales of thousands of kilometres-synoptic scales, air pollution effects taking place over days or weeks). Mesoscale (hundreds of kilometres which effects taking place over hours and days). Micro scale (one kilometre order-urban pollution, with effects over minutes or hours) (Danida, 1999). Air pollutants are eventually removed from the atmosphere in one way or another though there are some compounds that reside in the atmosphere for very long periods of time. The most effective removal processes are wet deposition and dry deposition (Butler, 1979).

2.8.1 Atmospheric Stability

Transportation and dispersion of pollutants depends on the stability of the atmosphere. A stable atmosphere is characterized by an increase in temperature with height, and in such circumstances vertical air mixing is suppressed and conditions for potentially intense air pollution are created. The atmosphere is said to be unstable if the temperature decreases with height such that the displaced parcel of air continues on an upward or downward motion. It is in the lower atmosphere (The planetary boundary layer) that dispersion of pollutants can be predicted through turbulent diffusion considering the mechanical forces like wind shear and surface friction and thermal forces due to solar heating. The lower atmospheric profile determines the stability of the atmosphere since the atmosphere is warmed from the surface (Stern, 1984).

The nature of the earth’s surface determines the rate of heating or cooling of the surface by solar radiation that sets up a cycle of heating and cooling of the atmospheric boundary layer, which is reflected strongly in the wind field. A stable stratified temperature profile results. At night air is stable because of the cooling and as the sun rises solar radiation heats up the ground faster than the air. Soon after dawn, stable air gives rise to turbulent flow. As buoyancy increases, the wind shear decreases with height and a warm thermal of air attain the same temperature as the ground. Near evening, the temperature of air exceeds that of the ground and heat flux to the ground causes a stable stratified temperature. Due to this, at sunset in Harare plumes of air pollution are noticeable in the western areas like Mbare, Highfield, Glen View giving visibility problems (Stern, 1984).

2.8.2 Inversion and temperature heights

Under normal conditions temperature decreases with height in the troposphere because the source of heat for the atmosphere is the earth's surface. However, there are situations, in the atmosphere, when temperature increases with height. This is usually because of the indifferent nature of the earth's surface is not evenly distributed and the ability of the atmosphere to correct this results in an increase in temperature. Situations where temperature increases with height are called *inversions*. From an air pollution stand point, situations where temperature increases with height are of great importance as the air will be very stable and little mixing of pollutants takes place. This is common in Harare especially in winter whereby in the morning visibility will be very low because of lots of pollutants trapped under the inversion in morning (Stern, 1984).

2.9 Current research on Total Dust Precipitation and $PM_{2.5}$ in Zimbabwe and in other parts of the world

The renewed interest in the light-scattering properties of aerosols in Europe was prompted by recent finding that manmade aerosols play a central role in the atmospheric radiation budget (IPCC, 1995). This has led to several studies being carried out across the world using the nephelometer.

2.9.1 Possible sampling techniques

Some examples of sampling techniques used for atmospheric particulates which could have been used are the sedimentation collection method, filtration method, impaction methods, centrifugal methods, electrostatic precipitation, use of Moss bags, Begerhoff method, nephelometer and many others.

2.9.2 Nephelometer

2.9.2.1 Operations of Nephelometer

The instrument is essentially an aluminium scattering chamber that is lined with light absorbing flock paper to minimize scattering off the walls of the chamber. The schematic representation of the chamber is shown on **Figure 2.1**. The aerosol is drawn into the chamber via the inlet port that has a valve enabling direct air sampling or filtered air sampling. The filtered air option is used to measure the Rayleigh scattering of the molecules and is used to measure the background scattering signal of the instrument due to wall scattering. During ordinary sampling the instrument can be contaminated if the air is much polluted. Therefore it is necessary to periodically measure the background signal to ensure that to the user is getting more accurate aerosol scattering coefficients. The air is blown into the instrument using the external blower capable of delivering a variable flow depending on the nephelometer. A lamp provides illumination via a light pipe and cosine diffuser. A backscatter shutter (Internal chopper) can be engaged if a backscatter is desired. The scattered light passes through a series of apertures and the reference chopper and then the lens before being split via colour filters into blue (B), green (G) and red (R) wavelengths which are detected by the photomultiplier tube (PMT) located at the end of the instrument. At the other end there is a light trap (Anderson *et al.*, 1998).

The reference chopper is a circular plate that makes a full rotation 23 times per second providing the instrument with measurements of the lamp signal PMT dark current and direct signal. Approximately half of the disc is open allowing the true scattering to pass through, about a quarter is opaque allowing transmission of the light source alone and the other quarter is dark allowing measurement of the noise signal due to the PMT. The back scatter shutter is located between the light source and the apertures when it is engaged and then rotated out of the way when the total scattering signal is desired. The restricted internal geometry of the nephelometer means that the angular integration is truncated to between 7 and 170 degrees (Anderson *et al*, 1996).

A temperature (T), pressure (P) and relative humidity sensor are also fitted to the nephelometer. Heating of the air can occur inside the instrument due to the lamp and through the sampling line. This generally ensures that the temperature inside the nephelometer scattering chamber is higher than ambient, avoiding condensation. A heater is provided to ensure that under all operating conditions sample temperature can be maintained higher than the inlet temperature (Anderson *et al.*, 1998).

The instrument has an onboard signal processing capability with both calibration constants and background scatter values stored in internal memory. Communication with the instrument is via the computer running proprietary TSI soft ware either Nephwin or nephlog. Alternatively data can be retrieved using a terminal interface via a serial port (Anderson *et al.*, 1999).

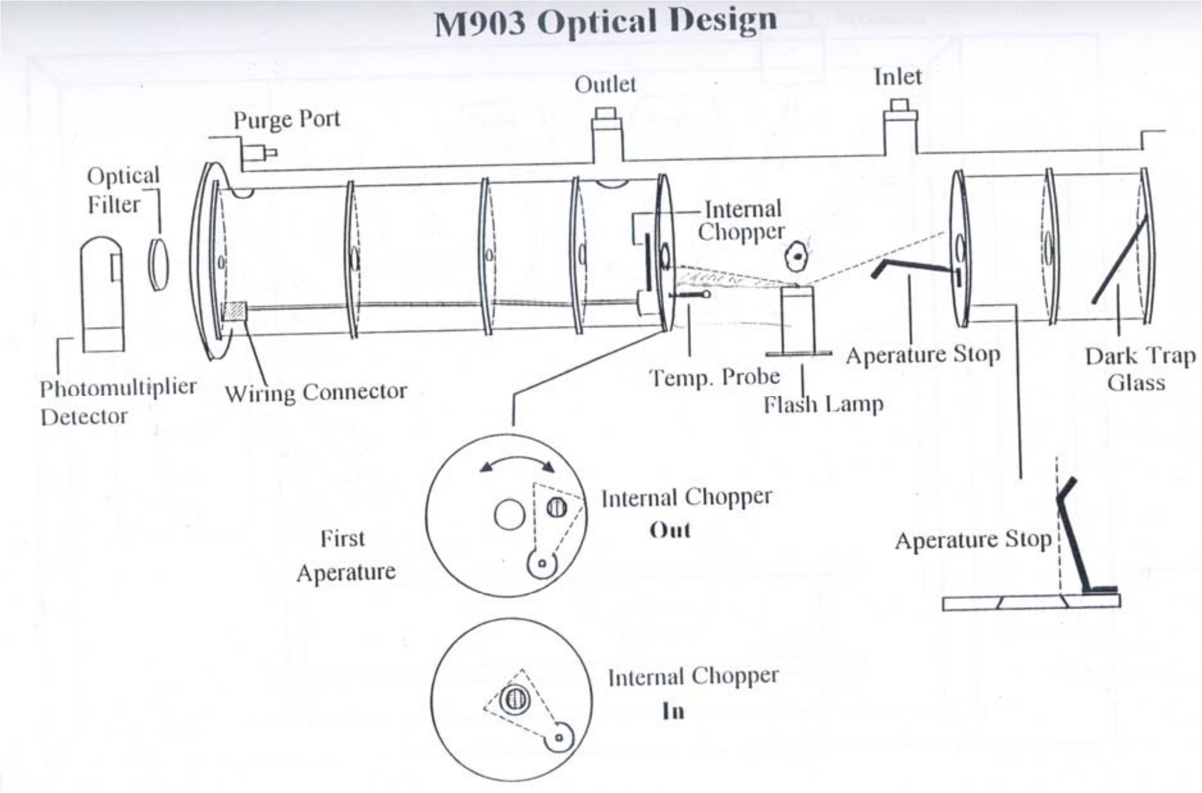

Figure 2.1 The optical design of nephelometer M903 version 2.37, which was used in the research. (Operations procedures M903 Nephelometer, 1998)

2.9.2.2 Theory of Operation of the nephelometer

The property that the nephelometer measures, is the extinction of light over a distance. Extinction is caused by both scattering and absorption of light by particles. The extinction coefficient b_{ext} is a measure of these, and is given by the formula

$$b_{ext} = b_{scat} + b_{abs} = \ln \frac{\left(\frac{I}{I_o}\right)}{x} \qquad (2.4)$$

x = length of light path
I = intensity of light after distance
I_o = initial intensity of light

b_{scat} and b_{abs} are the scattering and absorption coefficients. They are each divided into two components:-

$$b_{scat} = b_{ag} + b_{sp} \qquad (2.5)$$

$$b_{abs} = b_{ag} + b_{ap} \qquad (2.6)$$

b_{rg} = Rayleigh (gas) scattering coefficient
b_{sp} = particle scattering coefficient
b_{ag} = gas absorption coefficient
b_{ap} = particle absorption coefficient

The nephelometer measures b_{scat} and b_{rg} and subtracts b_{ag} to get b_{sp}. b_{ag} is usually negligible. The equation that governs the instrument is

$$B = \left(\frac{I_o}{y}\right)\left(\frac{b_{scat}}{2PI}\right) \qquad (2.7)$$

y = vertical distance from light source to sensor
B = flux of light detected by sensor

The nephelometer counts photons using the photomultiplier tubes. The photon counts are converted to counting frequencies and then scattering coefficients using calibration constants (Anderson *et al.,*1998)

2.9.2.3 Signal Processing

The process described in this section is carried out for each of the three colours. First, the raw photon count for each section (or gate) of the reference chopper is measured for total scatter and backscatter. There are a total of 18 data (3 colours x 3 chopper sections x 2 positions of backscatter shutter). These data are normalized by gate width to get a scaled count rate according to the equation

$$C_s = \left(\frac{360 \times C \times S}{G \times N} \right) \tag{2.8}$$

C = raw photon count
S = speed of chopper (Hz)
G = gate width (degrees)
N = number of revolutions
C_s = scaled count rate (Hz)

Note: The gate width is 40° less than the total section width. The first and last 20° are blank to separate the signals.

When a pulse of light is being registered on the PMT, it cannot register another pulse during that time. This "dead time" is a function of the pulse width of the PMT and must be corrected for using the equation

$$F = C_s \times (C_s \times K_1 + 1) \tag{2.9}$$

K_1 = pulse width constant
F = corrected count rate (Hz)

From time to time, the air sample entering the nephelometer is filtered in order to measure the scattering by the gas molecules (Anderson *et al.*, 1999). The nephelometer calculates raw scattering signals for filtered air and for aerosol as,

$$B_f = K_2 \times \left(\frac{S_f - D_f}{C_f - D_f} \right) \tag{2.10}$$

B_f = raw scatter signal for filtered air

C_f = scaled count rate of calibrate gate for filtered air (Hz)

D_f = scaled count rate of dark gate for filtered air (Hz)

K_2 = span gas constant

S_f = scaled count rate of signal gate for filtered air (Hz)
The same is done for the aerosol ('a' subscripts).

The Rayleigh scattering for filtered air and aerosol is then calculated as,

$$R_f = \left(\frac{K_3 \times P_f \times T_s}{T_f \times P_s} \right) \tag{2.11}$$

K_3 = Rayleigh scatter constant
P_f = Pressure of filtered air
T_s = Standard temperature (273.15 K)
T_f = Temperature of filtered air
P_s = Standard pressure (1.0133 bar)
R_f = Rayleigh scatter for filtered air

The same is done for the aerosol.

Three parameters are then calculated wall scatter (W), total scatter (B_s), and b_{sp}.

$$W = B_f - R_f \tag{2.12}$$

$$B_s = B_a - W \tag{2.13}$$

$$b_{sp} = B_s - R_a \tag{2.14}$$

B_a is the total absorption

R_a is Rayleigh scatter for aerosol

In order to calculate the backscatter coefficient (b_{bsp}), the same procedure is followed, and K_3 is multiplied by K_4, a backscatter constant.

The instrument error is +/- 0.2 mm^{-1} (Heintzenberg *et al.*, 1996).

2.9.2.4 Calibration of nephelometer

K_1 is based on the pulse width of the PMT and is set by the manufacturer. It is different for each colour.

K_3 is a known property of air and varies with wavelength, temperature and pressure. K_3 values for the span gases are also known.

K_2 is calculated from the scattering data of two span gases, 'low' and 'high.' The scattering coefficient for the low span gas is expanded to

$$b_{spl} = B_1 - W - R_1 \tag{2.15}$$

$$b_{spl} \equiv K_2\left(\frac{S_1 - D_1}{C_1 - D_1}\right) - K_3 \times \left(\frac{P_1}{P_s}\right)\left(\frac{T_s}{T_1}\right) - W \tag{2.16}$$

b_{spl} is scattering coefficient of low span gas

B_l is raw scatter for low span gas

R_l is Rayleigh scatter for low span gas

The scattering coefficient is 0 because there are no particles present. This equation also holds for the high span gas. The two equations are subtracted from one another. The W term drops out and the only remaining unknown is K_2 which can then be solved for.

K_4 is likewise calculated using backscatter data. The equation for the low span gas is

$$b_{sspl} = B_l - W - R_l \tag{2.17}$$

$$b_{sspl} = K_2 \times \left(\frac{S_l - D_l}{C_l - D_l} \right) - K_4 \times K_3 \times \left(\frac{P_l}{P_s} \right) \times \left(\frac{T_s}{T_l} \right) - W = 0 \tag{2.18}$$

The equation again is applied to the high span gas as well. The two equations are subtracted to eliminate W, and the only remaining unknown is K_4 (Anderson *et al*., 1999).

2.9.3 Bergerhoff Method

This method serves to determine the dust precipitation in the ambient air. Dust precipitation is the dry residue of the input of atmospheric matter collected in a collecting pot, during the period of exposure. In this method collecting pots are made of either glass or plastic. The use of plastic pots avoids measurements being lost due to frost breakage and can be obtained as they are using easily available, which may occur if Bergerhoff glass pots are used, that the reason why plastic pots were used in this project. The input of atmospheric matter is determined over the planned period of measurement, as a rule one month (30 ± 2), by exposing the collecting pots. The distilled water in the sample is evaporated and the dry residue is determined gravimetrically, the result being reported in g m^{-2} d^{-1} or mg m^{-2} d^{-1}.

2.9.3.1 Apparatus and materials needed for the Bergerhoff method

Collecting pots, domestic jar or plastic pot, whose dimensions are determined by the size of the protective basket. These pots must be thoroughly cleaned before measuring the dust precipitation.

Posts with protective basket need to be used for accommodating the collecting pot. The distilled water used should be checked at regular intervals to determine the mass of its evaporating residue. Balance with an accuracy of at least 0.1mg need to be used to weigh. Drying cabinet to dry the apparatus and tweezers to remove any insects or logs from the collecting pots.

2.9.3.2 Installation of measurement point

The opening of the collecting pots has to be horizontal; steps should be taken to ensure free inflow to the apparatus. Care should be taken that the site is not affected by emissions from immediately adjacent source which would limit the representative nature of the measurements required by the measurement task

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2.9.3.3 Determination of total dust precipitation (TDP)

After carrying out preparatory work, the collecting pots will be opened. The sample material (dust and liquid) adhered into appropriate collecting pots is rinsed with distilled water. The coarse impurities (for example leaves and insects) are removed using tweezers and the determination of TDP is done by weighing the total residue. In order to determine the weight of the evaporating dishes when empty, they are dried for an hour at 150 ^{o}C, in a drying cabinet, cooled for 30 minutes and then reweighed. The water from the collecting pots is poured into the evaporating dish and cabinet dried at temperatures below 80 ^{o}C, then cooled for 30 minutes.The weight of the dish and its contents is then determined. The difference between the pre-weighed dish and the dish with its contents gives the weight of the total dust precipitation.

2.9.3.4 Calculation of results

The collecting pots contents to be evaluated as dust precipitation are given by the difference G between the weight of the dish and contents after evaporation and weight when empty in g for each evaporating dish.

$$x = \left(\frac{G \times f}{A \times \tau} \right) \tag{2.19}$$

Where x is dust precipitation in g m $^{-2}$d^{-1} or mg m $^{-2}$d^{-1}

A is collecting area in cm^{2}

f =10000 cm^{2} m $^{-2}$ (conversion factor)

G is mass of the dust precipitation sample in g or mg

τ is the period of sampling (collecting time) in d (days)

2.9.3.5 Assumptions of the Begerhoff Method

- Since measurement is a mean of all the days considered have received the same pollutant levels
- No particulates remained attached to the wall of the containers when transferring to the evaporating dishes
- When removing the coarse impurities, no particulates are removed in the process
- No birds droppings will be collected by the pots.

2.9.4 General description of LI-6262 CO_2/H_2O vapour analyzer

The LI-6262 CO_2/H_2O vapour analyzer is a differential, non-dispersive, infrared (NDIR) gas analyzer. The CO_2 and H_2O measurements are based on the difference in absorption of infrared (IR) radiation passing through two gas sampling cells. The **reference cell** is used for a gas of known CO_2 or H_2O concentration, and the **sample cell** is used for a gas of unknown concentration. Infrared radiation is transmitted through both cell paths, and the output of the analyzer is proportional to the difference in absorption between the two.

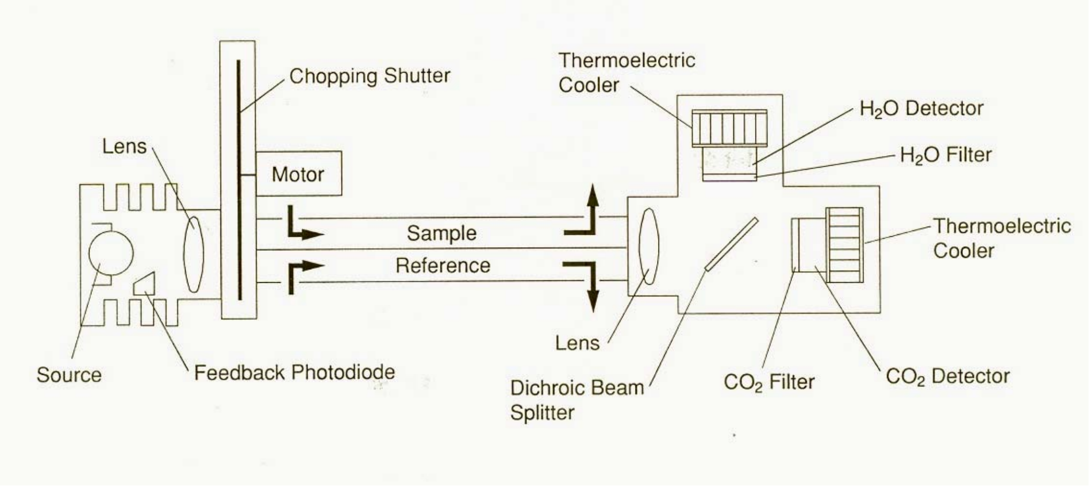


Figure 2.2 The schematic design of the LI-6262 CO_2/H_20 vapour analyzer (LI-6262 Manual, 1996)

The infrared source is vacuum sealed for long life (> 10,000 hours) and high stability. A separate optical feedback circuit with a photodiode maintains the source at a constant colour temperature (1250 K). A gold reflector surrounding the IR source maximizes the radiation output from the source and decreases the power required. The chopping shutter disc is spun by a motor, whose shaft turns on high precision bearings for long life and low noise. Rotation is precisely controlled at 500 hertz on a phase locked loop circuit. The optical path between the source and optical bench is sealed and continuously purged of CO_2 and H_2O by an attached tube containing soda lime and magnesium perchlorate. This eliminates interference due to ambient CO_2 or H_2O vapour.

2.9.4.1 Theory of Operation of LI-6262

The sample cells are gold-plated to enhance IR reflection and resist tarnishing over time. One set of sample cells is used for both H_2O and CO_2 measurements by using a diachronic beam splitter to provide radiation to two separate detectors. A 150 nm band pass optical filter is used to tune the CO_2 detector to the 4.26 micron absorption band for CO_2, and a 50 nm band pass optical filter tunes the H_2O detector to the 2.59 micron absorption band. Both filters provide excellent rejection of IR radiation outside the desired band, allowing the analyzer to reject the response of other IR absorbing gases. The filters are mounted directly on the detectors for thermal stability. Each detector is a lead selenide solid state device that is insensitive to vibration. The detectors are cooled and regulated to -5 °C by thermoelectric coolers, and electronic circuits continuously monitor and maintain constant detector sensitivity. The result of this detector circuitry is a detector system that is very stable. Infrared radiation from the source is focused through the gas cells and onto the detector by a lens at each end of the optical bench. Focusing the radiation maximizes the amount of radiation that reaches the detector in order to provide maximum signal sensitivity.

All of these features provide a CO_2 noise level that is typically 0.3 ppmn peak-to-peak (at 350 ppm) when using 1 second signal averaging, and 1 ppm peak-to-peak with 0.1 second signal averaging; the H_2O noise level is approximately 0.002 kPa at 2.0 kPa when using 1 second signal averaging, and 0.006 kPa when using 0.1 second signal averaging. Signal averaging times are selectable (in software) between 1 and 30 seconds and are used to achieve even lower noise levels. For example, with 4 seconds of signal averaging, the noise levels typically decrease 50 %.

CHAPTER 3 MATERIALS AND METHODS

Population growth, increasing urbanization of the population and increased energy demands in urban areas of Zimbabwean resulted in constant changes taking place in the environments. As most people in Zimbabwe are now resorting to the use of firewood because of power cuts this will lead to increased air pollution levels. Apart from that, the Zimbabwean fleet is known to have been increased and also industrialization which is taking place will lead to an inevitable rise in sulphur and nitrogen dioxides and particulate matter, especially PM $_{2.5,}$ in the cities.

Figure 3.1 The top-elevation of the study area at the University of Zimbabwe (www.googleearth.com/17^{o}46'57.63 S 31^{o}03'03.93 E) 12 April 2007

3.1 Study area

The main study area of this project was the University of Zimbabwe, which lies in the capital city of Zimbabwe which is Harare from 31º 25' E to 31º 60' E and 17º 77' N to 17º 87' N. The nephelometer's pump, carbon dioxide gas analyser and the automatic weather station (AWS) were installed on the roof of the Physics department building which is 1450 m above the sea level and 10 m above the ground (on the roof of the Physics department building surrounded by green mark on **Figure 3.1**). The study area shown in **Figure 3.1** is surrounded by busy roads namely Upper East to the East, Mount Pleasant Drive to the north, College Drive to the west and Churchill road to the south. These roads provide a source of pollution from passing vehicles. The study area itself is quite busy during the week days. This study area was chosen because the sampling equipment would be raised above the three storey building (Physics department). On top of the building, was a good position as it was away from ground, which is a source of dust which was likely to affect the measurements.

3.2 Chosen techniques

Out of the all possible sampling techniques mentioned in Chapter 2 (2.9.1), Begerhoff and the use of nephelometer were the only chosen techniques. When choosing methods to use, there are several factors that have to be looked into and they include cost of equipment, whether the equipment is user friendly, the effectiveness of the method to be employed and the availability of the equipment.

3.2.1 Bergerhoff method

The cost of measuring equipment is low and this allows a large number of measuring stations to be set up with low financial outlay if several measurements are required. No power supply is required and this allows the equipment to be set up in the open, the collecting pots can be changed by a semi-skilled person. The manageable size of the pots makes it easy to transport them.

There is an old saying as follows, “The quality of analysis is only as good as the quality of the sample”. This means that it is pointless carrying out expensive accurate analysis if the sample does not represent the parental material. The underlying principle of sampling is simply “the sample must represent the batch” (Mujuru, 2004).

3.2.1.2 Nephelometer

There are advantages associated with using the nephelometer which include:-

- It has got an internal memory which can store data averages and can be retrieved at any time using a computer. The current version will store up to 2 weeks of 5 minutes averages before downloading is necessary. Any computer with a serial port and terminal software can be used,
- Pressure and temperature are measured in the scattering volume and are used to correct for changes in air Rayleigh background,
- Ambient relative humidity is measured, and
- Averaging periods of up to 1 hour are user selected.

3.3 Experimental design

The study was divided into two parts namely $PM_{2.5}$ and the TDP (total dust precipitation) measurements. The $PM_{2.5}$ measurements were done using the nephelometer’s sucking pump on the roof of the Physics Department. Its time was synchronised with that of the CO_2 gas analyser. Measurements were averaged after every 5 minutes for both the nephelometer and the CO_2 gas analyser and measurements were taken everyday of the week. The measurement from the sensor of the automatic weather station and the CO_2 gas analyser were stored in CR23X (Campbell scientific, Edmantan, U.S.A.March/2000) data logger. The stored data was collected every 4 days using a laptop computer. The second part involved the use of collecting pots (Bergerhoff method). Initially 5 collecting pots were installed on the roof of the Physics Department building and the second set of pots was set up at 12 different parts of residential areas of Harare with 2 collecting pots per position. Trace element analysis was then carried for the 12 different sites using the TDP which was collected.

3.3.1. Use of the Nephelometer

The nephelometer has been used in different parts of the world to measure aerosols. In most cases the measurements which were carried out, used dry air. So the first thrust of this project was to determine the response of the nephelometer to wet and dry air samples.

3.3.1.1 Comparison between wet air sample and dry air sample measurements

The nephelometer set up was put in the MAGM (Masters in Agricultural Meteorology) laboratory as indicated on **Figure 3.3** and its pump was put on the rooftop of Physics Department building at 1.5 m above the roof’s floor. A tube was connected between the sucking chamber and sucking pump. The tube is coated with special material to avoid attachment of particulates on its walls as this was going to alter the measurement of the particulates.

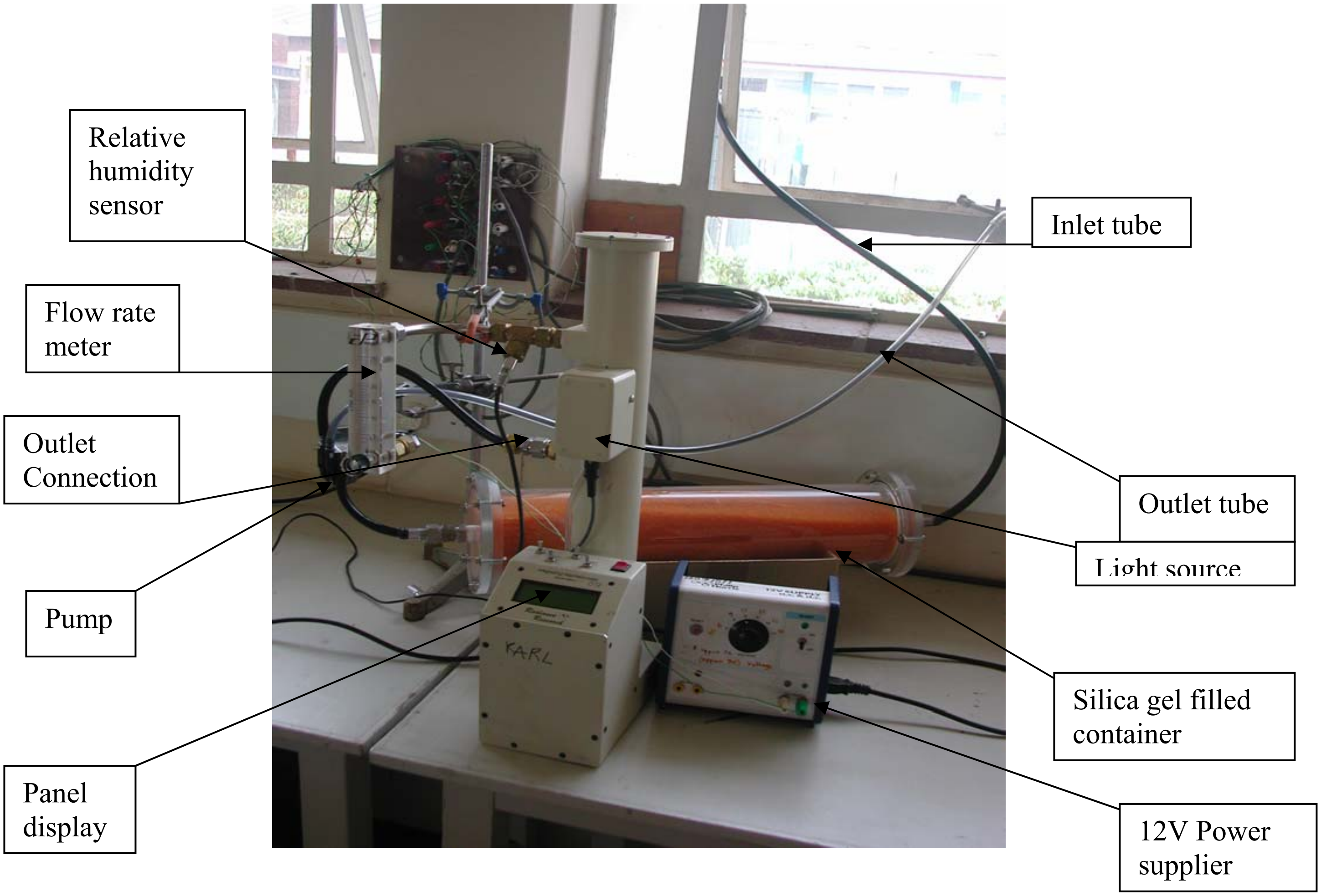


Figure 3.2 The M903 integrating nephelometer ROM Version 2.37 which was the main instrument used in this project

Ambient air which was drawn from the rooftop of Physics department building was passed through a 50 cm long tube which was filled with silica gel (which was used as the drying agent).The flow rate was set at 5 litres min^{-1} and the averaging time set at 5 minutes for a day. Relative humidity readings used were those which were produced by the nephelometer as they represented the degree of dryness of the air passed through the silica gel. These results were compared with those obtained when the silica gel containing tube was removed, so that the ambient air could remain wet. The averaging time was also set at 5 minutes and the flow rate maintained at 5 litres min^{-1}. The measurements of relative humidity used were those which were recorded by the humidity probe on the AWS on the roof.

The AWS was set up on the rooftop of Physics Department building. The following weather parameters were measured; air temperature and relative humidity sensor was set at a height of 1.2 m above the surface, solar radiation, rainfall wind speed and direction at 1.8 m above the surface. The sensors for the measurement of weather were connected to CR23X data logger. Those for the rain gauge were connected to CR23X data logger. A laptop computer was used to download data at regular intervals (after 4 days).

3.3.1.2 Comparison of $PM_{2.5}$ with meteorological parameters

The basic idea of the methodology is rather straight forward. All measurements done using the nephelometer, used dried air. These air measurements were taken from March 14 2007 to April 19 (2007). The nephelometer's averaging time was reduced to 1 minute. This allows a clear observation of the variation of particulates long averaging time tends to reduce the accuracy of the information obtained. The averaging time of all the meteorological parameters was set at 5 minutes for the entire sampling period.

Diurnal measurements of the particulate matter as well as of meteorological parameters were taken to observe how they vary with time of day and to investigate whether any relationship existed between meteorological parameters and particulate concentrations in the atmosphere. The system was run continuously and certain days were selected, especially those days on which rain had fallen and to determine the effect of precipitation on the composition of atmospheric particulate matter.

3.3.1.3 Comparison of particulate matter concentration during working week days (Monday to Friday) with weekends (Saturday and Sunday)

All measurements were taken for the entire week and then analysis of measurements was also done to observe the behaviour of particulate matter during the working week days and compare them with those of weekends. The 5 minute averages were converted to hour averages of all the measurements taken from March 14 to April 19 2007 to observe the temporal behaviour of particulate matter during the working weekdays and weekends.

3.3.1.4 Comparison of diurnal and weekly variation of particulate matter ($PM_{2.5}$) with carbon dioxide (CO_2)

The time of the nephelometer and that of the LI 6262 carbon dioxide/water vapour analyzer were synchronized and the averaging time was set at 5 minutes. The LI 6262 carbon dioxide/water vapour analyzer set-up was put on the Physics Buildings roof top were the sucking chamber of the nephelometer was positioned. The measurements from the CO_2 analyzer were compared with those of particulate matter taken by the nephelometer daily as well as weekly. The flow rate was set at 5 litres min^{-1}**.**

3.3.2 Bergerhoff method

Collecting pots which were used had 60 mm wide openings, were128 mm tall and had a holding capacity of 375 ml. These pots were cleaned with warm tap water and then soaked in water with detergents for a day to remove the oil. These pots were filled with 200 ml of distilled water and installed on the roof of Physics building from 26 November 2006 to 27 December 2006. Water levels were checked after every 4 days and more distilled water was added to mark if water levels went below the mark.

3.3.2.1 Site requirements

The collecting pots used were tagged with site name and start and end dates. These collecting pots were located at least 50 m from small-scale local sources, e.g. generators, coal or wood. This was done particularly to ensure that the sites were well exposed and not sheltered by tall vegetation closer to the collecting pots. The pots were installed with their openings being horizontal and pointing upwards to allow free flow of air and exposure to dust fall and rain. The collecting pots were exposed for the desired period (21 days).

3.3.2.2 Sampling procedure

The pots were marked at 200 ml level and distilled water was poured in, up to the mark. The water level was monitored after every 4 days and if the water levels decreased to levels below the mark, more water were then added so that it remained at the required level. In case of rainfall, where water levels exceeded the level, no water was removed as this was going to compromise the amount of collected particulate matter in the pots.

3.3.2.3 Collecting procedure

After 21 days of sampling, the pots were sealed and then taken to the laboratory for analysis. The samples were now ready for treatment and analysis/measurements. Normally there is a delay between this step and the time when measurements would take place. During this period samples were kept in a refrigerator. This was done in order to prevent growth of moulds and algae which were likely to affect to results.

3.3.2.4 Measuring procedure

Clean filter papers were weighed 15 times in order to determine the average weight of each filter paper and also in order to remove the noise or uncertainty that is normally associated with measuring mass. Mettler 240 Analytical balance which measures correct to 5 decimal places of grammes was used. The filter papers were the placed into funnels and placed on a vacuum pump. The water in the samples was then poured into the funnel and the particulates were then collected. **NB**. Distilled water was poured into the collecting pots, which were thoroughly shaken so that same particulates which may have stuck on the walls of the pots were collected. This distilled water was then filtered again, in order to capture those particulates which might have escaped during the first filtration.

The filter papers were then put into the desiccators filled with silica gel which acted as the drying agent for 24 hours. G (mass of dry precipitation in the sample) was then determined by subtracting the mass of empty filter paper from that of filter paper with precipitates on it.

$$G = X_1 - X_2 \tag{2.20}$$

Where X_1 is mass of filter paper and dust precipitation on it and X_2 is mass of an empty filter paper. x (dust precipitation in g/m^{2}d) was then calculated using equation 2.19.

3.3.2.4 Sampling procedures used

3.3.2.4.1 Sampling A (31 days sampling)

The first set of 5 pots was installed on the roof of Physics building from 26 November 2006 to 27 December 2006.These pots were filled with 200ml of distilled water and then put on the roof of Physics building from 26 November 2006 to 27 December 2006.

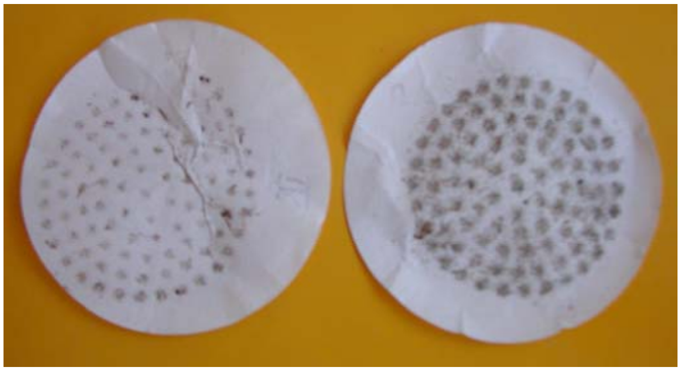


Figure 3. 3 Samples of total dust precipitation (TDP) on filter papers

3.3.2.4.2 Sampling B (21 days sampling)

For the second set, a total of 24 collecting pots were used in this experiment. A total of 2 collecting pot were put on top of the Physics department building and the remaining 22 were distributed to high and low density suburbs of Harare, two pots per station. The pots were filled with 200 ml of distilled water and the water levels were monitored for 21 days running from DOY 81 to DOY 102 2007 after which they were taken to the laboratory for further analysis.

3.4 Instruments

The determination of the quantity of given pollutant in the ambient atmosphere requires care and the use of sensitive instrumentation since the concentrations of the pollutants in the atmosphere is small (can be in ppm or ppb). In this research a nephelometer was used to measure $PM_{2.5}$, LICOR IRGA used to measure ambient CO_2 mixing ratio and the atomic absorption spectrometer (AAS) was used to measure the concentrations of the trace elements.

3.4. Instrument calibration

Instruments are always calibrated prior to field measurements. Calibration reduces instrument related errors. This is particularly true in the case where different types of sensors may be used whose specifications are manufacturer dependent. Calibration of sensors is carried out against an in-house standard and ensures firstly that the deviations from the standard are within the accuracy limits advertised by the manufacturers of the sensors and secondly that adjustments to the measurements can be affected where necessary (Mhizha, 2003).

3.4.1 Nephelometer

The M903 portable nephelometer is light weight, low power instrument designed for portable operation as well as general environmental monitoring. It measure light scattering extinction coefficient (σ_{sp}) using the geometry of a standard integrating nephelometer. Pressure and temperature sensors automatically correct for changes in air Rayleigh scattering. Relative humidity also monitored and recorded. The light source is variable rate flash lamp with a wavelength defining optical filter (545 nm).

The optical and electrical background noise is sufficiently low to allow measurement of (σ_{sp}) (for particles) less than 10 % of air Raleigh ((σ_{sp}) < 0.001km^{-1}) to greater than (σ_{sp}) 1 km^{-1}. The electronics are computer based, providing flexible menu driven programming of the instrument operation using panel display/switches or a serial port. Data averages can be stored internally in battery RAM and retrieved at any time.

3.4.1.1 Calibration of nephelometer

The nephelometer (Serial number; MPI-S/N MOA-0184) was calibrated by Frank , at Max Plank Institute for Chemistry and Biogeochemistry Department in Germany on DOY 264 (2006) and **Table 3.1** shows the results which he obtained before and after calibration.

Table 3 The values which were obtained after and before calibration of the nephelometer

	Zero set integer	Span set integer	Wall	Span value	Reference
Before calibration	17529	50985	41%	74.7	
After calibration	17730	50985	51%	74.7	32600

3.4.2. Gas analyzer

The LICOR IRGA is sensitive to temperature and pressure fluctuations. When it is moved from one place to another, the calibration values can shift easily. Over a period of time, calibration values drift. Therefore it is essential to calibrate the IRGA regularly and to adjust the zero and span from time to time. All calibrations were done, according to the recommendations of the manufacturer outlined in the IRGA user manual.

3.4.2.1 Calibration of Gas analyzer

For CO_2 calibration, two gas tanks with NIST traceable CO_2 at concentrations of 334.8 ppm and 335.6 ppm were used. Additionally, NIST traceable pure nitrogen gas was used to find the CO_2 zero. All gas tanks were fitted with regulators. Using the regulator fitted on the N_2 gas tank, the flow of gas was adjusted until it gave a reading of (1.2 ± 1) l min^{-1} on the rotameter connected to the IRGA sample inlet. A Gelman 1 µm filter was also connected to the sample inlet path. The gas was left to flow through the IRGA for an hour, by which time the reading on the IRGA had stabilized. Next, the 334.8 ppm CO_2 gas tank was connected to the IRGA sample inlet and using the same procedure as the N_2 gas, data was logged. Finally, the 335.6 ppm gas was used to get the final calibration point. The three data points for the CO_2 calibration were obtained by averaging the last 10 stable readings of CO_2 (mV) from the data logger outputs for each gas. A calibration line was then plotted of CO_2 concentration [ppm] against CO_2 [mV] from the gas tanks i.e. $c=c(u)$ from which any CO_2 signal from the IRGA could be converted to ppm or, preferably, µmol mol^{-1}. It was assumed that the relationship between the LICOR IRGA signal and the gas concentration was linear in the CO_2 range prevailing throughout the experiment.

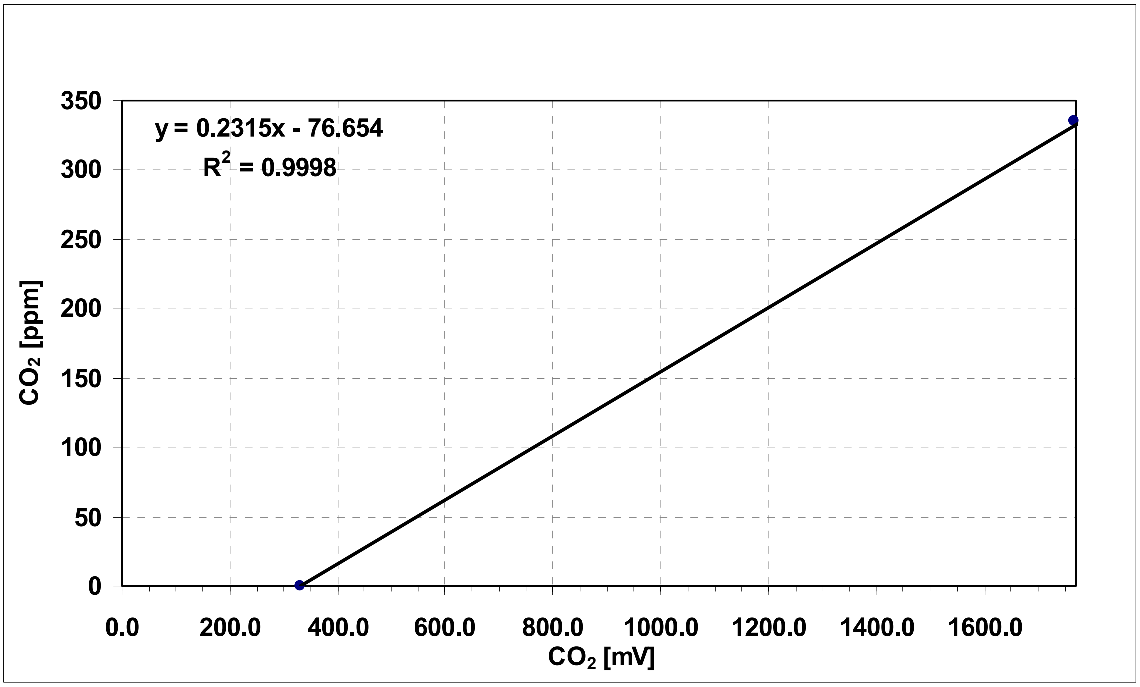


Figure 3. 4 Calibration graph for the LICOR CO_2 for the data taken on DOY 31 2007

3.5 Trace element analysis of total dust precipitation collected using the Bergehoff method

The 24 collecting pots which were collected from the 12 different sites of the residential areas of Harare were further analysed for the trace elements (lead (Pb), iron (Fe) and nickel (Ni)) using the Atomic Absorption Spectrometer.

3.5.1 Equipment used

A Varian Spectra (AA-6401 F) Atomic Absorption spectrometer fitted with graphite furnace accessory was used for analysis of the following metals Pb, Fe and Ni. For TDP to be separated from the filter papers into solution the filter paper were dipped in acids (see section 3.7.3). The solutions were analyzed for each element (iron, lead and nickel) with corresponding hollow cathode lamps and deuterium lamp was used for background correction. Argon (99.99%) was used to provide an inert atmosphere during drying and ashing to blow away the gases produced.

Figure 3. 5 The Atomic absorption spectrometer (AA-6401 F) used to analyse the trace elements

3.5.2 Reagents used

The analytical grade chemical reagents which were used for separating the TDP from the filter papers and dissolving the TDP into solution are nitric acid, hydrofluoric acid, perchloric acid, hydrochloric acid and neither de-ionized water nor the acids used showed significant blank. These reagents were either freshly prepared or were taken directly from the stock solutions.

3.5.3 Preparation of solutions

A filter paper was placed in 100 cm^3 Teflon beaker to which 5 ml of 50 % nitric acid was added. The beaker was then covered and heated for 30 minutes. The contents were heated to destroy organic matter and the residue was then re-dissolved in a mixture of 2 ml each of concentrated nitric acid and perchloric acid. The mixture was the heated to dryness and to the residue 1 ml of concentrated hydrofluoric acid was used to destroy the silica matrix. The mixture was then heated until fumes of perchloric acid were observed and the mixture was redissolved in 2 ml of 1 M nitric acid and the solutions diluted to 100 ml. The solutions were stored at low temperatures (4 ^{o}C) in plastic bottles, which had been soaked in 0.1 % nitric acid for 24 hours and then rinsed thoroughly with de-ionized water before use.

Blanks and standards containing 10 ppm and 10 ppb were prepared using serial dilutions of 50 ppm stock solution. Standard solutions were prepared using the corresponding pure metals and the stock solutions were stabilized by dissolving them in 0.1 % nitric acid. Fresh working standards were prepared each day to avoid loss of analyte on the container wall or leaching out of the element from the container.

3.6 Measurements of the Meteorological parameters

Three field campaigns were carried out (starting from DOY 257 2006 to DOY 119 2007). The first step was the installation of temperature and humidity sensor, wind speed and direction sensors, rain gauge and solar radiation sensor. All these sensors were connected to a data logger (CR23X) shown on **Figure 3.6** from which data was down loaded using a laptop computer after regular intervals (4 days). These sensors were installed on the roof of Physics department building.

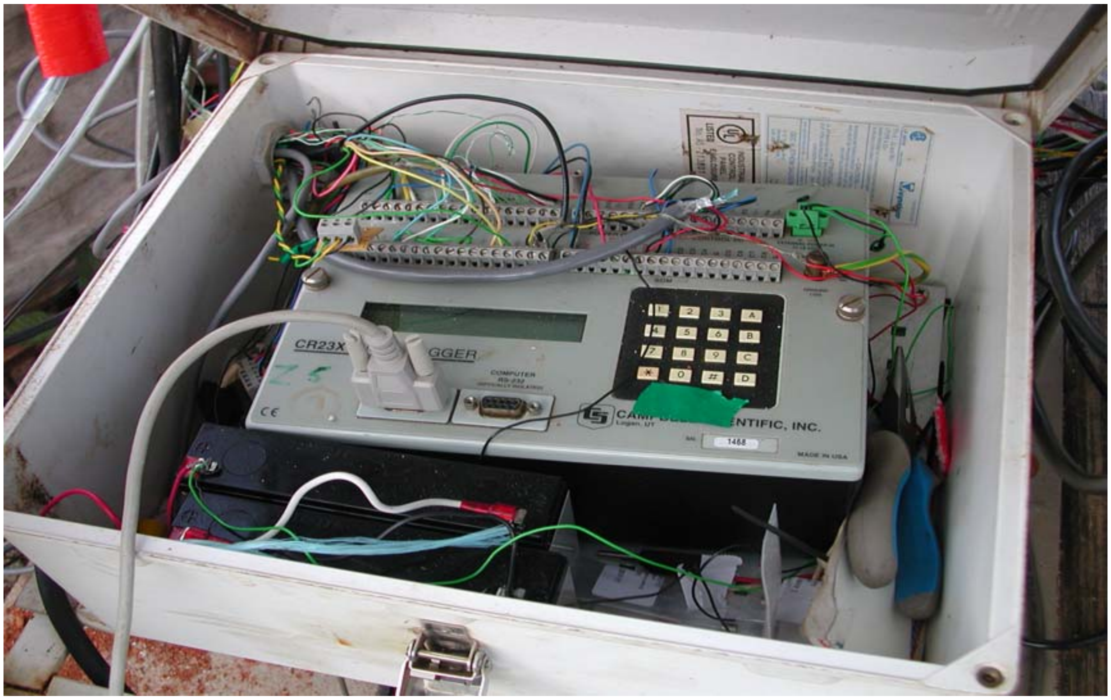


Figure 3.6 CR23X Micro logger on which all the meteorological sensors were connected during the sampling period DOY 257 2006 to DOY 119 2007

The data logger was put in a metal box to protect it from direct sunlight and rainfall damages.

3.6.1 Wind speed and direction

For wind speed an A100L2 cup anemometer (Vector Instruments, UK cup) was used and a 03001 wind sentry wind vane (R.M. Young Instruments, July 1995) was used to measure wind direction. This wind direction sensor has a measurement range of 360 ^{o} whilst the wind speed sensor has got a speed range of 0 to 77.216 m s^{-1} and operating temperature range of - 30 ^{o}C to 70 ^{o}C. The measurements were taken from the DOY 254 (2006) to DOY 119 (2007). Both the wind vane and the cup anemometer were raised to 1.6 m above the ground on the roof of Physics Department building.

3.6.2 Air temperature and relative humidity

Measurements for relative humidity and temperature were done using, the HMP45AC Temperature and Relative Humidity sensor (Campbell Scientific Ltd; Loughborough, UK). It was set at a height of 1.5 m above the ground on the roof.

3.6.2.1 HMP45AC temperature and relative humidity probe

The HMP45AC temperature and relative humidity probe contains a Platinum Resistance Temperature detector (PRT) and Viasala HUMICAP 180 capacitive relative humidity sensor. The temperature sensor has a measurement range of - 40 ^{o}C to + 60 ^{o}C with its accuracy at manufacture being greatest at 20 ^{o}C (0.2 ^{o}C) and lowest at 40 ^{o}C (0.4 ^{o}C). The relative humidity sensor has a measurement range of 0 to 100 %. Its accuracy at manufacture at 20 % is 2 % RH (0 % to 90 %) and 3 % RH (90 % to 100 % RH).

3.6.3 Rainfall

The measurement of rainfall was done using the tipping bucket rain gauge, model CSL500 which has measurement of 0.2 mm/tip. (Campbell Scientific, USA). The rain gauge was placed on the roof of the Physics Department (UZ). Measurements were done from DOY 2 to DOY 119 (2007).

CHAPTER 4 RESULTS AND DISCUSSION

The results which were obtained in this chapter are based on the procedures which were carried out in the methodology and the discussion will focus mainly on the temporal behaviour of $PM_{2.5}$ and carbon dioxide, the effects of the meteorological parameters (wind velocity, temperature, relative humidity solar radiation and rainfall) on the concentrations of the $PM_{2.5}$ and carbon dioxide and lastly on the determination of spatial distribution of TDP and trace elements in the residential areas of Harare.

4.1 Comparison between wet air sample and dry air sample measurements

A comparative analysis between the dried air (which was passed through silica gel) and wet air samples (air which was measured directly from the atmosphere, without any moisture being removed) was carried out to observe how the nephelometer responds to the two different situations.

4.2 Why was the ambient air dried?

The nephelometer responds differently to wet and dry ambient air, as a result some measurements were done using dry air and some using wet air were carried out to observe the best conditions under which the instrument could give best results. **Figure 4.1** shows that the variation of ambient relative humidity with that of ambient temperature which is almost mirror images of each other. The saturation vapour pressure depends highly on temperature (equation 2.3) so as temperature decreases from 1600 to 0600; the saturation vapour pressure will be decreasing. Since the saturation vapour pressure is the denominator (equation 2.2) it results in an increase in relative humidity. When temperature increases during the day saturation vapour pressure increases leading to lower relative humidity values. At 0505 relative humidity reached its maximum point of 92 % and temperature had reached its minimum value of 17.5 ^{o}C. At 0600 relative humidity will start to decrease because temperature will be increasing leading to increasing saturation vapour pressure. Aerosols, moving in gradient of relative humidity, change their shape or chemical structure. Leaving out chemical reactions, mass and shape of the droplet are influenced by these possible changes (Straubal, 1980).

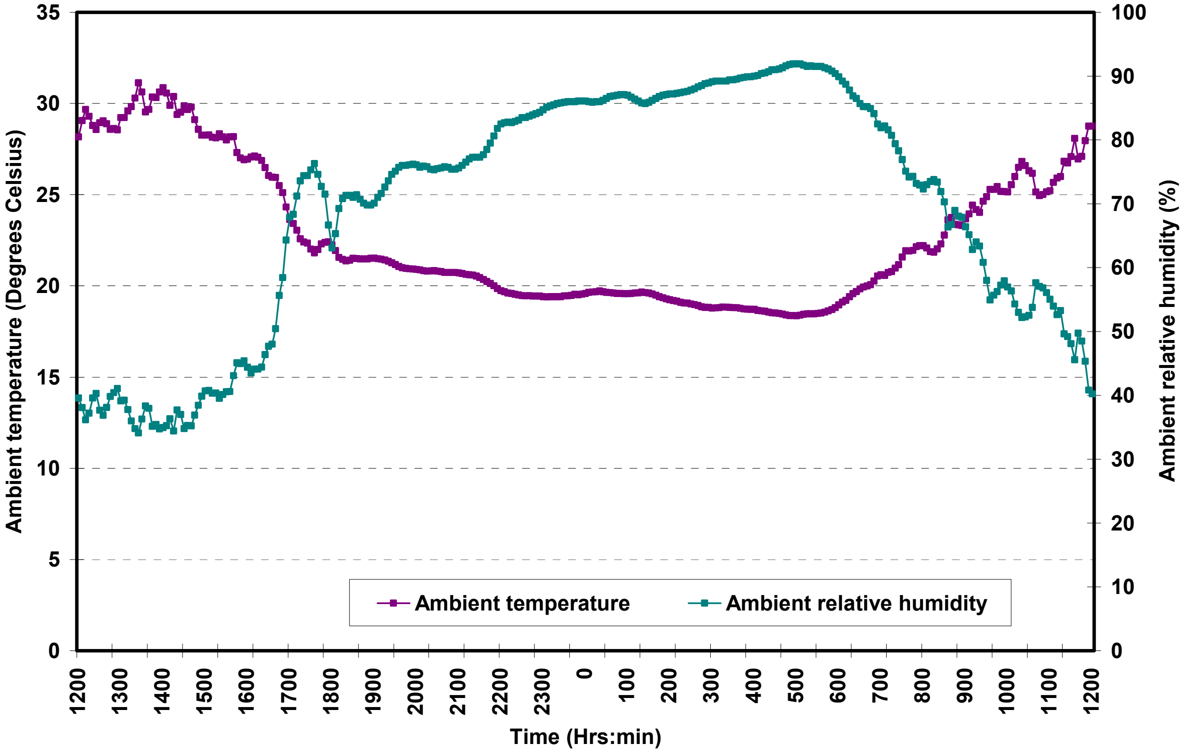


Figure 4.1 Diurnal variation in ambient relative humidity and ambient temperature on DOY 350 to 351 2006

The changes in the ambient relative humidity have got a profound effect on the readings of the nephelometer. As temperature decreases relative humidity will start to increase until it reaches the deliquescence point normally taken as 40 % RH (Ten Brink., 1996). At this point and above particulates in the atmosphere will start to accrete water molecules and they start to grow into large particulates which can not be recognized by the instrument.

This is evidenced by the decrease in particulate concentration which was observed in **Figure 4.2**, when the relative humidity was above 40 % back scattering was decreasing and it kept on decreasing as relative humidity increased because less concentration particulates of 2.5 µm aerodynamic diameter available in the atmosphere. Most of these particulates were converted into particulates of greater diameter beyond which can be detected within the 545 nm wavelength which could be detected by the nephelometer. Varying the relative humidity before reaching the screening volume, particle's size and shape can be changed by uptake of water. These changes can be very fast. The speed of the growing process depends on the initial size of the particle and relative humidity. Therefore the accuracy of the scattering device is reduced, as it is impossible to detect large molecules or to foresee this event (Straubal, 1980). As a result the nephelometer was duped by higher relative humidity and it will record lower back scattering values, which will not be a representative of what was in the atmosphere.

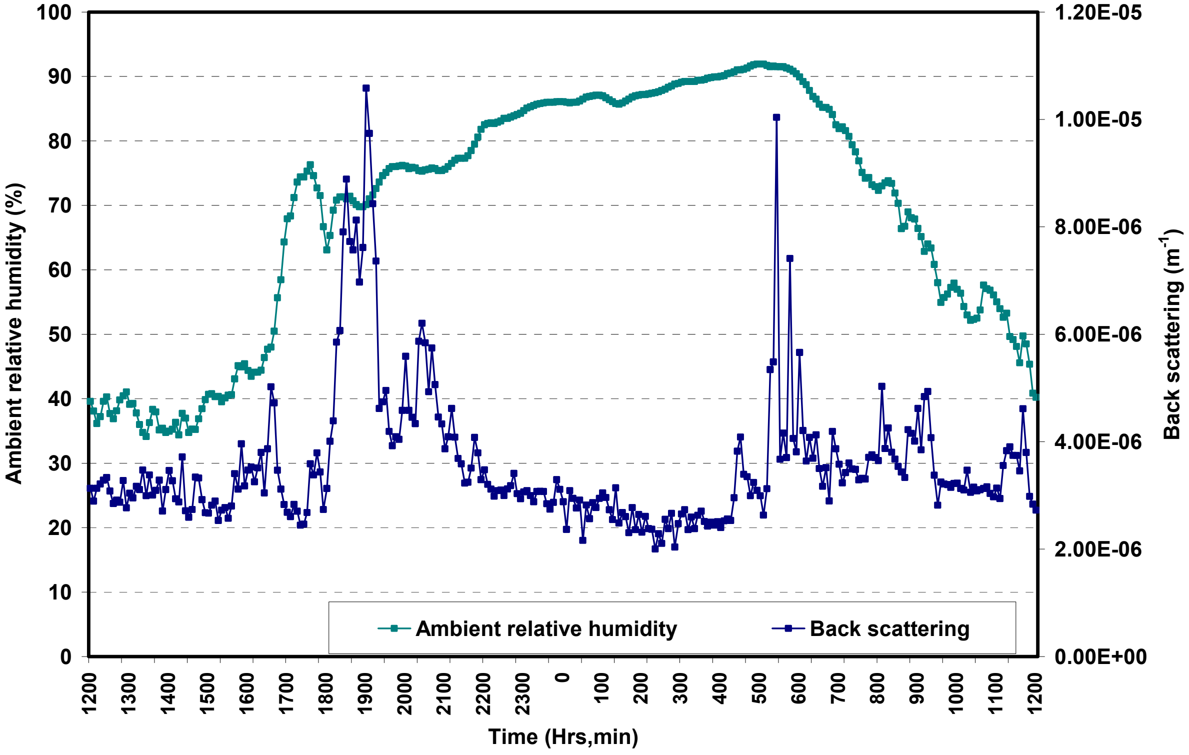


Figure 4.2 Diurnal variation of ambient relative humidity and back scattering on DOY 350 to 351 2006

As temperature starts to increase at 0550 at dawn water which will have adhered to the particulates surfaces will begin to evaporate thereby freeing the particulates back into the atmosphere. High back scattering values were noted after 0400 when relative humidity was decreasing and the lowest backscattering value of 2.00×10^{-6} m^{-1}was recorded just before the maximum point of the relative was reached. This shows that most of the $PM_{2.5}$ had crystallized leaving very few suspended in the atmosphere. **Figure 4.3** shows that there was a negative strong correlation coefficient of 0.6923 since back scattering values was observed to decrease with increasing ambient relative humidity.

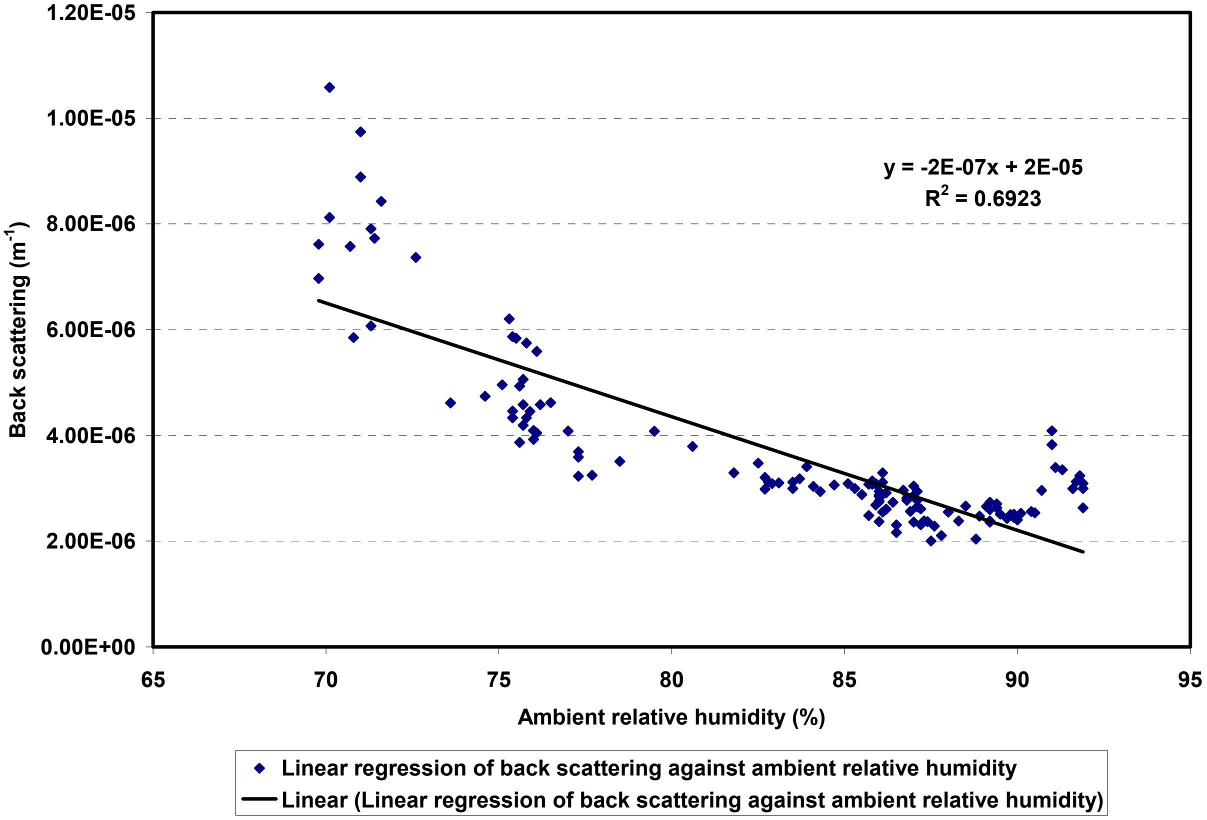


Figure 4.3 Relationship between back scattering and ambient relative humidity from 1900 to 0600 on DOY 350 to 351 2006

In contrast to **Figure 4.2**, **Figure 4.4** had relative humidity maintained between 6 % and 7 % below the deliquescence point where all the particulates do not grow. At this point they were at the lower branch of the hysteresis loop, were they remain dry. It is in this state were particulates do not crystallize and usually this gave an exact representation of the atmospheric $PM_{2.5}$ concentration. Unlike **Figure 4.2** which was produced when the nephelometer was duped when the particulates had been enlarged by the crystallization process and this resulted in lower values being recorded at midnight and high values during the day which are not representative of what exactly is in the atmosphere. For this reason all measurements which were used in this research was of dried air.

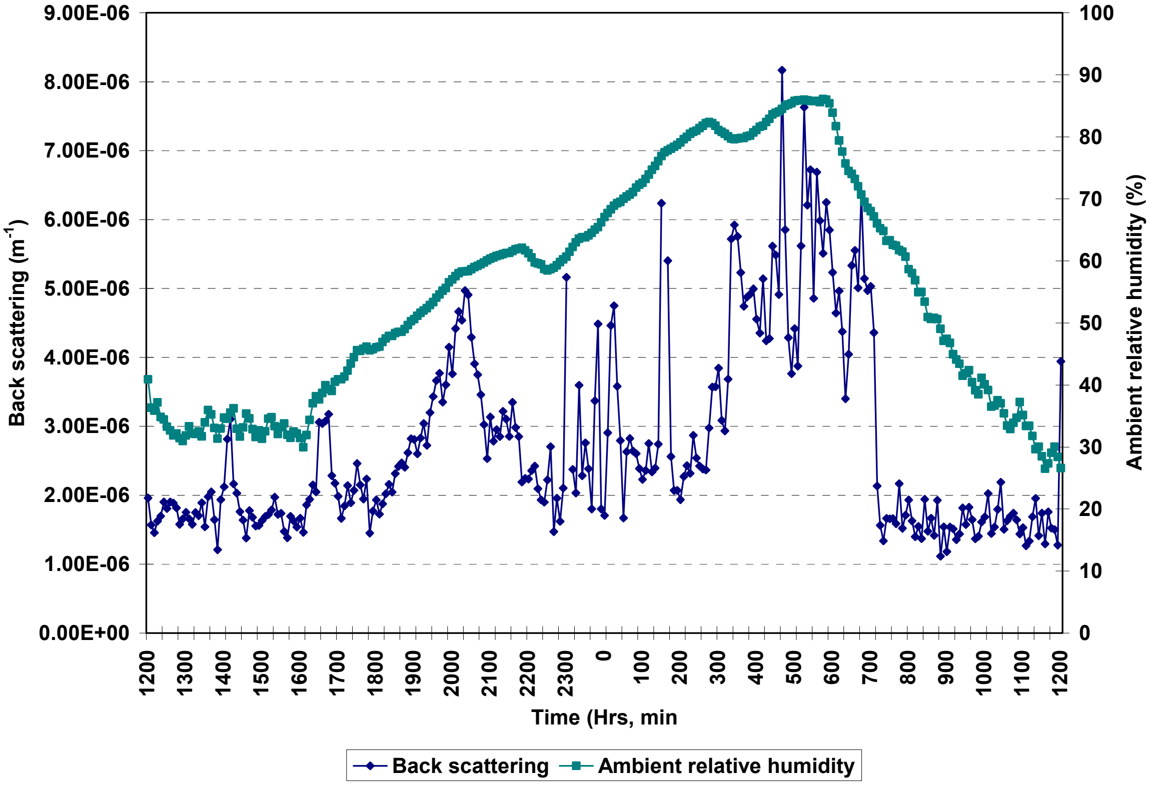


Figure 4.4 Diurnal variation of back scattering when inside tube humidity was maintained between 6 % and 7 % and ambient relative humidity on DOY 10 to 11 2007

Figure 4.5 shows a positive correlation coefficient of 0.2738, since back scattering was observed to increase as ambient relative humidity increased. This is what is expected as the boundary layer decreases, the atmosphere becomes stable and there will be less mixing of the air during the night. This results in increased concentrations of $PM_{2.5}$ during the night. This was in contrast to what was observed when ambient air was not dried. **Figure 4.3** shows that wet air tends to affect the concentrations of the $PM_{2.5}$ being measured by the nephelometer as increasing $PM_{2.5}$ concentrations in the atmosphere were being reduced by the increasing ambient relative humidity.

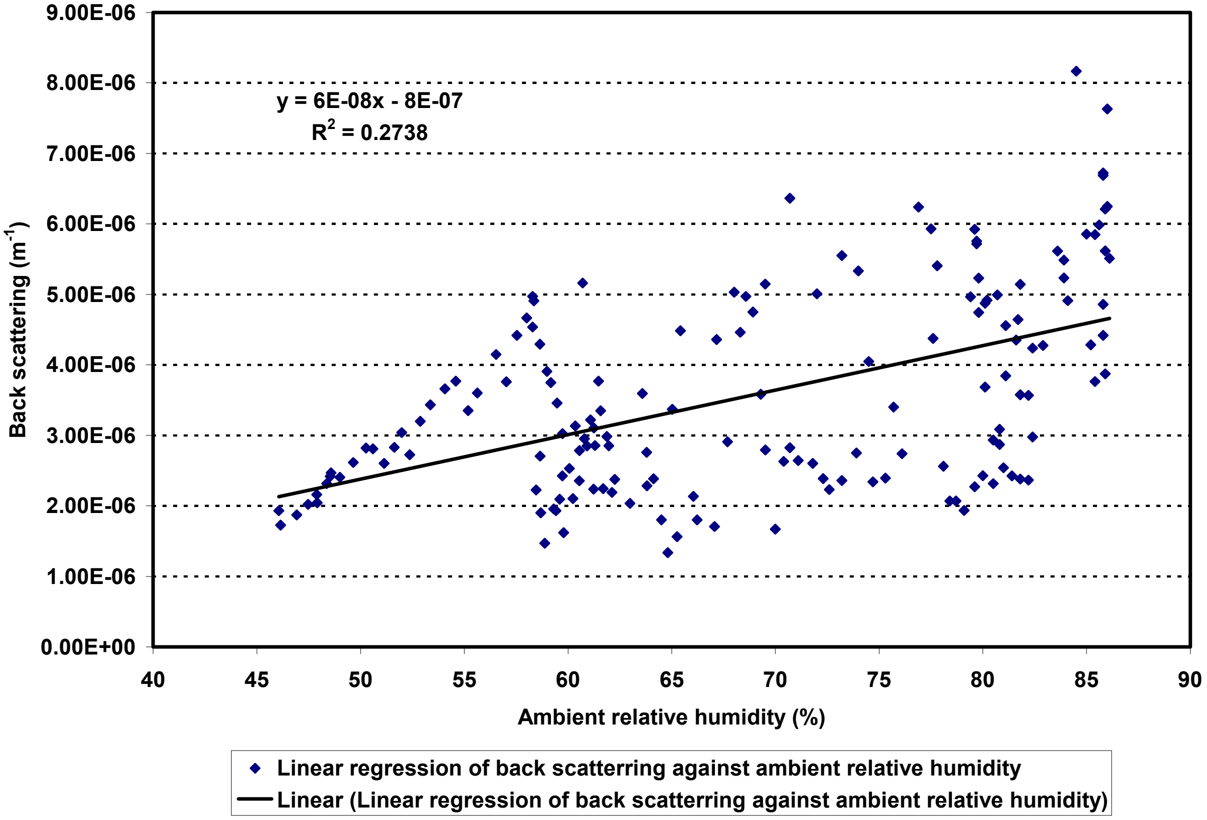


Figure 4.5 Relationship between back scattering and ambient relative humidity from 1900 to 0600 on DOY 10 to 11 2007

4.3 Effect of temperature on weekly diurnal variations of $PM_{2.5}$

Figure 4.4 shows that temperature was low (around 15 ^{o}C) during the night and was generally high during the day as it ranged from 26 ^{o}C to 28 ^{o}C. The temperature cycle curves for the entire week averages were smooth, whilst those of $PM_{2.5}$ had a lot of fluctuations. Fluctuations observed in back scattering values shown in **Figure 4.4** were observed not to follow the temperature cycle. At some points high back scattering values were recorded when the temperature was low, for example on Thursday 0800 a spike in $PM_{2.5}$ was observed whilst temperature low was at 15 ^{o}C. On Monday, Tuesday, Friday and Saturday at 0800 small spikes of $PM_{2.5}$ were noticed when temperature was low (around 15 ^{o}C see **Figure4.7**) like on Thursday. These peaks are due to the fact that, at this particular time traffic density will have increased and it tends to add some $PM_{2.5}$ into the atmosphere. These peaks occur just about when the temperature starts to increase and that's when the boundary layer will be decreasing and the atmosphere will start to stabilize. As a result there is no direct relation between temperature and $PM_{2.5}$, since temperature affects the atmospheric stability and then $PM_{2.5}$ will respond to the changes in atmospheric stability. The response takes same time as there is a time lag between the changes temperature are felt by $PM_{2.5}$. As a result there is no clear relationship between ambient temperature and atmospheric $PM_{2.5}$ concentrations. From **Figure 4.7** the correlation coefficient between ambient temperature and back scattering was found to be 0.00004. This value shows that there is no relationship between back scattering and ambient temperature.

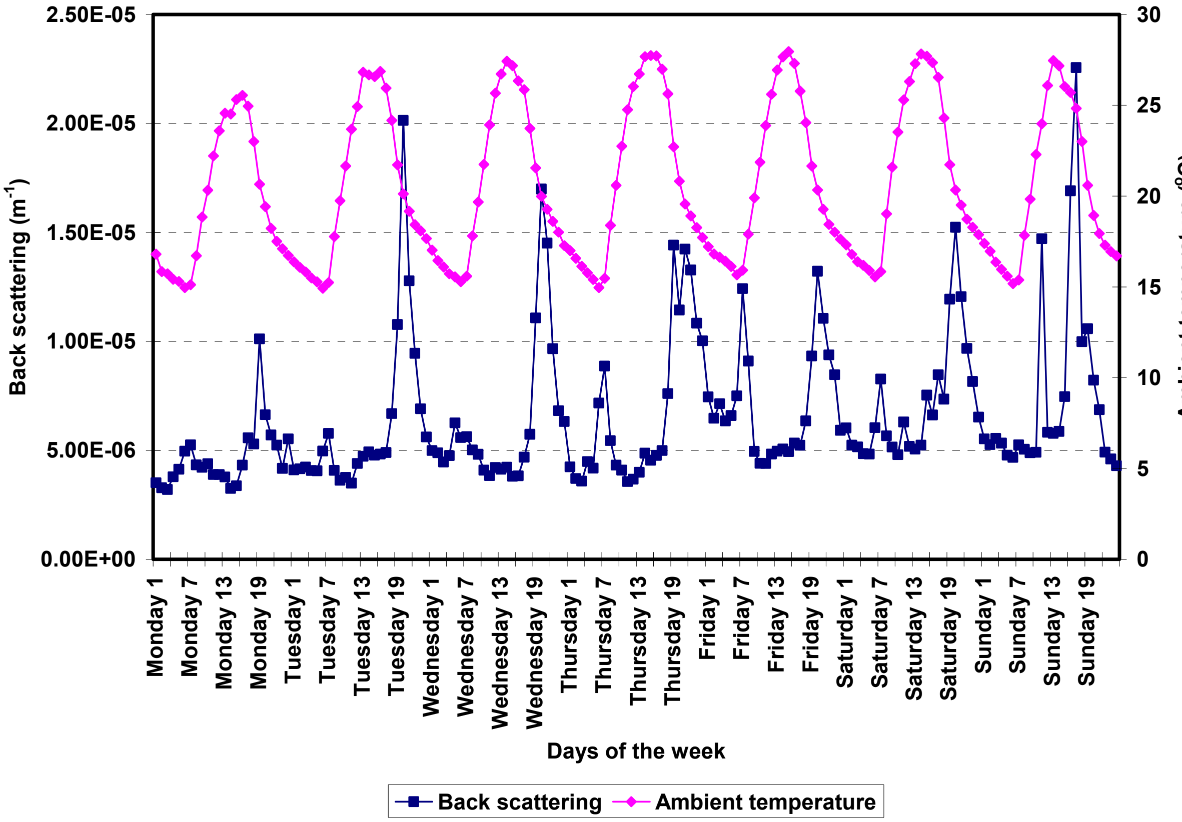


Figure 4.6 Diurnal variations of temperature and $PM_{2.5}$ averaged for 6 weeks from DOY 73 DOY 118 2007

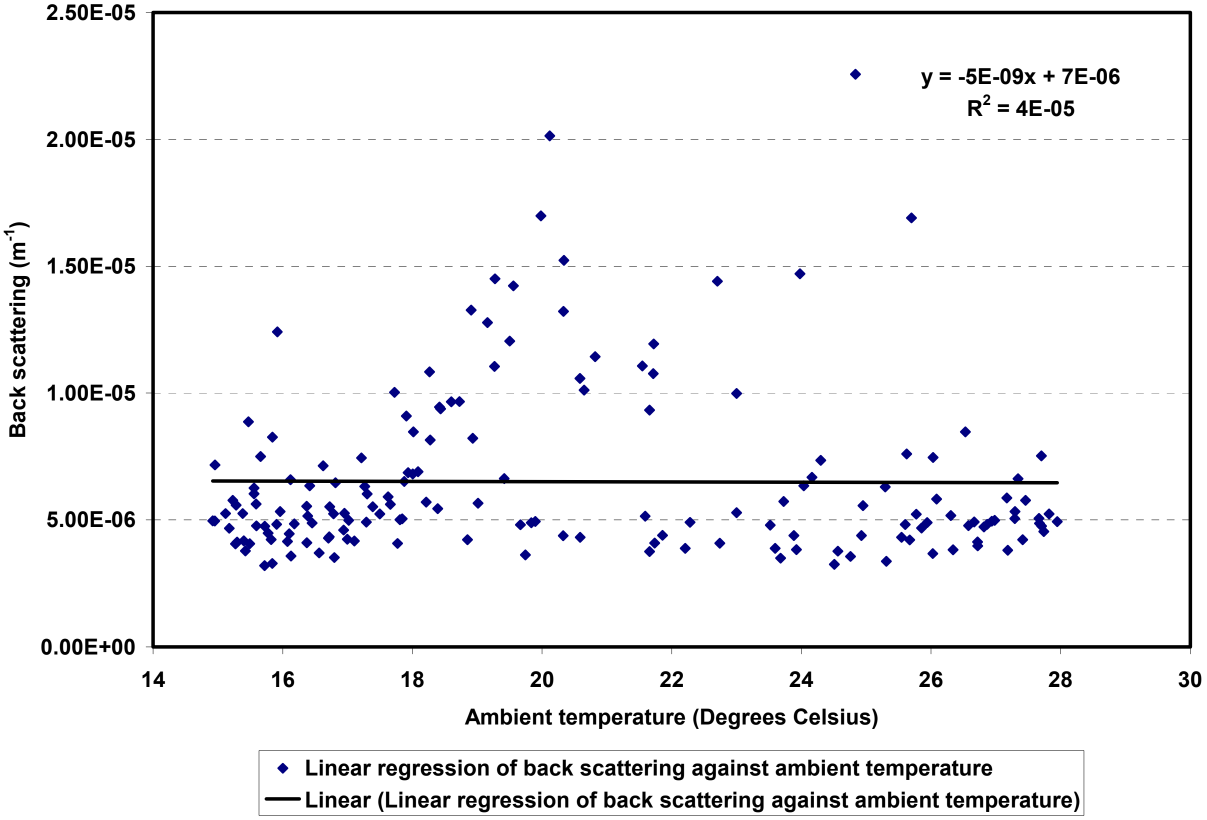


Figure 4.7 Relationship between diurnal variations of temperature and $PM_{2.5}$ averaged for 6 weeks from DOY 73 DOY 118 2007

4.4 Effect of wind speed on weekly diurnal variations of $PM_{2.5}$

Figure 4.9 shows that when wind speed was low (less than 4 m s^{-1}), back scattering was generally high (from 3 x 10^{-6} m^{-1} to 6 x 10 $^{-6}$ m^{-1}) even though the highest back scattering was found at 4.7 m s^{-1}. This was also observed in **Figure 4.8,** on Tuesday from 1700 to 2230 wind speed was low (2.5 m s^{-1}) and back scattering was high (2 x 10 $^{-5}$ m^{-1}). Similar trends were observed on Wednesday from 1700 to 2230 wind speed was around 2 m $s^{-1}$and back scattering was high 1.5 x 10 $^{-5}$ m^{-1}, on Thursday from 1700 to 2230 wind speed was 0.8 m s^{-1} whilst high back scattering values above 1.2 x 10 $^{-5}$ m^{-1} were recorded. Saturday from 800 to 900 wind speed was low 0.8 m s^{-1} whilst a sharp peak of back scattering was observed and between 1900 and 2330 there was a spike in back scattering which corresponded to low wind speed of 2.8 m s^{-1} was recorded. When wind speed was high (above 4.7 m s^{-1}). **Figure 4.9** shows that back scattering did not exceed 7.5 x 10 $^{-5}$ $m^{-}1$ when wind speed was above 4.7 m s^{-1}.This shows that there is an inverse relationship between wind speed and $PM_{2.5}$ concentration, but this relationship is weak because low wind speeds can be recorded against corresponding low $PM_{2.5}$ concentrations. For example from 0100 to 0300 Tuesdays, wind speed was low (2.6 m s^{-1}) and the corresponding $PM_{2.5}$ recorded was low as well (1.2 x 10^{-6} m^{-1}).The same scenario was observed on Wednesday from 0100 to 0300 and on Sunday from 0100 to 0600. **Figure 4.9** shows a negative gradient of -1 x 10^{-6}, which means that there is an inverse relationship between wind speed and back scattering. This inverse relationship is very weak as evidenced by the correlation coefficient of 0.1061.

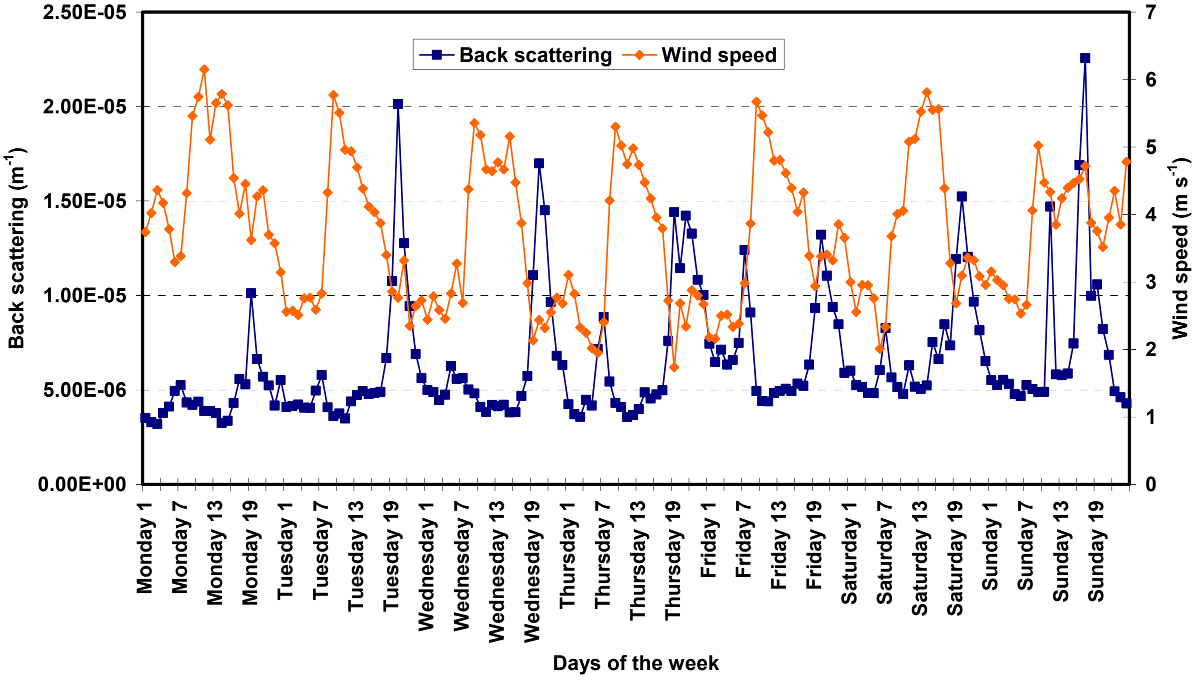


Figure 4.8 Diurnal variations of wind speed and $PM_{2.5}$ averaged for 6 weeks from DOY 73 DOY 118 2007

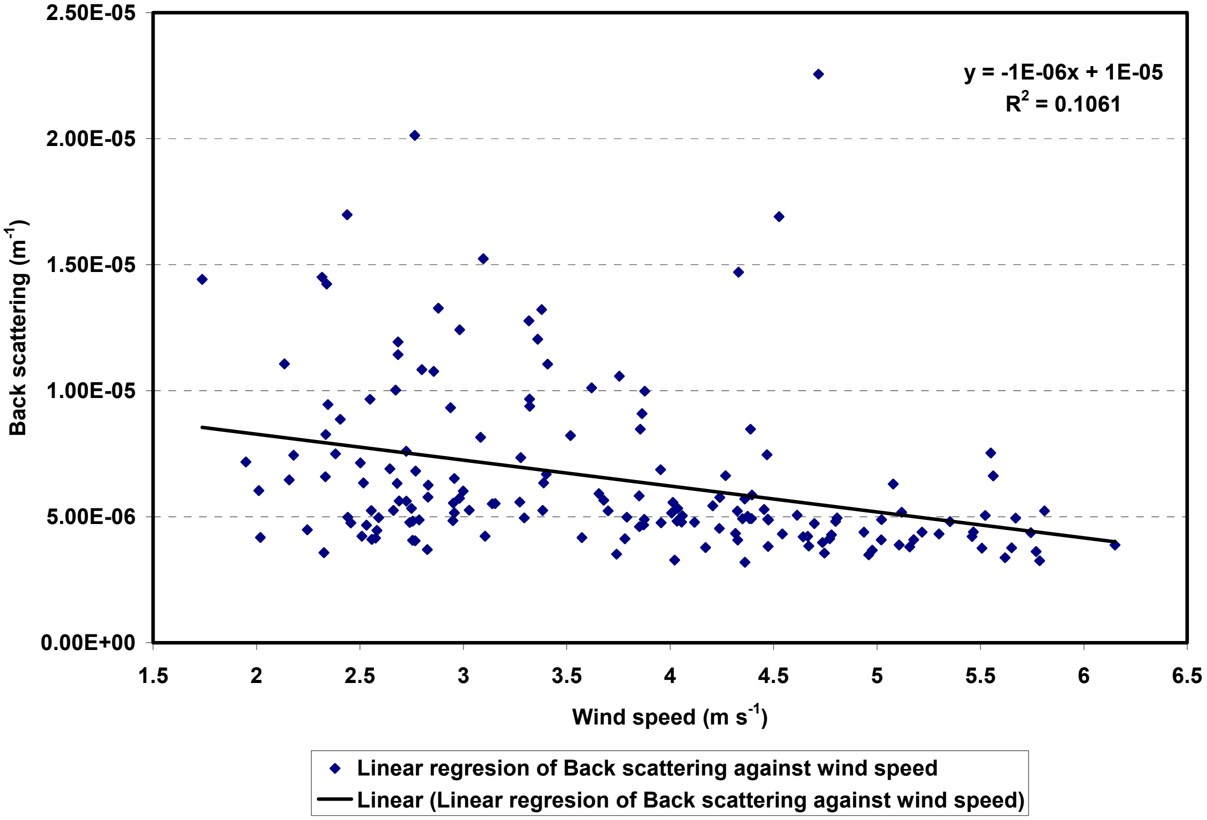


Figure 4. 9 Relationship between diurnal variations of wind speed and $PM_{2.5}$ averaged for 6 weeks from DOY 73 DOY 118 2007

4.5 Effect of temperature on weekly diurnal variations of CO_2

Figure 4.10 also shows that the graph of ambient temperature had smooth cycles unlike CO_2; its cycles have not been smooth as some spike were observed on every crest of the CO_2 cycles. The temperature and CO2 concentrations are in an antiphase. Whenever the curve of CO_2 showed the spikes temperature's curves remained smooth. **Figure 4.11** shows that CO_2 concentrations tend to decrease with increasing ambient temperature. The correlation coefficient of 0.2944 and the gradient was -0.942, shows a weak inverse relationship between CO_2 concentrations and ambient temperature. This shows that temperature was not influencing the changes which were observed in CO_2 mixing ratio, as the ambient temperature had smooth curve whilst CO_2 mixing ratios were fluctuating. In other words CO_2 cycle is independent of diurnal ambient temperature changes.

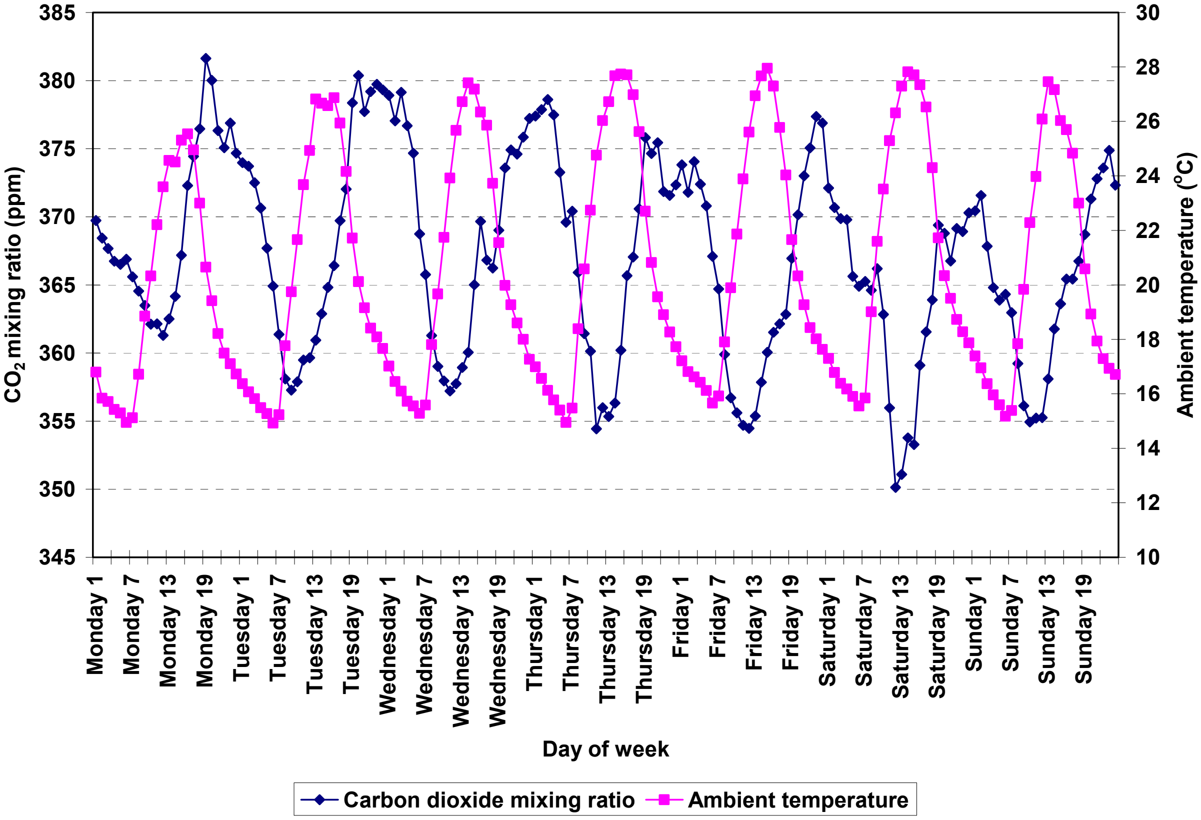


Figure 4. 10 Diurnal variations of temperature and CO_2 averaged for 6 weeks from DOY 73 DOY 118 2007

When the air parcel is heated by solar radiation at the earth's surface, its temperature rises above that of the surrounding air and it acquires buoyancy (Wark, 1981).In unstable (lapse) conditions which occur when the surface is strongly heated, vertical motion is enhanced by buoyancy. The amount of enhancement increases as the wind shear decreases, where the eddies are stretched vertically (Monteith and Unsworth, 1990). Parcels of superheated air rising from super heated earth's surface, and the slower descent of larger portions of the atmosphere surrounding these more rapidly rising air parcels and it results in strong thermal turbulences. The size and, hence, the scale of these eddies caused by thermal turbulence are larger than those of the eddies which are caused by mechanical turbulence (Boubel et al, 1994). This explains why low concentrations of both CO_2 and PM $_{2.5}$ were observed during the day. Since during the day high temperatures and high solar radiation values were observed which means that there were large vertical eddies, which resulted in the dilution of atmospheric pollutants (PM $_{2.5}$) and CO_2. During the day lower concentration values which were observed can be attributed to the unstable atmosphere, strong thermal turbulences and vertical eddies and increased mixing height.

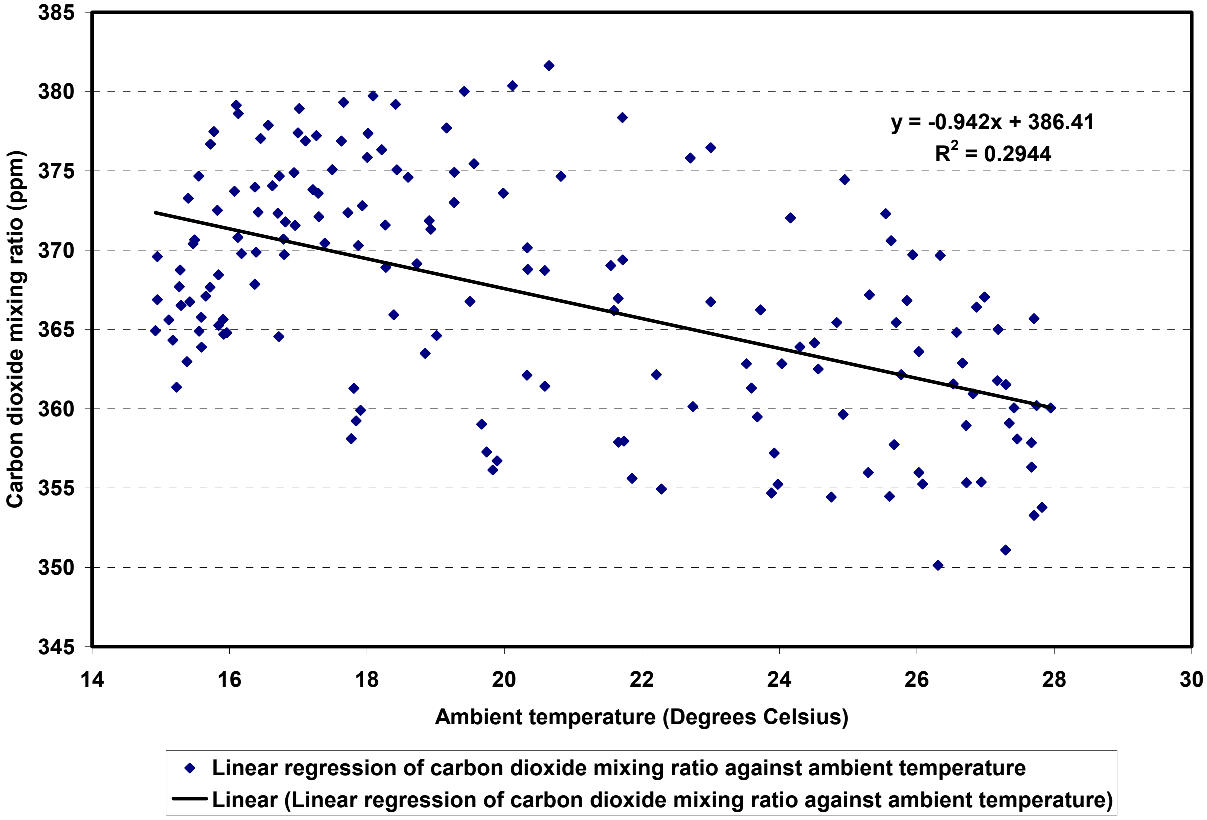


Figure 4.11 Relationship between diurnal variations of temperature and CO_2 averaged for 6 weeks from DOY 73 DOY 118 2007

4.5 Effect of wind speed on weekly diurnal variations of CO_2

Figure 4.12 shows that CO_2 mixing ratios are more sensitive to changes in wind speed as compared to $PM_{2.5}$ (**Figure 4.8**). This is evidenced by the fact that, for all the troughs in the CO_2 cycles which occurred from 0800 to 1600 of every day of the week were accompanied by high wind speed of above 5 m s^{-1}. Figure 4.13 shows the correlation coefficient of 0.4526 and a gradient of 0.4.6646. This shows that there was a strong inverse relationship between CO_2CO2 concentrations and wind speed. When wind speed was 3.75 m s-1 or less CO_2 concentrations were always above 360 ppm, whilst when the wind speed was above 3.75 m s-1 lower than 360 ppm CO_2 concentrations were recorded. High wind speed results in strong air mixing and well mixed air will lead to dilution of the CO_2 hence low mixing ratios. From **Figure 4.6** it was shown that ambient temperature was high during the day, which means that the atmosphere will not be stable as the high temperatures allow strong vertical motions. From 1800 to 0700 the CO_2 mixing ratios were high and the corresponding wind speeds were low (3 m s^{-1} or less) for every day of the week. Low wind results in less air mixing and less dilution, hence high CO_2 mixing ratios were recorded when the wind speed was low. Low wind speeds also results from a stable atmosphere which resists vertical motions of air and hence less turbulences.

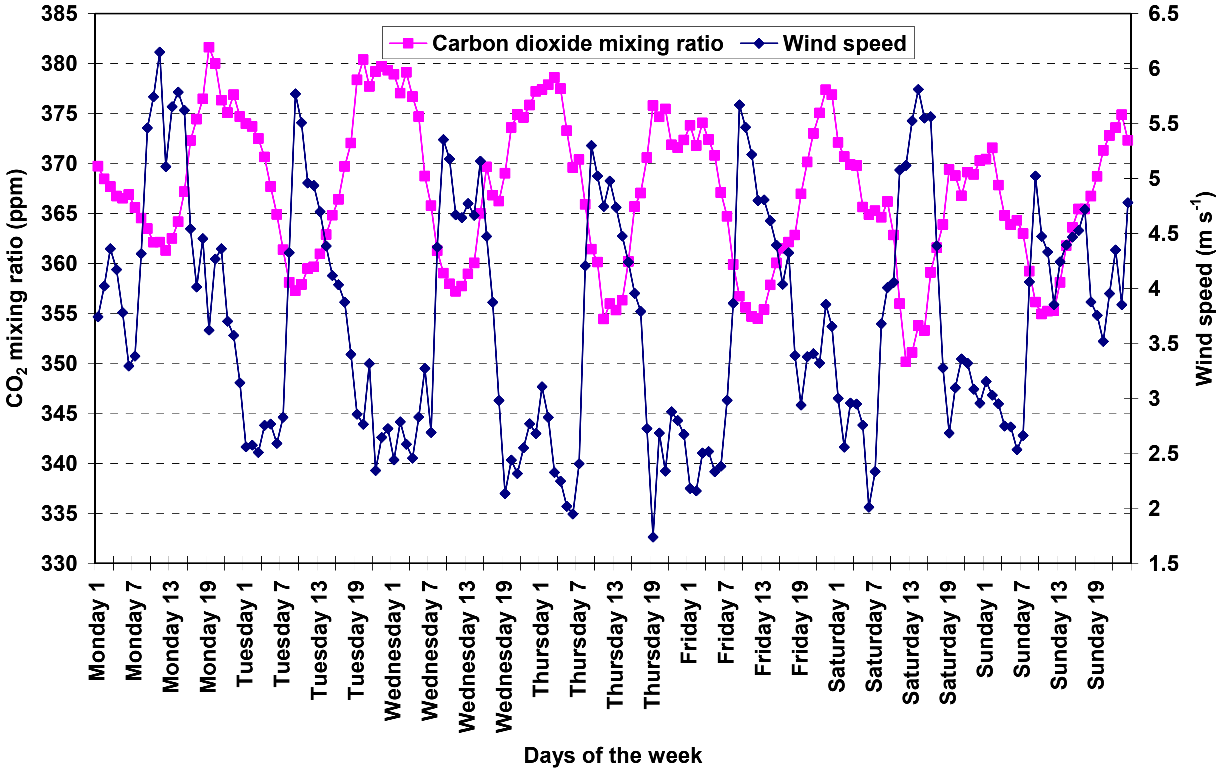


Figure 4.12 Diurnal variations of wind speed and CO_2 averaged for 6 weeks from DOY 73 DOY 118 2007

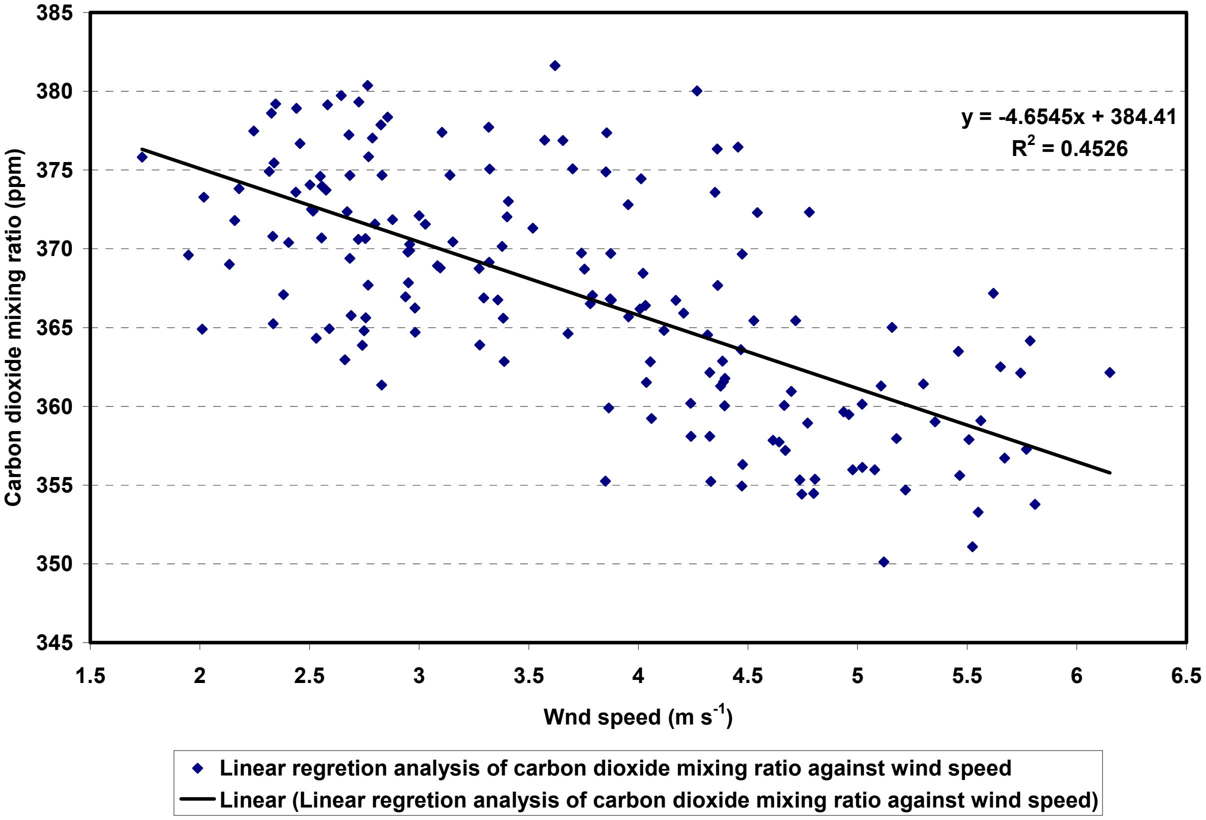


Figure 4.13 Relationship between diurnal variations of wind speed and CO_2 averaged for 6 weeks from DOY 73 DOY 118 2007

4.3 Weekly diurnal variations of CO_2 and $PM_{2.5}$

Figure 4.14 shows that CO_2 concentration diurnal variation with time is similar to that of $PM_{2.5}$. CO_2 concentration was low during the day (between 348 ppm and 358 ppm) whilst during the night it was high (between 372 ppm and 383 ppm). The observed diurnal CO_2 mixing ratio cycle follows the natural CO_2 cycle, whereby during the day plants will be photosynthesising using the CO_2 from the atmosphere to manufacture sugars. Photosynthesis tends to be the main sink of CO_2 during the day and it reduces atmospheric CO_2 mixing ratios during the day. The boundary layer will be high and there is generally strong thermal turbulence and vertical eddies during the day due to high temperatures and high solar radiations. These unstable atmospheric conditions tend to dilute the concentrations of both $PM_{2.5}$ and CO_2, hence lower values were observed during the day. During the night CO_2 mixing ratios were high (between 372 ppm and 383 ppm) and back scattering recorded some sharp peaks during the night ranging from 8 x 10^{-6} m^{-1} to 2.25 x 10 $^{-5}$ m^{-}

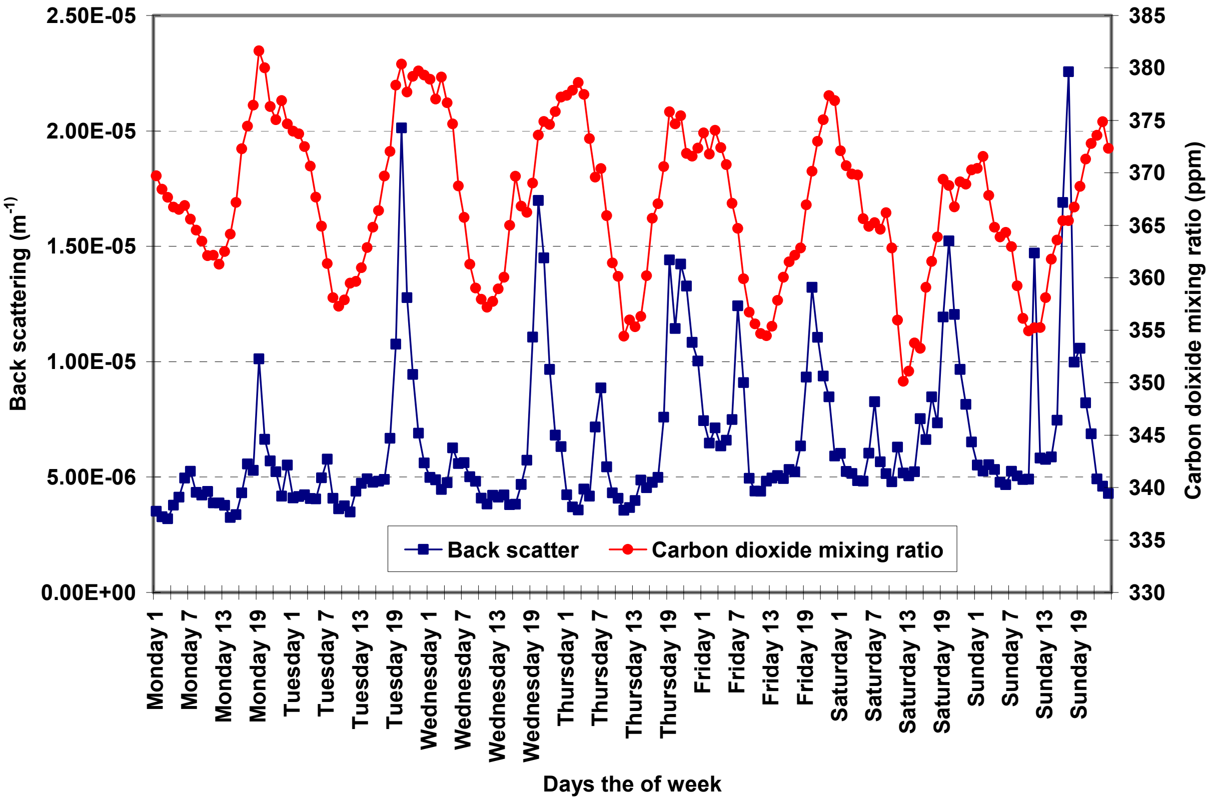


Figure 4.14 Variation of CO_2 concentration and back scattering values with time for 6 weeks averages from DOY 73 to 118 2007

During the night plants save as the main CO_2 source, because they will be respiring. Respiration is a chemical process whereby plants will be using oxygen in the atmosphere to convert sugars into energy. This chemical process results in the release of CO_2 into the atmosphere thereby increasing the atmospheric CO_2 mixing ratios during the night. The sharp peaks for back scattering (ranging from 1 x 10^{-5} m^{-1} to 2.25 x 10^{-5} m^{-1}) were mainly due to atmospheric stability, whereby the boundary layer will be low at night, no thermal turbulence horizontal eddies will replace vertical eddies and there will be less mixing of the air. These stable atmospheric conditions increase the mixing ratios of CO_2 during the night as there will be less mixing of the air, hence less dilution. **Figure 4.15** shows a gradient of 1 x 10^{-7} and correlation coefficient of 0.0772 between $PM_{2.5}$ against CO_2 concentrations. This shows that there was a weak direct relationship between CO_2 and $PM_{2.5}$ as $PM_{2.5}$ increased with increasing CO_2 concentrations.

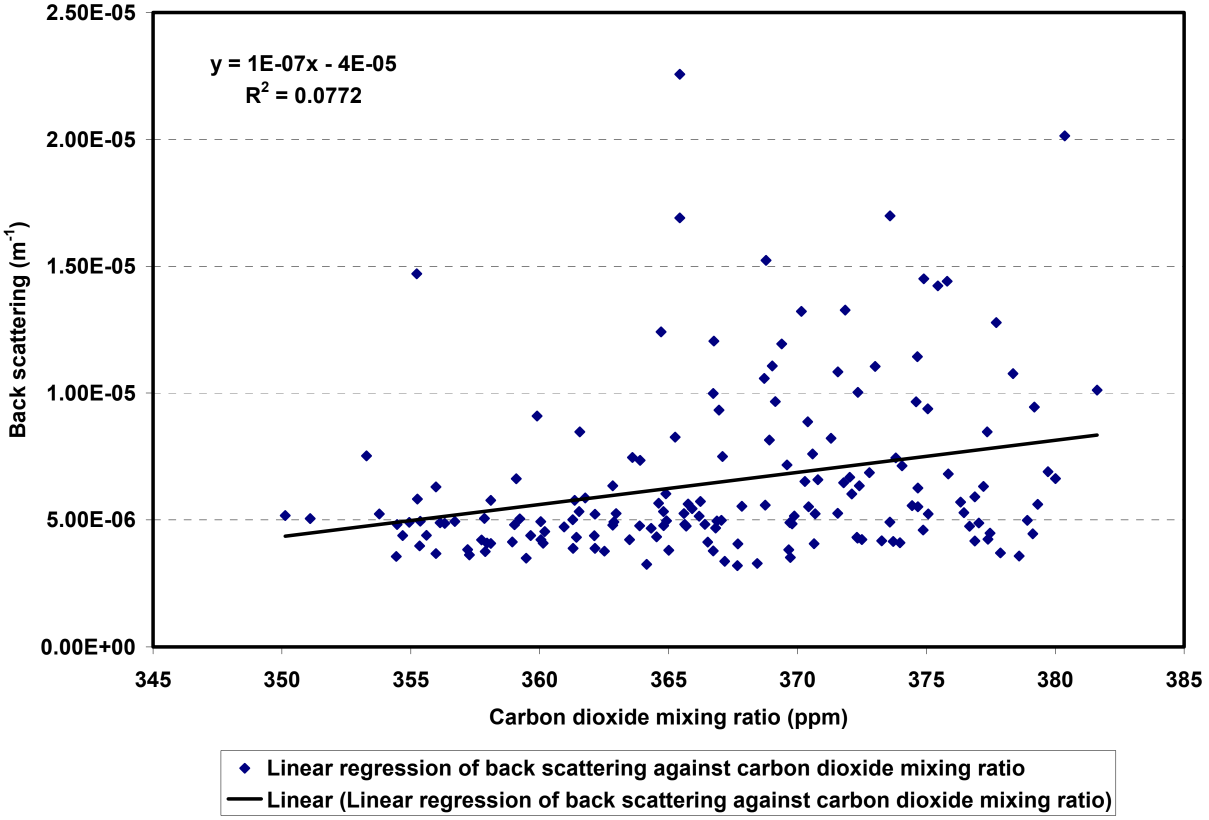


Figure 4.15 Relationship between CO_2 concentration and back scattering values for 6 weeks averages from DOY 73 to 118 2007

4.6 Effect of wind direction on weekly diurnal variations of $PM_{2.5}$ and CO_2

Figure 4.14 shows that the curve of CO_2 has got a similar trend with that of $PM_{2.5}$ that is peaks are mainly observed during the night and lower concentrations during the day when the atmosphere will be unstable and the boundary layer will be high up.

Figure 4.14 shows that from Monday to Friday the crests of the CO_2 were not smooth, as they had some spikes superimposed on them which corresponded with the sharp spikes of $PM_{2.5}$. These superimposed spikes were observed from 1930 to 2000 everyday from Monday to Friday and they were not observed on Saturday and Sunday. From 1930 to 2000, of everyday of the week the average wind direction was south easterly (0127 ^{o} to 0150 ^{o}). This means that the extra CO_2 was coming from the city centre, since the city centre is between south and south east of sampling point. The absence of the spikes on the CO_2 cycle on Saturday and Sunday correspond to the sharp peaks of $PM_{2.5}$, shows that the sources of CO_2 and $PM_{2.5}$ are not the same, even though the wind was coming from the south east on Sunday and Saturday it was not carrying enough CO_2 to cause significant changes on the smooth natural crests on the graph of CO_2. The main source of the CO_2 which caused the superimposed spikes could be traffic from the city centre and some industries which are to the south east, as these normally operate fully during the week and some industries will be closed or operate at low capacity during Saturdays and Sundays. Traffic density is usually low during the weekend, and this may have been the reason why the spikes sitting on top of the CO_2 crests were observed during the weekends. As for $PM_{2.5}$ peaks which occurred from 1930 to 2000, everyday of the week, their source could not be identified precisely. It was safe just to say that the source is to the south east of the University of Zimbabwe and it produces $PM_{2.5}$ every day of the week.

During the day (800 to 1700), wind was observed to be coming mostly from either north or north east. In this direction, there are no major sources of $PM_{2.5}$ and this direction is mainly composed of residential properties and Pomona Quarry which is 6 kilometres to the north east. Since it is situated in an area which is less polluted with the $PM_{2.5}$, as the air travels from the quarry to the sampling point it will have been strongly diluted and it will not cause significant changes to the concentrations at the sampling point.

The wind direction on Sunday 1700 was from 147 ^{o} and a sharp peak of $PM_{2.5}$ concentration was observed (2.26×10^{-5} m^{-1}). There was no corresponding CO_2 peak at 1700. The main reason was that on Sunday traffic density will be low; as a result the anthropogenic source of CO_2 was reduced. So even though the wind was coming from the south east (147 ^{o}), it carried mainly $PM_{2.5}$ with little CO_2 from traffic, as the traffic density was low. The presence of a weak peak in the CO_2 mixing ratio curve at 2000, whilst other days of the weak had profound spikes was due to the fact that, at 2000 traffic density will have eased out. So when the wind was coming from the south east (down town) it did not have a strong plume of CO_2 as most the traffic density will have decreased.

Wind direction has got a profound effect on the concentrations of $PM_{2.5}$, as it bring brings the $PM_{2.5}$ from their source to the sampling point. Wind direction can also assist the researcher to identify the source of the pollutants and it gives the direction from which the $PM_{2.5}$ will be coming.

4.7 Diurnal averages for carbon dioxide and particulate matter ($PM_{2.5}$)

From **Figure 4.16** the peak for $PM_{2.5}$ for working week days at 0730 is higher than that for the weekends. This is so because during the weekend especially on Sundays very few people go to work and traffic population will be low and some industries do not operate during Sundays and some operate half the day hence low emissions into the atmosphere. This results in low particulate matter concentrations being recorded.

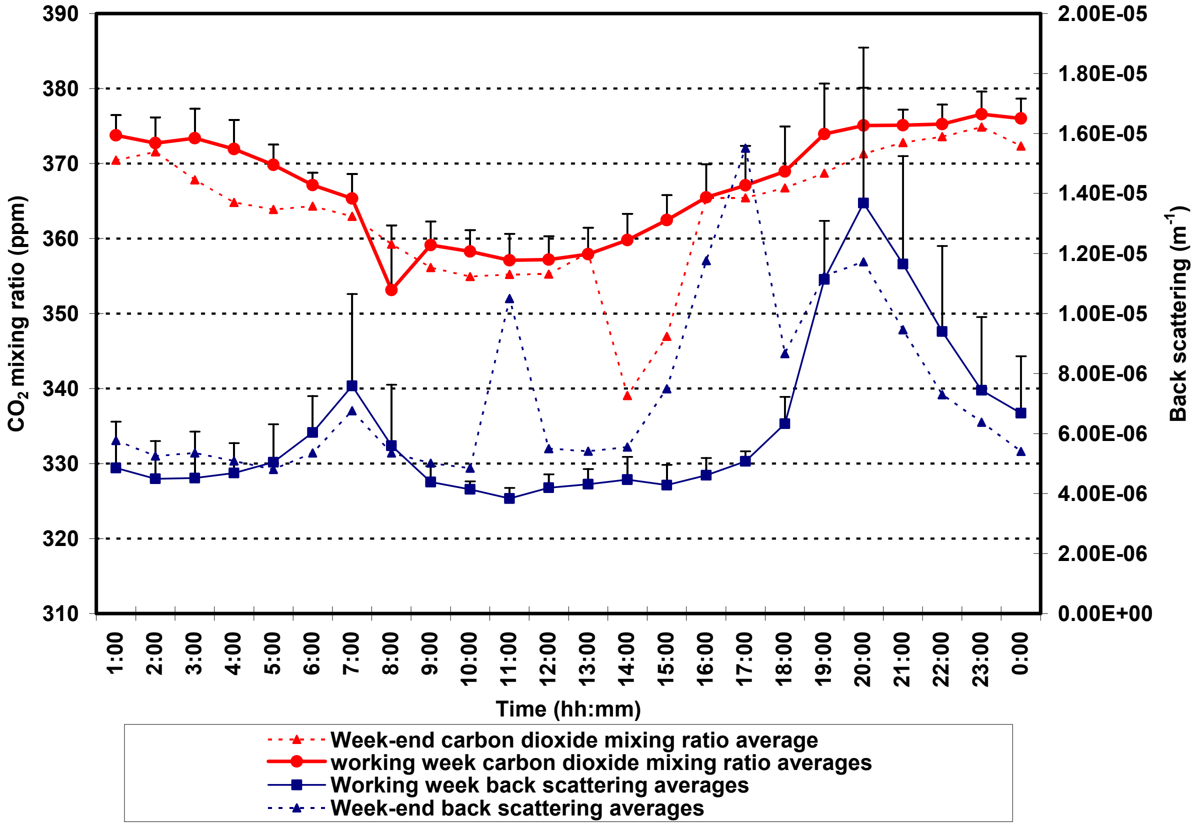


Figure 4.16 Variation of averaged working week days (Monday to Friday) and week-ends (Saturday to Sunday) for both CO_2 concentration and back scattering. The data was averaged for six week's measurements from DOY 73 to DOY 118 2007

The peak which is observed at around 2000 was higher and broader for the weekend averages than for week days. This is so because most of the averaged weekend days had long periods of low wind speeds as shown in **Figure 4.18**. The long periods of low wind speed resulted in the broadness of the peak at 2000. **Figure 4.17** shows a correlation coefficient of 0.0044 for weekend averages of back scattering against CO_2 concentration. This shows that there was no relationship between CO_2 concentrations and $PM_{2.5}$ whilst during the week there was a weak direct relationship as indicated by correlation coefficient of 0.3449.

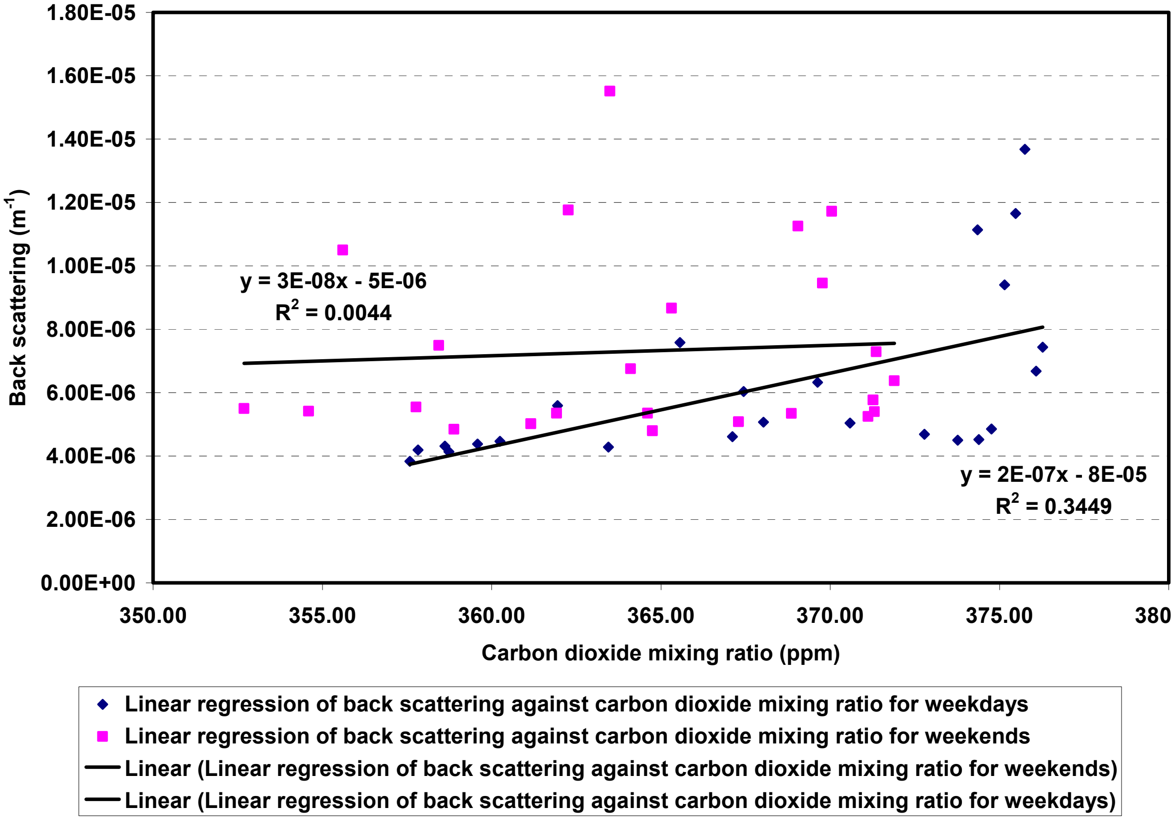


Figure 4.17 Relationship between CO_2 and back $PM_{2.5}$ variations averaged for working weekdays (Monday to Friday) and weekends (Saturday to Sunday). The data was averaged for six week's measurements from DOY 73 to DOY 118 2007

As the other source of CO_2 apart from natural source (plant) was identified to be to south east, it could have been coming either from the fuel combustion or from industries which are located to the south east of the University of Zimbabwe. For carbon dioxide the weekend averages were quite low compared to working week days. This was also due to the fact that most companies operate from Monday to Friday and they produce carbon dioxide during the process and most public transport is normally busy from Monday to Friday, thereby releasing a lot of carbon into the atmosphere. During the weekend public transport operations as well as industries operations are very low hence less carbon dioxide is emitted into the atmosphere.

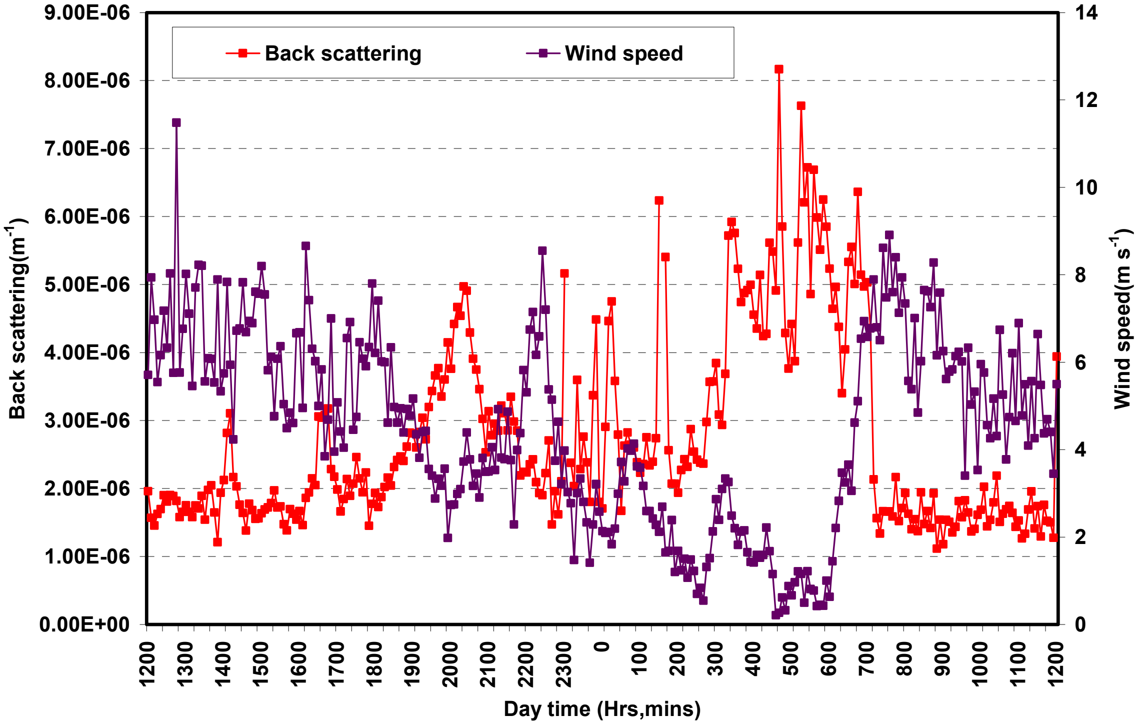


Figure 4.18 Variation of back scattering and wind speed recorded on DOY 76 to 77 2007

Figure 4.18 shows that period in which wind speed will be low correspond to the period in which $PM_{2.5}$ concentration will be high. As shown from 0100 to 0700 when the average wind speed was below 2 m s^{-1} and average back scattering was high (4 x 10^{-6} m^{-1}). When the average wind speed rose to above 4 m s^{-1} from 0700 to 1200 average back scattering decreased to 2.8 x 10^{-6} m^{-1}.

4.8 Effect of rainfall on atmospheric particulate matter concentration ($PM_{2.5}$) and carbon dioxide (CO_2) mixing ratios

From **Figure 4.19** it was be observed that rainfall tend to wash down the $PM_{2.5}$ from the atmosphere resulting in low measurements being recorded by the nephelometer. From **Figure 4.14** it was observed that low back scattering value which correspond to low $PM_{2.5}$ concentrations recorded during the day, but in this case rainfall reduced $PM_{2.5}$ during the evening to values below those recorded during the day. Back scattering value of 1.2 x 10^{-6} m^{-1} was recorded at 2150 soon after 14 mm of rainfall were received at 2145. After that deep back scattering values started to increase gradually signifying that the particulates were now accumulating into the atmosphere. The decrease in back scattering which is normally observed at around 0630 to 0730 **(Figure 4.14)** which is due to sudden increase in the mixing height and this could not be observed because the concentration of the $PM_{2.5}$ were pretty low. The $PM_{2.5}$ concentration was observed to decrease as soon as the rain started to fall, even with light showers. Rain out is the term which is normally used to describe the process by which atmospheric pollutants are removed (Boubel, 1994). **Figure 4.9** shows that, the rate of increase of back scattering from1558 was 1 x 10^{-8} m^{-1} min^{-1} before rainfall, but this rate dropped to 9 x 10^{-9} m^{-1} min^{-1}after rainfall (from 2200 to 0300) which shows that humid atmosphere reduces the rate of increase of particulate matter. The equations for the regression line before rainfall was y = 1 x 10^{-8} x - 1 x 10^{-6} and after rainfall was y = 9 x 10^{-6} x 4 x 10^{-6}.

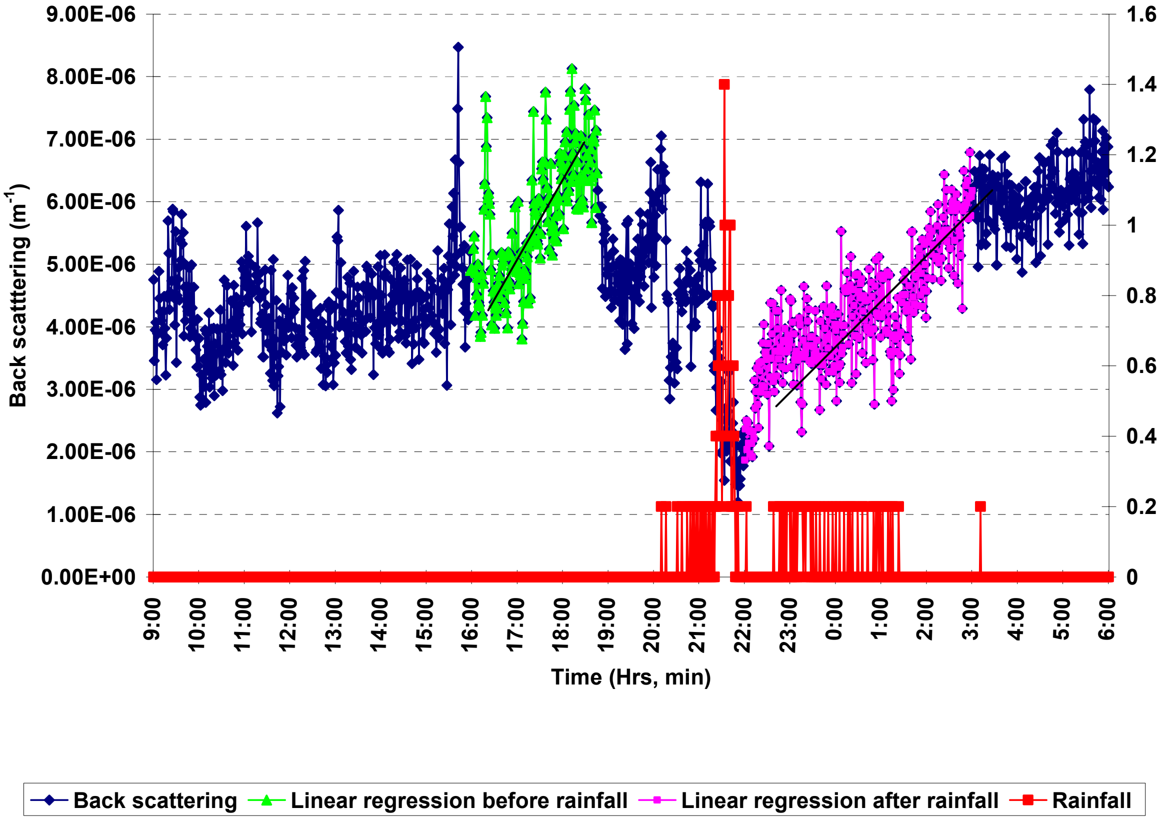


Figure 4.19 The effect of rainfall on the atmospheric particulate matter ($PM_{2.5}$) concentration on DOY 60-61 2007

Water droplets from rainfall are larger than those of the water vapour; as a result water droplets tend to absorb the $PM_{2.5}$ from their surroundings and the $PM_{2.5}$ concentrations were observed to decrease as soon as the rain started to fall, even with light showers. The water droplets absorb the $PM_{2.5}$ from the atmosphere into themselves. This reduces the amount of $PM_{2.5}$ available in the atmosphere. This shows that most of the $PM_{2.5}$ particles are hygroscopic, when they attract water they became heavy to an extent that their residence time in air is reduced and they fall to the ground a process known as sedimentation (settling by gravity) (Hanna *et al*, 1987). This resulted in lower concentrations of $PM_{2.5}$ in the atmosphere as most of them were washed down.

Unlike the $PM_{2.5}$, CO_2 concentrations are only affected by large amounts of rainfall as shown in **Figure 4.20**. Rainfall started at 2020 and the CO_2 mixing ratio did not respond to the light showers like what the $PM_{2.5}$ did in **Figure 4.19.** CO_2 started to decrease at 2110 hours after 2.2 mm of rainfall was received. Only significant drop was observed at 2135 when 1.4 mm of rain was received. The drop of CO_2 was from 374.02 ppm to 371.66 ppm whilst that of $PM_{2.5}$ was from 7×10^{-6} m^{-1} to 1×10^{-6} m^{-1}. This shows a decrease of 2.76 ppm of CO_2 concentration and the $PM_{2.5}$ decreased by 6×10^{-6} m^{-1}. This shows that the $PM_{2.5}$ concentrations in the atmosphere are greatly affected by rainfall as compared to CO_2 mixing ratios. The rate of increase of CO_2 rainfall was 80.672×10^{-3} ppm per minute before rainfall but after rainfall the rate decreased to 49.602×10^{-3} ppm per minute. So rainfall acts as a natural atmospheric $PM_{2.5}$ cleaner.

Scavenging of particles or gases may take place in clouds (rainout) by cloud droplets or below clouds (washout) by precipitation (Boubel, 1994). Wet deposition whereby the atmospheric contaminants are deposited to the ground in form of solutions has shown to affect particulate matter ($PM_{2.5}$) more than it does gases (CO_2).

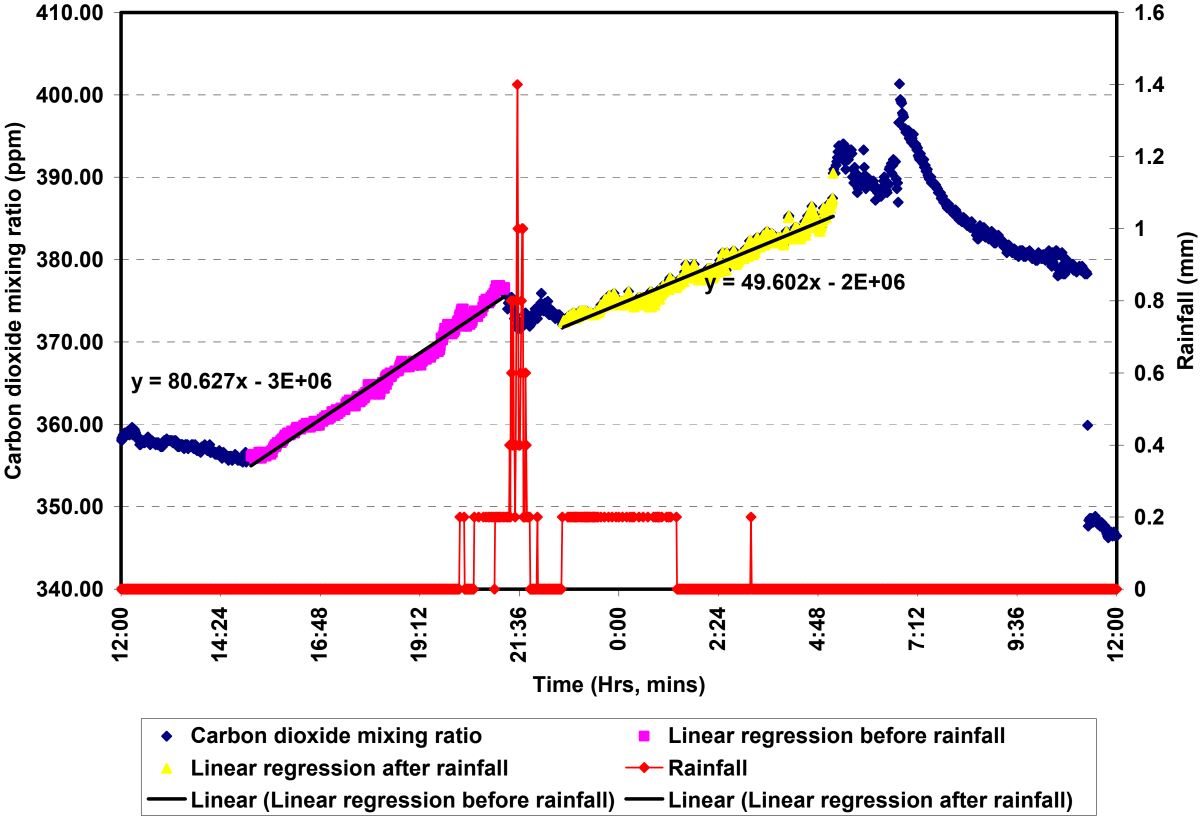


Figure 4.20 The effect of rainfall on the atmospheric CO_2 mixing ratios on DOY 60-61 2007

4.9 Spatial distribution of TDP (Total Dust precipitation) and the trace elements

The initial direction of transport of pollutants from their source is determined by the wind direction at the source. Air pollution concentrations from point sources are more sensitive to wind direction than any other meteorological parameter (Boubel, *et al*, 1994).

4.9.1 Spatial distribution of TDP (Total Dust precipitation)

The average TDP measured at UZ from DOY 330 to DOY 360 2006 shown in **Table 4.1** and from DOY 81 to DOY 102 2007 in **Table 4.2** were 0.04069 g $m^{-2}d^{-1}$and 0.04274 g $m^{-2}d^{-1}$ respectively. This shows that from November to December 2006 the atmosphere at the University of Zimbabwe was more polluted compared to from March to April 2007. The high value observed with a standard deviation of 0.007293, was due to the fact that the pots were located at

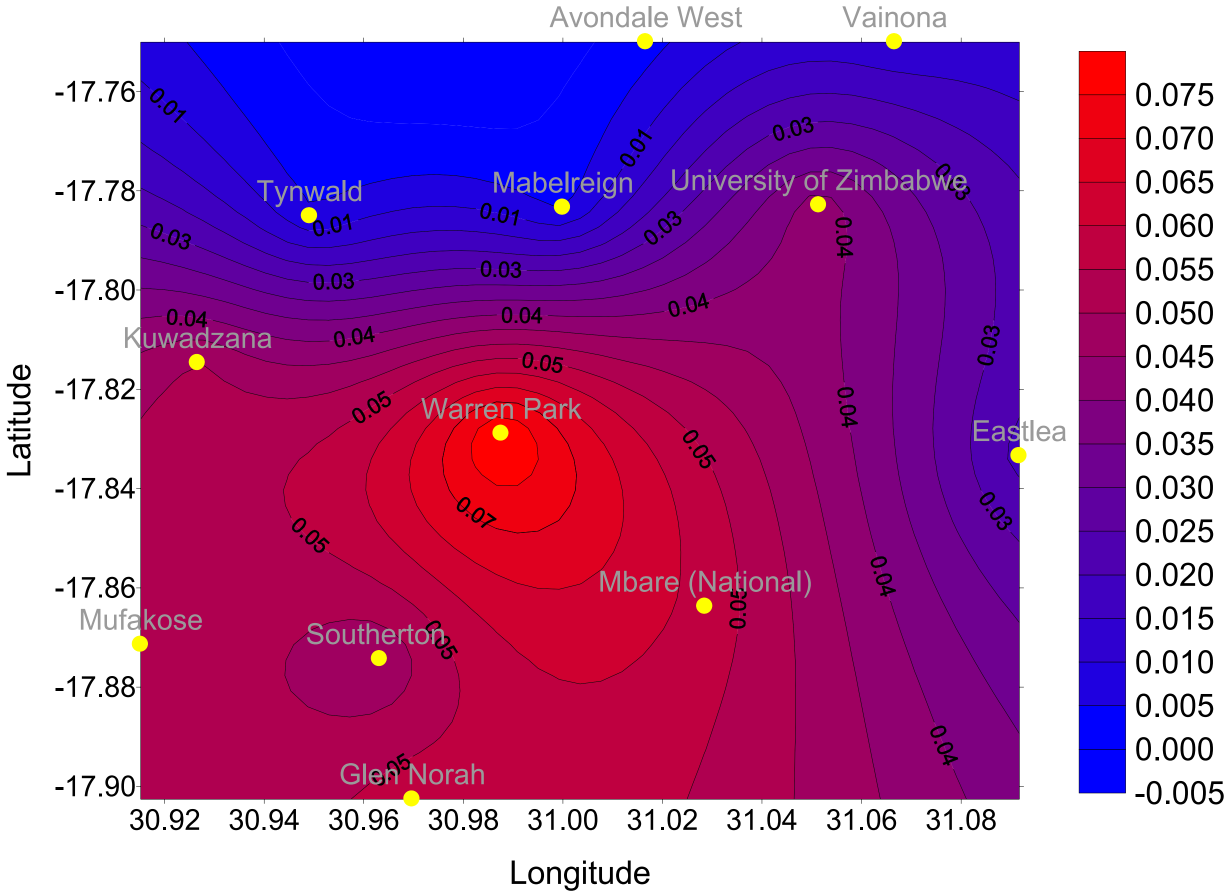
5 different points which were approximately 6 m apart on the roof of the Physics department. Pots A and B were at the centre of the roof top and recorded lower TDP than pots C, D and E which were on the edge of the building **(see Figure 3.1).** As a result high standard deviation was due to different site on which the pots were located.

Table 4.1 Masses and dust precipitation of TSP collected by 5 different pots from the Physics department building rooftop from DOY 330 to DOY 361 2006

Collecting pot	Mass of the Total Suspended Particulates (g) ($\pm$0.000005)	Total Dust precipitation ($g\ m^{-2}d^{-1}$)
A	0.01307	0.03728
B	0.01099	0.03135
C	0.01432	0.04084
D	0.01792	0.05111
E	0.01503	0.04287
Averages	0.01427	0.04069 $\pm$0.007293

Warren Park had the highest TDP value of 8.1 1x 10^{-2} $g\ m^{-2}d^{-1}$ and this was due to the wind blown dust from the nearby Warren Hill mountains where quarry dust is being taken, dust producing activities which take place and the closed dumping site which is close to 2km away. Mbare National showed a higher value of 5.82 x 10^{-2} $g\ m^{-2}$, because the area is exposed to wind blown dust from Graniteside, Workington and Southerton industries. In these industries there is a lot of coal combustion and other particulate producing activities which takes place. Apart from these industries as well there are some home industries which generate a lot of particulates into the atmosphere especially spray-painting.

In high density suburbs the soils are more exposed than in low density suburbs. For this reason the total dust precipitation in Mufakose, Kuwadzana, Glen Norah, Mbare, Warren Park and Southerton are higher than those in low density areas namely Vainona, Mabelreign, Eastlea and Avondale West. Eastlea had a slightly higher value of 4.12 x10^{-2} $g\ m^{-2}d^{-1}$ because there is a busy high way road nearby (Robert Mugabe Road) which was 10 m away, from which a lot of dust was produced and other particulates from fuel combustion.



Latitude (Degrees South) and longitude (Degrees East)

Figure 4.21 Spatial distribution of TDP in residential areas of Harare from DOY 80 to DOY 102 2007

The high value which was recorded at the University of Zimbabwe which is situated in Mount Pleasant was due to the fact the sampling pot was on top of a three storey building and there was no interference. Unlike the other pots which were at 1.5 m above the ground, these pot's measurements were greatly affected by trees, buildings and other objects which were taller than 1.5 m. There is a mining site 5 km northeast of UZ, where there is a lot of granite blasting. The particulates from this area may have been carried adverted to UZ, hence high value being recorded.

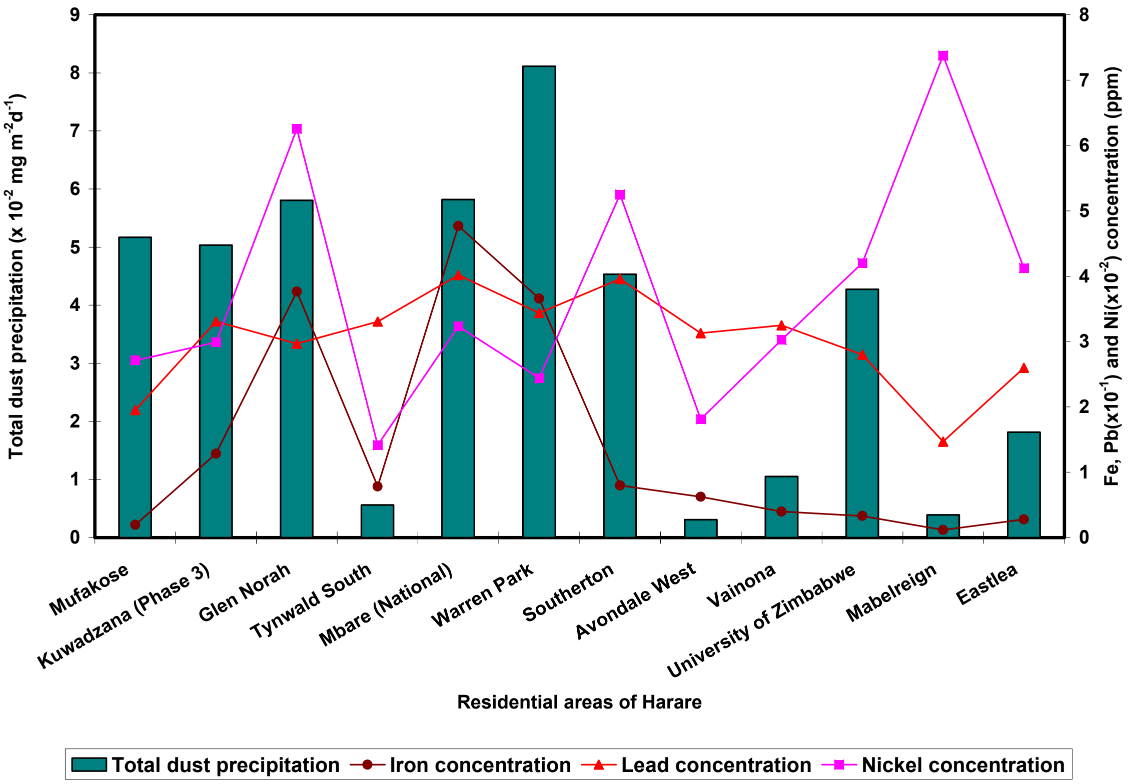


Figure 4.22 The variation of total dust precipitation in different residential areas of Harare DOY 80 2007 to DOY 102 2007

Avondale West had the least TDP because the area does not have any dumping sites or industrial site nearby and the area is surrounded by tall grass. As a result there is no major source of TDP. On the other hand the area is upwind as most of the time Harare wind is north easterly. From **Figure 4.22** other regions with the lower TDP are from the northern suburbs namely Tynwald, Mabelreign and theses areas are close to each other. As a result their TDP are also within the same range (0.015 and 0.005 g $m^{-2}d^{-1}$). From Warren Park to areas to the south, the regions with the same TDP were increasing going to the east. This shows that longer distances had similar TDP values.

Table 4.2 Masses and total dust precipitation of TSP collected at 12 different sites in the residential areas of Harare from DOY 80 2007 to DOY 102 2007

Residential area	Mass of the total dust precipitation of two collecting pots per gram (± 0.000005)	Total Dust Precipitation ($g\ m^{-2}d^{-1}$)
Mufakose	0.01228	0.0517
Kuwadzana (Phase 3)	0.01196	0.05034
Glen Norah	0.01379	0.05806
Tynwald	0.00133	0.00560
Mbare (National)	0.01389	0.05818
Warren Park	0.01927	0.08114
Southerton	0.01076	0.04533
Avondale West	0.0007	0.0031
Vainona	0.00250	0.01051
University of Zimbabwe	0.01015	0.04274
Mabelreign	0.00093	0.0039
Eastlea	0.00431	0.01815

4.9.2 Spatial distribution of the trace elements

Metals are emitted during high temperature processes, such as waste incineration, smelting, cement kilning, and power plant combustion. In such cases, heavy metals vaporise at high temperatures, they condense into soot and fly ash particles that are emitted simultaneously (Jacobson, 2002)

Mbare (National) had the highest values of lead and iron. These high values may have been due to the wind blown dust which was coming from the busy bus terminus which in the residential area. The major source of the two elements is the high density of the petrol powered vehicles which passes along Simon Mazorodze road which was close to the sampling point. Leaded petrol is known to contribute significantly to atmospheric lead concentrations. The area has got high density of home industries such as motor mechanics, welding which produces high concentrations of iron into the atmosphere and carpentry.

NB: The values shown in **Table 4.3** are of elements in the TDP collected from the 12 sampling sites**.**

Table 4.3 Distribution of iron, lead and nickel concentrations in selected residential areas of Harare

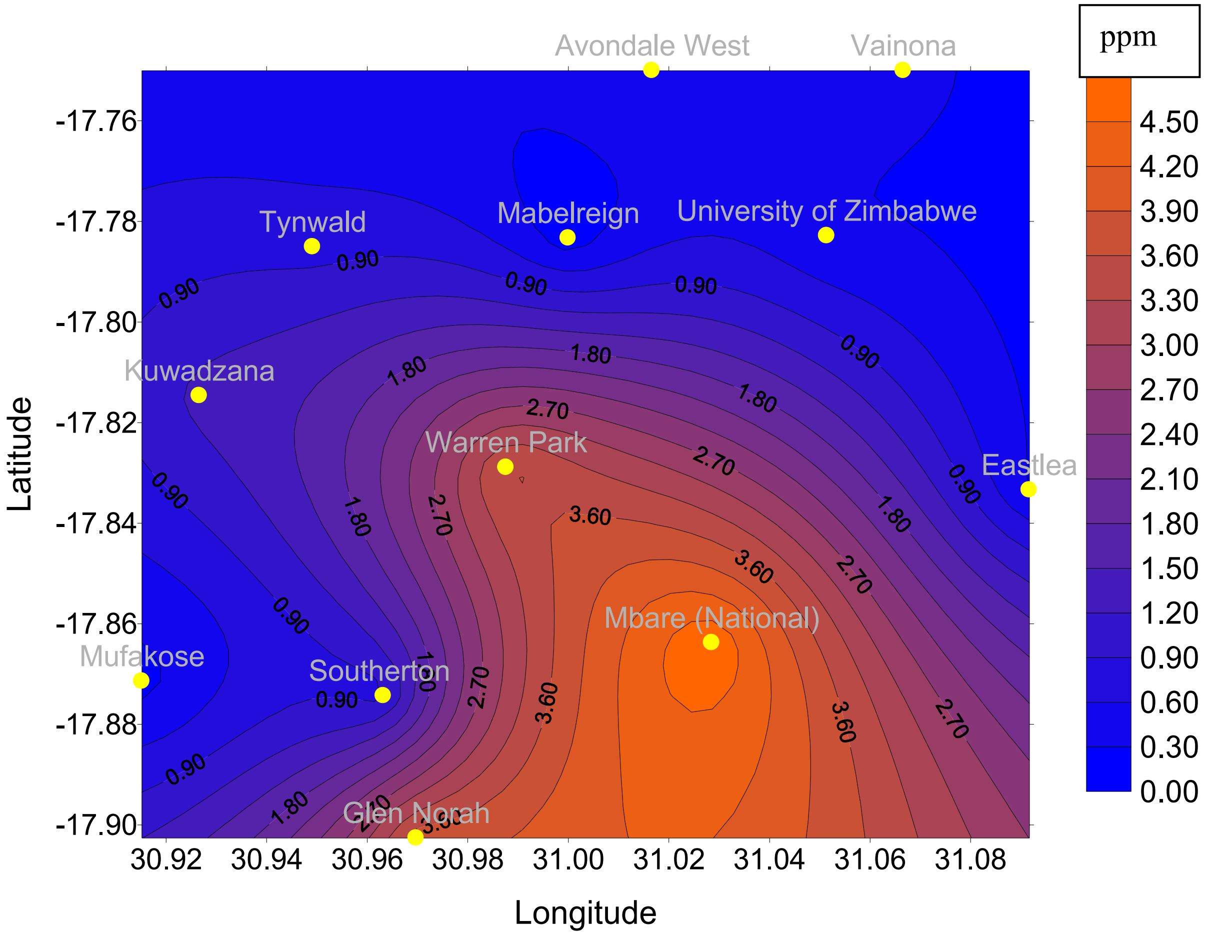
Residential area	Iron concentration / (ppm)	Lead concentration / (x 10^{-1} ppm)	Nickel concentration / (x 10^{-2} ppm)
Mufakose	0.1963	1.949	2.71
Kuwadzana(Phase 3)	1.2858	3.308	2.99
Glen Norah	3.7644	2.966	6.26
Tynwald	0.7837	3.304	1.415
Mbare (National)	4.7684	4.017	3.235
Warren Park	3.6565	3.438	2.44
Southerton	0.7986	3.958	5.25
Avondale West	0.6252	3.127	1.813
Vainona	0.3963	3.246	3.025
University of Zimbabwe	0.3325	2.799	4.205
Mabelreign	0.1168	1.467	7.375
Eastlea	0.2769	2.597	4.12
Average values	1.417	3.02	4.251
Standard deviation	1.648	0.69	2.908

4.9.2.1 Iron

From **Figure 4.23** the concentration of iron in the low density areas like Vainona was in 1.50 ppm region, University of Zimbabwe (Mount Pleasant) and Eastlea were in 1.20 ppm region and Tynwald was in 0.90 ppm region. These are all northern low density areas and the City of Harare had the idea of locating all low density suburbs in the northern side of Harare as the wind will be from the north. Since the northern side is the up wind, all industries are located to the southern part of Harare. The high density areas are located to the southern part of the city close to the industrial sites. These residential areas are prone to high risk of air pollution.

Low iron concentrations recorded by northern suburbs are due to the fact that the wind from north is less polluted as there is no source of air pollution in the northern part of Harare. The other fact is that, in these areas there are few dumped old vehicles carcasses and less if any home industries in which panel beating and welding are practised. As a result the amount of iron which will be emitted into the atmosphere is a minimum.

In high density areas like Glen Norah, Mbare National and Warren Park had the highest value of iron, 3.76 ppm, 4.77 ppm and 3.66 ppm respectively. This was due to the fact that there are a lot of dumped old vehicles and a lot of home industries which specializes in welding and panel beating. These activities, add a lot of iron into the atmosphere. Of all the high density suburbs Mbare had the highest iron concentration of 4.77 ppm. This was because Mbare has got high density of home industries such as motor mechanics, welding and other metallurgical works which emit high concentrations of iron into the atmosphere.



Latitude (Degrees South) and longitude (Degrees East)

Figure 4.23 Spatial distribution of iron (Fe) in the atmosphere of the residential areas of Harare from DOY 80 to DOY 102 2007

Mbare is surrounded by industrial sites namely, Southerton, Workington and Graniteside industrial sites. In these industrial sites there are a lot of companies which specialises in steel smelting and milling like Craster Metals industries which has got two companies one in Workington and the another one is located in Southerton. Both of these companies add iron into the atmosphere. Other companies have got oil and coal powered plants and these also add iron into the atmosphere around Mbare area. In Mbare there is a lot of biomass burning which occurs along Mukuvisi River.

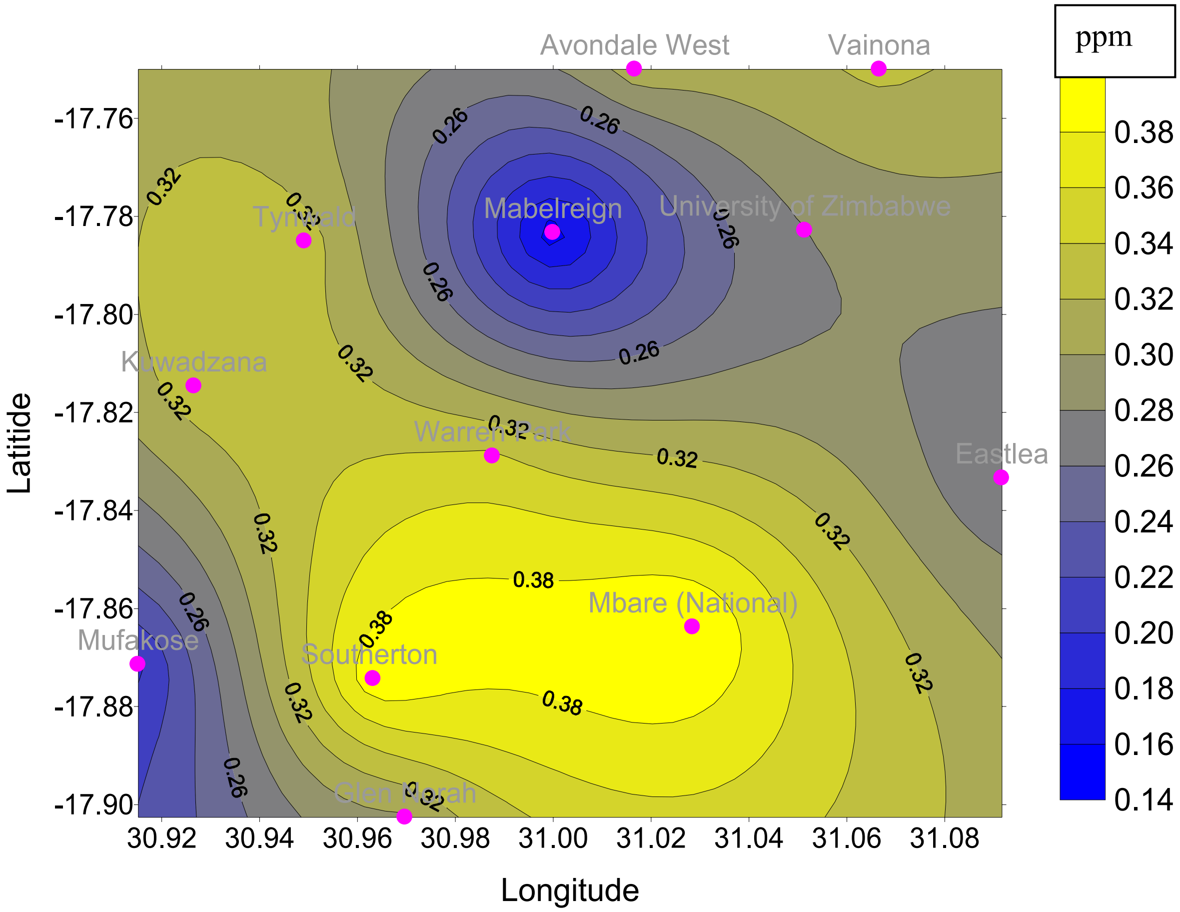
The high standard deviation value of 1.648 ppm which is far much greater than the mean value of 1.419 ppm for all the sampling sites shows that there were great differences between the sampling sites. This was due to the fact that northern low density suburbs recorded lower iron concentrations were far of the industrial and dumping sites than the southern high density residential areas counter parts which are close to dumping and industrial site.

4.9.2.2 Lead

Lead is a very toxic element, causing variety of effects at low dose levels. These include brain and kidney damage, reduced growth in children, decreased sperm count, in men and spontaneous abortion in woman. Lead is produced from leaded petrol (tetraethyl lead is added to gasoline to increase the octane rating), manufacture of batteries, paints, combustion of coal, incineration of wastes and fertilizer manufacture (WHO, 2000).

But pollutants can be adverted by wind. The lead concentrations recorded at Mbelreign and Mufakose were 0.18 ppm and 0.22 ppm respectively. These two sampling points had the least lead concentrations. For both Mabelreign and Mufakose the sampling points were far away from the busy roads. Mabelreign's sampling point was located in a close; as a result few vehicles have access the area. As for Mufakose the sampling area was at the extreme end of the residential area, where heavy vehicles and commuter omnibuses rarely reach.

Tynwald and Kuwadzana sampling regions fall in the 0.32 ppm to 0.34 ppm region. These two sampling areas are close to each other, but they are concentrations differ by 0.004 ppm with Kuwadzana having the higher concentration of 0.3308 ppm and Tynwald with 0.3304 ppm. This difference is due to the fact that there are commuter omnibuses and waste incineration in Tynwald which is a medium density area as most people own cars unlike in Kuwadzana most people use public transport which contributes a lot to lead concentration in the atmosphere.



Latitude (Degrees South) and longitude (Degrees East)

Figure 4.24 Spatial distribution of lead in the atmosphere of residential areas of Harare from DOY 80 to DOY 102 2007

Warren Park was 0.34 ppm mark as shown by **Figure 4.24** which is a higher value for lead concentration than its counter parts Tynwald and Kuwadzana. This is so because Warren Park's sampling site was close to busy Bulawayo Road. Lead from the leaded petrol will be emitted into the atmosphere. Apart from that there is a dumping site called Warren Hills Dumping site near by where waste incineration occurs and this also adds lead into the atmosphere.

Mbare recorded the highest lead concentration value of 0.4017 ppm which was in the same region with Southerton, of above 0.38 ppm, but Southerton had a slightly lower value of 0.3958 ppm. These high values recorded in Mbare may have been due to the wind blown dust which was coming from the busy bus terminus which is in the residential area. The major source of lead in the Mbare high density suburb is the petrol powered vehicles which pass along Simon Mazorodze road which was close to the sampling point. Leaded petrol is known to contribute significantly to atmospheric lead concentrations. The area has got high density of home industries such as motor mechanics, welding which produces high concentrations of iron into the atmosphere and carpentry. Chloride Batteries Company is located in Workington industrial site close to Mbare, where lead is used to manufacture vehicle batteries. This company also contributes to the highest value recorded in Mbare compared to other sampling sites.

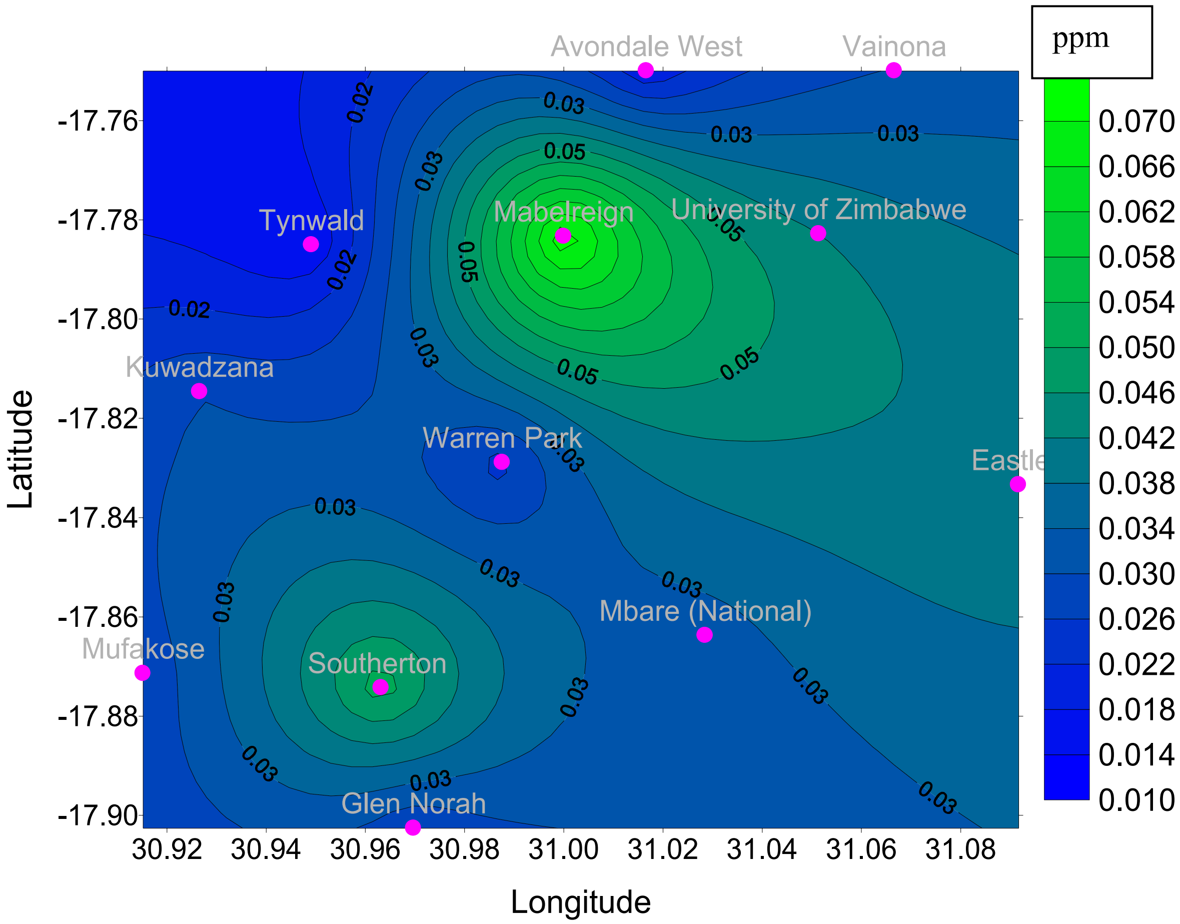
The reason why Southerton and Mbare, have similar concentrations is that the two areas are close to Southerton industrial area. Mbare is close to Tobacco Processing Company and British American Tobacco where tobacco processing takes place and tobacco processing contributes a lot to lead concentrations in the atmosphere. Southerton is also close to Lytton Tobacco Company and Tobacco Auction Floors where tobacco processing takes place.

In general there aren't huge differences in lead concentrations in all sampled areas as shown by the lower standard deviation value of 0.069. This lower standard deviation value may have been due to the existing fuel problem in the country as a result fewer vehicles are on the road hence less lead is being loaded into the atmosphere.

4.9.2.3 Nickel

Nickel (Ni) in TSP emanates for wearing of steel which contains nickel, for example stainless steel in which nickel is a major component. Major nickel anthropogenic source is combustion of oil (including gasoline) followed by non ferrous mining and its production. Wood combustion and waste incineration also contribute significantly to atmospheric levels of Ni (Nriagu, 1979).

Figure 4.17 show that Mabelreign sampling point recorded the highest nickel concentration of 0.07375 ppm. The main reason for this high value was that, there is an electrical substation close to the sampling site and electricians from ZESA are always on the station fixing same problems. Their problem solving is believed to contribute to the observed high nickel concentrations as it involves some metallurgical works. The regions with the same nickel concentrations as Mabelreign is UZ and then Eastlea seem to increase in distance and this may have been caused by wind which might have carried the nickel from Mabelreign down to Eastlea.



Latitude (Degrees South) and longitutdes (Degrees East)

Figure 4.25 Spatial distribution of nickel in the atmosphere of the residential areas of Harare from DOY 80 to 102 2007

In Glen Norah, the nickel concentration 0.026 ppm to 0.022 ppm.There is a dumping site nearby where a lot a burning of waste product which at times includes oils occurs. Old dumped vehicles contribute as well as same parts are made up of iron mixed with nickel. The same reasoning applies to Warren Park sampling site which was close to dumping site (Warren Hills). Warren Park recorded lower value of 0.0244 ppm whilst it was located in between Mabelreign (0.7375 ppm) and Southerton (0.525 ppm).

High value in Southerton and Mbare are attributed to combustion of coal, wear of steel objects and steel related industries nearby. Southerton sampling point is 1 km away from Craster Metals milling company as a result there was a lot of nickel recorded in Southerton unlike Mbare which is 3 km from Craster Metals sister steel milling company in Workington.

4.10 Relationship between TDP and the trace elements (lead, iron and nickel)

The R^2 value of 0.4882 shown on **Figure 4.26** indicates that there is a correlation between iron and TDP, but it's very weak. Areas with high TDP recorded high iron concentrations like Warren Park recorded a TDP concentration of 8.11 x 10^{-2} g m^{-2} d^{-1} had iron concentration of 3.76 ppm and same points with lower TDP concentrations like Vainona had 0.39 x10^{-2} g m^{-2} d^{-1} and iron concentration of 0.1168 ppm.

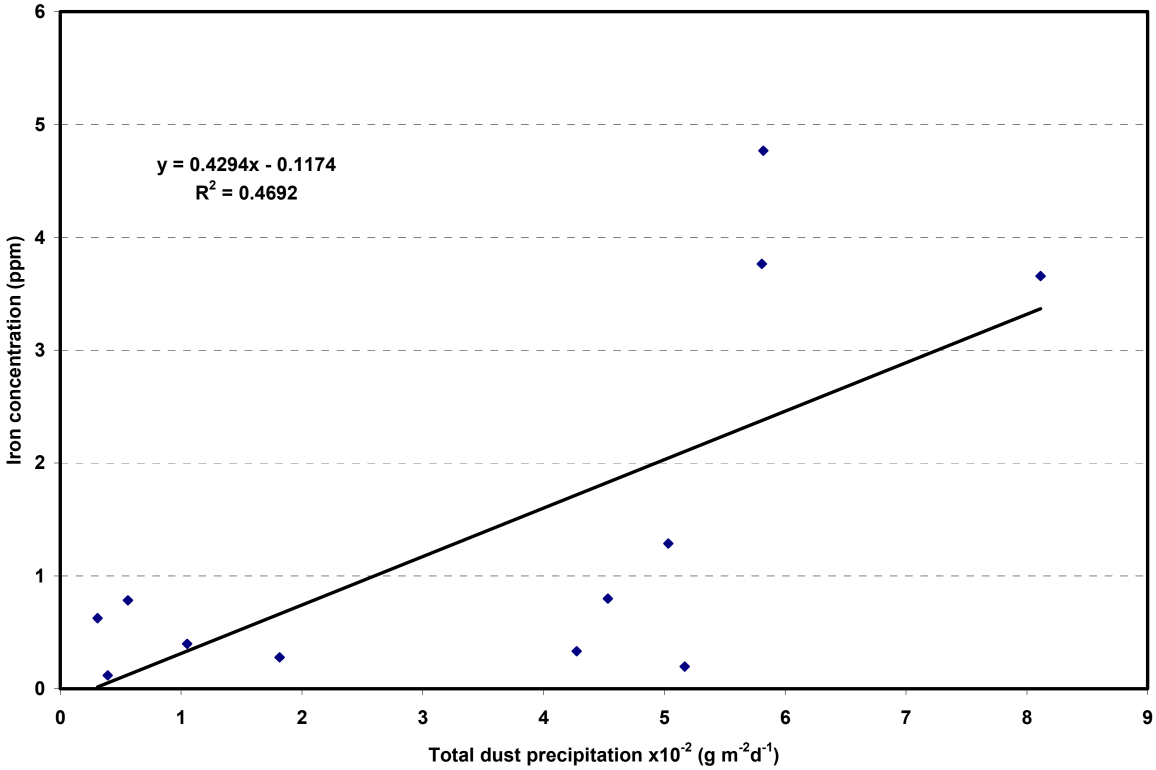


Figure 4.26 Relationship between iron and TDP

There were some areas with high TDP but with lower iron concentrations, which affected the correlation between TDP like Mufakose which had TDP concentration of 5.16 x10^{-2} g m^{-2} d^{-1} and iron contration of 0.019 ppm. As a result there was a weak correlation between TDP and iron concentration. Iron concentration tend to increase with TDP, but that relationship is not strong as indicated by some points which had higher TDP concentrations that is between 4 and 6.5 x 10^{-2} g

m^{-2} d^{-1} and these points went on to give low iron concentrations of below 1.3 ppm. These points affected the straight line relationship

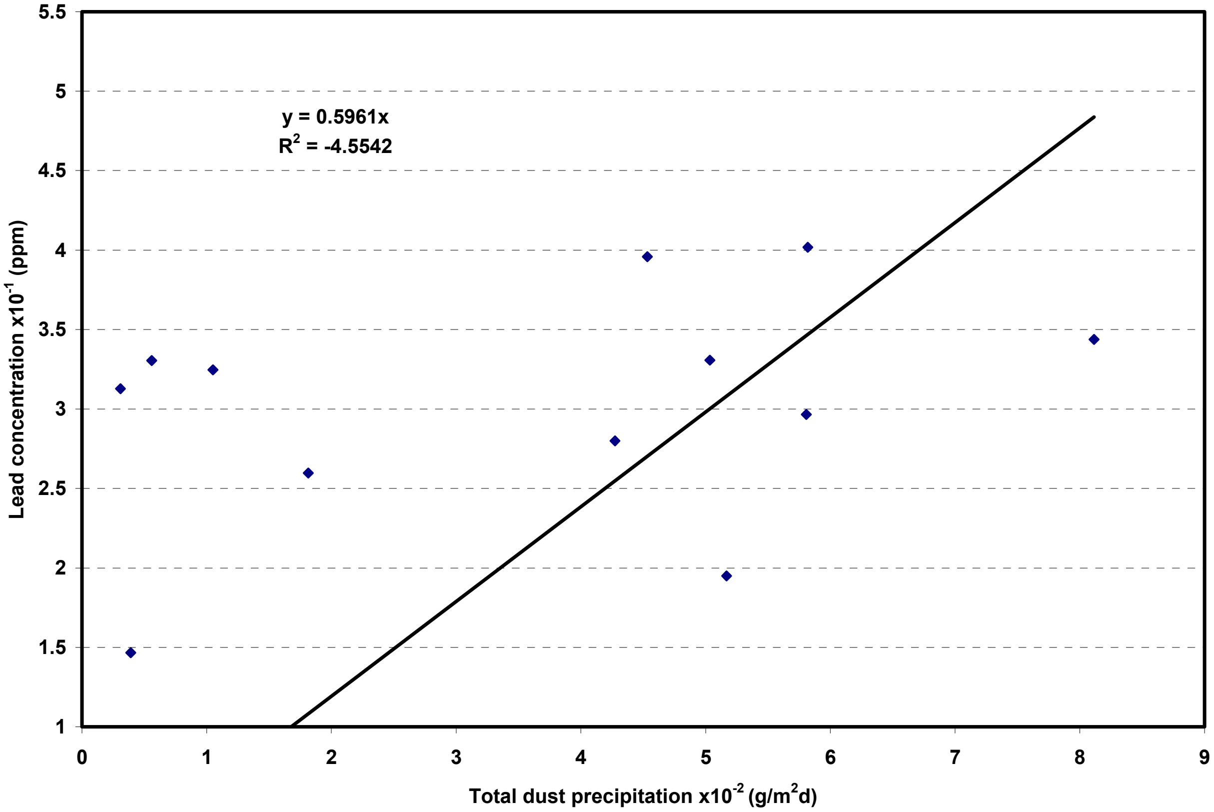


Figure 4.27 Relationship between lead and TDP

Figure 4.27 shows no relationship between lead and TDP as indicated by the correlation coefficient value of -4.5542. There was no relationship because some areas which had lower TDP recorded high lead concentrations like Tynwald which had 0.56 x10^{-2} g m^{-1} d^{-1} recorded lead concentration of 3.304 x 10^{-2} ppm whilst some areas which had high TDP recorded lower lead concentrations for example Mufakose had TDP of 5.168 x10^{-2} g m^{-2} d^{-1} and recorded lead concentration of 1.949 x10^{-1} ppm.

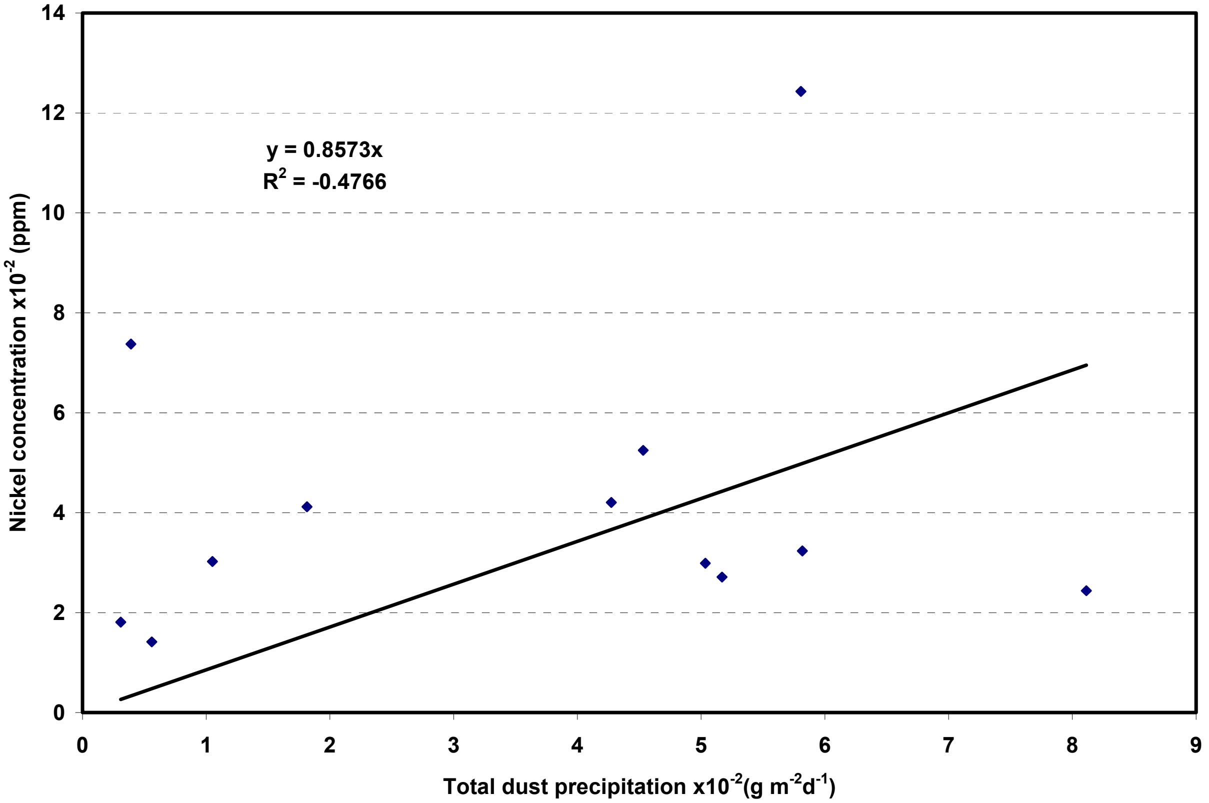


Figure 4.28 Relationship between nickel and TDP

Figure 4.28 shows that there was no correlation between TDP and nickel concentrations as, since those areas with high and lower TDP went on to record almost similar nickel concentrations. For example Vainona (low density area) had nickel concentration of 3.025 x 10^{-2} ppm and recorded lower TDP concentration of 1.05 x 10^{-2} g m^{-2} d^{-1} and Kuwadzana (high density area) had nickel concentration which was close to that of Vainona of 2.99 x 10^{-2} ppm but it had recorded high TDP of 5.03 x 10^{-2} g m^{-2} d^{-1} . This removed chances of any relationship hence small R^2 value of -0.4766.

The correlation coefficient between TDP and iron, TDP and lead and TDP and nickel concentrations were 0.4692, 0.1182 and -0.4766, show that there is no strong correlation between TDP and any one of the three trace elements namely lead, iron and nickel.

CHAPTER 5 CONCLUSION

This chapter presents conclusion of the study and list of recommendations for further study.

5.1 Conclusion

1. $PM_{2.5}$ concentration in the atmosphere can not be predicted by monitoring the behaviour of a single meteorological parameter, as the results may be misleading. For meaningful conclusion to be made, all the parameters namely wind speed and direction, temperature, solar radiation, relative humidity and rainfall need to be studied. This is because $PM_{2.5}$ concentration in the atmosphere depends on several meteorological factors**.**

2. It was observed that it was necessary to use dry air when determining the $PM_{2.5}$ using the nephelometer, since it was discovered that wet air tends to dupe the instrument. As the particles absorb water, they increase in size leading to some errors as the instruments will not be in a position to detect them, as they will have grown to larger sizes beyond what the instrument measure. The $PM_{2.5}$ concentrations were observed to behave in a cyclic manner, whereby the concentrations were high during the night and occasionally some sharp peaks were observed at 1700. During the day it was noted that the $PM_{2.5}$ concentrations were low. CO_2 was observed to follow its natural cycle, whereby the CO2 concentrations were low during the day and high during the night. Occasionally on top of the CO_2 concentration crests some superimposed peaks were observed which were due to anthropogenic sources. These small peaks on CO_2 natural cycle were observed to occur at the same time with the sharp peaks of $PM_{2.5}$ from 1700 to 1930. The average wind direction from 1700 to 1930 was observed to be from 127 ° (south easterly of the University of Zimbabwe). This direction means that the wind was coming from the city centre. It was concluded that the peaks on the CO_2 natural cycle and the sharp peaks of $PM_{2.5}$ at 1700 were due to pollution plume which was coming from downtown. On Sundays it was observed that the there was no peak of CO_2 concentration from 1700 to 1930, but the peak of $PM_{2.5}$ was prevalent and the wind direction was 147 °. This shows that the sources of CO_2 and $PM_{2.5}$ were not the same as the wind from the same direction on Sunday brought high concentrations of $PM_{2.5}$ and low CO_2 concentrations. It was also concluded that the main source of CO_2 from the southeast from

1700 to 1930 was fuel combustion from the traffic. On Sunday the traffic density will be low, hence low CO_2 concentrations was brought from the south east. The source of PM $_{2.5}$ is believed to generate these particle every day of the week as the peaks appeared on everyday.

3. Wind speed was observed to have a slight effect on the PM $_{2.5}$ and CO_2 concentrations, as low wind speed were associated with higher concentrations whilst high wind speeds were associated with low concentrations. High wind speed causes air mixing and this dilutes the concentrations of both CO_2 and $PM_{2.5}$. When the wind speed is low there will be less mixing and that's why low wind speeds were associated with high concentrations of CO_2 and $PM_{2.5}$. Wind direction was observed to have a profound effect on the CO_2 and $PM_{2.5}$ concentrations. This is evidenced by the fact that sharp peaks were observed when the wind was coming from highly polluted areas, for example from down town and small peaks when wind was coming from the north were there are few sources CO_2 and PM $_{2.5}$.

4. Temperature was observed to have no effect on CO_2 and $PM_{2.5}$ concentrations as the ambient temperature and the concentration cycles (CO_2 and $PM_{2.5}$). The concentrations of CO_2 and $PM_{2.5}$ had some fluctuations which were not observed on the ambient temperature cycle.

Rainfall was observed to have a strong effect on CO_2 and $PM_{2.5}$, as CO_2 molecules and PM $_{2.5}$ molecules are absorbed by water droplets, as these droplets fall to the ground they bring with the CO_2 molecules and $PM_{2.5}$, a process known as wet deposition. Wet deposition process reduces the concentrations of CO_2 and PM $_{2.5}$ in the atmosphere.

5. The spatial distribution TDP (total dust precipitation) which contained the heavy metals which were analysed was not uniform in residential areas of Harare. High density areas which are close to dumping site, busy roads and industrial site recorded high concentrations of TDP. For example Warren Park is close to Bulawayo Road and a dumping site recorded the highest TDP of 0.0114 g $m^{-2}d^{-1}$, whilst Avondale West which is a low density area and far from major sources of TDP had 0.0031 gm^{-2} d^{-1}. High nickel concentrations were recorded in Mabelreign because of proximity to an electric substation on which the electricitians would come regularly, to do operations which emitted nickel into the atmosphere.

6. High lead (0.4017 ppm) and iron (4.7684 ppm) concentration were recorded in Mbare because it is surrounded by an industrial area (Southerton, Graniteside and Workington) and there is a busy bus terminus in the area. Leaded petrol is the major source of lead, hence high lead concentration was recorded in the area and metallurgical works in home industries and the surrounding areas were responsible for high iron concentrations. Mabelreign recorded the least lead concentration (0.1467 ppm) and iron concentrations as it is upwind of the industrial sites and there is no busy bus terminus in the area as most people own car. Lowest nickel concentration was recorded in Avondale West (0.01813 ppm) because the area is also up wind of and away fro the industrial sites of Harare, hence low nickel concentrations.

5.2 Recommendations

1. There is a great need for continuous monitoring of $PM_{2.5}$ concentrations, in order to observe their variations with seasons. The same applies to CO_2, which is a greenhouse gas hence its concentration needs to be known. In order to get more information relating to sources of particulate matter, there is a need to establish metal ratios in $PM_{2.5}$ and PM_{10}. This information will enable researchers to differentiate between the contribution of wind blown dust and combustion sources.

2. There is a need to monitor the role played by Mbare Msika bus terminus and home industries in producing airborne pollutants in Mbare which is a densely populated residential area. Diesel emissions from long distance buses can cause a serious healthy problem considering the fact that such particulates fall within the $PM_{2.5}$ range. The levels of PAHs need to be studied, in order to determine the contribution effect of diesel and petrol vehicles to pollution. On the other hand those studies can then be used to differentiate windblown particulates from those from traffic fleet particulates.

3. The proposal by the Ministry of Energy and Power Development to ban or reduce the use of leaded fuel should be implemented as a matter of urgency. The prevailing situation in which it's cheaper than unleaded petrol actually encourages its use. There is also a need to measure some other forms of particulates like PM_{10} which are well known for causing respiratory problems.

4. Continuous measurements using the Bergehoff or any method to measure TSP need to be carried out, in order to monitor the behaviour and variation with seasons. Twelve sampling sites are too few to cover a city with more than 2.5 million people and also too few to be able to come up with a model for the city of Harare. So there is a great need to increase the number of sampling sites and cover all areas including the industrial sites.

5. There is a great need to record monthly pollution data and present it in a simpler way like Air Pollution Indices (APIs) which can be easily understood like weather data in local media.

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APPENDIX

Appendix A Day of the year (Julian) calendar

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Jan	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Feb	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59			
Mar	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Apr	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	
May	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151
Jun	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	
Jul	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212
Aug	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243
Sep	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	
Oct	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304
Nov	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	324	325	326	326	327	328	329	330	331	332	333	334	
Dec	335	336	337	338	339	340	341	342	343	344	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	361	362	363	364	365

Add 1 to values not in italics during leap year.