

SULPHUR DIOXIDE MEASUREMENTS IN NAIROBI

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


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ABSTRACT

Sulphur dioxide in ambient air at Nairobi's major Industrial area and its environs was measured using pararosaniline method. In this study, concentrations for a period of six months (June - November, 1993) at six sampling sites are presented.

The data was collected in Nairobi Industrial area and two residential areas, South B and Makadara. Sampling was done during morning hours, from 9.00 am to 11.30 am and from 2.00 pm to 4.30 pm for afternoon hours, to give the average concentration for a given day.

The monthly average concentrations was higher at the Industrial area (24.4-175.5mg/m³) than at the residential sites (14.2-72.5mg/m³). Sampling sites located closer to major Industries recorded higher values than those far away. Sites downwind of the industrial area recorded higher concentrations than sites located upwind.

In all sampling sites, higher concentrations were found in the morning hours (9.00-11.30am) than the afternoon hours (2.00-4.30pm). June-september period recorded generally high concentrations (14.2-175.5mg/m³). Climatological information indicated that this period is characterized by high frequency of stable conditions and calm winds. October -November period had lower concentrations (14.0 - 157.8mg/m³) due to favourable dispersion conditions (higher wind speeds and unstable conditions) experienced during this period.

The average monthly concentrations at the industrial area was found to exceed World Health Organization(WHO) guidelines on some occasions, implying this could pose serious health problems to the people staying nearby.

In the context of Sulphur dioxide emissions, the industrial development in Kenya has not reached a level where serious health problems may arise except during those months characterized by poor dispersion conditions and in those areas closer to industries.

CHAPTER ONE

1.0 INTRODUCTION

There are many different views as to what constitutes pollution of the atmosphere. Elsom [1987] defines atmospheric pollution as "the presence in the atmosphere of substances or energy in such quantities and of such duration liable to cause harm to human, plant, or animal life or damage to human made materials and structures, or changes in the weather and climate or interference with the comfortable enjoyment of life or property or other human activities".

Categories of air pollution to which exposure is possible are:-

- (i) Radiation: ionizing and non ionization
- (ii) Atmospheric gases: SO_2 , CO , CO_2 , NO , N_2O , NO_2 etc
- (iii) Dust: non biological air borne particles
- (iv) Biological particles/aerosols: viruses, pollen, bacteria etc.

Air pollution sources can be classified into natural and anthropogenic (man made) sources.

1.1 Natural Sources of Pollutants

The effect of volcanic eruptions have been noticed around the world, although, their emissions are significant only on an

intermittent basis . The effects of the 1883 eruption of Krakatoa in the East Indies reportedly caused spectacular atmospheric effects such as brilliantly red sunsets for more than two years afterwards [Williamson, 1973]. This resulted from great quantities of fine ash being thrown up to altitudes of at least 20 km. The gases emitted during volcanic eruptions include sulphur dioxide, hydrogen chloride, hydrogen fluoride and hydrogen sulphide. Nitrogen dioxide formed by electrical discharges, and ozone are also air pollutants resulting from natural sources. Particulate matter formed are dusts from deserts, ashes from forest fires, particles of sea salt, meteoric dust, plant pollen etc. [Bach,1972].

1.2 Anthropogenic Sources of Pollutants

These include domestic heating equipment, transportation, a wide range of industrial plants and power plants. Products emitted are suspended particulate matter (soot, smoke) and gaseous sulphur [Elsom, 1987]. The tremendous increase in the use of petroleum products, particularly in petrol powered motor vehicles, introduced several new pollutants These are mainly exhaust emissions of oxides of nitrogen, carbon monoxide, hydrocarbons, and lead. Waste energy inthe form of heat also contribute to the list of local pollutants, while nuclear power production and atomic weapons testing highlights radiation as a pollutant [Elsom, 1987].

In Kenya, indoor pollution poses a major environmental concern. This is because fuel wood is among the major sources of energy, others being petroleum fuels and electricity (Ottichilo et al., 1991). The main pollutants resulting from wood fuel usage is carbon monoxide. Petroleum fuel contribute to the environmental indoor pollution especially when it is used for domestic purposes. The major products are oxides of carbon (especially carbon monoxide) and sulphur oxides. Petroleum and wood fuels are used in most rural homes areas since the rural inhabitants do not have adequate electricity supply.

On the global scale, carbon dioxide increase primarily due to burning of fossil fuel has been a problem of major concern [Woodwell, 1983]. It is commonly accepted today that the presence of contaminants in normally inhaled has detrimental effect on health, whether in the short or long run. There are several cases where a pollutant has been diagnosed as the specific cause of a complaint or ailment, such as eye irritation brought by Los Angeles or Tokyo smog and chest disease due to certain industries [Gilpin, 1971].

Stimulus to the interest of health authorities in air pollution came largely through the dramatic and tragic acute episodes where obvious discernible mortality was found.

In early December 1930, a thermal inversion layer confined the pollutants of a number of industrial plants to a small valley of the Meuse River in Belgium. On the third day, many people were stricken and sixty people died before the week was out. Illness affected persons of all ages. Those with previous problems of heart and lung diseases were primary victims [Firklet, 1931]. A combination of several pollutants was associated with this disaster. Sulphur dioxides and fluorides have been implicated.

In Donora Pennsylvania in 1948, stagnant meteorological conditions and low temperature in the valley of the Monongalela River led to a smog which prevailed for about four days. There was a marked increase in illness and a few people died. Pre-existing disease of the cardio-respiratory system was present in majority of the fatal cases [Rouche, 1947; Schrenk, 1949]. Studies appear to indicate that no single substance existed in sufficiently high concentration to be considered the responsible factor, but the more likely combination of a number of irritant gases and fumes caused the illness and deaths

At Poza Rica, Mexico, in 1950 some people died and many others were hospitalized as a result of the malfunction of an oil refinery sulphur recovery unit; large quantities of hydrogen sulphide were vented to the atmosphere. There was a pronounced low altitude

temperature inversion which prevailed at this time [McCabe and Clayton, 1952].

In London, 1952, two inversions, one close to the surface and the other caused by descending air higher up, confined the fog which covered the Greater London close to the ground [Douglas and Stewart, 1953]. Many people died during this episode. Most of the people who died during and immediately after the fog had previous respiratory and cardio-vascular diseases, mainly of chronic nature.

There seems to be some demonstrative association between mortality and morbidity and demonstrated air pollution events. The fact that most of these episodes occurred when there were not many good developed air pollution measuring methods makes it difficult to find a specific correlation between the pollution concentrations and the meteorological parameters existing then. It could have been possible that some episodes occurred in areas without a good meteorological network.

1.3 General effects of atmospheric pollutants

Gaseous pollutants in the atmosphere affect human health, visibility, climate, vegetation and materials [Sellers, 1984].

In this section the effect of air pollutants on human health and, weather and climate will be discussed.

1.3.1 Effects on health

There has been accumulated evidence to correlate air pollution with increased mortality from cardio-respiratory causes, increased susceptibility to respiratory disease and interference with normal respiratory function [McCormac, 1971]. This evidence comes primarily from three types of investigations. First, from statistical studies of past morbidity and mortality which correlate geographic factors with air pollution. Second, from prospective epidemiological studies of morbidity, mortality and respiratory functions to variations in air pollution. Third, there are laboratory studies of response by animals and by humans, in some cases, to exposure to various pollutants singly or in combination.

Sterling et al., [1969], in a study of urban morbidity and air pollution in Los Angeles, found a significant correlation between pollution and fluctuation of rate of admissions to hospitals for disease categories including allergic disorders, inflammatory diseases of the eye, respiratory infections, influenza, bronchitis and certain cardio-vascular diseases.

Hudson [1970] conducted a study of the short term effects of air pollution on mortality in New York City, analyzing data on

mortality, air pollution, and meteorological factors during the period November 1962 through May 1965. He concluded that the level of respiratory and heart disease mortality over time is quite significantly related to environmental conditions, and that a large percentage of the variation in mortality from heart and respiratory diseases was explained by concurrent variations of air pollution and temperature, with pollution being the more important explanatory variable.

1.3.2 Effects of general air pollution on weather and climate

As early as 1929, Ashworth [1929] claimed to have found that there was thirteen percent less rainfall on Sundays than on Weekdays at Leicester, England over a 10 year period, presumably due to reduced emissions on Sundays.

Chanson [1968] found that since 1925, there has been a 30 to 40 percent increase in precipitation at La Porte with a concurrent rise in smokiness and steel production in Chicago.

Perhaps the greatest concern of global atmospheric pollution during the past two decades has been the issue of carbon dioxide. From climate model simulations of increased CO₂, there is a prediction with considerable confidence that there will be a global mean temperature increase. With much less confidence other more specific regional climatic changes are inferred, including relatively

greater polar temperature increase and summer dryness in middle latitudes e.g. the latitudes of the United States [Gunter et al., 1983]. The global warming rate consistent with assumed equivalent doubling of the concentration of CO₂ by the year 2050 and an estimated 4 °C equilibrium warming of this doubled concentration is about 0.3 °C per decade. A transient climate warming simulation experiment, reported by the Goddard Institute for space studies (Hansen et al., 1988), indicates a warming rate of 0.35 °C per decade for a similar greenhouse gas scenario. Routine monitoring for CO₂, established in 1958 and expanded significantly during the 1980s, has provided a reasonably comprehensive picture of the temporal and spatial trends in atmospheric CO₂ in the recent past. Analysis of air trapped in polar ice cores has extended this information yet further backwards in time, to about 100,000 years BP (before present) [UNEP, 1989, 1991]. On the basis of this observational evidence, it is concluded that the global average concentrations of atmospheric CO₂ has increased from pre-industrial levels of around 270 parts per million by volume (ppmv) to a 1991 value of 355 ppmv (IPCC, 1992b).

1.4 Sulphur Dioxide: Sources and Effects

In this section, sources of sulphur dioxide and its effects on animal, plant life, materials and weather will be discussed.

1.4.1 Sources of SO₂

Sulphur dioxide present in the atmosphere comes from both natural and man made sources. Natural sources of SO₂ include microbial activity and volcanic activity; and sea salt spray adds to atmospheric sulphate [Williamson, 1973]. Natural emissions account for about half of all atmospheric SO₂; these are not increasing as natural sulphur is simply recycled. On the other hand, man made SO₂ is increasing especially in the northern hemisphere, where an estimated 90 percent of all man made SO₂ is created.

Most man made SO₂ is formed when fossil fuels are burned. These fuels contain sulphur compounds which when oxidized produce sulphur oxides mainly sulphur dioxide [Williamson, 1973].

1.4.2 Effects of SO₂ on plants

The effect of SO₂ on plants can be acute or chronic. Acute injury is caused by absorption of high concentrations of sulphur dioxide in a relatively short time, resulting in a rapid accumulation of sulphite which is toxic to the metabolic process. Long term absorption of SO₂ at sub-lethal concentrations results in chronic injury. This becomes a manifest as a yellowing of the leaf [Kate et al., 1939]. Potentially damaging concentrations to vegetation are 0.25 ppm for 8 hours; 0.35 ppm for 4 hours; 0.55 ppm for 2 hours and 0.95 ppm for 1 hour [Dreisinger, 1965].

1.4.3 Effect of SO₂ on rain water and materials

The presence of strong acids in aerosol particles has been known for many years and quantified since the mid 1960s [Junge and Screech, 1971]. The formation of sulphuric acid in the atmosphere, principally by oxidation of anthropogenic SO₂, is the major source of acidity in aerosols. Further, in the absence of complete neutralization, these acidic aerosols constitute a major source of acid in precipitation. Presence of sulphuric acid will corrode metals, especially iron, steel, zinc, copper and nickel [Elsom, 1987]. The calcium carbonate in limestone and other building materials is readily converted into soluble calcium sulphate by sulphur dioxide.

1.4.4 Effects on Aquatic Ecosystems

Most measurements suggest that sulphuric acid is the major component of acid rain in most regions [Record et al., 1982 and Swedish Ministry of Agriculture, 1982]. Since SO₂ is the major precursor of sulphuric acid, the major component of acid rain arises from SO₂. Thus SO₂ affects the aquatic ecosystems indirectly through the action of acid rain. Most concern for the impact of acid rain on aquatic ecosystems is focused on the effects on the fish population. It is generally accepted that increasing lake acidification due to acid deposition has caused fish kills and stock depletion. Einbender et al. [1982] report the existence of at least 212 fishless lakes in the Adirondacks, the loss of all fish in 140 Canadian lakes, the near total depletion of buffering capacity in 3000 lakes in the

Eastern United States, the acidification of more than 10,000 lakes in Sweden to pH 6 or below and reduced populations of salmon and trout in major rivers in southern Norway.

1.4.5 Effects of SO₂ on Human health

At concentrations above 20 ppm, sulphur dioxide has a marked irritant effect on the eyes, nose, throat and airways, causing tearing, choking, wheezing, coughing and sneezing [U.S. Department of Health, Education and Welfare, 1974].

In a study of Norwegian pulp and paper workers, Staple [1964] reported excess coughing, sputum production, and shortness of breath in workers exposed to sulphur dioxide concentrations in the range of 2 to 36 ppm. Lee and Fragment [1969] reported an eightfold excess in respiratory cancer mortality among arsenic smelter workers. Investigations revealed that persons with high exposure to sulphur dioxide were most at risk. It was postulated that sulphur dioxide in the work environment may have enhanced the likely carcinogenic action of arsenic.

Shy [1978] concludes that sulphur dioxide alone is not a potent pulmonary irritant unless concentrations exceed 10 to 20ppm; levels that are virtually never encountered in ambient air and rarely in work room environments. The apparent reason for this low

potency is that inhaled sulphur dioxide is nearly completely absorbed in the upper airways and does not reach the lung.

Study Area.

Nairobi is located at about 37°E and 15°S. Most of this area has a daily range of temperature of about 15°C during the hot, dry season (Mid December to mid March) [Mwebesa, 1979]. The main rainy season is from mid March until the end of May, and there is a short rainy season from mid October to mid December. Throughout most of this area the months between the two rainy seasons, especially from June to August tend to be rather cloudy and cool, but are generally dry. Day time temperatures are sometimes less than 20 during July and August. September and early October are much warmer and more sunny, but only a few showers develop. January to March are the hottest months. The mornings are often overcast throughout most of the year. The average annual rainfall at Nairobi is about 875 mm.

The major industrial area is close to the city center (figure1). There has been a rapid industrialization in Nairobi with many industries increasing by about a hundred percent over the last two decades (table 1).

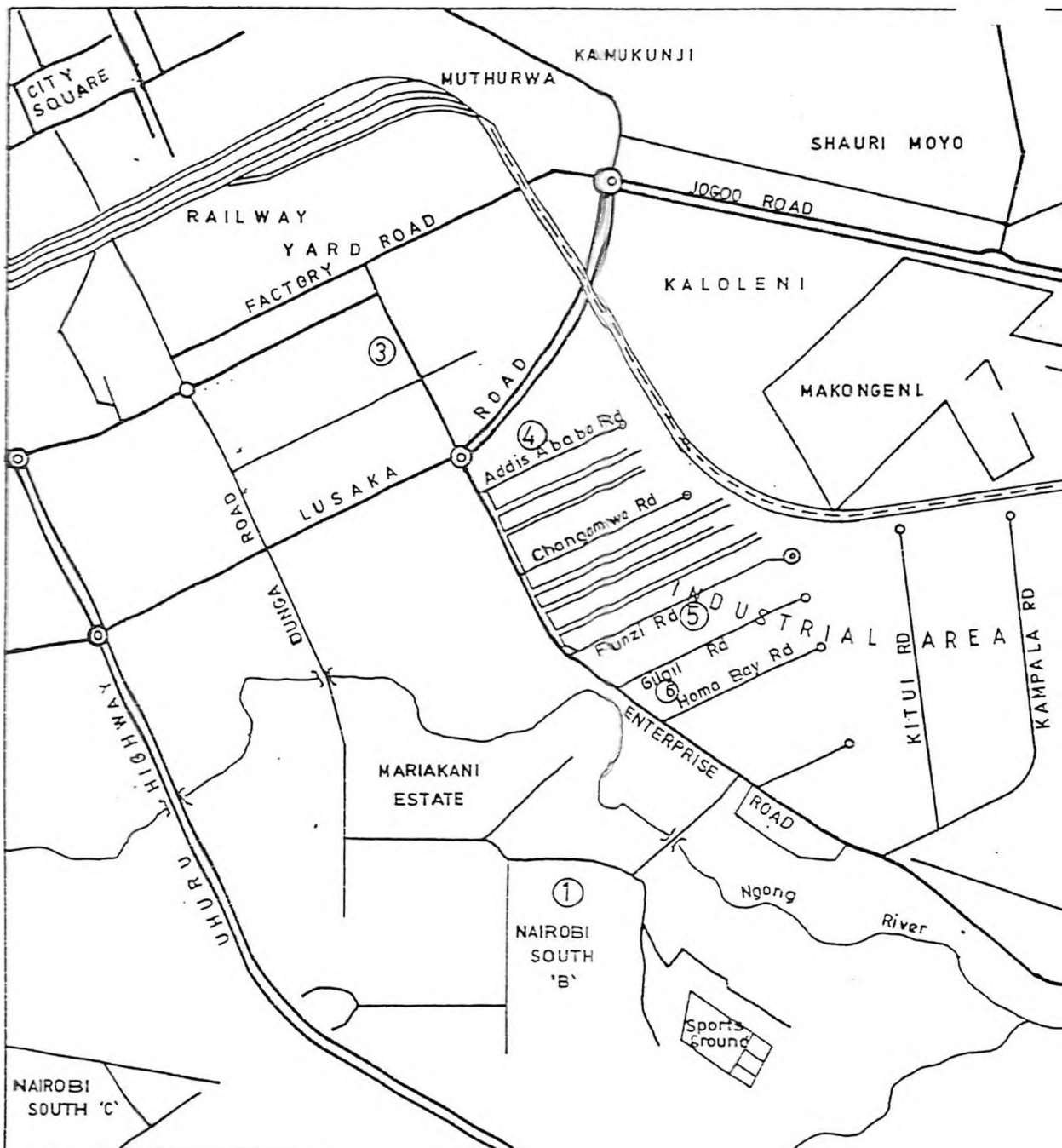
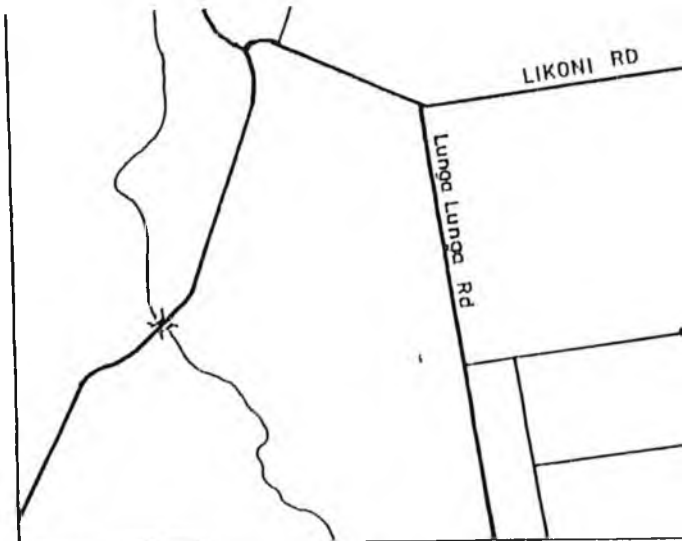
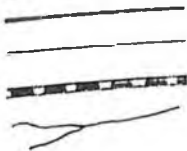


Fig.1 A map of Nairobi showing sampling sites



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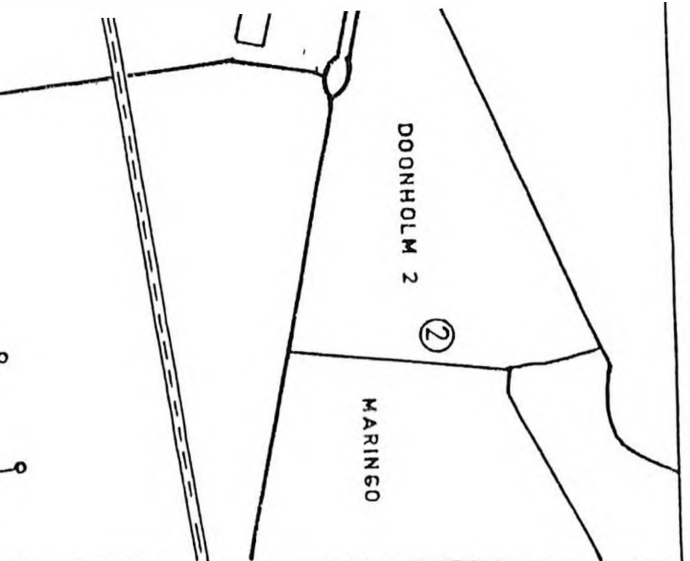


Major Roads

Minor Roads

Railway Line

River



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Table 1. A list of some of the major industries and their emission products in Nairobi.

Type of industry	1978	1993	Type of Pollutants
Grain milling	8	14	Particulates
Wood and cork	4	10	Particulates
Pulp and paper	29	49	Particulates, Sulphur dioxide, carbon monoxide, hydrogen sulphide
Rubber	8	20	Particulates, organic compounds
Plastics	33	83	Particulates, gases
Basic metal industries	10	17	Particulates, carbon oxides and fluoride
Motor Vehicle Assembly	10	27	Particulates
Clay and glass	6	10	Particulates
Liquor and malt	4	5	Particulates, hydrocarbons
Meat and dairy	4	12	Particulates, smoke, nitrogen oxides
Petroleum refineries	2	7	Particulates, hydrocarbons, organic compounds
Metal and Steel industry	21	36	Particulates
Bakery industry	7	15	Particulates, smoke, nitrogen oxides
Sugar and Confectionery	5	8	Carbon monoxide, Particulates
Bevarages	12	20	Particulates, sulphur oxides, hydrocarbons
Tobacco	1	1	Particulates, carbon monoxide
Chemical industry	13	31	Particulates, sulphur oxides, nitrogen oxides

1.7 LITERATURE REVIEW

Various methods have been used to determine pollution concentrations in the atmosphere. The most commonly used are: use of air quality models, the actual measurement of the pollutant concentrations and analysis of the chemical composition of rainwater as an indicator of pollution levels. Recently, satellite information has been used to study pollution levels [Lyons et al., 1977].

Turner et al [1973] estimated annual SO_2 and total suspended particulates for the New York air quality control region in 1969 using six different dispersion models. A good estimate of the mean and maximum SO_2 concentration was found using the climatological dispersion model. By using a model which depicts the catalytic oxidation of sulphur dioxide to sulphuric acid in dispersing stack plumes Freinberg [1976] investigated the effect of temperature and relative humidity on the conversion of sulphur dioxide to sulphuric acid in dispersing plumes. He found that at 5°C the fractional yield of sulphur dioxide is sensitive to relative humidity in the range of 40-80% while at 30°C it is sensitive to relative humidity only when the relative humidity is higher than 90%. Thus relative humidity plays a more or less important role in determining the extent of oxidation of sulphur dioxide, depending on temperature. The one dimensional steady state model has been used to study the influence of clouds and rain on the vertical distribution of sulphur dioxide [Gravenhorst et al., 1977]. The calculated sulphur dioxide volume mixing ratio were found to decrease from 1ppbv at the ground level to 0.01ppbv in 15km altitude. The

estimates of emissions and meteorological data, have been used to predict dispersion and deposition over Europe [Eliassen and Saltbones, 1983]. The wet depositions were found to exceed the predictions of the model, i.e. it could not be accounted for by European emissions. The excess is thought to reflect long range transport (from north America) or a complex recirculation of European emissions (including those from north east Europe). Rolph et al., [1992], compared three - month averages of modeled air concentrations of SO_2 and SO_4^{2-} with measurements from five National Oceanic and Atmospheric Administration / Air Resources Laboratory dry deposition sites. The modeled values tended to under predict air concentrations of SO_2 and over predict air concentrations of SO_4^{2-} .

Gaussian plume models are routinely applied in studies of environmental impact [Huber, 1990]. This form assumes that the plume spread has a Gaussian distribution, the wind affecting the plume is uniform and the plume is perfectly reflected at the surface. Applications of this equation to environmental studies are reported in literature [Turner, 1970 and Pasquill, 1974]. This equation is used to provide estimates of pollutant concentrations depending on the persistence of the wind direction.

The diffusion models generally assume that the pollutants remain in the atmosphere, with perfect reflection at the underlying surface [McCormac, 1971]. This is usually a satisfactory assumption for travel distances of a few hundred meters in the absence of fog or precipitation. Most models assume that the surface structure is

uniform, thus assuming that mechanical eddies, thermal eddies and wind structure are constant. It is very rare that surface structure remains homogeneous over a relatively long distance. Hence wind structure, atmospheric stability will not remain constant. This is more so, especially in urban areas. Hence actual measurement of pollutant concentrations gives a better presentation of pollution levels than calculations based on diffusion models.

Chemical composition of rain water study has also been used as an indicator of pollution in most urban cities. Most of the available information is based on samples of bulk precipitation. This means that the collectors are open to the atmosphere at all times and collect rain, snow, and dry fallout. Bromfield [1974] studied the deposition of sulphur and sulphates in the rainwater in northern Nigeria. Highest concentrations were found in April and October and lowest in August collection period, when rainfall was highest. High April concentrations were attributed to the anthropogenic sulphur in the form of ash and gaseous sulphur that is released just before the onset of the rains by farmers clearing and burning natural fallows for planting. Parurgo et al., [1990] found that the rain samples collected in the Gulf of Mexico were very acidic. Sulphate and nitrate ions were found to be the major constituent pollutants of the rainwater. This method is now widely acknowledged to be of limited value because of its poor sampling characteristics for dry deposition [Gate, 1991]. For many ions, particularly those residing on large airborne particles, urban bulk sampling yielded considerably higher concentration than found in samples collected in wet only samplers. The sulphate and nitrate ions

were among those ions with some tendency to occur in higher concentration.

In an effort to determine sulphur dioxide levels in the atmosphere, various measurements have been carried out. Previous studies of SO₂ tended to concentrate on developed countries presumably due to their high emission rates. De Bary and Junge [1963] at the monitoring stations in Europe and North America, found higher SO₂ concentrations in winter than in summer. Raynor et al. [1974] measured SO₂ concentrations in the suburban Long Island (United States). Sulphur dioxide concentrations were found to be minimum at noon, in the late afternoon or evening, and after midnight. Maximum concentrations were found in the morning soon after sunrise. On the annual cycle, highest concentrations occurred in winter and lowest in summer. Similar results were found by Cleroux et al., [1980], who found 150% higher sulphur dioxide concentration in winter than in summer, in Montreal. The SO₂ pollution was found to be locally dependent on emission sources, mainly near the oil refineries.

On large scale basis, Georgii [1977] found that measurements of the horizontal distribution of SO₂ showed a decrease of the concentration from the continent to the oceans. He found higher winter values than summer concentrations. The higher winter values are caused by additional anthropogeneous sources and secondly by lower mixing-heights during winter. The difference between winter and summer values were only found in the lower troposphere up to 3 km altitude. Smith et al., [1977] studied the transport of sulphur dioxide in power

plant plumes from aircraft measurements. The sulphur dioxide emitted during morning hours was found to undergo rapid mixing near the plant. The plume however maintained its identity on being mixed through the mixing layer. Sulphur dioxide emitted at night remained decoupled from the ground and was shown to be transported more than 300Km by midnight in the light wind region aloft. The sulphur dioxide emitted at night remained decoupled from the ground and experienced much less dilution.

De Wiest [1978] made a survey in Belgium of air pollution increase due to the atmospheric conditions. Atmospheric concentrations of SO₂, NO and CO were measured. Highest concentrations were characterized by meteorological parameters; low wind speeds, negative air temperature, strong temperature inversions - all encountered at the same time.

Despite the numerous study undertaken for SO₂ concentration in urban atmospheres, the continental background of SO₂ in regions not directly influenced by anthropogenic emissions has remained largely unexplored. Breeding et al. [1973] has summarized the few data in existence. For example, Georgii [1970] measured 0.75 ppbv in Colorado, Lodge et al. [1974] found 0.1-1.3 ppbv in the American tropics. Fischer et al., [1968] reported a range of 0.3-1.4ppbv for Antarctica.

Whereas detailed studies on pollution measurements especially sulphur dioxide has been done in developed countries, little work has been

carried out in developing countries. However, it is usually considered unlikely that air in tropical areas can become polluted to harmful levels. Peterson [1966] estimated that the air pollution potential (inability of the atmosphere to disperse pollutants) of most tropical regions is low. More recently Ng'ang'a [1980] concluded that in tropical regions "air pollution may not become such a serious problem unless or until the rate of industrialization is dramatically increased". There are however, a number of examples of pollution problems in the tropics. Gerish [1972] found that atmospheric conditions in 'tropical' Florida could lead to severe pollution episodes.

In Africa, Egypt has a fairly extensive SO₂ measurements reported in literature. Measurement at a number of sites found monthly means to be regularly in the range of 100-300 µgm⁻³ [Commins, 1987]. Seasonal means of SO₂ concentrations were 140-430 µgm⁻³ in city center locations and 60-140 µgm⁻³ in residential sites. Annual means were 260-290 µgm⁻³ in the city center and 90-110 µgm⁻³ in the residential areas. Generally, higher concentrations were found in the summer months and the lowest concentration in winter. The data presented is however, unreliable. This is because the main monitoring method used was acidimetric titration (hydrogen peroxide). It was shown that due to high atmospheric ammonia concentrations and high temperatures this method was unreliable [Nasralla et al., 1984a; Commins, 1987].

In Kenya, the only known SO₂ measurement done was in 1977-1978 for the GEMS (Global Environmental Monitoring System) data, [WHO, 1980]. The data is however, inconclusive since no more than

eight measurements were carried out at each site in each year. Ng'ang'a and Ngugi [1987] estimated the acid deposition due to industrial activities in some major towns in Kenya. The central part of Kenya (Nairobi and Thika) were shown to have the highest deposition rates. This was attributed to the large industrial areas in these places. Ng'ang'a [1989] studied the chemical composition of rainwater in Kenya. It was found that chemical composition of rainwater in Kenya is not significantly affected by emissions from man-made sources. He concluded that the industrial development in Kenya has not reached a stage where emission levels can have significant impact on the rainwater from the point of view of acidification.

1.7.1 Objectives of the present study

From the foregoing discussion, it is evident that at high concentrations, sulphur dioxide can cause detrimental effects on human health, plant life and materials. The aim of the study was to assess the air quality in Nairobi in the context of sulphur dioxide. The effect of meteorological factors such as wind speed and direction, temperature, humidity, cloudiness and rainfall on the concentration of sulphur dioxide have also been investigated.

The study was carried out at the Industrial and residential areas (Fig 1). This was to find whether or not there was any significant contribution of sulphur dioxide from the industries.

The study is important in determining the influence of specific emission sources or groups of sources on local air quality. The information is

important in planning of pollution control and industrial and municipal zoning strategies. Areas with high pollution potential could be zoned off from residential development. By knowing the relationship between concentrations and meteorological parameters, emission rates could be reduced during those months characterized by poor dispersion conditions.

1.7.2 Description of Sampling sites

Six sampling sites were chosen for the study as shown in figure 1. Most of the sampling points were at the Industrial area which is South east of the city centre. Four sites were chosen at the Industrial area. These are Prisons (site 3), Addis Ababa (site 4), Funzi road (site 5) and Gilgil road (site 6). Prisons and Addis Ababa are situated closer to a number of Industries, on the north eastern side of the Industrial area. These sites are down wind of the Industrial area. Funzi road and Gilgil road are almost at the centre of the Industrial area. South B (site 1), is located at about 1 Km, on the South westerly of the Industrial area, while Makadara (site 2) is about 1.5 Km north of the Industrial area.

CHAPTER TWO

2.0 THEORY AND METHODOLOGY

2.1 Sulphur Dioxide

Sulphur dioxide is a colourless gas at room temperature, non-flammable with a pungent odour and acid taste. It is readily absorbed by snow, humid soil and plants. Sulphur dioxide has a melting point of -76.1°C and boiling point of -10°C . It combines readily with water to form sulfurous acid (H_2SO_3) and thereafter, is more slowly oxidised to sulphuric acid (H_2SO_4). Sulphur dioxide is one of the most widely encountered contaminants of the air environment.

The beneficial effect of sulphur dioxide are the relief of sulphur deficiencies in soils and control of certain fungal diseases, such as 'black spot' in roses [John and Fletcher, 1977].

Once sulphur dioxide is released in the atmosphere, various factors will determine its removal from there. Such removal mechanisms are discussed in section 2.2

2.2 Removal Mechanisms of SO_2 in the atmosphere

There are several ways in which sulphur dioxide is removed from the atmosphere.

2.2.1 Dry deposition

This is the transport of particulate and gaseous contaminants from the atmosphere into surfaces in the absence of precipitation. Gases are sometimes reversibly adsorbed onto surfaces, whereas particles may be deposited and subsequently resuspended [Lindberg et al., 1989]. The physical and chemical properties of the surface onto which the gases are deposited determines the ultimate fate of contaminants, once deposited. A relatively nonreactive smooth surface may result in rapid bounce off of particles and may not permit absorption or adsorption of certain vapours. A

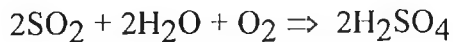
rougher, more reactive surface favours greater deposition rates. For gases, solubility and chemical reactivity are the dominant factors affecting uptake by the surface.

2.2.2 Oxidation

In the atmosphere, as the exhaust plume containing sulphur oxide disperses, oxidation of SO_2 to SO_3 continues. Since SO_3 is hygroscopic, it will dissolve in water, thus forming sulphuric acid.

Much of the remaining gaseous SO_2 may then be oxidized as it diffuses to the droplets and is dissolved. The oxidizing agent is molecular oxygen which has also been dissolved in the droplets.

The reaction proceeds according to the following overall equation:

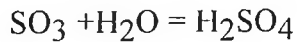
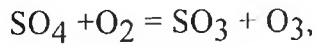
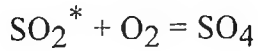


Iron and manganese have been known to catalyze this process [Calvert et al. 1985]. These particles serve as nucleation sites for droplet formation and at high concentrations of SO_2 often emitted in industrial plumes, molecules of SO_2 can readily diffuse into the interior of a droplet where they may come into contact with the nucleating particle. Oxidation will then proceed throughout the droplet. This production of H_2SO_4 lowers the vapour pressure of the droplet, and encourages more water molecules to diffuse through the air to the liquid surface and condense.

Metal oxides such as Magnesium oxide, Iron oxide, Zinc oxide and Manganese oxide react with the surrounding sulphuric acid to form metal sulfates, with the result that the liquid of the droplet is maintained as a relatively neutral solution. This makes possible the absorption of still more SO_2 from the air.

The other mechanism responsible for some oxidation of SO_2 in the atmosphere involves the photoexcitation of the SO_2 molecule through its absorption of solar radiation. $\text{SO}_2 + E = \text{SO}_2^*$, where E is the absorbed solar energy, and SO_2^* represents an excited sulphur dioxide molecule

whose electrons describe orbits with a higher total energy than that of the unexcited molecule. The excited sulphur dioxide readily reacts with certain atmospheric constituents such as molecular oxygen [Leighton, 1961]. Several other reactions then follow to complete the oxidation to sulphuric acid.



Experiments indicate that the reaction rate for bright sunlight is still fairly slow, less than 2% of the SO_2 is oxidized during an hour. This process is thus not as effective as the catalyzed oxidation in a humid atmosphere.

Naturally occurring ammonia (NH_3) is a key factor which determines the mean life time of SO_2 in the troposphere [Williamson, 1973]. When tropospheric NH_3 is absorbed in water droplets together with SO_2 , it will neutralize the solution as the SO_2 oxidizes and will thus encourage more absorption of SO_2 and accelerate its removal from the atmosphere. This process is accelerated appreciably at lower temperatures such as those commonly found at a height of several kilometers above ground [McKay, 1971].

Vegetation too plays a very important role in the scavenging of gases in the atmospheres SO_2 being one of them. For most forest tree species, gas exchange is modulated by the equation:

$$U = \frac{C_a - C_{i/s}}{r_{bl} + r_s + r_{m/s}} + \frac{C_a - C_{sfl}}{r_{bl} + r_{sfl}}$$

[Benett et al, 1973 and O'Dell et al. 1977].

In the above equation the uptake flux density to the leaf (U) is proportional to the gradient of pollutant concentration between the air (C_a) and the concentration at leaf surface (C_{sf}) or at the uptake sites inside the leaf ($C_{i/s}$). Uptake to the leaf surface is limited by the boundary layer resistance (r_{bl}) of the leaf and the additional resistance to uptake due to the leaf surface (r_{sf}). Uptake to the internal sites is limited by the boundary layer resistance, the resistance through the stomata on the leaf surface (r_s), and the internal, mesophyll resistance ($r_{m/s}$).

The concentration of gases such as SO_2 affect the stomata size [Majernick and Mansfield, 1970]. At relative humidities above 40%, stomatal opening occurred at SO_2 levels as low as 25 ppm. At lower relative humidities in the same range of exposure, the stomata closed. When exposures were for a few days, permanent opening was observed.

2.3 Methodology

There are a number of methods employed in the measurement of sulphur dioxide in the atmosphere. A few methods are discussed here.

2.3.1 Colorimetric Methods-West-Gaeke

In the modified West-Gaeke colorimetric method SO_2 is collected in sodium tetrachloromercurate (II) (TCM) to form a dichlorosulfitomercurate complex (DCSM) which resists oxidation by either the oxygen in the air or that dissolved in the absorbing solution. Heavy metals that could oxidize sulphur dioxide before DCSM formation is complete are complexed by addition of ethylenediamine tetraacetic acid disodium salt (EDTA) to the TCM absorbing solution [Scaringelli, et al 1970].

A major source of error associated with the analysis of sulphur dioxide by the West Gaeke colorimetric procedure is the widely differing collection efficiency reported for the Greenburg-

Smith and midget impingers when atmospheric concentrations decrease to the $26\mu\text{g}/\text{m}^3$ (10 ppb) level [Adams, 1972].

2.3.2 Other colorimetric methods

Attari [1970] absorbed sulphur dioxide into a solution of ferric ammonium chloride, perchloric acid, and phenanthroline dye. A color complex with an absorbance at 510 nm was formed. The colour which developed within 10 minutes, tended to fade with time. Hydrogen sulfide was found to interfere.

2.3.3 Conductivity Methods

The most common method is that which is exemplified by the Thomas Autometer [1962]. In this method, the conductivity of a dilute sulphuric acid - hydrogen peroxide reagent changes due to the absorption of pollutants. The change in conductivity is assumed to result primarily from sulphur dioxide absorbed from the sampled air and oxidized to sulphuric acid. Sensitivity limit of these instrument generally averages $131\mu\text{g}/\text{m}^3$ (50 ppbv); however, they are nonspecific, since conductivity change may result from any material which is collected by the absorbing solution which alters its conductivity. If other pollutants are also present, their solubility, or their collection efficiency in the scrubber may be significantly lower than that for sulphur dioxide.

2.3.4 Iodometric Methods

In the iodine method, the sulphur dioxide is collected in an impinger containing a standard solution of sodium hydroxide. After sample collection, the absorbing solution is acidified and the liberated sulphurous acid is titrated with standard iodine solution [Jacobs, 1960]. This method responds to the total reducing gases present in the sample, including hydrogen sulfide and methyl mercaptan. The method is unsuitable for field application, unless laboratory facilities are available for immediate titration of the samples.

2.3.5 Filtration Methods

Pate et al. [1963] collected SO_2 by filtering air through potassium bicarbonate impregnated type AA Millipore filters. The filters are then analyzed for collected sulfate. The collection efficiency of impregnated filters is dependent upon humidity, temperature, and the atmospheric concentration of sulphur dioxide. The collection efficiency was however found to decrease rapidly below 25% relative humidity.

2.3.6 Determination of sulphur dioxide by Fluorescence

Continuous and automatic monitoring of sulphur dioxide by fluorescence is based on the fact that if SO_2 is irradiated with ultraviolet light, fluorescent radiation is emitted in a continuous spectrum between 240 and 420 nm, with a maximum at about 320 nm, Schwarz et al. [1974].

Fig. 2 illustrates a typical instrument. Light from a UV source is focused by lens and passed through a filter to suppress the wavelengths that are in the range of the fluorescence spectrum of SO_2 (longer than 300 nm). This is necessary because otherwise stray light reaching the detector would be taken to be fluorescence radiation. Ambient air is passed through the measuring cell at a constant rate. Sulphur dioxide, if present in the air, will be excited and will emit fluorescent radiation, which is picked up by a photomultiplier provided with a filter and a honeycomb structure to remove, as far as possible, stray light that might contribute to the signal.

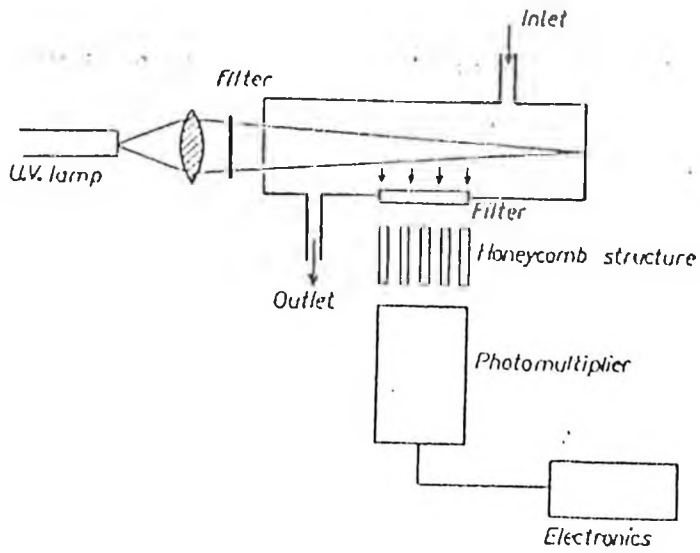
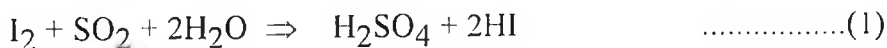


Figure 2 Fluorescence SO₂ monitor. Ultraviolet light from a source passes through a filter to remove light of longer wavelengths into the measuring cell. The fluorescence radiation in the direction perpendicular to the incoming beam is filtered and passes by way of the honeycomb structure (to interrupt stray light) to the photomultiplier. (Source: Strauss, 1978)

2.3.7 Rapid Quantitative method

This is the method which is currently employed by Kenya's Ministry of Labour. It is based on the classical chemical reaction between iodine and sulphur dioxide (Equation 1)



2.3.7.1 Reagent and Apparatus

1. Iodine 0.1N solution. 1.27g of iodine and 4.0g of potassium iodide are weighed in a small beaker. About 15 mL of distilled water is added and stirred until it is dissolved. This is then transferred into a volumetric flask of 100 mL and filled up to the mark with distilled water. The contents are then kept in a dark bottle.

Since the atomic weight of iodine is 127g, 1.27g of iodine in 1 litre of water gives a normality (N) of $1.27/127 = 0.01\text{N}$ iodine. In 100 mL of water the normality will be 0.1N iodine.

2. Iodine 0.0001N solution. A fresh solution is prepared. 1 mL of 0.1N iodine solution is pipette into a volumetric flask of 1000 mL and filled up with distilled water to the mark.

According to reaction(1), 1 mL of 0.0001N iodine solution corresponds to 0.0032 mg of SO_2 . This is so because 1 mL of 0.0001N iodine solution contains $1/1000 \times 0.0001/2$ moles of iodine. Hence for complete reaction $1/1000 \times 0.0001/2$ moles of iodine will react with the same number of moles of sulphur dioxide.

SO_2 has molecular weight of 64 g; therefore $0.0001/2 \times 1/1000$ moles of SO_2 will have a weight of $0.0001/2 \times 1/1000 \times 64$
 $= 32 \times 10^{-7}$ g of SO_2 or 0.0032 mg.

3. Starch, 1% solution. 1g of starch is mixed with 10mL of distilled water in a beaker and 90ml of boiling distilled water added. The mixture is heated on a water bath for 5 minutes and cooled. In this method, starch is used as an indicator.
4. Sampling air pump. A T-glass joint with tubing at the two ends is attached between absorbing tube and a pump to regulate input and output of air. The sampling pump was calibrated by setting a suitable flow rate (fig. 3).

2.3.8.2 Procedures

10ml of 0.0001N iodine solution is placed into an absorber (impinger tube) and 1 drop of starch solution added. This turns the solution blue in colour.

The air sample is drawn through the solution by a pump until the blue colour just disappeared. The volume of air drawn through the iodine solution is noted.

2.3.8.3 Calculation

SO₂ concentration is calculated using the following equation.

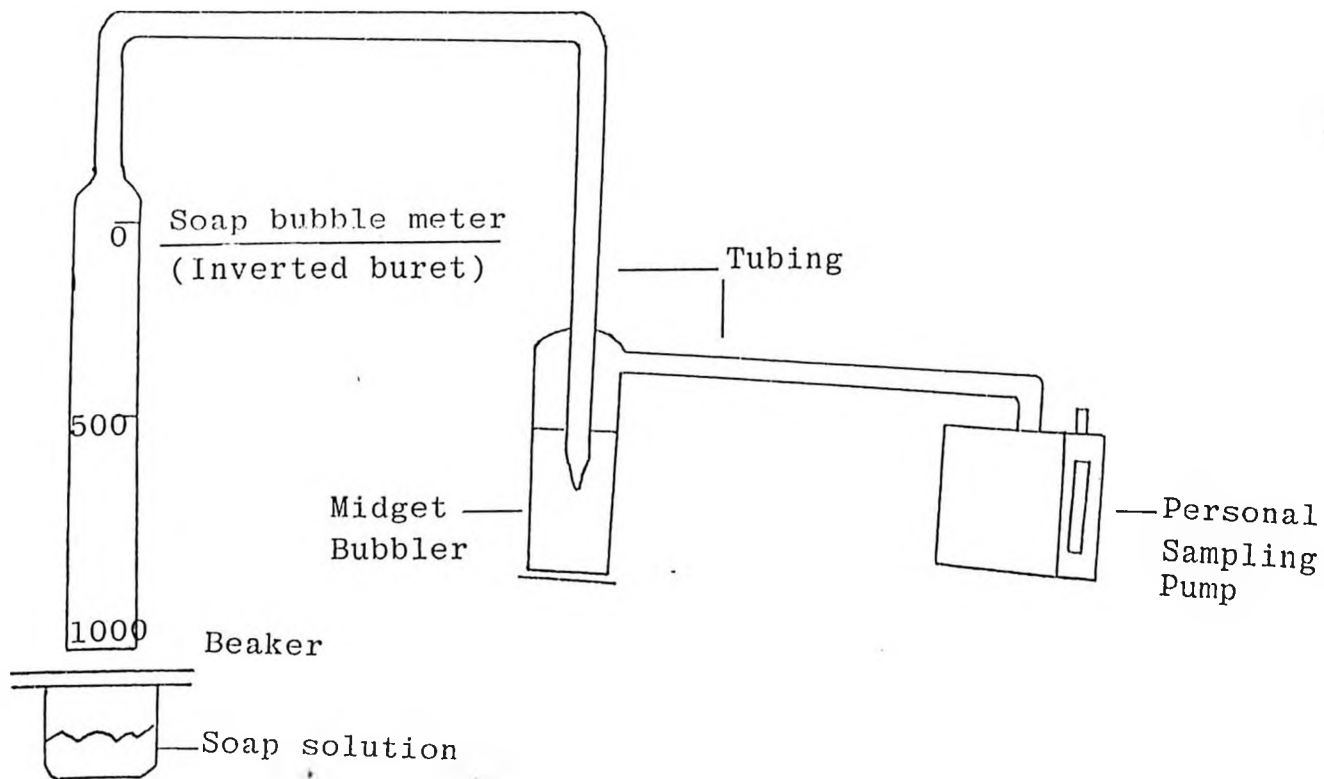
$$\text{ppmSO}_2 = \frac{10 \times 0.0032 \times 22.415}{V \times 64.06} \quad \dots\dots\dots (2)$$

Since 10ml of iodine solution is used, for complete reaction the number of SO₂ moles will equal

$$\frac{10 \times 0.0032 \times 10^{-3}}{64.06}$$

At room temperature, 1 mole of ideal gas occupies a volume 22.415 litres . Assuming SO₂ behaves like an ideal gas

Fig. 3: Calibration set up for personal sampling pump with midget bubbler



$$\frac{10 \times 0.0032 \times 10^{-3}}{64.06} \text{ moles will occupy } \frac{10 \times 0.0032 \times 22.415}{64.06}$$

litres of SO₂.

The above litres are contained in a volume V litres of air.

Therefore SO₂ concentration in ppm equal

$$\frac{10 \times 0.0032 \times 10^{-3} \times 22.415 \times 10^6}{64.06 \times V} \text{ ppm SO}_2$$

2.3.9 Pararosaniline Method

The Pararosaniline method is based on the absorption of SO₂ from the air in a solution of (trans-1, 2 cyclohexylenedinitrilo) tetraacetic acid (CDTA). Sulphur dioxide, in ambient air sample, is collected in a buffered formaldehyde absorber solution, which enhances the collection efficiency and stabilizes the resulting sulfite from oxidative loss. Potassium hydrogen phthalate is used as the buffer in the absorber and formaldehyde as the stabilizer for the sulfite species which forms the oxidation resistant species, hydroxymethanesulfonate [Dasgupta et al. 1980]. The intensely coloured pararosaniline methylsulfonic acid is the basis of the analytical measurement.

2.3.9.1 Range and Sensitivity

Atmospheric sulphur dioxide concentrations measurable by this technique range from 10ppbv (parts per billion by volume) to about 5ppmv (parts per million by volume). Below 10ppbv, collection efficiency falls off rapidly. The lower limit of detection is 0.3 microlitre(μL) gaseous SO₂ in 15mL of formaldehyde absorber representing a concentration of 10ppbv (26μg/m³) SO₂ in an air sample of 30L. One cannot extrapolate to lower values by taking larger volumes of air.

Beer's law is followed through the working range from 0.1 to 0.7 absorbance units (up to 30μg in 25mL final solution).

2.3.9.2 Interferences

The principal known interferences in SO₂ sampling are oxides of nitrogen, ozone and heavy metals (e.g. iron, manganese, and copper). In this method the interferences have been minimized or eliminated. Sulphuric acid eliminates interferences by oxides of nitrogen. Delaying the analysis lets the ozone to decompose while the interference by the transition metals is eliminated by trans-1, 2 cyclohexylenedinitrilo) tetraacetic acid (CDTA).

2.3.9.3 Precision and Accuracy

The precision at the 95% confidence level is 2.7% for SO₂ concentrations of 1µg/mL in the absorber [Dasgupta et al. 1980].

2.3.9.4 Apparatus

In this study, Midget impinges were used as the absorbers, personal air sampling pumps were used for volume measurements and the spectrophotometer for colour measurement. The GL-tubes were used for storage of SO₂ containing solution prior to analysis.

2.3.9.4 Reagents

1. Purified pararosaniline dye, is recommended for use in this method [Stern, 1976]. During the project exercise impure pararosaniline was used because it was not possible to obtain the dye in the purified form.

The influence of dye purity on analytical procedure has been considered by several authors [Pate et al., 1962 and Scaringelli et al., 1970]. Purity of the pararosaniline dye affects the sensitivity of the colorimetric procedure although not necessarily the accuracy or reproducibility when a standard curve of absorbance versus concentration is prepared for each dye lot, and all other analytical conditions are held constant.

2. Distilled water; was used as a solvent.

3. Sodium hydroxide, **4.5M (molar)**. This was made by placing 18 grams of solid NaOH and about 80mL water in 100mL volumetric flask. After NaoH had dissolved and the solution cooled, the final solution was diluted to the mark and then stored in a plastic bottle.
4. A 5×10^{-2} M stock CDTA solution; was produced by dissolving 1.82g CDTA and approximately 0.4g NaoH in water then diluting to 100mL.
5. Buffered formaldehyde absorbing reagent. By diluting 5.30 mL of 37% formaldehyde solution, 2.04g of potassium hydrogen phthalate and 20ml of the 0.05M Na₂ CDTA solution to 1 L (litre), buffered formaldehyde absorbing reagent was formed. This reagent could be stored for one year.
6. Buffered formaldehyde absorber, working reagent. This was produced by diluting the buffered formaldehyde absorbing reagent tenfold with water.
7. Sulfamic acid, 0.6%. This was obtained by dissolving 0.6 of sulfamic acid in 100mL of water and then by addition of dilute NaoH dropwise to adjust to pH 4. When protected from air the reagent could be kept for a maximum of ten days.
8. Hydrochloric acid, 1.0N. Was produced by diluting 83mL of 12.1M acid (37% Hcl) to 1L.
9. Pararosaniline reagent. 133mL of the 0.2% purified pararosaniline solution and 114mL of concentrated HCL was diluted to 1 L with distilled water.

10. Standard sulfite solution. 0.300g of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) was dissolved in 500mL reagent quality water.

11. Dilute sulfite solution. 2mL of standard sulfite solution and 10mL of the buffered formaldehyde absorbing reagent was pipet in 100mL volumetric flask and filled to the mark with distilled water. This sulfite solution is stable for one month and is used to prepare working sulfite standards.

2.3.9.6 Air samples collection Procedure

The air samples collection procedure is shown in fig.3. 15mL of the buffered formaldehyde absorbing solution which was then placed in a midget impinger. The sampling probe-to-absorber linkage was kept short and direct using less tubing. Further downstream of the absorber, a sampling pump calibrated to 0.5 L/min flow rate was used to determine the volume of air sampled. The duration of sampling will depend on the concentration of SO_2 in air. With midget impingers, a sampling rate of up to 0.5L /min is satisfactory. Sampling rates within that range will generally have an absorption efficiency of 98% or greater. The absorber was shielded from direct sunlight by covering it with aluminum foil. By use of a stop watch, the time sampled was noted and volume of air sampled, determined by multiplying flow rate with time. Before every sampling, the flow rate of the pump was checked in the laboratory to ensure that it had a constant flow rate. The same thing was done after every sampling. During the period of study, a flow rate of 0.5 L/m^3 was maintained.

2.3.9.7 Analysis

After collection, 1ml of 0.6% sulfamic acid solution was added to the sample solution. Subsequently, the sample could be stored at room temperature for up to one month with no significant degradation of the collected sulfite [Dasgupta and Decesare, 1982]. For analysis, 1mL of 4.5M NaOH was added from a dispensing pipet to the collected sample. The resulting solution

was carefully mixed, then rapidly added to 5mL of the pararosaniline working reagent in a 25mL GL-tube. The sample pararosaniline solution was immediately capped and mixed by inverting several times. The sample was added to the acidic pararosaniline and not in the reverse order, to prevent lower absorbance values and poor precision [Stern, 1976]. After mixing, water was added to the contents of the culture tube to bring the level up to the neck, giving 25mL of total volume. The absorbance of the resulting colour was measured between 10-15 minutes after preparation at a wavelength of 580nm. Distilled water was used in the reference cell.

2.3.9.8 Calibration

The dilute sulfite solution prepared in 3.3.9.5 contains approximately 8µg/mL of SO₂. A standard calibration series is prepared by diluting x mL of the sulfite standard with (15-x) mL of the absorbing solution. This series of standards was then analyzed as described in section 2.3.9.7. The total absorbance of each solution was plotted against total micrograms of SO₂. This gave a linear relationship. The intercept with the vertical axis of the line best fitting the points usually is within 0.03 absorbance units of the blank (zero standard) reading [Stern, 1976]. Under these conditions the plot need be determined only once to evaluate the calibration factor (reciprocal of the slope of the line). This factor was used for calculation results provided there were no radical changes in temperature or pH.

2.3.9.9 Calculations

The concentration of sulphur dioxide in the sample was computed by the following formula:

$$\text{SO}_2 \text{ concentration in ppm} = \frac{(A - A_0) 0.382B}{V}$$

where

A = the sample absorbance

A₀ = the reagent blank absorbance

0.382 = the volume (μL) of $1\mu\text{gSO}_2$ at 25°C , 101.3kPa

B = the calibration factor, $\mu\text{g}/\text{absorbance unit}$

V = the sample volume in litres corrected to 25°C ,
101.3 kPa (by $PV = nRT$).

2.3.9.10 Effects of Storage

Dasgupta and Decesare, [1982] found that sulphur dioxide solutions collected as hydroxymethanesulfonate were very stable from loss of sulfite when protected from direct sunlight. Samples stored at 22°C for 40 days had a loss of 2.6% sulfite. The loss increased to 12% in 19 days for samples stored in direct sunlight.

CHAPTER THREE

3.0 RESULTS

The results presented are for a period of six months, covering June 1993 up to and including December 1993. The initial plan was to have data for a period of ten months, but using the rapid quantitative method (a method currently used by the Ministry of Labour), the colour change was found to be dependent on temperature. Sulphur dioxide concentration which is related to the colour change of iodine solution was thus found to increase with temperature. This is illustrated in figures 4 and 5, where scatter diagrams of sulphur dioxide concentration versus temperature were plotted during the morning and afternoon sampling periods respectively. Moreover, values obtained using the rapid quantitative method were found to be too high. In some cases, during sunny hot days the iodine solution even after addition of starch was colourless. These coupled with the fact that the method also responds to the total reducing gases present in the atmosphere like hydrogen sulphide necessitated the discontinuation of the method.

The pararosaniline method was employed in favour of rapid quantitative method. This method is described in chapter 4. Sampling was done in the morning hours from 9.00 am to 11.30 am and 2.00 pm to 4.30 pm in the afternoon hours.

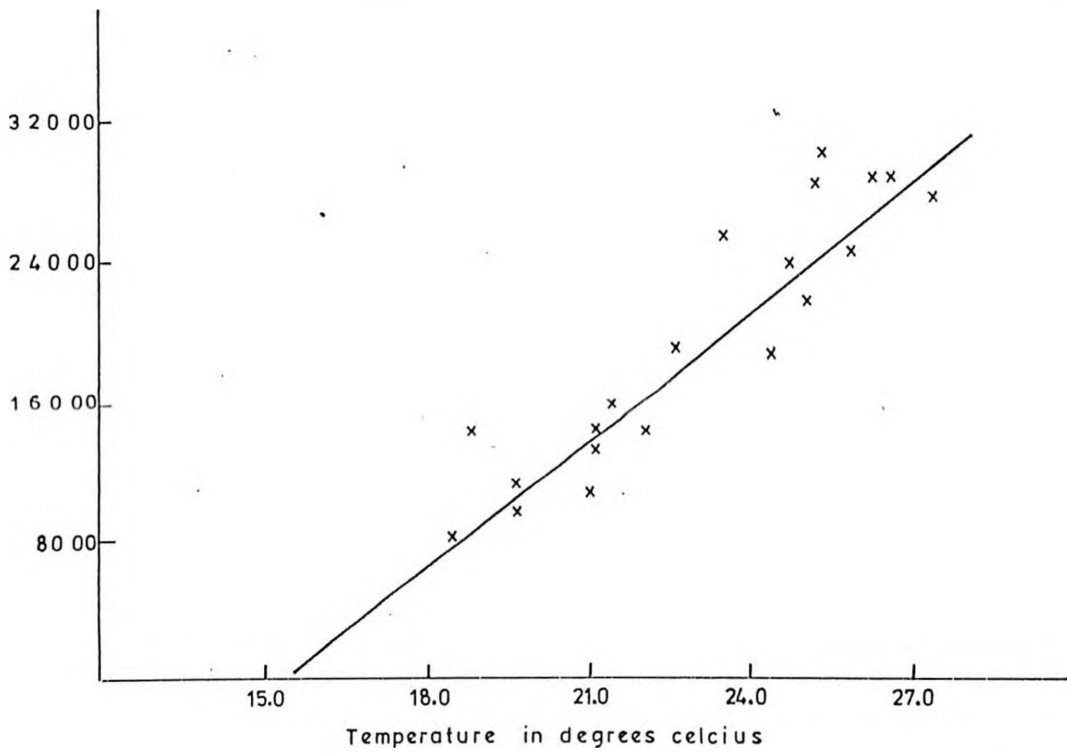


Fig. 4. Variation of morning sulphur dioxide concentration with temperature using rapid quantitative method.

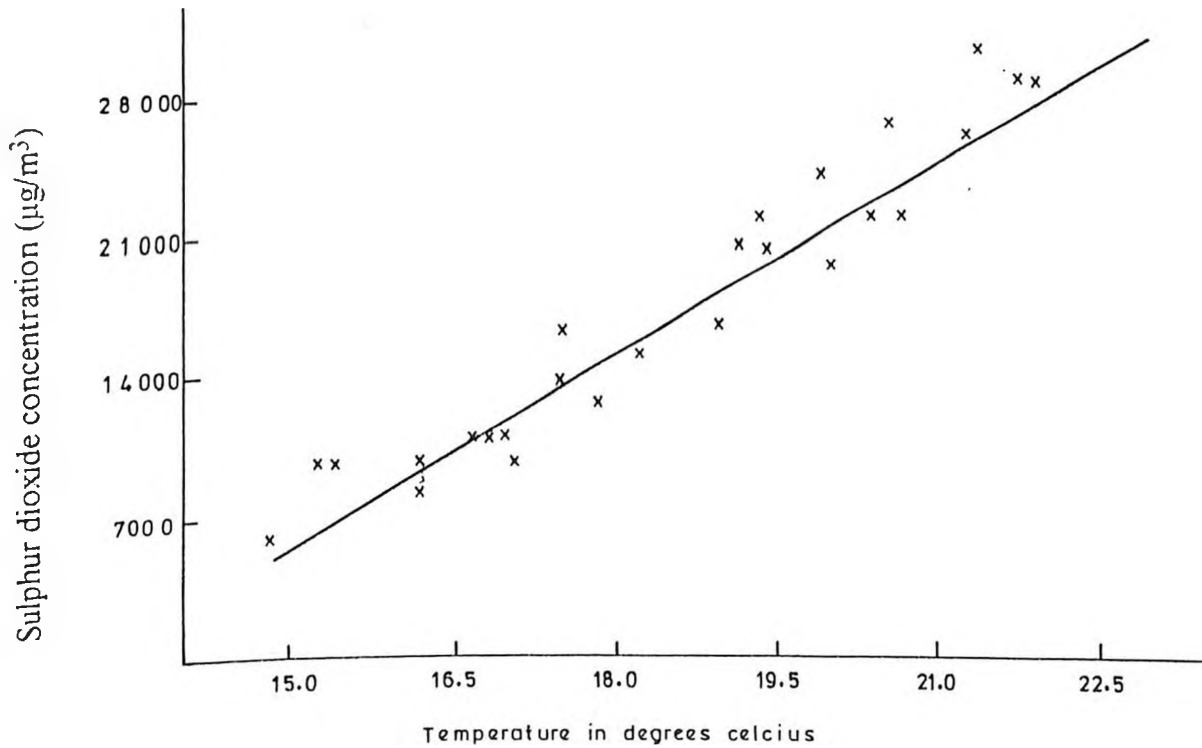


Fig. 5. Variation of afternoon sulphur dioxide concentration with temperature using rapid quantitative method.

3.1 Calibration Curves

The calibration curves were prepared as detailed in section 2.3.9.8. Two calibration curves were prepared, one for the month of June and the other for October (figures 6 and 7). The second calibration curve was plotted when a new pararosaniline solution was prepared in October. In both cases the reciprocal of the slope which is used to calculate SO₂ concentration (section 3.3.9.9) was found to be almost the same. The reciprocal was found by subjecting, Absorbance (Y) and total amount of sulfite as sulfite (X) to regression analysis. The reciprocal of the coefficient of X was then calculated.

For the calibration graph prepared in June, the coefficient of X was found to be 0.007494, giving a reciprocal value of 133.0. The calibration graph prepared in October gave the coefficient of x equal to 0.007484 yielding a reciprocal value of 134.0.

Fig.6 Calibration curve for the month of June

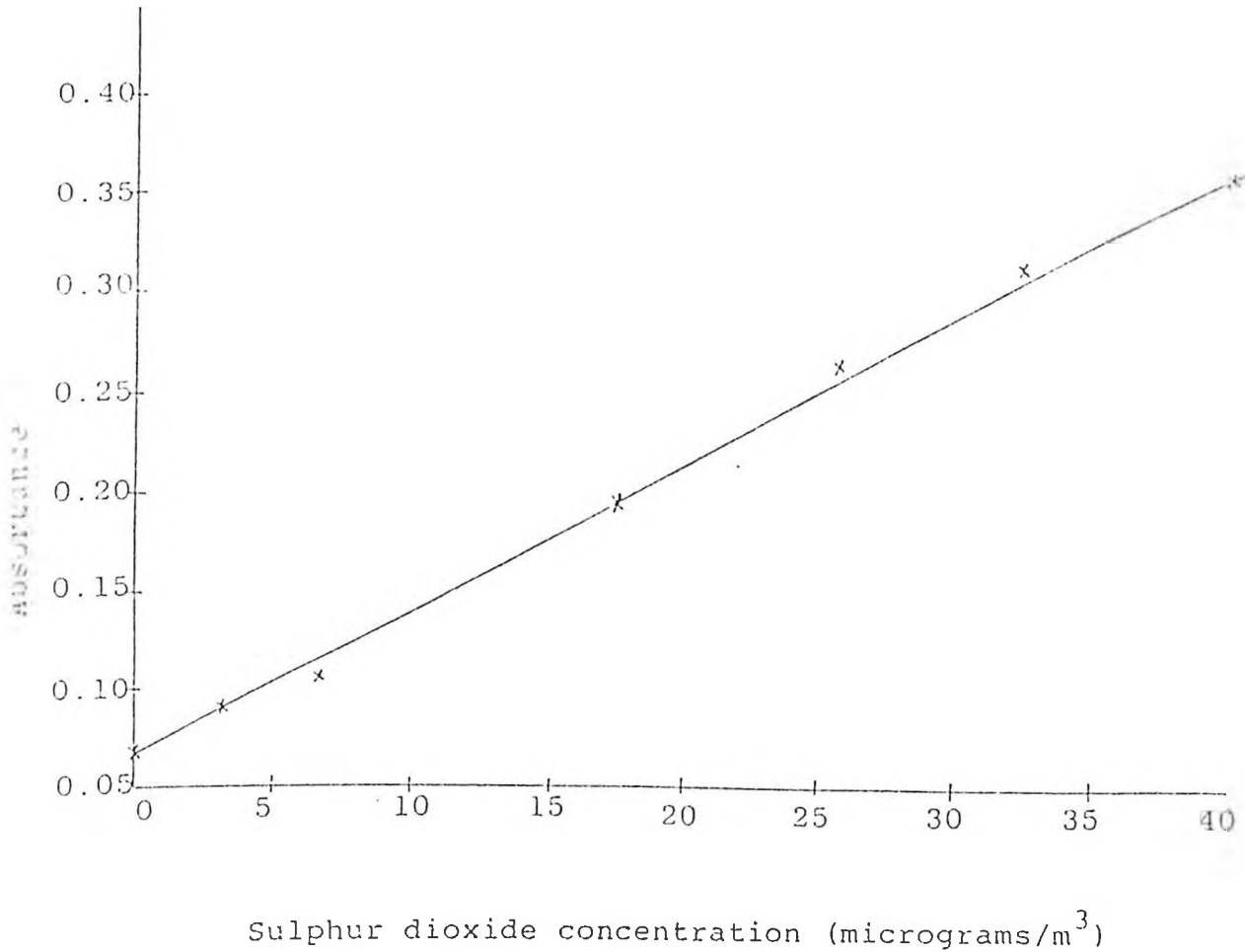
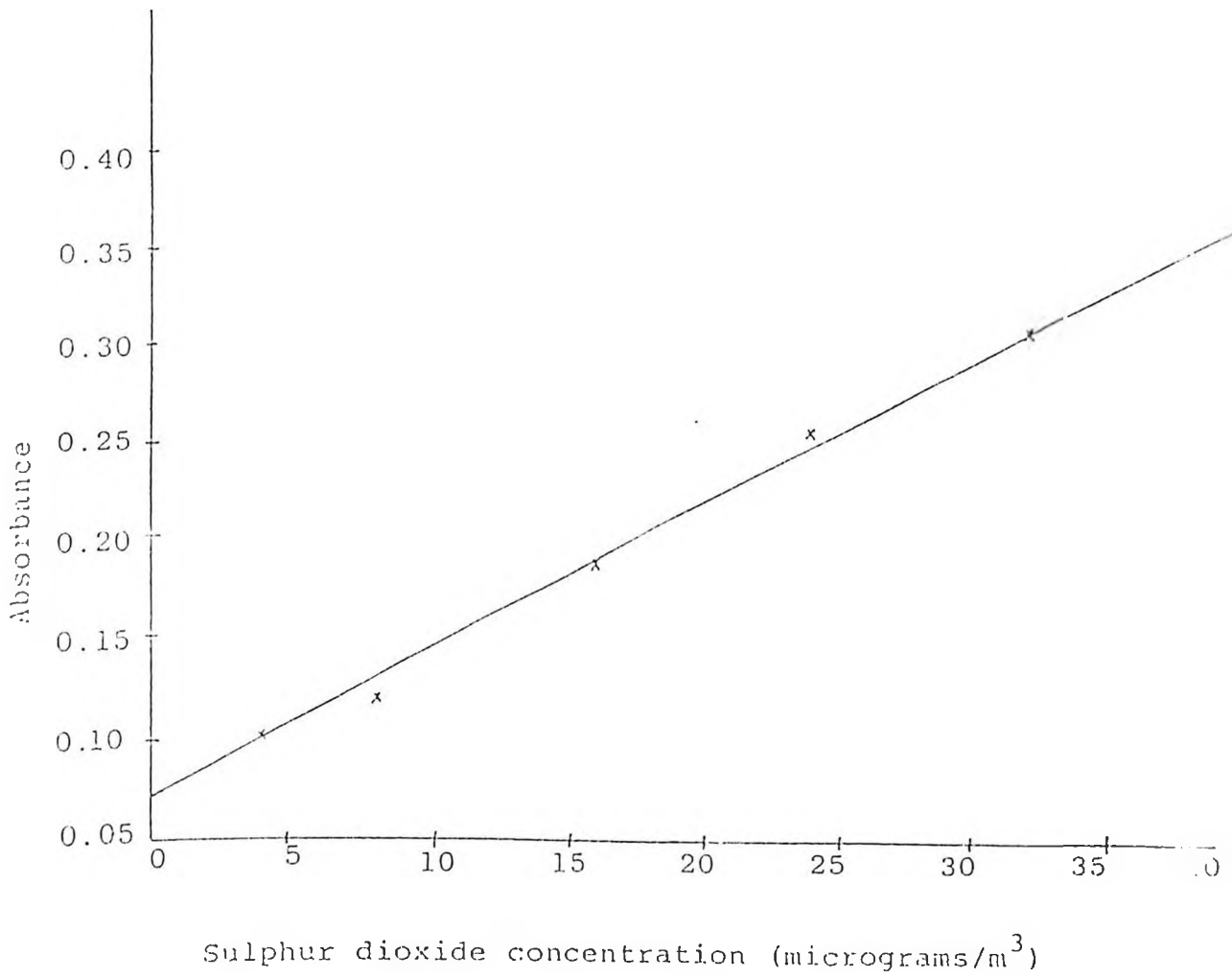


Fig.7 Calibration curve for the month of October



3.2 Correlation analysis

The degree of dependence between two variables is expressed in terms of the population correlation coefficient ρ . In practice an estimate of ρ is obtained by determining the sample correlation coefficient r from a sample of observations selected from the population of all possible observations. The correlation coefficient r is a pure number without units or dimension and r always lies in the interval -1 to $+1$. Positive values imply a tendency for both variables to increase (or decrease) together, negative values indicate that large values of one variable are associated with small values of the other variable.

From a sample of simultaneous observations for two variables (x and y), the correlation coefficient (r) is given by

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\left[\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2 \right]}}$$

Where \bar{x} and \bar{y} are the arithmetic means of simultaneous observations, n is the number of observations and i is the i th observation.

The significance of the correlation coefficients obtained were tested by using students t -test.

3.2.1 Correlations at various sampling sites

Correlations of SO_2 concentration with various meteorological parameters are shown in Table 2. At prisons near the Ministry of labour the correlations were negative with temperature and wind speeds with fairly high correlations with temperature ($r = -0.62$). SO_2 concentration was positively correlated with relative humidity ($r = 0.51$) and cloud cover ($r = 0.32$).

At Addis Ababa Road sampling point, the SO₂ concentration was negatively correlated with wind speed ($r = -0.35$) and temperature ($r = -0.65$). Correlations with relative humidity were quite high ($r = 0.67$). Cloud cover was also positively correlated with SO₂ concentrations although the correlation coefficient was low ($r = 0.30$).

At Funzi road SO₂ concentration showed good correlations with wind speed ($r = -0.66$) and temperature ($r = -0.66$). There was positive correlation with relative humidity ($r = 0.59$) and cloud cover ($r = 0.45$).

Gilgil road sampling site had highest correlations with meteorological parameters. Correlations with wind and temperature were all negative ($r = -0.83$) in each case. Correlations with relative humidity and cloud cover were positive $r = 0.72$ and 0.52 respectively.

At Makadara sampling site SO₂ was negatively correlated with wind speed ($r = -0.27$) and temperature ($r = -0.50$). SO₂ was poorly correlated with cloud cover ($r = 0.02$) and showed fairly high correlations with relative humidity ($r = 0.48$).

At South B SO₂ was negatively correlated with wind speed ($r = -0.45$) and temperature ($r = -0.40$). With relative humidity the correlations were a little bit high ($r = 0.50$) and weakly correlated with cloud cover ($r = -0.09$).

In all sites SO₂ concentration was negatively correlated with wind speed and temperature. Correlations with temperature was most significant in most sites. Except for South B where SO₂ concentration was weakly correlated with cloud cover ($r = -0.09$), correlations, between the concentration and, humidity and cloud cover was positive although correlations coefficients with cloud cover were quite low at most sites.

From these correlations, wind speed, temperature and humidity are the most important meteorological parameters affecting SO₂ concentrations.

The volume of air into which the effluents are emitted is directly proportional to the wind speed, and the concentration of the effluents is inversely proportional to the wind speed.

This is well illustrated by the Gaussian plume equation (Eq. 4.2).

$$\chi(x,y,z) = \frac{Q}{(\pi u \sigma_y \sigma_z)} \exp -1/2 \left(\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2} \right) \dots\dots\dots 4.2$$

Where:

Q is the quantity of material released in unit time

u is the average wind in the x direction

χ is the instantaneous concentration at a sampling position

σ_y is the standard deviation of the cross wind displacement of the material

σ_z is the vertical displacement of the material above the boundary

If the wind speed doubles, other conditions being equal, the pollutants are emitted into twice the volume of air downstream from the source. This explains why lower SO₂ concentration was found during higher wind speeds and higher concentrations during calm conditions. This is in agreement with the results of other authors. For example Niemeyer, 1960 found lower concentrations of pollutants in the afternoon than during morning hours. Higher wind speeds in the afternoon as opposed to low wind speeds in the morning favour the dispersion of the pollutants. High relative humidity in most cases occurred in the morning hours. This is the time when temperatures and wind speeds are low. Generally in an open country, with at least a moderate wind speed and a thoroughly cloudy sky, the

smoke trail from a source forms into a fairly straight well defined trail with discernible steady increase in width and height as distance from the source increases. If however, the wind is light and there is sufficient sunshine to warm the ground surface, a much greater degree of irregularity appears in the form of the plume. The smoke is heated by the absorbed solar radiation and the movement of the air itself leads to a rapid spread of the smoke in the vertical, and to an erratic variation in the direction of travel of successive sections of the smoke plume. The result is that the plume has a meandering and sometimes even disconnected form, and rapidly reaches a stage when it is no longer visible. On the other hand at night, if the sky is sufficiently clear to result in appreciable cooling of the ground, and the wind is light, the vertical spread is considerably reduced and the smoke trails off downwind in a compact visible form for appreciable distances. The above described constitute the classification of diffusive conditions, i.e near zero gradient (neutral stability), lapse or decrease of temperature with height (unstable) and inversion or increase of temperature with height (stable). The concentrations within the plume tend to be relatively lower in unstable conditions and relatively high in stable conditions. When the reverse in transition of stability sets in, as it happens in the morning hours, a temporary occurrence of very heavy concentrations, even at great distances from the stack, may result from the fumigation action due to unstable conditions occurring below the plume and stable conditions aloft. That is why generally high SO_2 concentrations were observed in the morning hours. High wind speeds generally occurring in the afternoon resulted into low observed SO_2 concentrations.

Table 2: Correlations with meteorological parameters at various sampling sites.

	Wind speed	Temperature	Relative humidity	Cloud cover
Prisons	$r = 0.12$	$r = -0.62$	$r = 0.51$	$r = 0.32$
Addis Ababa road	$r = -0.35$	$r = -0.65$	$r = 0.67$	$r = 0.30$
Funzi road	$r = -0.66$	$r = -0.66$	$r = 0.59$	$r = 0.45$
Gilgil road	$r = -0.83$	$r = -0.83$	$r = 0.72$	$r = 0.52$
South B	$r = -0.45$	$r = -0.40$	$r = 0.50$	$r = -0.09$
Makadara	$r = -0.27$	$r = -0.50$	$r = 0.48$	$r = 0.02$

3.3 Average monthly concentrations

Figures 8 to 13 show the average monthly concentrations for SO₂ measured at various points in Nairobi. The monthly averages represent the morning and afternoon concentrations averaged over the sampling period in a month.

In some months sampling was done more often than other months, depending on the availability of transport. In each month, different sampling sites were visited on different occasions. Since sampling periods for pararosaniline method was more than one hour, it was possible to visit more than two sites on each sampling day.

Monthly results are for sampling sites Prisons, Addis Ababa road, Funzi road, Gilgil road, South B and Makadara.

The average monthly concentrations for Industrial area increase from about 92 micrograms/m³ in June to about 105 micrograms/m³ in July and peak concentration of 116 micrograms/m³ occur in August. Thereafter the concentrations decrease to about 80 micrograms/m³ in the month of September, 75 micrograms/m³ in October and goes up slightly to about 80 micrograms in November. The pattern is similar for different sampling sites at the industrial area. Except for July and October when concentrations were highest at Prisons sampling site. The highest monthly concentrations were found at Addis Ababa sampling site. Save for the months of June and November, the monthly average concentrations at Prisons and Addis Ababa sampling points were quite close. This could be due to their proximity to one another.

The other sampling points in industrial area (Funzi and Gilgil roads), depicted similar month to month variation as Prisons and Addis Ababa sampling sites. In most cases, monthly concentrations at Funzi road were higher than at Gilgil road sampling site. It is

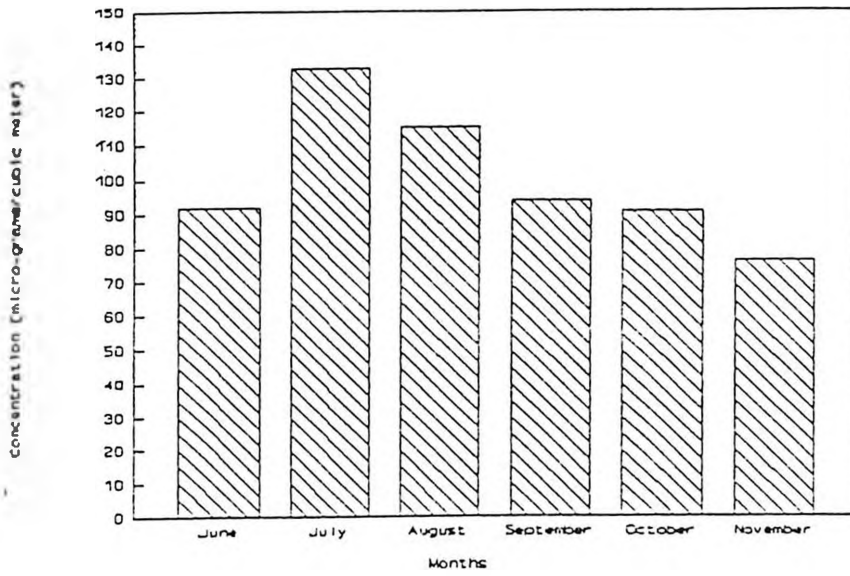


Figure 8 : sulphur dioxide concentration at Prisons.

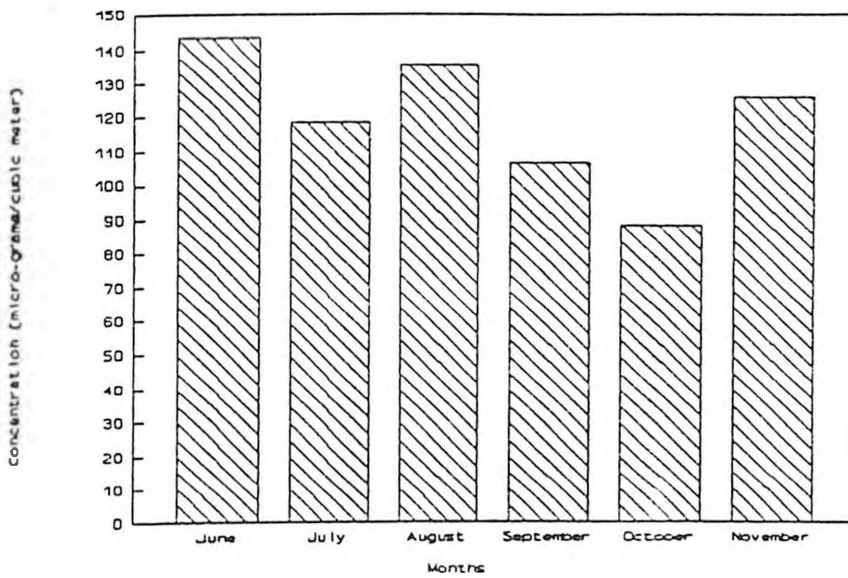


Figure 9 : Sulphur dioxide concentration at Addis Ababa.

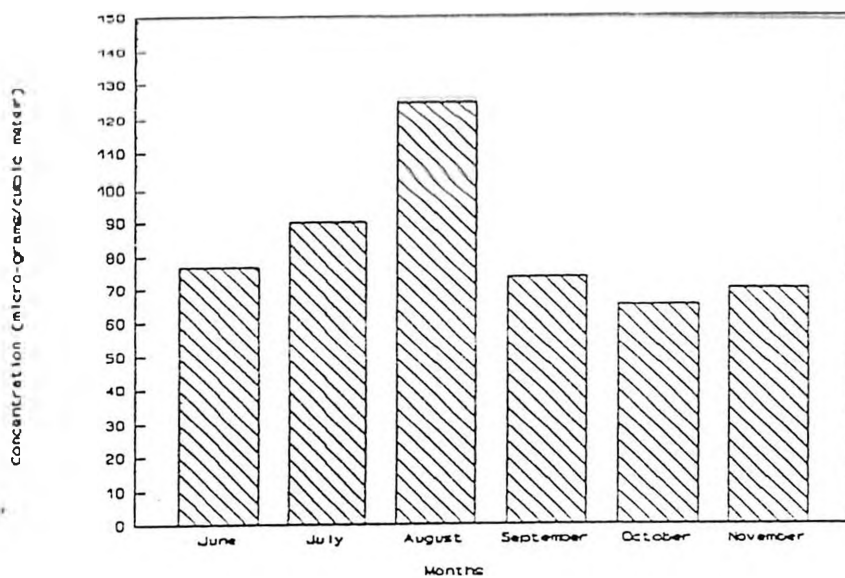


Figure 10 : Sulphur dioxide concentration at Funzi road.

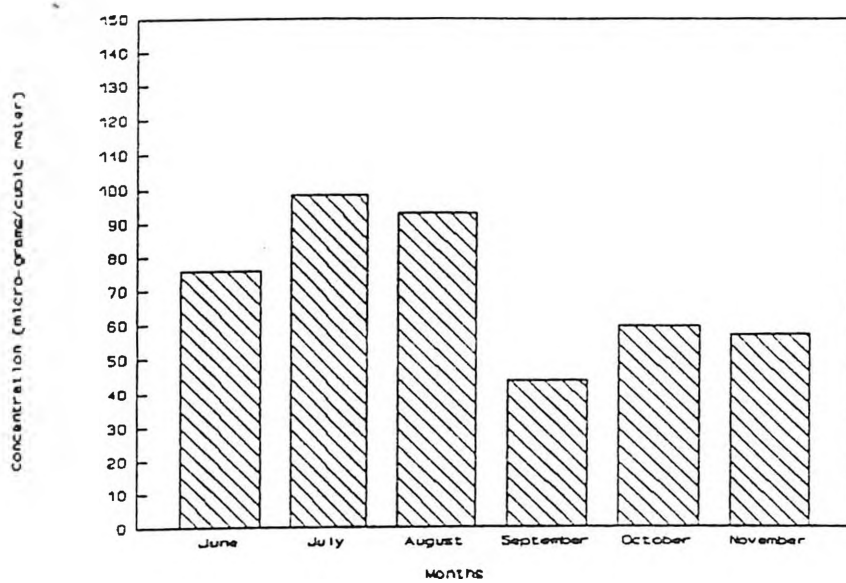


Figure 11 : Sulphur dioxide concentration at Gilgil road.

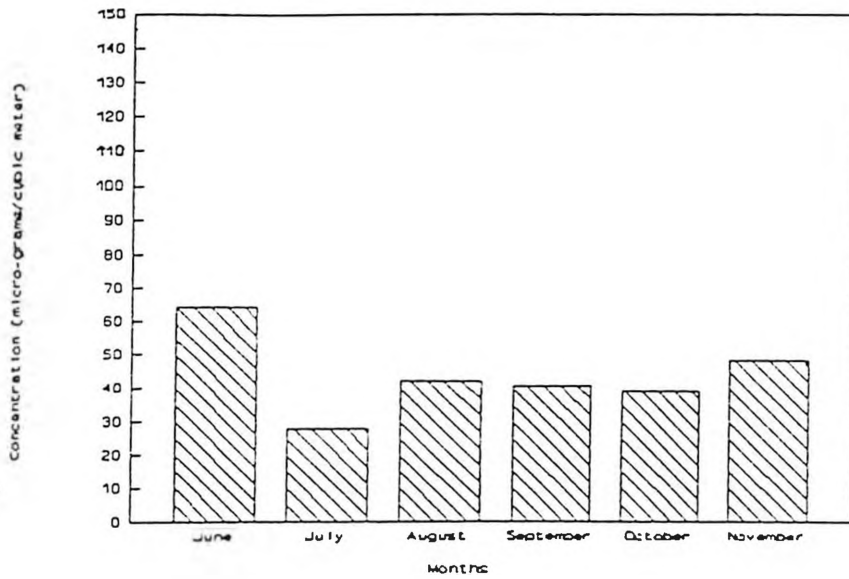


Figure 12 : Sulphur dioxide concentration at South B.

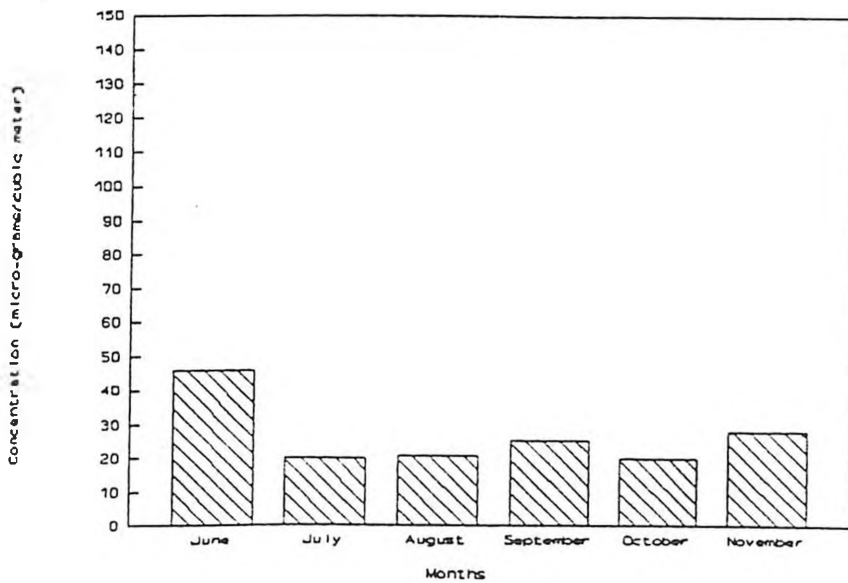


Figure 13 : Sulphur dioxide concentration at Makadara

also worthwhile to note that average monthly concentrations at both sampling sites are quite similar. There was a remarkable difference between monthly concentrations at Prisons and Addis Ababa road sampling sites, and at Funzi and Gilgil road sites. The former were showing much higher concentrations than the latter sites. This could be due to the major sulphur dioxide sources being closer to Prisons and Addis Ababa road sampling sites. In fact, Prisons sampling site is located to the west of many industries. These industries emit a lot of gases and SO₂ could be one of the major gaseous pollutants originating from them. Indeed, during sampling days especially on cool mornings and afternoons, some offensive choking gases could be noticed from these industries. This was evident up to a distance of about 400 meters from the main factories. Prison workers residing nearby were complaining of the emissions which they claimed caused constant coughs. During the period of sampling, the wind direction was characterised by a higher frequency of ESE. Thus prisons and addis ababa sites, being downwind of the industrial area, will tend to receive most of the pollutants. These sites could also be located close to the major sulphur dioxide producing sources.

The other sampling sites were located outside the major industries. Makadara site was north of the industrial area, whereas South B was on the south of the main industrial area. Both sites are almost the same distance from industrial area, although South B site is a little bit closer. Highest concentrations were recorded in the month of June at South B (about 60 micrograms/m³). The concentrations then decreased to about 25 micrograms/m³ in July, then rose to about 40 micrograms/m³ in August and about the same concentration in the subsequent months.

Makadara sampling site also had highest recorded average monthly concentration in June. The concentration decreased from about 40 micrograms/m³ in June to about 18 micrograms/m³ in July and August. In September the concentrations rose slightly to

about 22 micrograms/m³, decreased to about 18 micrograms/m³ in October and rose to about 25 micrograms/m³ in November. One notable observation about the monthly concentrations in these two sites is that in all cases the average monthly SO₂ concentration in both sites is less than in industrial area. In all the months covered the monthly SO₂ concentration at South B is far much more than at Makadara. Monthly average SO₂ concentration at Makadara does not show much variation from one month to another as other sites. This could be due to the fact that most of the SO₂ recorded at Makadara is of domestic origin. The variation in domestic usage of SO₂ producing fuel does not vary much from one month to another.

From the foregoing discussion it is evident that highest concentrations are found during those months characterized by low temperatures and wind speeds and high cloudiness and humidity. The months of June, July and August, depicted this kind of weather.

3.4 Morning and Afternoon monthly concentrations.

Morning concentrations were obtained between 9.00 a.m to 11.30 a.m while afternoon concentrations were obtained between 2.00 p.m to 4.30 p.m. Like the monthly average concentrations, sites located at the Industrial area recorded higher concentrations than those at the residential sites. Higher concentrations was recorded during those months with poor dispersion conditions for morning and afternoon monthly concentrations. For all stations, higher concentrations was recorded in the morning than afternoon hours (figures 14 and 15). The pattern was quite similar to that of the average monthly concentrations. Average concentration ranged from 44.2 μg/m³ at the residential estates to 112 μg/m³ at the Industrial areas, during morning hours. Afternoon concentrations ranged from 26 μg/m³ at the residential areas to 74.6 μg/m³ at the Industrial area. Similar results have been found by many researchers. Holzworth [1967] found, in the afternoon hours, lower relative concentrations than in the morning hours. This was due to higher

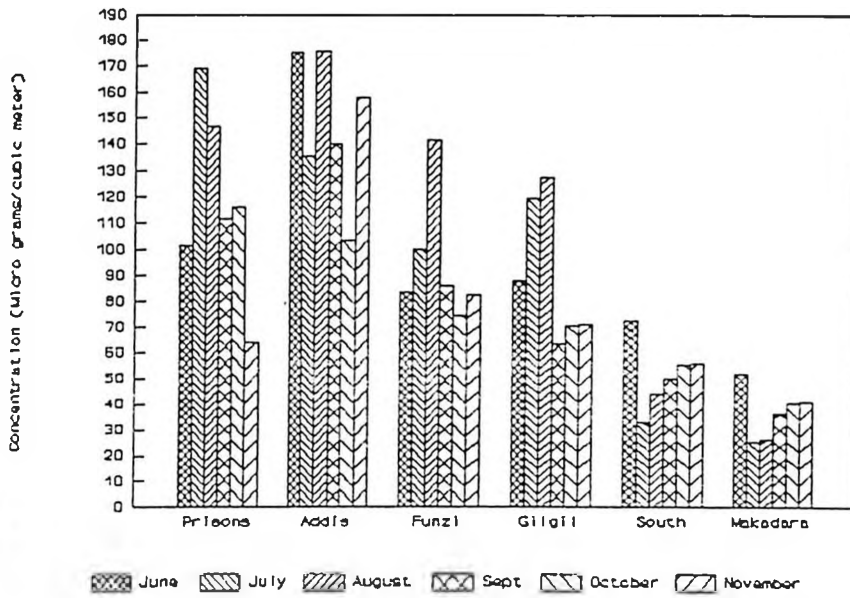


Figure 14 : Monthly variation of sulphur dioxide concentration during morning hours.

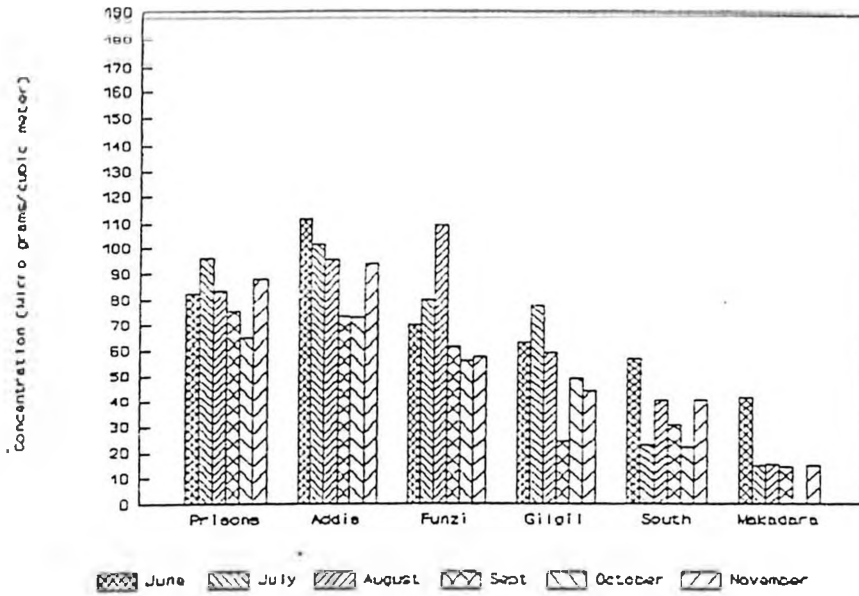


Figure 15 : Monthly variation of sulphur dioxide concentration during afternoon hours.

wind speeds and mixing depths in the afternoon hours than in the morning hours. Ng'ang'a [1976] found that in Nairobi, the morning hours are usually characterized by low wind speeds whereas higher wind speeds occurred during the afternoons. At Mombasa, Kimani [1990] found higher total suspended particulates during morning hours than afternoon hours. He attributed low afternoon concentrations to good dispersion conditions. This explains why higher concentrations were found in the morning hours than in the afternoon hours. On the monthly basis, the period of June to September recorded higher concentration than the October-November period. The difference is attributed to the dispersion conditions during these months. Ng'ang'a [1976] found that the months of June to September experienced high frequency of stable conditions and low wind speeds. Similar findings have been found by other researchers [Ngugi, 1982 and Kimani, 1990]. These conditions are favourable for high concentrations of pollutants.

The concentrations obtained were compared to World Health Organization (WHO) air quality guidelines. Table 3 shows the summary of sulphur dioxide concentrations at various places in Nairobi, whereas table 5 represents a summary of WHO air quality guidelines.

Table 3. Sulphur dioxide concentration in micrograms/m³, parts per billion by volume(ppbv) in brackets

Site	No. of Samples	Mean	S.D	Minimum value	Maximum value	C.V
Prisons	104	92.9 (35.6)	47.4 (18.2)	LD (LD)	255.9 (98.4)	0.48
Addis Ababa	64	116.3 (44.7)	46.8 (18.0)	51.4 (19.8)	242.6 (93.3)	0.64
Funzi	56	80.4 (30.9)	27.3 (10.5)	45.6 (17.5)	168.5 (64.8)	0.53
Gilgil	48	66.3 (25.5)	30.6 (11.8)	LD (LD)	43.3 (16.7)	0.52
South B	44	43.1 (16.6)	19.0 (7.3)	LD (LD)	72.5 (27.9)	0.49
Makadara	44	25.0 (9.6)	23.6 (9.1)	LD (LD)	72.5 (27.9)	1.00

Table 4: Average monthly meteorological parameters during June-November period for morning hours(A.M) and afternoon hours (P.M.) at Jomo Kenyatta International Airport (JKIA)

Meteorologic al parameters	Wind speed in knots		Wind direction		Temperature in degrees celcius		Relative humidity in %		Cloud cover in octas	
	A.M	P.M	A.M	P.M	A.M	P.M	A.M	P.M	A.M	P.M
Months										
June	4.0	6.0	ESE	ESE	17.5	22.1	76.0	52.0	7	6
July	5.0	7.0	ESE	ESE	16.1	21.1	70.0	48.0	6	7
August	4.0	9.0	ESE	ESE	16.7	23.3	71.0	41.0	7	5
September	5.0	10.0	ESE	ESE	18.5	25.3	62.0	34.0	5	4
October	7.0	11.0	E	E	20.1	26.0	60.0	35.0	5	5
November	10.0	12.0	ENE	E	19.8	24.9	74.0	45.0	6	5

Table 5: A summary of WHO Air Quality Guidelines of SO₂ Concentration (micrograms/m³)

Time-weighted average	Averaging time
500	10 minutes
350	1 hour
100-150	24 hours
40-60	1 year

Source: W.H.O, 1982.

These guidelines indicate the level and exposure time at which no adverse effects on human health are expected.

The period for sampling was usually one hour on each sampling session, i.e hourly concentrations in the morning and in the afternoon. Results of SO₂ concentration obtained were compared to the 1 hour averaging time concentration given by WHO. From table 3, there is no site which recorded a maximum value higher than that given by WHO air quality guideline (table 5) for 1 hour averaging time. The mean SO₂ concentration given in table 3 are for the averaging time of six months. Since it was not possible to do sampling for the whole year, values obtained for six months averaging time are compared to the World Health Organization(W.H.O) guideline for one year averaging time. This was found to be reasonable because the sampling period covered the months that have previously been found to be associated with poor dispersion and thus high air pollution concentration levels (Ng'ang'a, 1976). This means the contribution from other months can only lead to lower average concentration levels. The mean concentrations at the Industrial

areas were found to exceed the WHO guidelines, whereas at the residential areas, the mean values were found to be within the WHO guideline. Higher concentrations at the Industrial areas could be due to the proximity of the SO₂ producing Industries in the sampling sites found

One possible explanation for the relatively low values obtained could be due to relatively fewer number of industries in Nairobi producing sulphur dioxide (table 1). The fact that sampling was done from 9.00 am to 11.30 am in the morning and from 2.00 pm to 4.30 pm in the afternoon, imply that only a few hours were covered on each sampling day. The concentrations obtained on each sampling day might not have been representative of the daily mean concentration. This is especially so in the early morning hours when low temperatures and low-level inversion conditions persist. The periods when no insolation and strong or weak outgoing terrestrial radiation accompanied with weak wind speeds, as it happens during early morning hours, characterize extremely stable or very stable conditions. Such conditions are favourable for poor dispersion of pollutants, leading to higher ground level concentrations. This extreme case of poor dispersion was not covered during this study because it was not possible to do the sampling at night. Moreover, at night the emission rate is different since there are few industries and motor vehicles operating.

3.5 Log normal plots

The observed values are plotted along the horizontal axis. The data values are ordered before plotting. The vertical axis corresponds to the expected normal value based on the rank of the observation.

Let $x_{(1)}, x_{(2)}, \dots, x_{(N)}$,

represent the data values after ordering from smallest to the largest. The subscripts (j) is the rank order of the observation. If N is the total frequency, the vertical plotting position corresponds to the expected normal value for the relative rank (j out of N) of the observation. The expected

normal value is estimated as

$$\Phi^{-1}[(3j-1)/(3N+1)],$$

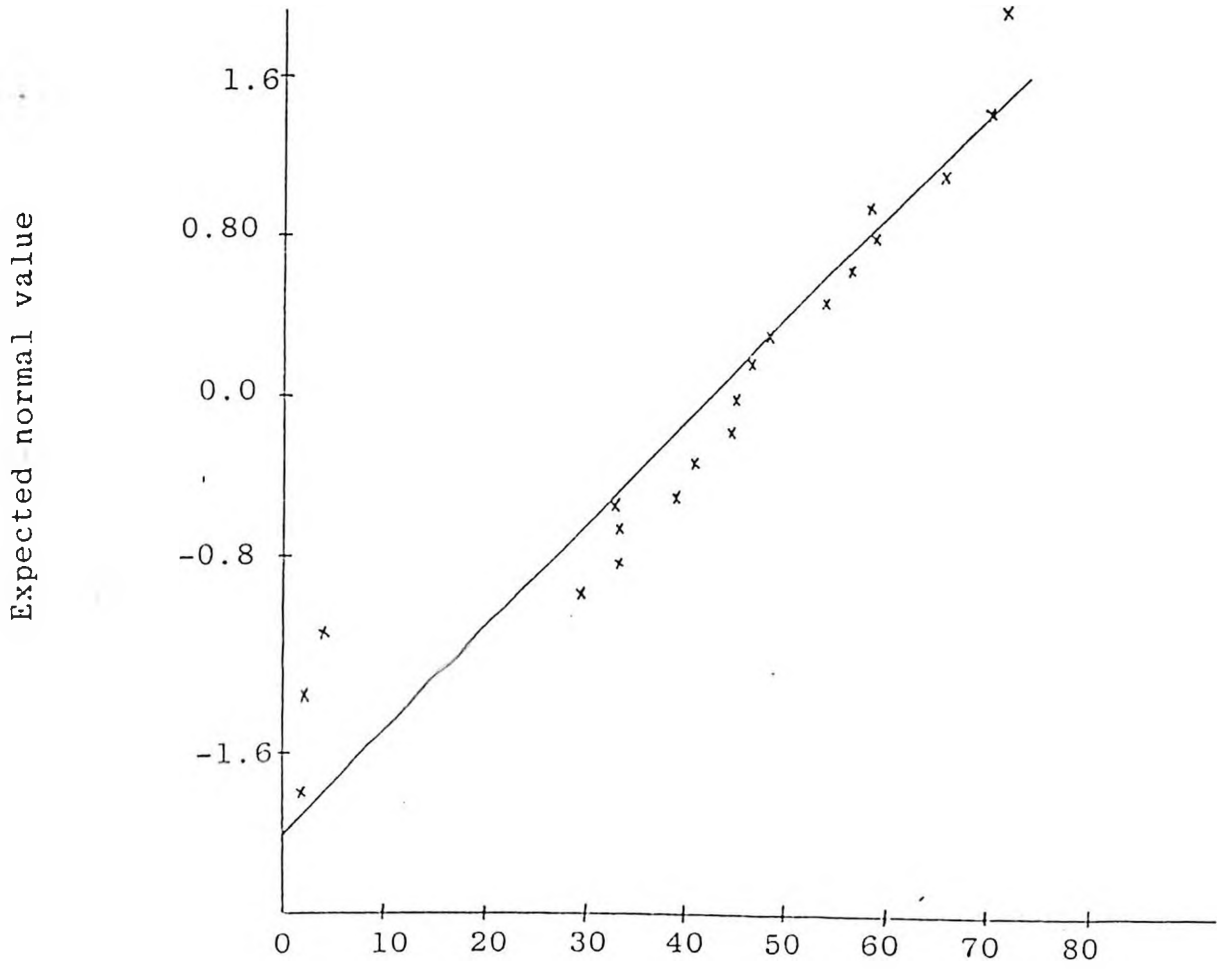
the standard normal value corresponding to the probability $(3j-1)/(3N+1)$. If the data are from a normal distribution, this line will be straight except from random fluctuations.

In contrast to the normal distribution, which is symmetrical about mean (μ), distribution of air contaminants exhibits a positive skewness. Despite difficulties in asserting the correct probability density function of air contaminants, there is a general agreement that a logarithmic transformation of the data closely approximates the normal distribution [Larsin et al., 1967]. This distribution is generally referred to as the log-normal distribution.

The results for log normal plots are shown in figures 16 to 21. With pararosaniline method, the lowest sulphur dioxide detection limit is $26 \mu\text{g}/\text{m}^3$. Any concentration which was lower than this was assumed to be zero. This explains why there was a clustering of points at lower levels with sampling sites South B and Makadara. Since these sites recorded the lowest concentrations, they also recorded concentrations below detection limit on a number of occasions.

As shown in figures 16 to 21, the logarithmic transformation of the data at most sampling points closely approximates the normal distribution. Thus the data for SO_2 concentration in Nairobi is in conformity with the distribution of air contaminants.

Fig.16 Lognormal plot for sulphur dioxide at South B



Sulphur dioxide concentration in micrograms/m³

Fig.17 Lognormal plot for sulphur dioxide at Makadara

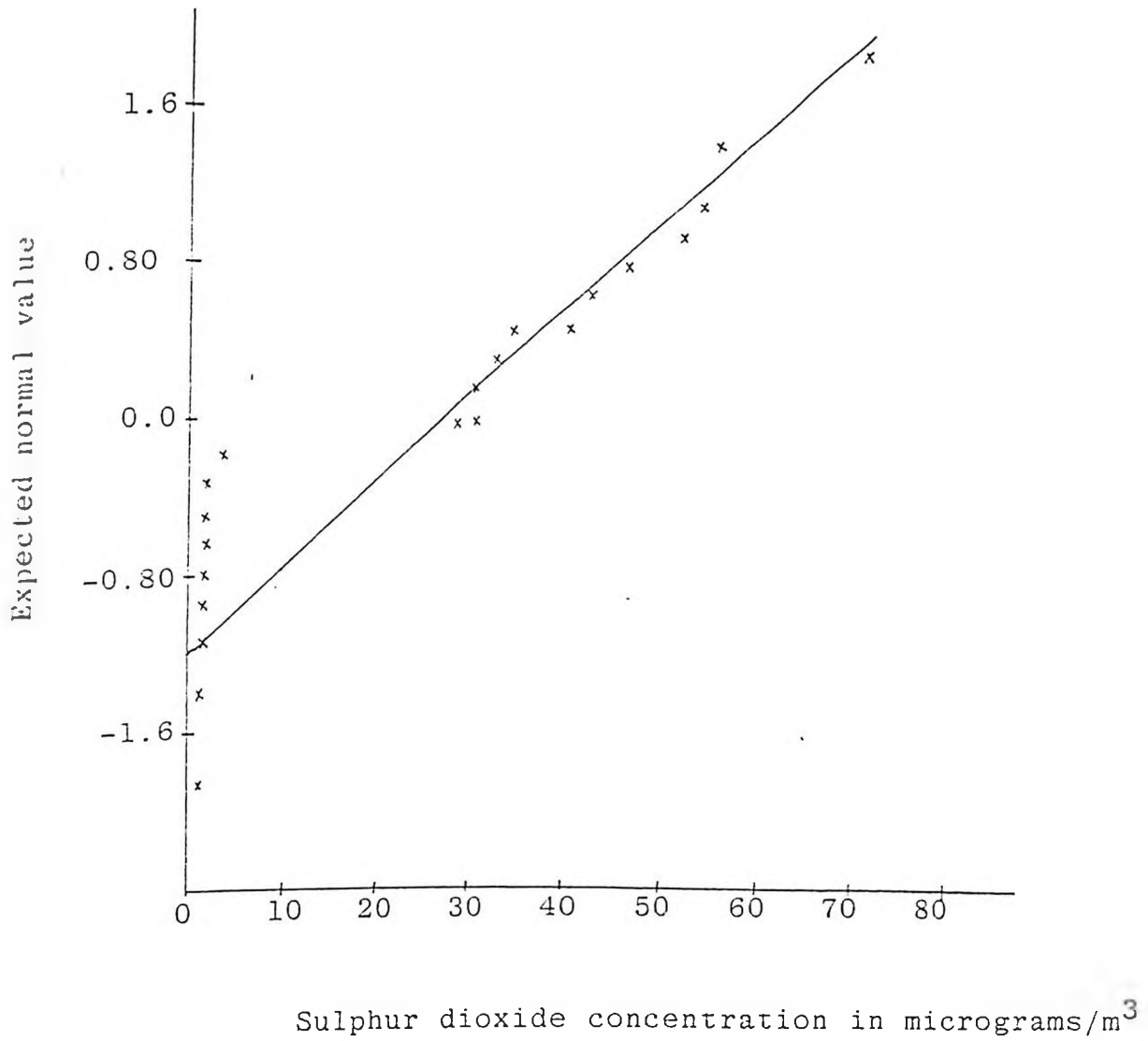
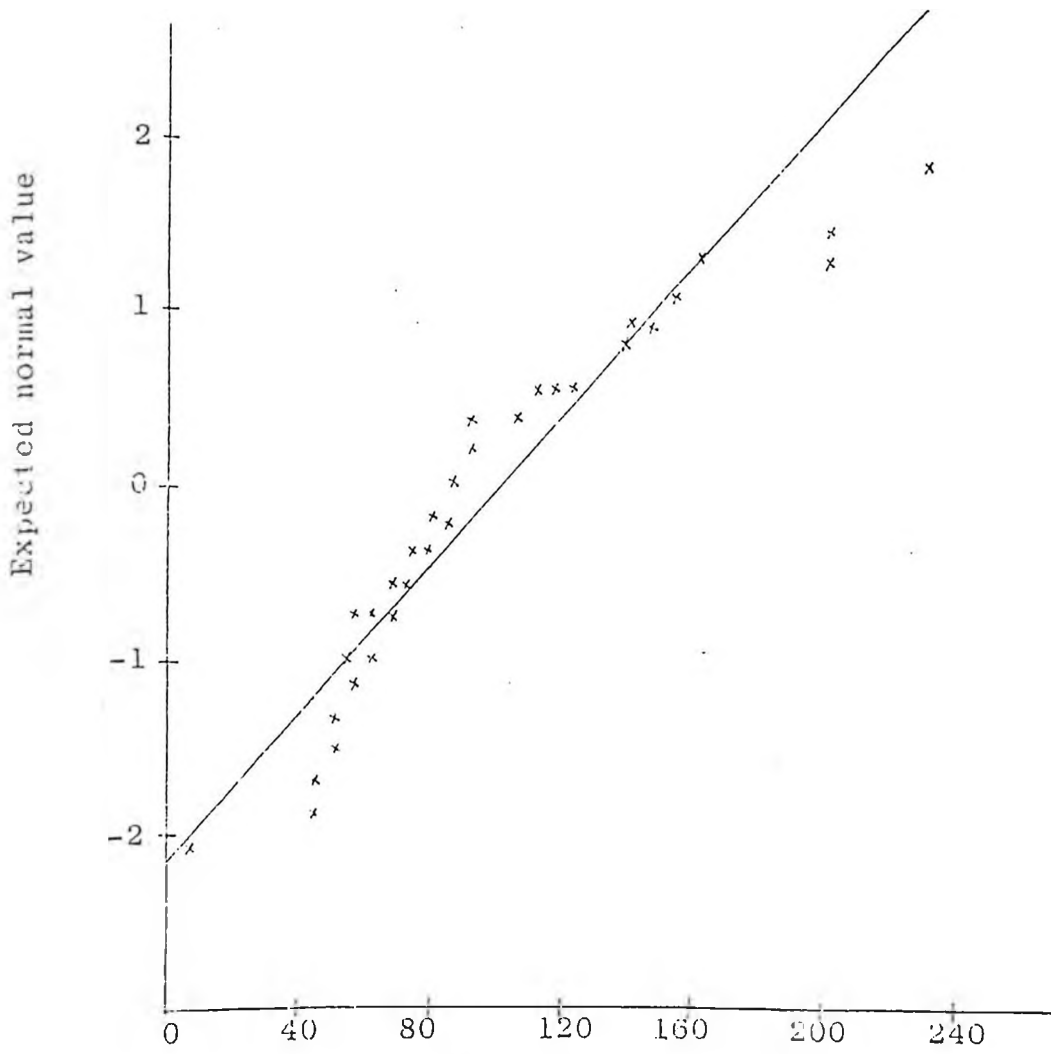
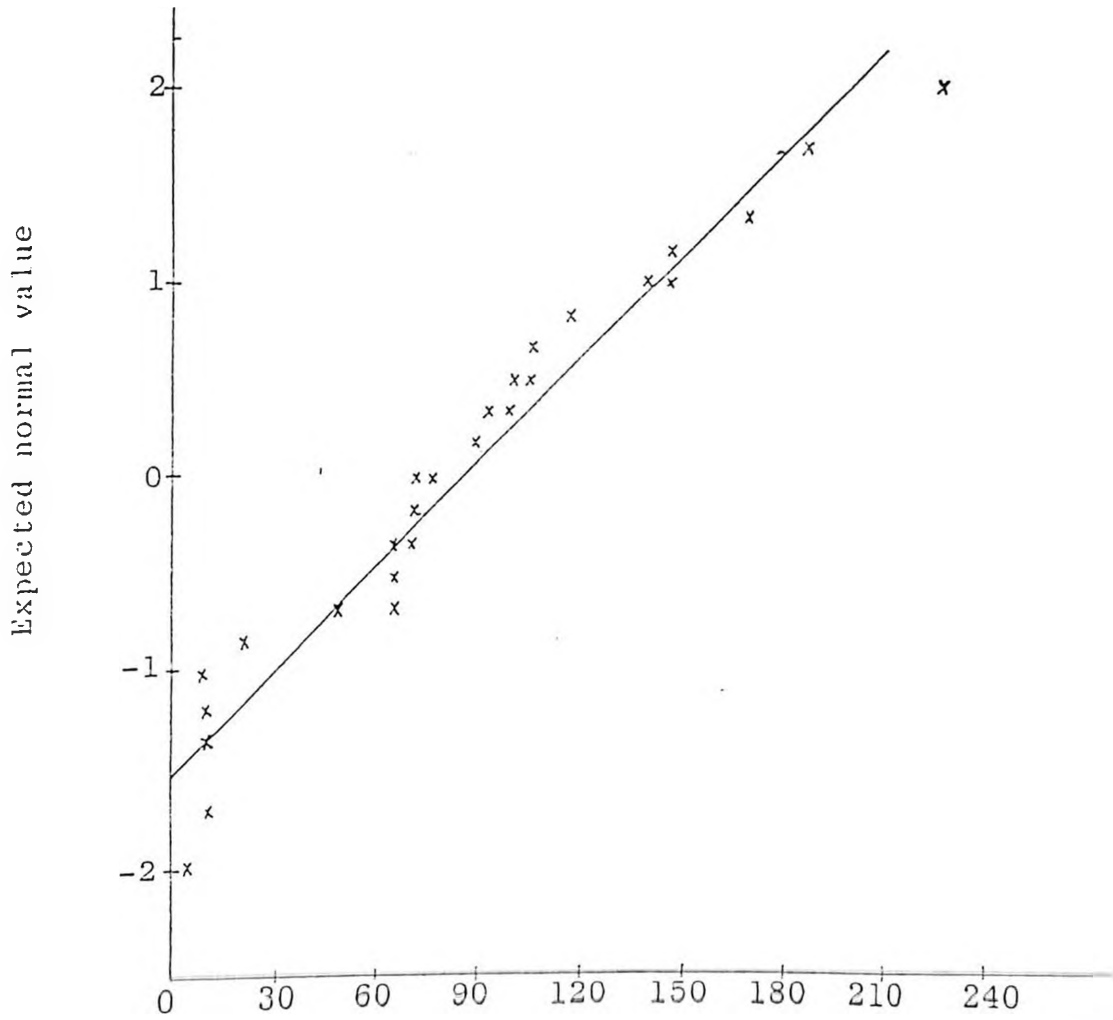


Fig.18 Lognormal plot for sulphur dioxide at Prisons



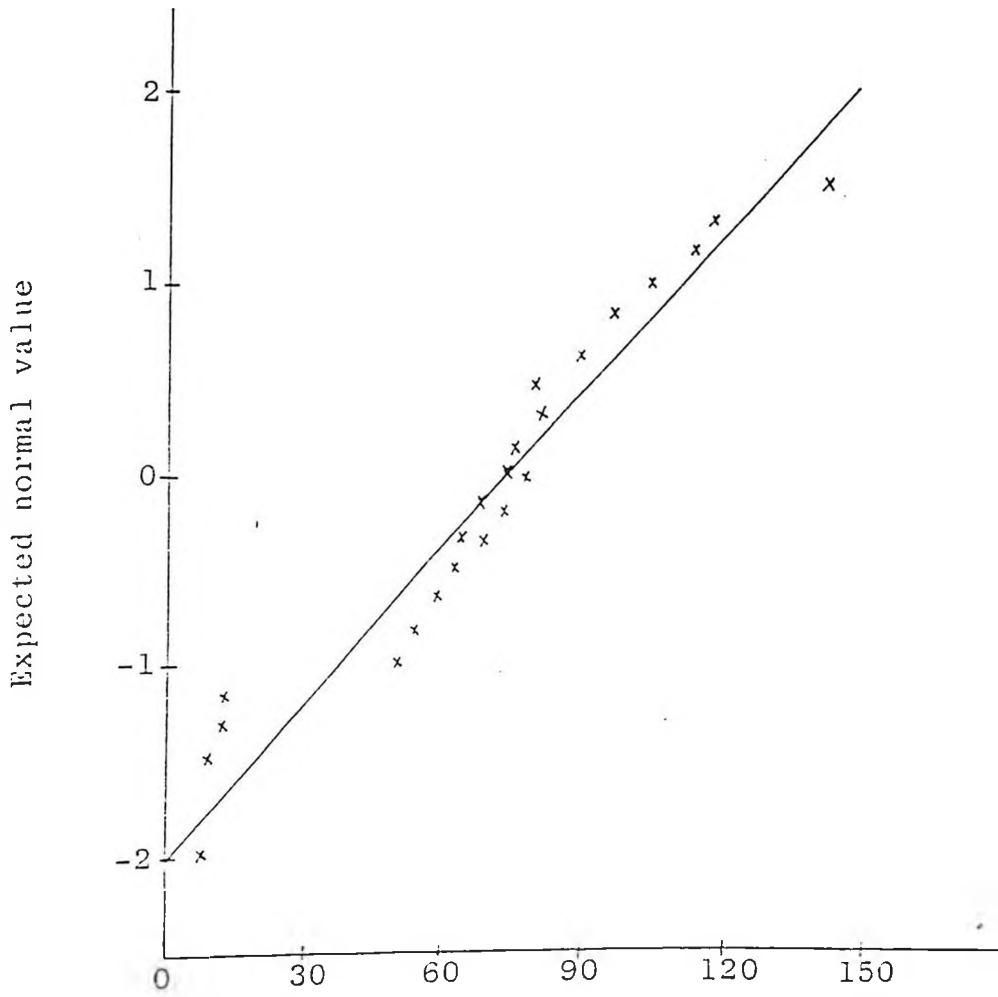
Sulphur dioxide concentration in micrograms/m³

Fig.19 Lognormal plot for sulphur dioxide at Addis Ababa road



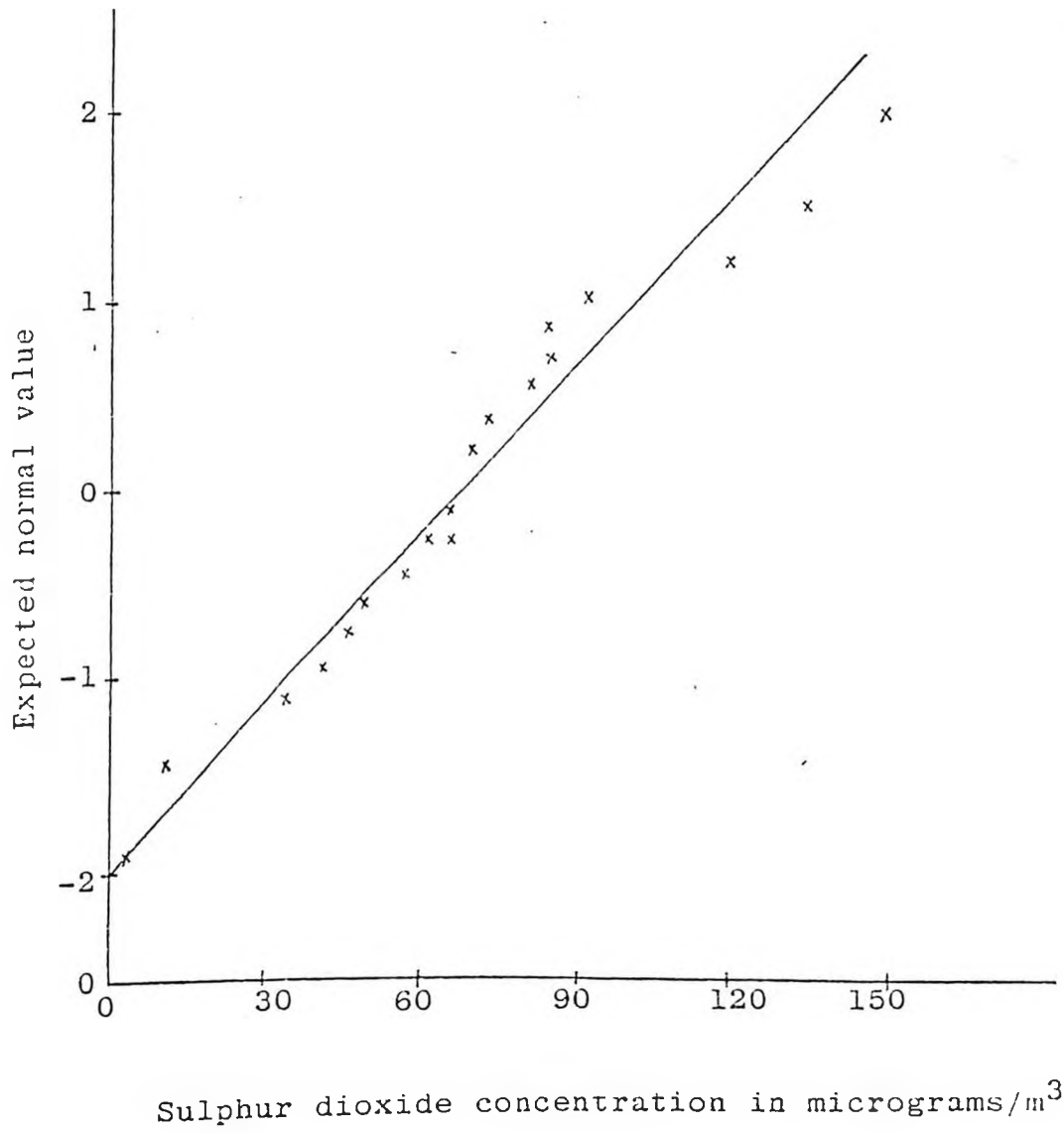
Sulphur dioxide concentration in micrograms/ m^3

Fig.20 Lognormal plot for sulphur dioxide at Funzi road



Sulphur dioxide concentration in micrograms/m³

Fig.21 Lognormal plot for sulphur dioxide at Gilgil road



3.6 CONCLUSION

Since measurements for different sites were not carried out at the same times, satisfactory comparisons of concentrations at different sampling points could not be obtained. Nevertheless, some observations were made about sulphur dioxide concentrations in Nairobi.

Average concentrations are higher in industrial area than in the residential areas, implying that some proportion of sulphur dioxide in Nairobi is of industrial origin. Even at the Industrial area, higher concentration was found at those sites closer to the higher number of factories, most probably SO_2 producing industries. The concentrations are high during those months characterized by low temperatures, wind speeds and high relative humidity. The regions down wind of industrial area experience relatively higher sulphur dioxide concentration than those areas upwind. The average concentration at each site does not show much variation from month to month.

The one hour concentrations are far below the one hour weighted average guidelines given by WHO. From this work, it looks like Sulphur dioxide does not pose a serious pollution problem in Nairobi. This however, could only have been verified if sampling was done throughout the twenty four hours of a day. High SO_2 possibly exceeding the WHO guideline, could have been recorded especially in the morning hours when poor dispersion conditions normally prevail. Wind speed, temperature and relative humidity are the most important parameters affecting sulphur dioxide concentrations. In most sampling sites, sulphur dioxide concentration is positively correlated to relative humidity and negatively correlated to wind speed and temperature.

The data obtained is in conformity with the distribution of air contaminants, exhibiting near normal distribution at all sampling sites.

3.7

Recommendations

The work carried on sulphur dioxide should not be taken to be conclusive. The following recommendations are made regarding more work to be done in order to have a wider understanding of pollution problem in Nairobi.

1. Sampling periods should be extended to cover 24 hours. This is important in finding the diurnal distribution.
2. Sampling should be carried out even during weekends and public holidays to find if there are any significant changes in concentrations during the week.
3. More sampling points should be installed in industrial area to have a large areal coverage. Residential areas should also have more sampling points. At least each residential area surrounding the industrial area should have a sampling point.
4. Some measurements should also be carried out in the city center to have a knowledge of motor vehicle emission levels.
5. Monitoring should be extended to major gaseous pollutants like oxides of nitrogen, hydrogen sulphide and carbon monoxide. An emission inventory should be carried out to estimate the amount of pollutant emitted by different sectors.

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