DETERMINATION OF THE LEVELS OF HEAVY METALS IN SUSPENDED PARTICULATE MATTER (SPM) IN KIBERA (NAIROBI)

BY

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DECLARATION

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

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DEDICATION

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Abstract

High population density, industrialization and increased vehicle use have led to severe deterioration of air quality in most urban centres. The most obvious air pollutant is the increased load of suspended particulate matter, which is known to have serious implication on human health. Health effects are mostly associated with particles in the size range of about 10 micrometres and below. It was therefore the aim of this study to determine the levels of suspended particulate matter in Kibera, the variation of the particulate matter levels with weather parameters such as rainfall, humidity and temperature, their heavy metal content and to correlate these levels with incidences of acute respiratory infections (ARI) of children under five years of age. Dustfall in a typical office working environment was also monitored by way of exposing preweighed coarse filters in the office and laboratory environment.

In this study, data on suspended particulate matter (SPM) collected over a one year period in Kibera, a suburban area of Nairobi is presented and discussed. The SPM was monitored as PM_{10} using the "Gent" Stacked Filter Unit (SFU) at heights of two (2) and four (4) metres above the ground level. The suspended particulate matter (SPM) was analysed by gravimetric, atomic absorption spectrometry (AAS) and energy dispersive X-ray fluorescence (EDXRF) techniques. The data analysis included calculation of interelement correlations (pearson-product moment) and enrichment factors.

For the acute respiratory infections (ARI) incidences, a questionaire administered to the mother elicited information on the symptoms. A total of 146 children were followed throughout the year. The ARI incidences ranged from (29.9-59.6%).

The mean PM_{10} values varied from (77.6-159.1μg/m^3) for samples collected at a height of two (2) metres and (60.9-138μg/m^3) at four (4) metres above the ground. These values are

higher than previous data (30-80μg/m^3) reported for a sub-urban site in Nairobi. The PM$_{10}$ data obtained in this work is lower than that reported in urban sites in Asia (15-219μg/m^3) and higher than that reported in urban and sub-urban sites in United States of America (1-97μg/m^3) and Europe (2.1-74.2μg/m^3). The PM$_{10}$ levels also varied with the weather conditions. The levels of particulate matter were found to increase with temperature, while low values were registered during high humidity. Samples collected after a rainy day and during a drizzle recorded low SPM values (10.8-22.7μg/m^3) for coarse particles and (8.10-14.3μg/m^3) for fine particles. This was probably due to the washing away of some of the particulate matter. Mean monthly values showed a strong seasonal trend with the highest values being observed in the cold (51.3-227.4μg/m^3) and dry (60.8-269.6μg/m^3) seasons. This was probably due to the high levels of soil dust during the dry season and increased residential emissions from the domestic heating (mainly wood/charcoal and kerosine fuels) during the cold season.

Concentrations in (μg/m^3) for elements analysed varied as follows:- potassium (1.435-4.533), calcium (5.185-7.109), titanium (0.387-0.809), manganese (0.381-0.790), iron (3.485-6.025), copper (0.119-0.169), zinc (0.143-0.247), lead (0.168-0.337), bromine (0.029-0.064), and zirconium (0.046-0.152) for coarse particle samples collected at a height of two (2) metres.

Higher values (0.046-7.11μg/m^3) were observed in the coarse particle fraction for elements calcium, potassium, iron, titanium and manganese which are associated with crustal dust. The elements copper, zinc, bromine and lead which are associated with anthropogenic origin had lower levels (0.029-0.337μg/m^3). Most of the highest concentrations were observed in the dry period (September- October). For most of the sites calcium, titanium, zirconium, potassium, iron and manganese showed high correlations (0.612-0.984) with the suspended particulate matter (SPM) in the coarse particle fraction suggesting soil dust to be the probable source. For some of the sites potassium and calcium also registered low correlations (-0.642-0.482) with SPM. This pointed to other possible sources for these elements apart from soil dust, e.g, burning of urban refuse and residential emissions. Copper, zinc, bromine and lead had low correlations (–0.793-0.386) with SPM in the coarse particle fraction indicating possible anthropogenic sources. However lead and zinc registered high correlations (0.658-0.773) with SPM in the coarse particle fraction for some of the sites.

At the height of four (4) metres the variation (μg/m^3) was as follows:- potassium (3.83-4.75), calcium (1.55-1.97), titanium (0.233-0.541), manganese (0.277-0.656), iron (2.31-6.29), copper (0.095-0.117), zinc (0.118-0.165), lead (0.120-0.222), bromine (0.045-0.054), and zirconium (0.036-0.095) for coarse particulate samples.

Lower concentrations were observed for most elements in the coarse particulate fraction for samples collected at four (4) metres height than at two (2) metres. However, bromine registered a slight increase in concentration at four (4) metres height. The elements calcium, titanium and zirconium showed reduction in concentration by higher factors (0.288-0.704) than for copper, zinc, and bromine (0.745-1.2) in the coarse particulate fraction. This pointed to resuspended soil dust at two (2) metres height as being responsible for the high levels observed for these elements in the coarse particulate fraction.

For fine particulate samples collected at two (2) metres height concentration (μg/m^3) for elements analysed varied as follows:- potassium (1.503-2.25), calcium (4.77 6.298), titanium (0.133-0.280), manganese (0.079-0.110), iron (0.862-1.102), copper (0.075-0.135), zinc (0.106-0.150), lead (0.165-0.250), bromine (0.031-0.055) and zirconium (0.011-0.027).

The elements potassium, calcium, titanium and iron still registered higher values (0.133-6.3μg/m^3) than most of the other elements. Potassium, calcium, titanium, manganese and iron showed both high (0.515-0.925) and low (-0.981-0.453) correlations with SPM at different sites. This may suggest various sources for these elements in the fine particulate fraction (e.g, soil dust, residential emissions and metal/welding works in the area). Zirconium registered high correlations (0.570-0.927) with SPM at all the sites.

For the fine particulate samples collected at height of four (4) metres the variation (μg/m^3) was as follows:- calcium (1.45-1.65), titanium (0.222-0.245), manganese (0.107-0.192), iron (0.326-0.818), copper (0.088-0.115), zinc (0.081-0.116), lead (0.162-0.225), bromine (0.031-0.034), and zirconium (0.012-0.022).

Levels for most elements remained in the same range as observed at two (2) metres height except for calcium, bromine and iron. Higher reduction factors were observed for calcium (0.262-0.303), bromine (0.618) and iron (0.378-0.742) than for titanium, copper, zinc, lead and zirconium (0.773-0.900). Manganese registered an increase in concentration at this height.

Low enrichment factors were observed at both heights for potassium (0.265-1.699), calcium (0.401-9.637), titanium (0.790-6.42), manganese (3.476-17.02) and zirconium (2.43-9.24) suggesting soil dust to be the main origin. However marginal enrichment for calcium (6.28-9.64) in the fine particulate samples at two (2) and manganese (10.48-17.02) at four (4) metres height were observed hinting at other possible sources apart from soil dust. The high enrichment factors observed for copper (10.77-228.3), zinc (12.385-124.6), lead (59.37-1967.0) and bromine (152.49-3038.7) at both heights suggested anthropogenic activites (i.e, industrial operations, automobile exhausts and residential emissions) to be the major contributors.

Bromine/lead ratios varying from (0.137-0.392) were observed at both heights hinting at vehicular emissions as the major sources of these elements at some of the sites.

Elemental concentrations in this study were found to be higher by factors ranging from (1.3 to 6.0) for most elements (calcium, potassium, titanium, manganese, iron, zinc and zirconium) except for copper, bromine and lead than previous reported case for a sub-urban site in Nairobi. Compared to studies in other parts of the world (Europe and Asia) data obtained from this study was found to be higher.

The average Acute Respiratory Infections (ARI) incidences was 8.49±4.01 episodes per child per year. The ARI incidences point prevalence showed a seasonal trend with both the cold and dry seasons having high point prevalence. Regressional analysis of monthly mean ARI incidences of children under five (5) years of age on PM_{10} and the fine particulate levels showed no significant correlation.

Dustfall sampled in a typical working office environment varied from (0.449 to $2.03 \mu g/cm^2/day$). The levels of dustfall sampled in the various offices (four) were found to depend on the position of the filter in the room (near windows, doors and height from floor), opening of windows, doors and the use of dust blowers and floor sweeping.

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Chapter One

1.0 Introduction

Air pollution has been a problem in many urban and industrialized communities for many years. The problem and concern of air pollution can be traced down to the thirteenth century. As early as 1257, Eleanor, Queen of Henry 3 left Nottingham for Tutbury because of smoke resulting from the use of coal in furnaces (Parker, 1978). In 1273 the use of coal was prohibited in London as it was considered that the clouds of smoke were prejudicial to health (Parker, 1978). It is the effect of air pollution on the environment that has aroused the awareness in man, resulting in numerous studies about the subject all over the world. Consequently much valuable knowledge is now documented concerning the effects of air pollution on human and animal health, property and plant life.

For centuries urban air pollution has been the focus of attention of those concerned with the health and welfare of city dwellers. This is essentially due to the magnitude of urban pollution sources and close proximity to densely populated residential areas.

Most of the air pollution to which a human being is exposed is of commercial, industrial, natural and domestic origin, it include solids, liquids and gases. These pollutants are introduced into the atmosphere through both natural sources such as volcanic activities, soil erosion, desertification, forest fires, pollen from plants, bacteria, sea spray and by anthropogenic sources such as industrial and motor vehicles.

Pollutants introduced into the atmosphere are mainly classified into two categories: primary and secondary pollutants (Seinfield, 1975). Primary pollutants are those directly emitted into the air which include particulate matter and gases. These pollutants are mostly from stationary sources such as factories and power plants. Other primary pollutants include hydrocarbons and nitrogen oxides most of which are emitted from mobile sources associated with transportation, i.e, automobiles. The secondary pollutants are as a result of chemical transformation of the primary pollutants in the atmosphere, example include the conversion of gas to particles. The primary air pollutants found in most urban areas are carbon monoxide, nitrogen oxides, sulfur oxides, hydrocarbons and particulate matter. However the most obvious air pollutant in most cities is the suspended load of particulate matter.

As the industrialization progresses and the cities continue to grow, the demand for heat, light, electric power and transport increases correspondingly. The burning of coal, wood and fuel oil to produce these essentials contribute to the enormous emission of pollutants. Increased number of factories as the cities grow also leads to increased waste chemical production. Vehicular emissions also contribute to increasing pollution levels in the urban areas (Khandekar *et al*, 1980; Karue *et al*, 1992; Tripathi *et al*; 1989).

The composition of the pollutants changes with changing technology, adding more exotic and often more dangerous products in the air. The greater the urban agglomeration the higher are it's air pollution levels. NAMP (1973) observed a progressive increase of the mean annual concentration of suspended particulates with city size in United States of America.

High morbidity and mortality rates have been blamed on acute exposure to air pollutants. Several epidemiological case studies have shown that elevated levels of total suspended particulate (TSP), PM_{10}, sulfur dioxide and acid aerosols are positively associated with mortality (Pope *et al*, 1992; Dockery *et al*, 1992; Bart, 1993). In all these epidemiological studies PM_{10} has been found to have a strong association with respiratory morbidity and mortality than the other pollutants such as sulphur dioxide and acid aerosols. These findings have been replicated in diverse communities all over the World (Editorial, 1993; Bart, 1989). These studies have also demonstrated associations between effects on health and particles from a wide range of sources. These include primary emissions from motor vehicles. Industrial sources or coal fires and secondary aerosols derived from gaseous emissions, including sulphur dioxide and oxides of nitrogen from industrial and vehicular emissions (COMEAP(a), 1998). The health effects of suspended particulate matter is most pronounced in children. Several epidemiological studies have established strong correlations between the rates of chronic cough, bronchitis and chest illness with all measures of particulate pollution (TSP, PM_{15} PM_{10} and $PM_{2.5}$) but less strongly with concentration of gases such as sulphur dioxide and nitrogen dioxide (Dockery *et al,* 1992). Pope, (1989) study in Utah valley revealed that PM_{10} levels were strongly correlated with hospital admissions for pneumonia, pleurisy, bronchitis and asthma. He also found that the PM_{10} levels were more strongly correlated with children's admissions than with adult admissions. As a result of these epidemiological case studies, evidence on adverse health effects has been used in setting emissions and concentration standards designed to protect public health. These are concentrations that cannot legally be exceeded during a specific span of time in a geographical area. For example in the United States of America, the National Ambient Air Quality Standards (NAAQS) has set the standard for particulate matter with the indicator pollutant being the PM_{10} as $150\mu g/m^3$ for 24 hours period and of $50\mu g/m^3$ as the annual average (Editorial,1993).

It will be aknowledged that air pollution is made up of many different components that affect the environment, directly or indirectly the health of people. The main components include sulphur dioxide, suspended particulate matter, carbon monoxide, reactive hydrocarbon compounds, nitrogen oxides, ozone and lead. In their study of the size distribution of nine metals aluminium (Al), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) present in Glasgow's atmosphere, McDonald *et al* (1979) established that the most toxic metals studied, cadmium (Cd), nickel (Ni), and lead (Pb) had extremely high proportions in the smallest particle size range which can easily enter the respiratory tract and lodge in the alveoli.

There is no systematic air quality monitoring in Nairobi, however some scattered measurements have been carried out which give some indication about the concentration of some pollutants in the air. Several studies on air quality done in Kenya have dealt mainly with the determination of the total suspended particulate matter (TSPM). The earliest recorded study on suspended particulate matter was in 1977\78 (UNEP, 1987). This was a study carried out by a team from the ministry of health through a World Health Organisation (WHO) program (GEMS\AIR). They had two sampling sites, city centre and residential, the suburban and industrial area respectively. Using high volume sampler for both sites, the concentration of TSPM was found to range from 35-128μg/m^3 with the later site registering the highest levels. Measurements carried out in 1982 revealed higher concentrations of suspended particulate matter in Nairobi industrial area-252μg/m^3, Buruburu-80μg/m^3, South C-103μg/m^3, Shauri moyo-92μg/m^3 and Woodly-83μg/m^3 (Ngugi, 1983). Another study (Karue *et al,* 1992) carried out in 1992 indicated increased levels with respect to total suspended particulate matter. TSPM collected at industrial area was 397.7μg/m^3 higher than that measured in 1982. This study also indicated that the air quality had deteriorated by a factor of 14.6 μg/m^3 particulates per year from 1983 (Karue *et al*, 1992). Several other studies (Gatebe *et al*, 1996) have been carried out in the subsequent years to assess the general air quality and to pinpoint the sources of pollutants. However, these studies used PM$_{10}$ as assessor of pollutant. Concentration of PM$_{10}$ ranged between (30-80μg/m^3) in a suburban area of Nairobi (Gatebe *et al,* 1994). PM_{10} standard is the most recent revision of the National Ambient Air Quality Standard (NAAQS-United States of America) for particulate matter. This replaced the previous particulate matter standard that regulated the concentration of total suspended particulates (TSP). This revision reflected the recognition that a size-fractionated index of particulate exposure was more biologically appropriate than TSP which included particles of all sizes (Editorial,1993). These studies have pointed out a deteriorating air quality and the major source of air pollution being the industrial emissions. Despite this documentation, no effort has yet been made by most countries to enact laws aimed at regulating emissions into the atmosphere. There has also been an attempt to use bioindicators to assess the metal burden of urban air. Njogu (1997) found high concentrations of manganese (Mn)-500μg/g and lead (Pb)-191.3μg/g in the barks of *mimosa folia*, *tipauna tipu* and *Ficus benjamina* trees in Nairobi.

This study attempts to identify the inorganic components i.e, heavy metal content of the airborne particulate matter (PM_{10}) in Kibera and also investigate acute respiratory infections (ARI) incidences of children under five years of age.

1.1 Air pollution and health

Despite vast improvements in health globally over the past several decades, environmental factors remain a major cause of sickness. One in five children do not live to see their fifth birthday, largely because of environmentally related diseases (World Resources, 1998). That number translates into eleven million childhood deaths each year, mostly due to illnesses such as diarrhea and acute respiratory infections (World Resources, 1998). For more than a century, severe air pollution incidents in cities such as London, Meuse Valley (Belgium) and Danora Valley (Pennysylvania) have shown that breathing dirty air can be dangerous and at times deadly (UNEP, 1991). For instance in 1880, 2200

Londoners died in one such incident when coal smoke from home heating and industry combined to form a smog of sulphur dioxide and air borne combustion particles (UNEP, 1991). But the concern about health effects of outdoor air pollution did not attract attention until the late 1940's and 1950's when air pollution disasters raised an alarm.

In 1948 in the small town of Denora, Pennysylvania (United States of America), 50 people were estimated to have died in a killer smog and in 1952, a London smog is estimated to have killed 4000 people (IAEA, 1996). These smogs were associated with widespread use of dirty fuels. The events acted as catalysts for governments to tackle urban air pollution. Many nations since then have adapted ambient air quality standards to safeguard the public against the most common and damaging pollutants which include sulphur dioxide, suspended particulate matter, ground level ozone, nitrogen dioxide, carbon dioxide and lead. For instance in the United States the clean air act of 1963, amended in 1970 mandates that Primary National Ambient Air -Quality Standards (NAAQS) be set low enough to protect the health of all sensitive groups within the population (STA, 1996). Although smogs or pollution episodes experienced in the early 19th century have gone, recent research works have shown that the numbers of deaths currently caused by air pollution are probably higher than was previously imagined (IAEA,1996). According to a report from the Committee on the Medical effects of air pollutants (COMEAP(a), 1998) United Kingdom, it's estimated that air pollution hastens the deaths of between 12,000 and 24,000 vulnerable people a year and is associated with 14,000 and 24,000 hospital admissions and re-admissions This report also indicates that in urban areas of Britain particulate matter is responsible for bringing forward the deaths of 8,100 people a year while SO_2 hastens the deaths of 3,500 people (BMJ, 1998).

Urban air pollution has worsened in most large cities in the developing world. This situation is propelled by population growth, industrialization and increased vehicle use. Despite pollution effects, air quality has approached the dangerous levels recorded in London in the 1950's in a number of megacities such as Beijing, Delhi, Jakarta and Mexico city (WHO/UNEP, 1992). In these cities pollutant levels sometimes exceed WHO air quality standards by a factor of three or more. In some of China's major cities, particulate levels are as much as six times the WHO guidelines (Liu *et al,* 1997). The developed world is no exception, a recent assessment by the European Agency found that 70 to 80% of 105 European cities surveyed exceeded WHO air quality standards for at least one pollutant (Derek, 1996).

The health consequences of exposure to dirty air are considerable. On a global basis, estimates of mortality due to outdoor air pollution run from around 200,000 to 570,000 representing about 0.4 to 1.1% of the total annual deaths (Lopez *et al*, 1996). However these mortality estimates alone do not tell much about the huge toll of illness and disability that exposure to air pollution brings at a global level.

Health effects span a wide range of severity from coughing and bronchitis to heart disease and lung cancer. Several epidemiological studies indicate that exposures to respirable particulates were associated with work-related symptoms of cough, itching, difficult or laboured breathing, chest tightness and wheeze (Gable *et al,* 1975). Vulnerable groups include infants, the elderly and those suffering from chronic respiratory conditions including asthma, bronchitis or emphysema. Stebbings *et al* (1972) established that elevated levels of respirable suspended particulates were associated with excerbations of cardiopulmonary disease symptoms, while Kerrebijn *et al* (1975) found children living in highly polluted area showing a higher preference of cough than their counterparts in less polluted areas. It is estimated that air pollution in developing world cities is responsible for some 50 million cases per year of chronic coughing in children younger than 14 years of age (World Bank, 1992). Many of air pollution's effects such as bronchitis, tightness in the chest and wheezing are acute or short term and can be reversed if air pollution exposures decline. Other effects appear to be chronic such as lung cancer and cardiopulmonary diseases.

In epidemiological case studies which compared death rates among United states of America cities with widely varying pollution levels, it was established that mortality rates were 17 to 26 percent higher in cities with the dirtiest air compared to those with the cleanest air. The one's with the dirtiest air had significantly higher rates of lung cancer and cardiopulmonary diseases (Dockery *et al,* 1995., Dockery and Spengler, 1993).

Fewer studies have been done in developing countries, and those that have been done have relied on calculations of health impacts in developed countries. However, the few studies done suggest that urban air pollution may have a tremendous impact on health. For instance Bart (1994) in his estimation of the health effects of air pollutants in Jakarta found that approximately 1,400 deaths, 49,000 emergency room visits and 600,000 asthma attacks could be avoided each year if particulate levels were brought down to WHO standards ($50\mu g/m^3$) 24 hour average and ($150\mu g/m^3$) annual mean.

In Kenya, a study on domestic air pollution from biomass burning in a rural area by Boleji *et al,* 1989, did not detect any relationship between the number of acute respiratory episodes of the children and indoor air quality. Gikungu (1993) considered the total monthly and seasonal variation of pneumonia in Nairobi. He established that the months corresponding to the onset of the long rain seasons had the highest number of patients. He also noted higher number of cases of pneumonia during the cold seasons. He attributed the high number of pneumonia cases during the onset of rainy season to the characteristic dry and dusty conditions prior to the onset of rains hence probability of viruses and bacteria being transported in the dust and when inhaled resulting in the diseases.

1.2 Rationale of the study

One of the main reasons has to do with the effects of air pollution on health. Although air particulates are known to have serious implications on human health, there is little information available on their trends in Kenya especially within the industrialized urban centres such as Nairobi. It is also evident that there is an unabated increase in the number of activities associated with increasing levels of air particulates within the country.

Health problems associated with airborne particulate matter are starting to be regarded with great concern in many countries and particularly those in the developing countries where, in some highly populated cities, the amounts of total suspended particulates are often far in excess of WHO guidelines (WHO/UNEP, 1992). Chemical characterisation of the airborne particulate matter is important since it leads to the identification of the main source of the pollutant. For example, lead (Pb) and bromine (Br) are associated with motor vehicle emission and manganese (Mn), iron (Fe), calcium (Ca) and titanium (Ti) with soil brown dust (Parr *et al*, 1996).

In many polluted cities the most direct consequences are, reduced visibility of the atmosphere, irritation of eyes and throat. However, much more important are the longer term effects on health. Several studies (COMEAP(b), 1998; Pope, 1989) have indicated that the health effects are mostly associated with particles in the size range of about 10μm and below (i.e, PM_{10}). Hence, these are the particles that are of greatest interest. Scientific studies have linked particulate matter especially fine particles (alone or in combination with other pollutants) with a series of significant health problems (US-EPA, 1997).

The groups most at risk from exposure to fine particles include the elderly, individuals with pre-existing heart or lung disease, children and asthmatics. The reported associations between levels of particles and effects on health principally reflect a real relationship. The only major difficulty in reaching any firmer conclusion about causality is the lack of established mechanism of action (COMEAP, 1998).

Acute respiratory infection (ARI) is a leading cause of morbidity and mortality especially in developing countries (Francisco *et al*, 1993; Graham *et al*, 1990). Reports from several countries indicate that approximately 30% of children who are seen as outpatient and (20-30)% of those admitted to hospitals present with ARI (Wafula *et al*, 1990). Among deaths in hospitals (20-27)% are reported as due to ARI. The experience in Kenya is similar to that reported for other developing countries, in 1980 ARI was the second most common cause of death among all ages, accounting for 19% of deaths (Wafula *et al*, 1990). Severe forms of ARI occur much more in developing countries than in developed countries (Wafula *et al*, 1990). This study also attempts to determine if there is any correlation between monthly acute respiratory infections (ARI) incidences of children under five years of age and levels of PM_{10} in Kibera in an effort to reflect on possible human health effects.

1.3 Objectives of the study

a) Determine the concentration of PM_{10} in the area of study .

b) Analyse variation of PM_{10} levels with atmospheric conditions.

c) Determine the heavy metal content of the airborne particulate matter (PM_{10})

d) Correlate the PM_{10} levels with the reported acute respiratory infections (ARI) incidences in children under five years of age.

Chapter Two

2.0 Literature Review

2.1 Introduction

Airborne particulate matter can be described as a mixture of solid and liquid particles suspended in gaseous state (Parr *et al,* 1996). Airborne particulate matter has an extremely wide diversity of chemical composition. Organic matter, nitrogen compounds, metals such as copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb) and radionuclides occur in the particulate matter in polluted urban atmospheres. Generally the size frequency of the particles has a distribution with two size modes at 0.2μm and 10μm equivalent aerodynamic diameter. These two size modes can also be classified according to their sources.

Large particles ranging from about 2.5 microns to 100 microns in diameter, comprise smoke and dust from industrial processes, agricultural activities, construction and road traffic as well as pollen and other natural sources. Smaller particles, those less than 2.5 microns in diameter, generally come from combustion of fossil fuels. These particles include soot from motor vehicle exhausts, which is often coated with various chemical contaminants such as metals, fine sulphate and nitrate aerosols that form when sulphur dioxide and nitrogen oxides condense in the atmosphere (World Resources, 1998). The largest source of fine particles is coal-fired power plants, but petrol and diesel engine exhausts are also prime contributors, especially along busy transportation corridors. Studies (Thurston *et al* 1985; Dockery *et al* 1989; Dockery *et al* 1992) indicate that particulate levels in North America and Western Europe rarely exceed 50μg/m^3. However, levels in many developing countries are much higher often exceeding 100μg/m^3 (WHO, 1994). For instance the ambient concentrations of total suspended particulates (TSP) in the developing countries are among the worlds largest (World Resources, 1998). In 1995 all but two of the 87 cities monitored for TSP in China far exceeded WHO's guideline of 50 $\mu g/m^3$ annual mean concentration (NEPA 1996).

2.2 Health effects of suspended particulate matter

Of the several pollutants that taint the urban air, fine suspended particulate matter, sulfur dioxide and ozone pose the most widespread and acute risks (World Resources, 1998). Bart and Susy (1989) determined the separate health consequences of ozone and particulate matter using a large cross-sectional data collected for six years in United States of America. The results indicated an association between smaller size particles (fine particles) and both minor restrictions in activity and respiratory conditions severe enough to result in work loss and bed disability in adults. Ozone was found to be only associated with minor restrictions. Adverse health effects appear to be related to injury of the surfaces of the respiratory system. Particulate matter may produce direct injury upon the surface of the respiratory tract or the injury may extend beyond the surface of the tract. The fraction of particles deposited in the three respiratory tract compartments as a function of particle diameter is shown in Fig 2.1 (Perkins, 1974).

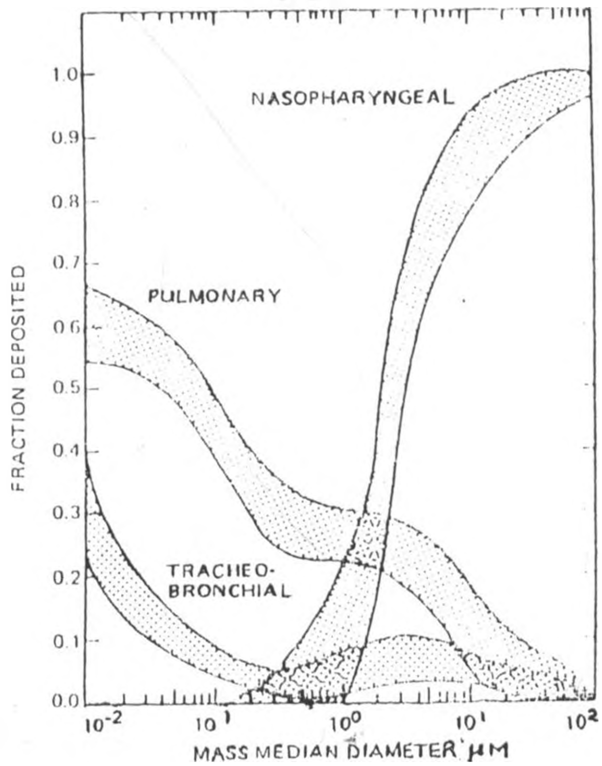


Fig 2.1: Fraction of particles deposited in the three respiratory tract compartments as a function of particle diameter (Perkins, 1974).

Studies on the effects of chronic exposure to air pollution have singled out particulate matter as the pollutant most responsible for the life-shortening effect of dirty air (Pope, 1989; COMEAP(a), 1998). The health effects of particulates are strongly linked to particle size. Particle with a size greater than 10 microns diameter are generally too large and heavy to travel very far and those that do reach a human body are filtered off by the nose. It is the smaller particles generally referred to as PM_{10} having a size of around 10 microns or less that are the most hazardous (IAEA, 1996). This is because they can be inhaled deeply into the lungs (Fig 2.1). The constituents in small particles also tend to be more chemically active and may be acidic as well and therefore more dangerous (WHO, 1994). This explains the increased interest of sampling and analysing the suspended particulate matter in two or more size fractions with more emphasis on the fine particulate range (IAEA, 1996).

Several epidemiological studies mainly done in the United States and Europe have associated particulate pollution with acute changes in lung function and respiratory illness (Pope, 1989; Dockery *et al,* 1996), resulting in increased hospital admissions from respiratory infections, or aggravation of chronic conditions such as asthma and bronchitis (Deborah, 1996;). Recent epidemiological studies (STA, 1996; BMJ, 1998; COMEAP(a), 1998) have shown daily fluctuations in PM_{10} levels to be associated with acute respiratory hospital admissions in children, to school and kindergarten absences, to increased medication use in children and adults with asthma. Pope (1989) studied respiratory diseases associated with community air pollution and found an association between PM_{10} levels and hospital admissions for pneumonia, pleurisy, bronchitis and asthma. He also found that during months when 24 hour average PM_{10} levels exceeded 150μg/m^3, average admissions for children nearly tripled, in adults the increase was 44%. High particulate levels have also been associated with higher infant mortality rates (Woodruff *et al,* 1996).

A number of epidemiological case studies have also linked short term increases in particulate levels, such as those that occur during pollution episodes with immediate increases in mortality. This pollution induced mortality rate ranges from 2 to 8 percent for every 50μg/m^3 increase in particulate levels. Dockery *et al* (1992) estimated the effect of inhalable particles (PM_{10}) and fine particles ($PM_{2.5}$) on daily mortality in St Louis and eastern Tennessee in United States of America. He found that total mortality in St Louis increased by 16% for each 100μg increase in PM_{10} and by 17% in eastern Tennessee. He found weaker but positive associations with $PM_{2.5}$. These findings have been replicated on several continents, in cities as widely divergent as Athens, Sao Paolo, and Philadelphia (Bart, 1993;

mechanism of filtration of suspended particles is a product of several processes including impaction, diffusion, precipitation and electrostatic attraction. Hence efficiency of filtration is a complex function of many variables, including pore size, particle size, face velocity and filter loading.

Atmospheric phenomena play an important role in the determination of ambient air quality. Diurnal and seasonal fluctuations in source emissions tend to be reflected in ambient air pollution levels. For example, in their studies Ngugi (1983) and Wilson (1984) found a diurnal variation of total suspended particulates (TSP). Meteorological parameters have varying degrees of influence on ambient air quality. The parameters of major significance are atmospheric stability, windspeed and direction and precipitation. Other influences may be attributed to temperature, humidity and solar radiation.

Temperature tends to have it's main effects due to the resulting changes in domestic heating requirements during colder weather. Humidity can affect air quality in a variety of ways. Low humidity can result in increased suspended particulate concentrations due to suspension of surface dust. Karue *et al* (1992) found TSP collected to increase with temperature and windspeed and decreased with relative humidity. High humidity as exhibited in fog conditions can block solar heating of the ground surface and thereby prolong the life of inversion layers.

2.3.2 Description of the "Gent" Stacked Filter Unit (SFU)

The concept of separating particulate matter into at least two size fractions by partial filtration dates back to work done in the 1950's by the United States Navy during atmospheric testing on nuclear weapons (Cahill *et al*, 1994). Compelled by the need to sample the particulate matter that is able to penetrate to the lungs and hence of great concern to health, several samplers have been designed. These include the cascade impactors and stacked filter units. The Gent stacked filter unit air sampler is specifically designed using the principle of sequential filtration (IAEA, 1996) for the collection of airborne particulate matter in the inhalable (PM_{10}) size fraction. Sequential filtration (SQF) is a method for size fractionation of aerosols, which exploits the well defined geometry of nucleopore filters. The filter separates the large particles by letting the smaller particles pass on to a backup filter. The SQF constitute a simple, practical and economic method for fractionating aerosols in such a way that the samples are suited for further gravimetric, chemical or microscopic analysis. Nucleopore filters are thin (6-10)μm homogeneous non-hygroscopic polycarbonate membranes with mass density of 0.95 g/cm^3 punctuated by circular pores normal to the surface which are randomly distributed (Heidem, 1981). The blown-up view of the sampler is shown in Fig 2.2 (Parr *et al*, 1996), it was designed at the University of Gent, Belgium for a co-ordinated Research Project supported by International Atomic Energy Agency (IAEA) and with 20 participating countries (Parr *et al*, 1996).

The sampler uses an open face type stacked filter unit, in which two 47mm nucleopore polycarbonate filters are employed for the collection of APM. Separation of the APM into the two size modes is done by placing the appropriate nucleopore filters in front of a final absolute filter in a sequence or stacked configuration. The sampler uses two types of filters, 8.0μm and 0.4μm pore size otherwise refered to as coarse and fine filters respectively. The coarse filter collects particles larger than 2μm (EAD) and fine filters the particles less than 2μm EAD. The filter unit is inserted in a cylindrical container hence the filters are well protected during transport and are only handled in the laboratory.

The cylindrical container is provided with a pre-impaction plate for the collection of particles larger than 10 micrometres (Fig 2.2). The impaction plate is usually coated with apiezon oil or vaseline for reducing particle bounce off. Since the impaction plate uses

The "Gent" SFU has been calibrated by Maenhaunt and his co-workers (Maenhaunt *et al,* 1992) and is now utilized extensively in PM_{10} sampling exercises.

The filter unit, a pump and timer forms an inexpensive sampling system and by having the same air stream pass through both filters the technique is subject to fewer flow problems than are other devices that rely upon either on split or parallel sampling parts (Maenhaunt *et al,* 1992). The Stacked Filter Unit (SFU) sampling line is shown schematically in Fig 2.3. It consists essentially of the following components:

a) a double (stacked) filter cassette.

b) a black polyethylene container (which includes a pre-impaction stage for PM_{10})

c) an orange-coloured rain protection cover.

d) a 40cm long soft transparent tubing to connect the stacked filter cassette to the poly-flo tubing.

e) poly-flo tubing (3/8 inches outer diameter, 1/4 inches inner diameter) with connection from the transparent tubing to the pump set-up.

f) a needle valve to regulate flow rate.

g) a vacuum gauge.

h) a gas flow meter (Rotameter).

i) a precision gas volume meter (volumeter).

j) a time switch and an hour meter.

The needle valve, the vacuum gauge, vacuum pump, the rotameter, the volume meter and timing devices (items f through j) are assembled in a pump set-up and enclosed in a housing (box) which consists of a grey PVC base plate and transparent polycarbonate material for the sides and top.

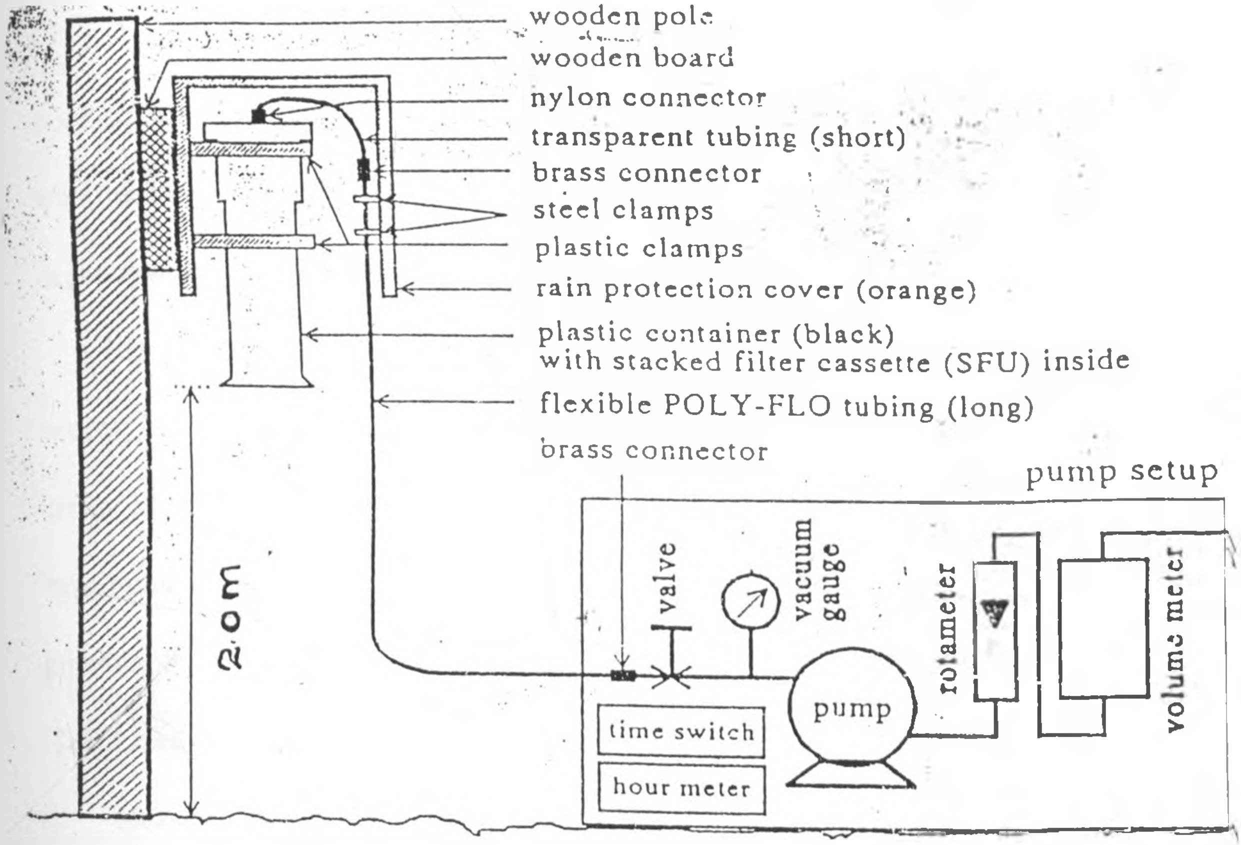


Fig 2.3: Schematic diagram of the SFU sampling line (Modified after Maenhaunt *et al*, 1992)

2.4 Air pollution by heavy metals

2.4.1 Introduction

From history, the rate of emission of most metals has always been low due to the low volatility of most metals, but with the advent of high temperature processes such as metal smelting fossil fuel combustion, biomass fuel combustion and other industrial activities, the rate of emission for some metals has substantially increased

(Hien *et al*,1997; Galloway *et al*,1982). The dynamic nature of the atmosphere makes some of these metals to be deposited in areas remote from their initial sources. This has resulted in increased metal concentrations in the atmosphere and their atmospheric deposition.

The greatly increased circulation of toxic metals in soil, air and water results in their build-up in the human food chain. The increased environmental exposure is implicated in the well documented elevations in the concentrations of several trace elements in body fluids and organ systems of contemporary populations (Drasch,1983).

The number of persons suffering from subclinical metal poisoning is believed to be several millions. A large portion of the cases are in the developed countries especially in the urban areas which have become centres of metal pollution and the population being susceptible to environmental toxins (Nriagu, 1988). Hence, as a global problem, the potential health effects of metallic hazards should be a matter of public health concern.

2.4.2 Heavy metal pollution studies

Heavy metals can be categorised into two broad categories, essential and non-essential. Essential heavy metals are those that are necessary for specific physiological functions in organisms (Mortz, 1981). Examples of essential metals to human beings include zinc (Zn), iron (Fe), manganese (Mn) and molydenum (Mo) whereas those regarded as toxic even when present in traces include mercury (Hg), cadmium (Cd), tin (Sn), lead (Pb) and chromium (Cr). Non-essential heavy metals are those that do not have any known biological functions in living tissues. They are acquired and accumulate in the body as heavy metal contaminants.

Since the industrial revolution production of heavy metals such as lead, copper, and zinc has increased exponentially (World Resources, 1998). The toxicity of these metals have also been documented throughout history. Greek and Roman physicians diagnosed symptoms of acute Lead poisoning long before toxicology became a science. Exposure to heavy metals has been linked to developmental retardation, various cancers, kidney damage and even death in instances of very high exposures (World Resources, 1998).

A metal can be regarded as toxic if it interferes with the growth or metabolism of cells when it is present above a given concentration (Oduor, 1992). Almost all metals are toxic at high concentrations and some are severe poisons even at low concentrations. In assessing the potential impact of a metal in the environment or in the target itself, example human being, the terms critical concentration and threshold levels are often used. This refers to the lowest level of exposure which is necessary to produce a detectable adverse health effect (WHO, 1976 and 1987).

World-wide, the known natural sources of metals into the atmosphere are soil, sea water, volcanic dust and gases. The anthropogenic emissions are from industrial gases, particulates, and fossil fuel combustion. Lead and arsenic are notable exceptions. the principal sources of these elements being the use of leaded gasoline and the use of arsenic pesticides. Metal pollution in soils is derived mostly from atmospheric fallout, coal flyash, urban refuse, animal wastes, agricultural and food wastes. On the other hand, the principal sources of pollutant metals in natural waters are the discharge of domestic and industrial (including mine and smelter) waste waters and the dumping of sewage sludge.

In recent years there has been an increased interest in trace metals in the atmosphere and their environmental effects, this is to a large extent because metals such as cadmium, mercury, and lead accumulate in the atmosphere and may be toxic to living systems (Barne *et al*, 1987). Knowledge about the levels of metals in atmosphere has been derived from studies of airborne particulate matter (APM), biological samples, and soil samples. This mainly involved determination in total suspended particulate matter, but this has since shifted to inhalable particulates in two or more size fractions (fine and coarse) as shown by some of the recent studies (Winchester *et al*, 1984; Foltescu *et al*, 1994; Xiande *et al*, 1995). By measuring heavy metal concentrations separately in coarse and fine particle size ranges, clues may be obtained as to which processes (example Soil dust, vehicular emissions and industrial emissions) are responsible for releasing the metals into the atmosphere. Kroger *et al* (1994) analysed fine and coarse particulate samples collected 13 kilometres from a copper smelter in Chile and found sulphur, copper, zinc and arsenic to be quite enriched in normal operation periods relative to non-operational periods. Further elemental characterisation of soil samples by radioactive source analysis demonstrated that this group of elements did not come from airborne soil dust. The elemental composition of airborne particulate matter has been determined in several areas around the world and shown to be influenced by distribution of local sources and meteorological conditions. Rhodes *et al* (1970) found lead (Pb) and bromine (Br) concentrations in almost all the samples from 38 sampling stations related to vehicular emissions. Ogunsola *et al* (1993) indicated that lead (Pb), bromine (Br) and zinc (Zn) were highly enriched in the atmosphere with lead (Pb) concentration exceeding the threshold limit prescribed by Nigeria Federal Environmental Protection Agency for over 50% of the samples analysed. Other studies (Cornille *et al*, 1990; Foltescu *et al*, 1994) done in Europe and Asia have also indicated major source of bromine and lead to be vehicular emissions. However, other sources of bromine and lead have also been identified which include natural marine sources and open burning of refuse (Annegarn *et al*, 1983; Xiande *et al*, 1995; Hien *et al*, 1997). Elevated levels of heavy metals have been observed in soils, vegetation and ambient air in urban areas. It has been observed that population living in industrial areas have relatively higher concentrations of metals like lead and cadmium in their blood (Wanjie, 1991; Oduor, 1992; Tripathi *et al*, 1989). Hong *et al* (1996) observed a positive correlation between lead (Pb) concentration and other trace elements in the urine of exposed workers and environmental samples. Vousta *et al* (1996) found elevated concentrations of lead, zinc, chromium and manganese in leafy vegetables with the airborne particulate matter being highly enriched with zinc, cadmium, lead and manganese in the greater industrial area of Thessaloniki, Northern Greece.

The metals pollute the environment either by direct toxicity, interference with the respiratory and photosynthetic balance or by impairment of the diversity and stability of the ecosystem. Lead (Pb) and cadmium(Cd) are among the most hazardous elemental pollutants. They are known to have comulative effects, so that even small quantities consumed may show effects later in life (Lucas, 1975). McDonalds *et al,* (1979) studied particle size distribution of metals in the atmosphere of Glasgow, they observed that the toxic metals cadmiun (Cd), nickel (Ni) and lead (Pb) had extremely high proportions in the smallest particle size range which can easily enter the respiratory tract and lodge in the alveoli.

Toxic elements are taken in through food, water and air. Of these three, air intakes are the most readily assimilated into the body. It is well established that inorganic species are intimately linked with the biosphere with some exceptions: calcium (Ca), nitrogen (N), phosphorus (P), potassium (K) and sodium (Na). Most of the essential heavy metal elements, cobalt (Co), chromium (Cr), manganese (Mn), nickel (Ni), selenium (Se), silicon (Si), tin (Sn) and vanadium (V) are also toxic when taken in excess, example too much copper causes nercotic hepatitis (Tyagi, 1992). Noll *et al* 1990, analysed TSPM samples from Los Angeles Basin (Claremont), California and Chicago and demonstrated that the elements could be divided into two groups according to their origin, namely those of crustal origin aluminium (Al), calcium (Ca), iron (Fe) and silicon(Si) and anthropogenic origin cadmium (Cd), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). Mahadevan *et al* (1989) analysed aerosol samples from a remote background site in India for 18 elements.

He established that the concentration levels of lead, potassium, zinc and bromine showed marginal enrichments relative to their crustal abundances. Chih-Shan Li (1994) analysed PM_{10} samples for elemental content in Taipei and came up with two groups of elements. He established that potassium, calcium, titanium, manganese and iron had lower enrichment factors (close to 1) which indicated they were most likely derived from soil dust. However, sulphur, chlorine, zinc, bromine and lead appeared to be highly enriched suggesting anthropogenic sources such as industrial operations, automobile exhausts and refuse burning. Several other studies (Maenhaut *et al*, 1987; Raad *et al,* 1991) have come up with similar findings.

In urban atmospheres, enhanced concentrations of heavy metals are observed due to the presence of industries, burning of fossil fuels and dense traffic. Malean *et al* (1977) reported lead levels of 0.01mg/m^3 for urban areas and 0.002mg/m^3 for non-urban areas. Xiande *et al*, (1995) studied elemental content data for aerosol samples collected from 24 sites in South Eastern Australia. He found low concentrations of lead (less than 20μg/m^3) for sites in rural areas as compared to values (240-340μg/m^3) observed for urban sites. Several research works have also shown that children living in cities have relatively high concentrations of toxic metals like lead (Pb), cadmium (Cd) in their blood (Cohen *et al,* 1973; Woldran, 1975). Wanjie (1991) evaluated lead (Pb) and cadmium in selected Kenyan urban population and detected cadmium (Cd) in blood samples (highest 32.30μg/dl) indicating that the metal was becoming more abundant in the atmosphere. Determination of heavy metal concentrations in the atmosphere is therefore important with a view to understanding the dose inhaled by human beings and also for knowing the sources of these elements.

In Kenya heavy metal pollution studies have mainly concentrated on the determination of total suspended particulate matter and recently on PM_{10}, soil, plants and water. A study by Karue *et al* (1992) evaluated the elemental concentration of the particulate matter using energy dispersive x-ray fluorescence in the city of Nairobi. He observed high levels comparable to those reported in other cities in India and Japan. This study established that Lead (Pb) levels were within the WHO guidelines (0.5-1.0μg/m^3). It further established that lead (Pb) and bromine (Br) mainly came from motor vehicles while manganese (Mn) and iron (Fe) were from industrial sources: potassium (K), calcium (Ca), titanium (Ti), zinc (Zn) and zirconium (Zr) were attributed to crustal dust. Gatebe *et al* (1996) evaluated the elemental concentration of PM_{10} samples in a suburban area, he obtained bromine/lead ratios ranging from 0.3-0.51. This study also attributed the sources of lead (Pb) and bromine (Br) to vehicular emissions.

Local studies in environmental pollution of the lithosphere include those to determine the concentration levels of selected heavy metals in soil samples in urban centres. Oduor (1992) evaluated the concentration of lead (Pb) and cadmium (Cd) in roadside soils and vegetation in Nairobi and Kiambu. In Nairobi he found that lead (Pb) concentration levels ranged from 0.0306-350ppm in soil and 0.00771-45.8ppm for plants. Cadmium (Cd) concentration ranged between 0.110-0.387 ppm in soils and 0.092-0.249ppm for plants. Regression analysis between the concentration of metals in the samples and traffic volume, established a strong correlation for lead (Pb). Hashim *et al* (1998) analysed soil samples along major highways of Kenya, he found lead (Pb) levels to be higher along the busy Nairobi-Mombasa highway than for areas situated along Thika highway leading to the conclusion that leaded gasoline continues to be the major contributor of lead (Pb) in the atmosphere.

2.5 Some heavy metals and their environmental implications

2.5.1 Lead

Lead is widespread and probably the most serious toxic metal (Tyagi, 1992). Its effect as a harzadous metal has been recognised since early civilisation. The metal being easily smelted has been used by man for making tools and vessels for either cooking, eating or wine storage. The main uses of lead are in the manufacture of lead accumulator, tetraalkyl compounds used as gasoline additives, cable sheathing, lead pigments and alloys (Fergusson, 1986). The uses of lead most commonly associated with poisoning are lead glazed pottery, solder plumbing, in paint and as additive to petrol (Fergusson, 1986; WHO, 1987).

In recent times lead has played a major role in occupational health diseases among smelters, miners and spray painters (UNEP, 1980). This has subsequently led to a lot of research work on lead as an environmental pollutant. One important feature is the significant amount of lead assimilated into the body from air intakes. This is due to the high absorption factor of 0.4 as compared with 0.1 for food and water. Lead intake in an average man depends on his working and domestic environment (Malean *et al*, 1977). The limit suggested by WHO for a tolerable intake of lead per day for an adult is 430μg, while the minimum lethal dose of inorganic lead for man has been estimated to be in the range of 300 to 700mg/kg body weight or blood lead (Pb) levels of 0.8mg/L (Tyagi, 1992). Children's toxic blood level is lower at 0.1 to 0.2 mg/L.

The major sources of lead emission into the atmosphere are auto exhausts, primary and secondary lead smelting, combustion of leaded fossil fuels and lead containing paints. Lead(Pb) from automotive exhausts is in the form of lead halides such as leadbromochloride (PbBrCl). Particulates represent the form of emissions from other sources. Xiande et al (1995) analysed data collected at 24 sampling sites in South-Eastern Australia and concluded that other additional sources of lead exists apart from motor vehicle exhausts, this is further confirmed by Wanjie, 1992 who analysed brands of cigarretes and found high levels of lead ranging from 6.52-8.82µg/g which indicated that smoking could be another probable source of airborne lead. The major contributor of airborne lead remains vehicular emissions as evidenced by several studies (Xiande *et al,* 1995; Tripathi *et al,* 1989). The particle size of auto-exhaust lead is usually less than 0.1µm, consequently it has been reported that about 40% of lead airborne particles are retained beyond the bronchioles and hence are completely absorbed by the human body (COBEAP, 1971). High concentrations of Lead (Pb) has also been found in crops, soil, dust near roads with high traffic density (Nasralla., 1994; Oduor., 1992; Vousta *et al,* 1996; Hashim *et al*, 1998). Lead (Pb) has been found to be a special hazard to young children, studies have shown that lead exposures can significantly reduce the intelligent quotient (IQ) of school-aged children (Goyer, 1996). A review of 17 studies from different parts of China found that between 65 and 99.5 percent of children living in industrial and heavy traffic areas had blood lead levels above 10µ g/dl (Jerome *et al,* 1996). Among the possible sources of exposure, soils and dusts have been shown to be responsible for a significant amount of lead burden in children (Sedman, 1989). Children take in dusts/soils by mouthing fingers, palms and eating foods exposed to dust or dropped on the floor, by absorption through the skin and inhaling the airborne dusts.

The health toll of lead exposure is particularly high among poor populations of developed and developing countries. This is because exposures are typically higher and the populations are more susceptible. In urban areas for instance, the poor may live in older housing where the risks from lead-based paint are greater (World Resources, 1998).

The toxicity of lead is based on the fact that it is a potent enzyme inhibitor because it binds with sulphydryl groups. Lead poisoning affects the blood forming mechanism. It inhibits a number of enzymes involved in the biosynthesis of haem, the porphyrin in haemoglobin and cytochromes. The principal danger areas are the haemopoietic system, leading to anaemia in serious cases, the nervous system leading to irreversible brain damage, i.e, acute encephalopathy and the renal system (Tyagi, 1992).

Early symptoms of lead poisoning are restlessness, irritability, headaches, muscle pains, heartburn and constipation. In the advanced stages lead intoxication can lead to epileptic convulsions, mental impairment, drowsiness and even comma (Bach, 1995). Lead poisoning can also cause early death, a survey in Chicago showed that out of 405 children with chronic lead poisoning, only 257 recovered completely, with the rest having permanent mental retardation and epileptic seizures (UNEP, 1984). A report involving lead poisoning in a physician family in America in 1969 revealed that six members of the family experienced fatigue, poor appetite, vague pains in the stomach and vomiting, with unexplained personality changes being observed in children and parents. Their blood lead levels were found to be 1.94mg/l (Wolbott, 1978).

At the lead levels usually found in the environment (i.e, reported by research workers) the symptoms of lead (Pb) poisoning may not appear. However, it has been established that the inhibition of certain enzymes, such as aminolevulinic acid dehydratase (involved in haemebiosynthesis) can occur at lead levels below 40μg of lead per 100 grams of blood (Sukurai *et al* ,1974).

2.5.2 Cadmium

Cadmium occurs in zinc-copper ores. The Cd/Zn ratio for a number of ores and ore concentrates lies in the range 0.001-0.0001(WHO, 1987). Cadmium and zinc are found in the same periodic group, have similar chemical properties, but zinc is biochemically active while cadmium is not. Cadmium'is less used than lead but its more toxic. Approximately 25-

50% of inhaled cadmium is absorbed into the body while from food the absorption is about 6%. The WHO tolerable intake per day per person is given as 57-71μg (Mehra,1992).

The metal is used for plating, in pigments, in batteries (Ni-Cd cells), stabilisers for plastics in alloys and in autoparts such as tyres, seats and radiators (Hiscock, 1979, WHO, 1987). Airborne cadmium emissions results when products that contain cadmium (Cd) are incinerated, such as autoparts (tyres and seats), plastic bottles and during the smelting of zinc, copper, lead and during the production of fertilisers and insecticides (Bach 1975). Rubber tyres can contain 20-90μg/g of cadmium (Lagerwerftetal, 1970) due to the use of zinc compounds such as zinc oxide and zinc diakyl carbamates in the vulcanisation process. The abrasion of tyres on the road adds cadmium (Cd) to street dust and mean levels of 2μg/g and greater have been reported (Tyagi, 1992).

Tobacco also contains around (0.5-3μg/g) (WHO, 1987) of cadmium (Cd), hence smoking acts as a source of airborne cadmium. This fact has been corraborated by work done by (Wanjie, 1991) who analysed some local brands of cigarettes and found cadmium (Cd) levels ranging from (0.84-1.25μg/g).

Cadmium toxicity result due to its similar chemical properties with zinc. Its toxic action seems to involve the replacement of zinc in key enzyme sites resulting in inhibition of their proper functioning (Pulves, 1977). Acute cadmium (Cd) poisoning is accompanied by a large array of symptoms and diseases including vomiting, loss of appetite, dizziness, excessive secretion of saliva, diarrhoea, bladder infection and pulmonary infection. Chronic cadmium (Cd) poisoning involves the kidneys and the liver. It also causes bone softening (Bach, 1975). The most serious case of hazards of cadmium (Cd) in the environment occurred in the jinzu river basin in Japan. Exposure to cadmium occured through the ingestion of rice grown in fields irrigated by industrially polluted water (UNEP, 1980). The affected subject developed a syndrome that began with renal dysfuntion and eventually resulted in painful bone changes. These conditions were exclusively found among the inhabitants of the polluted area for which cadmium was considered responsible (Shunichi *et al,* 1986).

2.5.3 Manganese

Manganese (Mn) occurs in fairly large quantities in the earth's crust. It was first isolated in 1774 (WHO, 1981). Manganese is widely used in the steel industry to reduce oxygen and sulfur levels. Further, manganese emissions occur during the process of manufacturing dry cell batteries, welding, coloring, bleaching of glass, producing potassium permanganate and other manganese compounds. Acute manganese poisoning mainly affects the respiratory system as manifested in nasal congestion, chest pain, and pneumonia. Chronic manganese intoxication mainly involves the central nervous system. The disorders associated with this disease include aimless running around, purposeless laughter or weeping, high irritability, impairment of judgement and memory spells of fear and hallucinations (Waldron, 1980).

2.5.4 Iron

Iron and steel industries are the major sources of Iron dust. Other sources of Iron emissions include welding, electric ore furnaces and fuel oil combustion.

Compared with other metals in the atmosphere, Iron occurs at a higher concentrations ranging from 0.1μg to 6.1μg/m^3. Karue *et al* (1992) in their study of a Kenyan urban area observed concentration ranging from (6.014-23.698μg/m^3) in total suspended particulate matter.

Iron oxide has been found to cause shortness of breath and coughing. Short term exposure to this dust is known to have caused spells of metal fever (Tyagi, 1992). Since Iron oxide acts as a carrier for benzo(a)pyrene transporting it deeply into the lungs, hence its inclusion in the class of agents inducing cancer (Wilfrid, 1975)

2.5.5 Titanium

Titanium (Ti) occurs rather abundantly in the earth's crust and is used in a large variety of industrial processes (Mason, 1966). Emissions of titanium into the atmosphere originates from processes involving paints, pigments, coatings, ceramics, fibre glass and alloys. Titanium mainly interferes with two types of enzyme action. It inhibits bone growth and interferes with the carbohydrate metabolism (Braunwald *et al*, 1987).

Chapter Three

3.0 Analytical techniques

3.1 X-Ray Spectrometry

3.1.1 Introduction

X-ray spectrometry (i.e, x-ray fluorescence) is an emission spectroscopic technique that has found wide utility in many fields which require elemental identification and determination. The technique depends upon the emission of characteristic x-ray radiation, usually in the 1-60 keV range following excitation of atomic electron energy levels by an external energy source such as charged particle, x-ray beam or δ-rays.

X- rays were discovered by Rontgen in 1895. It was H.G.J. Mosely who developed the relationship between atomic structure and x-ray emission and in 1913 published the first paper on x-ray spectrometry (Jenkins, 1976). The developement of routine instrumentation, leading to the x-ray spectrometer known today, took place over the following decades after Mosely experiments.

3.1.2 Properties of x-rays

X-ray phenomena of particular significance in x-ray spectrochemical analysis include :

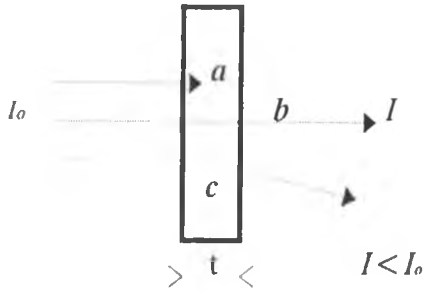
3.1.2.1X-ray Absorption

X-rays impinging upon a target undergo interactions with the elements of the target which are of prime concern to the x-ray spectroscopist. These processes are absorption and scatter. Absorption of the radiation may occur by specific interactions which are of importance in sample excitation process in x-ray spectrometers, or it may occur by more general interactions which have important influences on the emitted x-ray intensity from the sample. Scatter of x-rays leads to background intensity in the absorbed spectra.

When an x-ray beam passes through a material. The photons may interact with electrons in the orbits of the target elements in rather specific ways resulting in atttenuation of the intensity of the x-ray beam. The interaction may result in photoelectric ejection of electrons, or scatter of the x-ray beam, the overall result is frequently described in terms of an exponential decrease in intensity with the pathlength of the absorbing material.

Figure 3.1 below illustrates a perfectly collimated, monochromatic radiation beam of intensity I_o which is incident on an absorber having length of t cm and density ρ (g/cm^3). The incident beam may undergo absorption, transmission or scatter. The emergent collinear beam consists of the transmitted rays and has intensity I given by the Beer-lambart's law (Bertin, 1980) where,

$$I = I_0 \exp(-\mu t) \quad \text{.......(1)}$$



a-Photoelectric absorption *b*-transmission *c*-Scatter

Figure 3.1: Schematic representation of attenuation.

$\mu(cm^{-1})$ is the linear absorption co-efficient of the absorber. The negative sign indicates that the intensity always decreases, that is x-rays always undergo attenuatuion on passing through matter. In terms of mass absorption coefficient the equation becomes :-

$$I = I_0 \exp\left[-\left(\mu/\rho\right)\rho t\right] \quad \text{.......(2)}$$

where (μ/ρ) is the mass absorption coeffiecient (cm^2/g) of the absorber and ρt is the area density in g\cm^2. The mass absorption coefficient is related to the probability that radiation will interact with matter. It's an atomic property of chemical elements and is a measure of their x-ray "stopping power". It is a function only of wavelength, atomic number and is independent of the chemical combination or physical aggregation.

X-ray absorption can also be expressed by use of the concept of cross-section. This is a measure of the probability for those interactions to occur in a material. It exhibits a characteristic dependence on the energy, as well as on the atomic number of the atom in which the interaction takes place. If equation (1) is written in terms of numbers of x-ray photons incident upon n_o and transmitted by n, an absorber of thickness t cm and linear absorption coefficent μcm^{-1}, one gets.

$$n = n_o \exp(-\mu t) \qquad (3)$$

If the volume of the absorber traversed by the x-ray beam contains n_{a_t} atoms/cm^3, each of which presents an imaginary target area or cross-section σ cm^2 to the photons,

$$\mu = n_{at}\sigma \quad \text{or} \quad \sigma = \mu / n_{at} \qquad (4)$$

then cross-section and mass absorption coefficient are related as follows (Bertin, 1980):

$$\mu / \rho = \sigma\left(N / A\right) \qquad (5)$$

where

N is the Avagodro number

A is the Atomic Weight

The fundamental unit of atomic cross-section is the barn (1 barn= 10^{-24} cm^2) and mass absorption coefficients are often tabulated as barns per atom. The linear absorption coefficient and therefore the mass absorption coefficient gives a measure of the total absorption of the radiation which passes through the material, regardless of the mode of interaction, hence

$$\mu = \tau + \sigma + \pi \qquad (6)$$

$$\mu/\rho = (\tau/\rho) + (\sigma/\rho) + (\pi/\rho) \qquad (7)$$

where, τ, σ and π represent losses by photoelectric absorption , scatter and pair production (Bertin, 1980).

3.1.2.2 Photoelectric Effect

This is one of the processes leading to absorption of x-rays as they pass through matter.It involves the ejection of electrons from the orbitals of elements in the x-ray target. This process is a major contributor to the absorption of the x-rays, and is the mode of excitation of the x-ray spectra emitted by elements in samples. Primarily as a result of the photoelectric process, the mass absorption coefficient decreases steadily with increasing energy of the incident x-ray radiation, leading to sharp discontinuities in the absorption versus energy curve for a given element. These results from characteristic energies at which the photoelectric process is especially efficient. Energies at these discontinuities are called absorption edges (Bertin, 1980., Tertian and Claisse, 1982).

In an atom, the innermost electrons are bound most tightly while the outer electrons are only loosely bound. The more loosely bound an electron is, the lower the exciting radiation energy needed to eject it (i.e, absorption edge). For example, in an atom the closer to the nucleus an electron is, the higher the incident radiation energy needed to eject it. Hence the wavelength of an x-ray beam needed to eject an L-shell electron is longer (less energy) than that which is neeeded to eject an electron from K-shell.

On photoejection of an electron, unstable states in the electron orbitals of atoms are created. Once the vacancies in the inner orbitals are formed, the excited state relaxes by filling the vacancy with an electron from an outer orbital which results in the emission of characteristic secondary radiation. Only certain transitions are allowed because of quantum mechanical rules called selection rules (Tertian and Claisse, 1982). The quantum numbers of the initial and final energy levels must obey the following selection rules.

$\Delta n \geq 1$

$\Delta l = \pm 1$

$\Delta j = \pm 1$ or 0

where n is the principle quantum number l is the angular quantum number $j = l + s$ is the vector sum of l and s, where s is the spin quantum number. The transitions predicted by the selection rules are shown in figure 3.2 which contains the lines that are of most interest to the analyst.

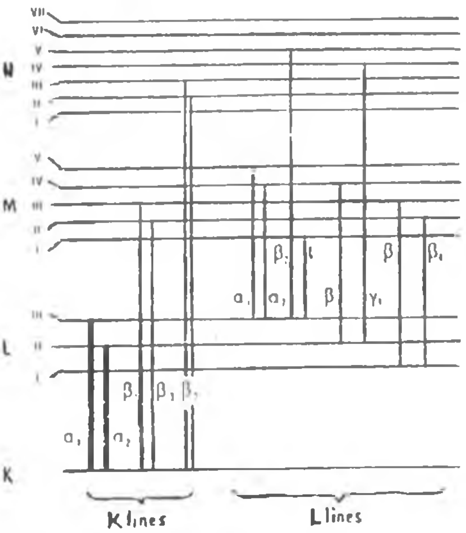
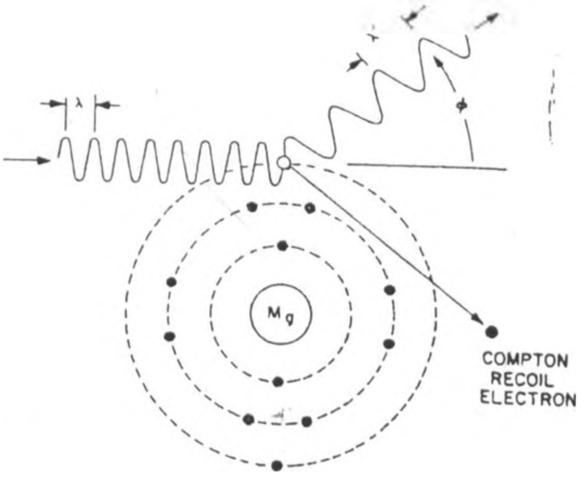


Fig 3.2: Partial energy level diagram showing the origin of the main lines in the K and L spectra (Tertian and Claisse, 1982).

3.1.2.3 Auger Effect

When an electron is ejected from an atomic orbital by the photoelectric process, there are two possible results, secondary radiation and auger or secondary electron ejection. The secondary radiation may succeed in getting out of the sample in which case characteristic x-rays are observed. On the other hand, it may be energetic enough to knock off an electron from one of the higher shells, e.g. L. This process is considered to be radiationless since it does not lead to the observation of characteristic x-rays. It's referred to as the auger effect and the ejected electron as the auger electron. The effect may also be visualised as the reabsorption of the characteristuc x-ray internal to the atom. Therefore, auger electron prodution is a process which is competitive with x-ray photon emission from excited atoms in a sample. The fraction of the excited atoms which emit x-rays is called the flourensence yield i.e, electron and the scatter is incoherent otherwise known as compton scatter (Fig 3.4). It should be recognised that, although the total amount of scattered radiation increases with increasing atomic number because of the greater number of electrons, a larger observed scatter is seen from samples with low atomic number matrices because there is less absorption by the sample.



where λ and λ' are wavelengths(cm) of the incident and modified scattered x-rays and

ϕ is the angle between unscattered and scattered x-rays.

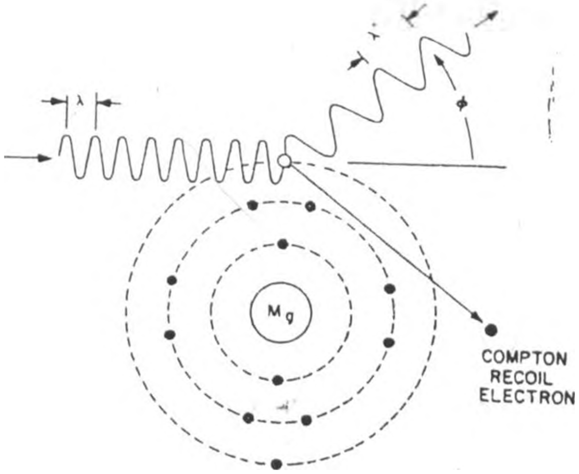
Fig 3.4: Schematic representation of modified (compton scatter) of an x-ray photon by an atom (Bertin, 1980).

3.1.2.5 Pair production

In pair prodution, x-ray photons interact with the atom's nuclei, expending all their energy in creating and imparting kinetic energy to electron-positron pairs (e, -e⁻). This phenomenon occurs only at photon energies ≥1.02 Mev and is of no importance in x-ray spectrometry.

3.1.2.6 Energy Dispersive X-ray- Fluorescence(EDXRF) technique

Is a non-destructive instrumental method of qualitative and quantitative analysis for electron and the scatter is incoherent otherwise known as compton scatter (Fig 3.4). It should be recognised that, although the total amount of scattered radiation increases with increasing atomic number because of the greater number of electrons, a larger observed scatter is seen from samples with low atomic number matrices because there is less absorption by the sample.



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3.1.2.6 Energy Dispersive X-ray- Fluorescence(EDXRF) technique

Is a non-destructive instrumental method of qualitative and quantitative analysis for chemical elements based on measurements of the wavelength and intensities of their x-ray spectral lines emitted by secondary excitation (Bertin, 1980., Nguyen, 1997). The primary beam from an x-ray tube or a radioisotope source irradiates the specimen (sample or standard), exciting each chemical element to emit secondary spectral lines having wavelengths characteristic of that element. The detector receives excited lines of all the specimen elements at once and generates a pulse of electric current proportional to its photon energy.

3.1.2.7 EDXRF set up

The x-ray fluorescence spectrometer used in this work consists of the following parts:

(1) The excitation source which excites characteristic x-rays in the specimen. Radioisotope ^{109}Cd was used as excitation source.

(2) Specimen presentation system, which holds the sample in a precisely defined geometry during analysis and provides for introduction and removal of the specimen from the excitation position.

(3) Computer and memory unit which also incorporates x-y recorder and printout display units.

(4) The x-ray spectrometer consisting of the Si(Li) detector(Canberra S1-30180), High voltage bias supply (EG and ORTEC Type 459), amplifier(EG and ORTEC Series 571), preamplifier (Canberra Model 2008), and the multichannel analyzer. A schematic representation is shown in Fig 3.5 a.

The detector is a crystal of lithium drifted silicon that is processed to form a diode. In operation, the x-rays are absorbed in the lithium-drifted layer. The x-rays enter the cryostat through a thin berrylium window. Each absorbed x-ray photon transfers it's energy to a photoelectron, which in turn expends its energy producing electron-hole pairs. The more energetic the x-ray photon, the more electron-hole pairs it can produce providing the basis for proportionality of detector output pulse height and x-ray photon energy in Si(Li) detectors. Lithium drifting serves to compensate for impurities in the silicon crystal hence minimizing other sources of charge carriers. The detector is maintained at liquid-nitrogen temperature (77°K) in its vacuum cryostat at all times (Fig 3.5 b). This reduces noise, ensures optimal resolution and minimizes diffusion of the highly mobile lithium atoms and enhances the life time of the detector. Vacuum operation is required to prevent condensation of moisture on the detector.

The information of the absorbed radiation from the detector is presented as a burst of charge (pulse) collected at the detector terminal. The purpose of the pre-amplifier is to convert the burst of electrons into a voltage signal which may be conveniently transmitted to the measurement system while retaining the proportionality of the energy deposit. The pre-amplifier is also required to keep the electronic noise low, a field effect transistor (FET) is built into the system for the purpose.

The pre-amplifier is coupled to the amplifier which serves to shape and amplify the signal for eventual presentation to the multichannel analyser for pulse height analysis. The MCA also includes a micro-processor which is pre-programmed to perform simple data analysis operations like: energy calibration, integration and subtraction of background, etc.

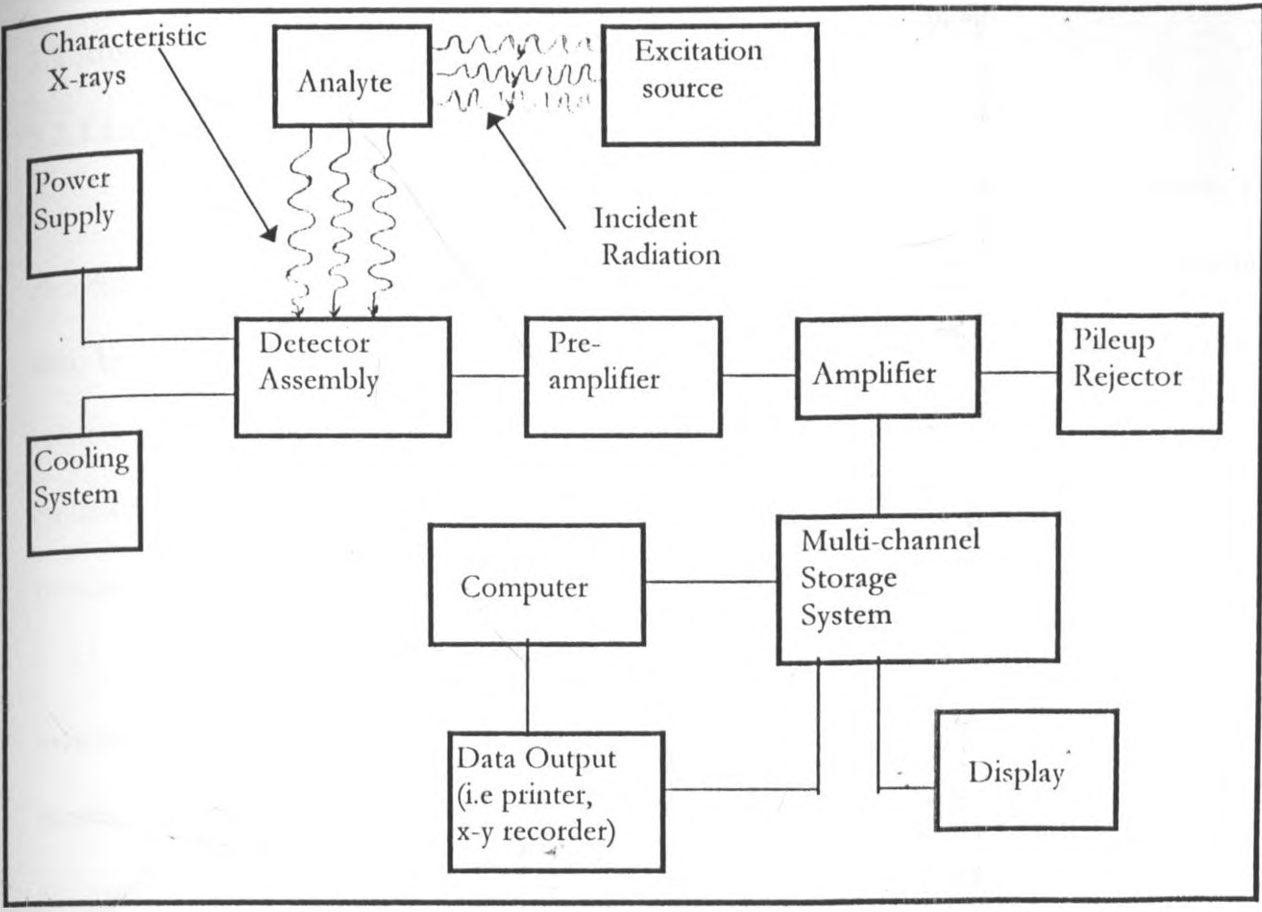

Fig 3.5a: A schematic representation of the X-ray spectrometer(Jenkins *et al*, 1981).

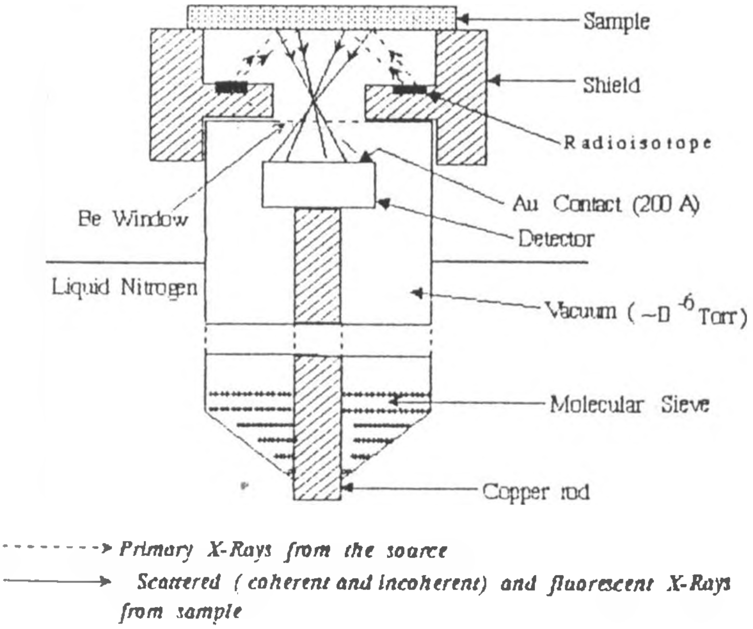

Fig 3 5b Cryostat with geometry of radioisotope source for exciting the sample

3.2 Atomic Absorption Spectroscopy (AAS)

3.2.1 Introduction

Atomic absorption spectrometry is an analytical technique for determination of elements based upon the absorption of optical radiation by ground state atoms in the gaseous state (Weltz, 1985). Interaction of ground state atoms with radiation energy results in three related spectroscopic processes which can be used for analysis, these are absorption, emission and flourescence. Atomic absorption is the most widely used of the three processes because of the reproducibility and long range of concentration measurements.

The phenomenon of the atomic absorption of radiation by atoms has been used for investigation in physics since the early nineteenth century, when Frauehöfur observed a number of dark lines in the sun's spectrum (Weltz, 1985). The first application of atomic absorption was to the determination of mercury by Muller in 1930 (Pinta, 1978). Not until when Walsh (1955) and Alkemade in 1969 in Europe (Pinta, 1978) established the principle for the determination of a chemical element by means of it's atomic absorption spectrum was real analytical atomic absorption spectroscopy born. Hollow cathode lamps or gas discharge tubes served as background source of radiation. This led to improved instrumentation, more reliable sources of radiation, hotter flames and non-flame atomizers (e.g. electrothermal atomizers) which enabled the technique to be extended for analysis of every metallic element in the periodic table. In a relatively short period of two and one-halve decades since their development in 1955, atomic absorption has become one of the most important analytical tools for the analysis of elements.

3.2.2 General principles of Atomic Absorption Spectrometry (AAS)

Atomic absorption is a physical process involving absorption of radiation by ground state atoms (i.e, free atoms) at a wavelength specific to that element, e.g, nickel absorbs at

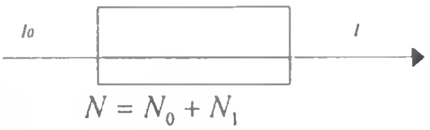

Fig 3.7: Schematic representation of absorption of radiation by atomic population *N*.

In the flame the total number of atoms *N* is distributed into N_0 atoms in the ground state and N_1 excited atoms, i.e, $N = N_0 + N_1$. It can be assumed that thermodynamic equilbrium exists in the flame because the atoms and the molecules all have the same mean velocity. The proportion of the excited to ground state atoms in the population at a given temperature is given by the statement of Maxwell -Boltzman law (Strobel, 1973).

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-\frac{E_1}{KT}} \qquad \text{.........(10)}$$

where, g_1 and g_0 are the statistical weights of the excited and ground atomic states ($g = 2j + i$, where j is the internal quantum number).

E_l is the excitation energy.

K is the Boltzman constant

T is the absolute temperature

0 and *1* represent ground and excited states respectively.

At most temperatures likely to be encountered in flames and electrothermal atomizers, all the atom's with electrons in higher states than the first excited states can be neglected. Unless *T* is very large, the exponential term is very small. The specific wavelengths at which an atom's valency electrons in the ground state can absorb radiation are called resonance wavelengths.

To determine how much radiation is absorbed by a cloud of atoms, consider the incident beam of monochromatic radiation I_0 on absorption cell of length b containing C atoms

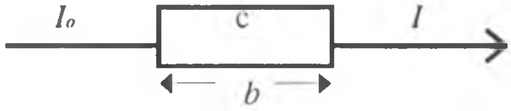

Fig 3.8: Atomic absorption cell of length b

The transmittance is given by:

$$T = \frac{I_1}{I_0} = e^{-kbc} \quad \text{.......(11)}$$

where T is the transmittance, b is the cell length, c the concentration of the analyte atoms in the flame and K the absorption coefficient (i.e, the fraction of energy absorbed per unit area per unit length). Taking logarithmns of both sides

$$Log\frac{I_0}{I_1} = kbc \quad \text{.......(12)}$$

The expression $Log\frac{I_0}{I_1}$ is defined as absorbance

$$Log\frac{I_0}{I_1} = A = kbc \quad \text{.......(13)}$$

where A is the absorbance and K is constant for a given system .

This expression (equation 13) known as the Beer-Lambert law (Weltz, 1985) predicts a linear relationship between absorbance and concentration as long as k and b remain constant. Hence an establishment of a calibration curve by ploting absorbance against concentration forms the basis of quantitative analytical technique for AAS.

3.2.3 Instrumental principles of Atomic Absorption Spectrometry

The most important component of AAS are:

(a) Radiation source

Hollow cathode atomic spectral lamps are the most common radiation sources for atomic absorption spectroscopy. These lambs can produce resonance radiation of narrow line width typically < 0.01 angstroms for most elements that are determined by atomic absorption. The cathode is constructed from the metal or an alloy of the element being determined. A small current is passed between the cathode and anode resulting in ionization of inert gas atoms. Atoms of the cathode metal (analyte) are sputtered from the surface due to interaction with these ions. Excitation results from collisions between analyte atoms and inert gas atoms in the discharge tube.

(b) Atomization System

To have atomic absorption its necessary to produce free ground-state atoms of the elements of interest. This occurs in the atomizer. A variety of commercial atomizers are available for use with atomic absorption equipment, the most common being flames and furnaces.

(c) Signal processors

A Photomultiplier tube sensitive to radiation over the wavelength range 1900-8000 angstroms is commonly used. Signals generated by this device are very small (in nanoampere range). The photomultiplier is a current source. The intensity of the current produced is proportional to signals strength. Micro-processors have recently been introduced into atomic absorption equipment mainly for setting of integration time, scale expansion, for instrument calibration and curve correction

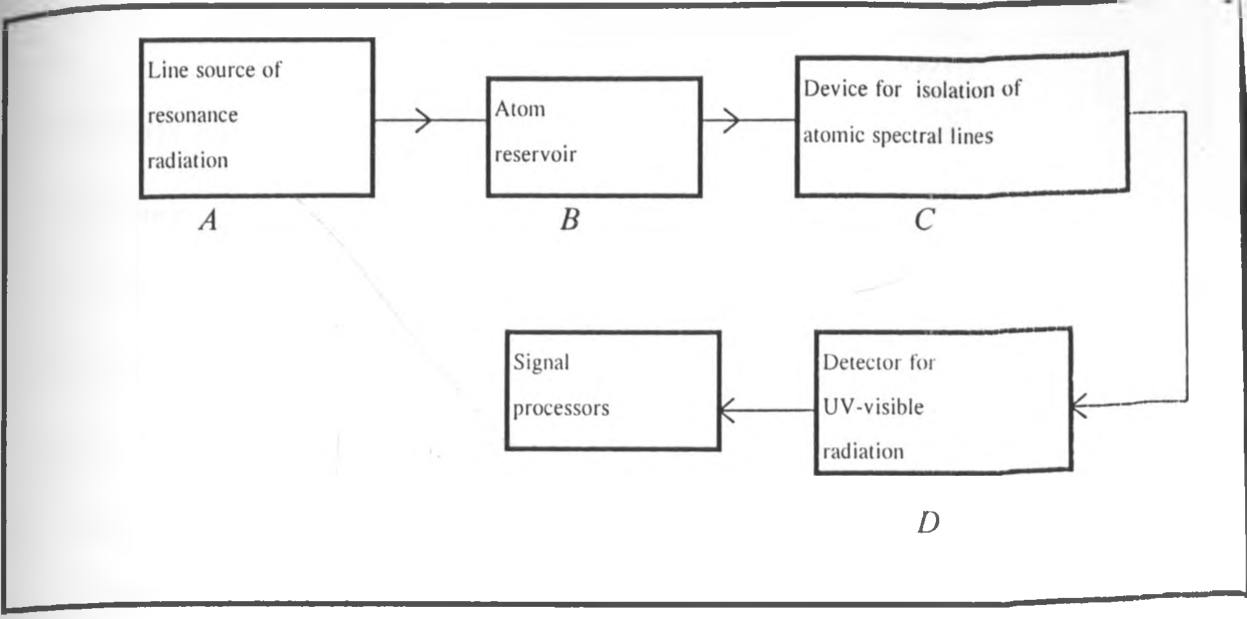

Fig 3.9: Schematic representation of atomic absorption spectrometer

A- hollow cathode lamp

B- a flame or electrothermal device

C- a grating monochromater

D- a photomultiplier

The principle of operation of atomic absorption spectrometer is simple, the hollow cathode lamp emits radiation characteristic of the cathode material, usuallly a single element (analyte). The beam consisting largely of resonance radiation, is electronically or mechanically pulsed. Analyte atoms are produced thermally in the reservoir. Ground state atoms, which predominate under the experimental conditions absorb a resonance radiation from the lamp, reducing the intensity of the incident beam. The monochromator isolates the desired resonance line and allows this radiation to fall on the photomultipler, an electrical signal is generated. The electronics of the unit are designed to respond selectively to the pulsed radiation emanating from the radiation source, signal processing occurs, which results in electronic output proportional to the absorption by the analyte atoms.

Chapter Four

4.0 Experimental procedures

4.1 General description of the study area

Kibera is a high density settlement area, covering three square kilometres with a total population of 122,643 people. This is among the highest densely populated area in Kenya apart from Mathare, Majengo and Korogocho which are also slum areas with population densities ranging from 44,000 to 55,750 (CBS,1989).

Kibera has a total of 42,722 households according to the 1989 census (CBS,1989). It is situated 7 kilometres southwest of city centre and 5 kilometres southwest of industrial area. On the northern side is boundered by high class residential estates, i.e, Kabarnet and Woodley Estates. The area is drained by two streams which end up into Nairobi dam on the lower side (Fig 4.1). The rivers are used for garbage dumping, hence they are usually clogged with urban refuse and minimal flow of water. This subsequently leads to the decay of the garbage which produces bad odour. The houses are built on the valleys of these two rivers with some being at a distance of one metre from the bank. The houses, made up of mud and wood, and roofed with corrugated iron sheets, are smoothened on the outside with concrete mixture. The houses are of uniform height, forming rows and columns of housing units, with a space of about one metre between the parallel units. Figure 4.2(a) shows the aerial view of the study area. Some of these spaces serve as the drainage trenches for dirty water and also for garbage dumping. There are only very few open spaces which are bare, with no vegetation cover and most are used as garbage dumps and play grounds for children. Only one major tarmac road (Kibera Drive) bounders the area on the upper side. From this road, the interior of the slum is served by dusty unpaved roads. A railway line passes through the slum area on the lower side (Fig 4.1).

Activities of environmental concern include battery charging which involve changing of battery acid (i.e, sulphuric acid), welding works, timber works, "posho" milling, gasoline and kerosene pumps, "busaa" brewing and commercial cooking of various foods in the open. The later activity was found to be a prominent feature in this area. Main fuels found to be used included wood, charcoal, sawdust and paraffin oil. Other activities of environmental concern include the burning of the refuse in the open.

4.2 Description of the sampling sites

There were five sampling sites designated A-E (Fig 4.1) covering the lower and the upper part of the area. All the sampling sites were located on the small open spaces between the housing units except for site C at Olympic Primary School which was located on a compound partly covered by grass on one side and paved road on the other side.

Site A

This was situated on the lower side of the slum area after the railway line about 10 metres from a dry weather road and is usually dusty during the dry season.

Site B and D

These two sites were located on the upper side of the study area at a distance of 20 metres and 3 metres respectively from dry weather roads which were usually dusty during the dry seasons. The ground was bare with no vegetation cover.

Site E

This site was located in an open space between several housing units, with the nearest road being 50 metres away.

Site C

It was located on a large compound which was partly covered by grass and paved on the other side. It was next to Olympic shopping centre and about 30 metres from a dusty road which was rated to be busy in terms of human traffic.

4.2.1 Sampling

Sampling was done using the "Gent" Stacked Filter Unit (SFU). Fine (0.4 micron pore diameter) and coarse (8.0 micron pore diameter) nucleopore membranes were used. These filters have several advantages over other filter types. They are very thin ($1 mg/cm^2$) and thus produce little x-ray scatter. The filters collect aerosols at the surface and are analysed directly. This is important since x-ray absorption of the incident and the generated characteristic x-rays in the filter material has to be taken into account because of the low trace element concentration (IAEA, 1996). Sampling was done for an average of eight hours per day starting at between 8.00 to 9.00 a. m. in the morning and ending at around 4.00 to 5.00 p.m. Hence, only one sample could be collected in a day. Sampling was started in May 1998 and ended in May 1999. Sampling from May to November 1998 was done at a height of 2.0m from the ground while from December 1998 to May 1999 it was done at 4.0m. Figures 4.2(a)-4.2(f) shows the SFU air sampler at various heights above the ground for the five sites. On average two sets of samples were collected per month for all the sites except for site B and E whose frequency was increased to four from September to December 1998.

With each sample the following information was recorded:-

a) The sample code. This was done for each sample such that it reflected the site, sample collected, type of filter membrane used and month of sampling. Example sample E18598 was collected at site E (Fig 4.1) in May, 1 refers to the first sample for that month, 8 refers to the coarse filter (i.e, 8.0 micron pore filter) and 5 refers to the month of May while 98 refers to the year 1998.

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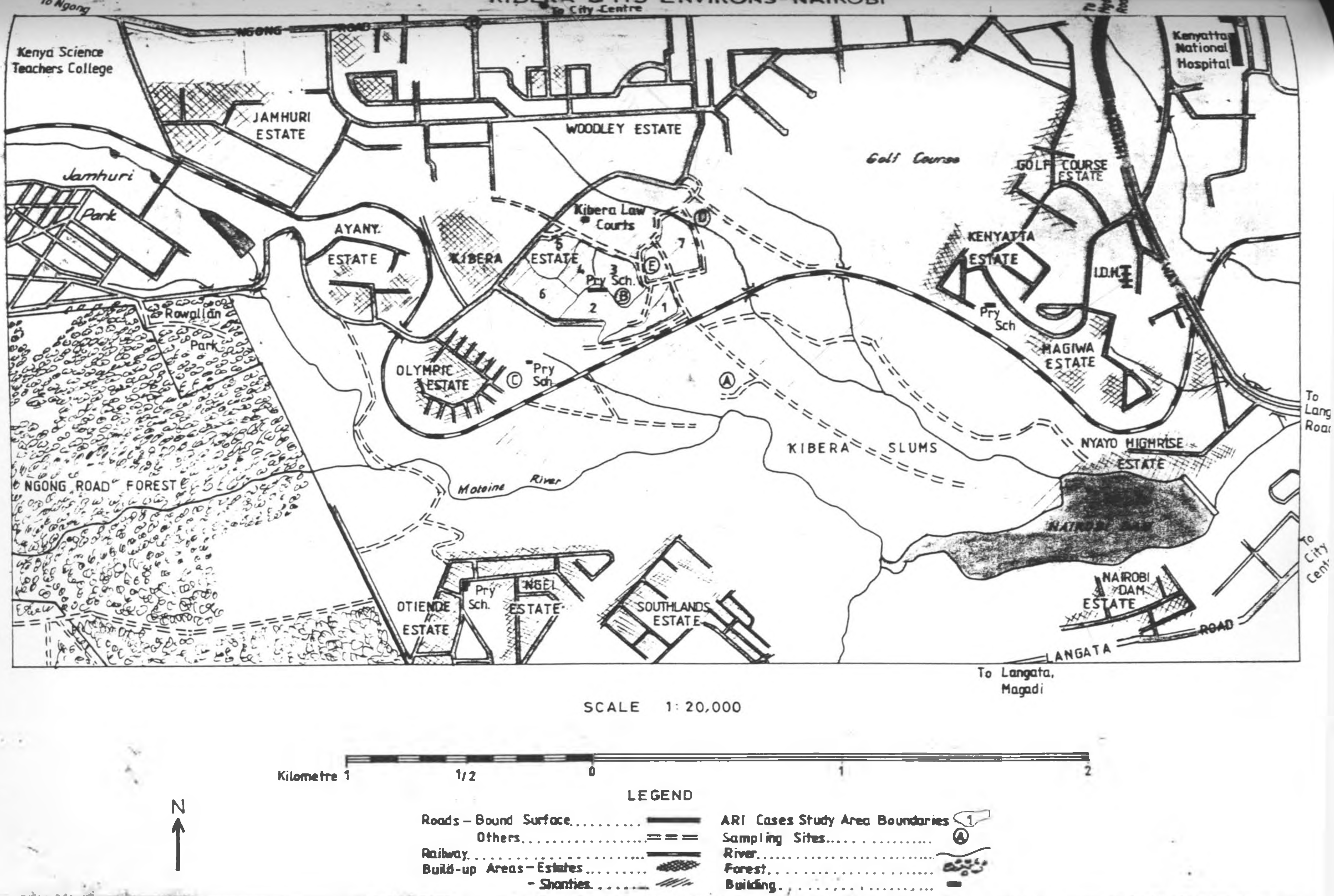

b) Start and end time of the sampling exercise.

c) Initial and final volume (as read from the volumeter).

d) Rotameter flow rate at the begining and end of sampling.

e) Initial and Final pressures (as read from the pressure gauge).

f) Weather conditions (i.e, sunny, cloudy, etc).

After every two weeks of sampling the SFU was dismantled into the various parts and cleaned thoroughly with ethanol. This was necessary to remove any particles which may have accumulated in the holding.

4.3 Sampling of dust fall at a typical office environment

Sampling of dust fallout was done at the Institute of Nuclear Science offices at the University of Nairobi. This was done by placing a coarse filter (i.e, 8.0 micron pore filter) in a petri dish which was thoroughly cleaned with ethanol. The filters were then left at the top of cabinets in various offices for 20 days each month. This exercise was carried on from January to December 1998.

Fig 4.2a: Aerial view of the study area

Fig 4.2b: Site A, "Gent" SFU sampler at a height of four (4) metres above the ground

Fig 4.2c: Site B, “Gent” SFU sampler at a height of two (2) metres above the ground .

Fig 4.2d: Site C, "Gent" SFU sampler at a height of four (4) metres above the ground .

Fig 4.2e: Site D, "Gent" SFU sampler at a height of four (4) metres above the ground.

Fig 4.2f: Site E, "Gent" SFU sampler at a height of four (4) metres above the ground.

4.4 Weighing of filters

Filters were weighed in an air conditioned laboratory using 1μg sensitivity (Ainsworth Type 24N) weighing balance before and after sampling. The balance pan was wiped clean with a piece of cotton wool soaked in ethanol. This was necessary to ensure the filters were not contaminated by dust particles which may have previously accumulated.

Prior to weighing all filters were left to equilibriate for 24 hours in the weighing room and irradiated with ^{241}Am α-emmiting source (5μCi) to remove the static build up before and after sampling. Filter loading on the SFU was done indoors (i.e, in the air-conditioned laboratory). Loaded filters were stored prior to analysis in thoroughly cleaned millipore petri dishes. The method provides satisfactory results, with less than 1% loss of the material (IAEA, 1996). All the filter handling was done using plastic tweezers to avoid contamination by grease from fingers and by heavy metals from metallic tweezers.

4.5 Acute Respiratory Infections (ARI) incidences.

The study of the acute respiratory infections (ARI) incidences cases was mainly concentrated on the upper part of the area (Makina). The children under study were visited twice a month by a team of officers from Kenya Medical Research Institute (KEMRI). The number of children involved in the study varied from 1066-1231 children all under five years of age. The advantage of studying the influence of air pollution on respiratory diseases occurence in children is that the respiratory tract in children is sensitive to environmental hazards, effects of cigarrete smoking and occupational health hazards have not yet come into play (Kerrebijn *et al*, 1975).

The data on the health status of the children was elicited by the use of a questionnaire which was administered to the mother. The questionnaire elicited information concerning the

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The data on the health status of the children was elicited by the use of a questionnaire which was administered to the mother. The questionnaire elicited information concerning the child's respiratory symptoms, date and duration of the sickness (KEMRI\JICA, 1998). For the first eight (8) months (January-August) 1998 the number of contacts ranged from one (1) to two (2). However the number of contacts was increased to four(4) from September to December 1998 (KEMRI\JICA, 1999).

4.6 Physical calibration and optimization of the Energy Dispersive X-ray fluorescence spectrometer (EDXRF)

4.6.1 Introduction

Instrumental calibration is one of the most important steps towards quality analysis. It has been established (Kump, 1993) that calibration may be done in the forms involving physical calibration, efficiency calibration and sensitivity calibration. The first form entails any adjustments made on the physical apparatus to ensure that they are operated at optimum conditions. Efficiency calibration is a procedure carried out as a prerequisite for sensitivity calibration. Sensitivity calibration determines the sensitivities of all elements of interest that are excited in a chosen excitation range. The excitation mode can either be continuous or monochromatic. Calibration of the x-ray fluorescence spectrometer using monochromatic excitation usually yields accurate evaluation of the energy distribution of excitation radiation. The evaluation of geometrical constants for the set of elements is a test for the suitability of the performed calibration. Deviations in the evaluated geometrical constants for the elements are due to errors arising from the ambiguity in detector parameters and from unstable composition of compounds used. Inaccurate data about the detector dead layer or Be window thickness for example could lead to errors in sensitivity and efficiency values.

4.6.2 Optimization of the Energy Dispersive X-ray Fluorescence.

The Si(Li) detector used in this work had an active diameter of 6mm, a sensitive depth of 5mm, a nominal Be window thickness of 25.4μm located at a distance of 5mm from the crystal. The detector was operated at -500Volts reverse bias so as to establish an electric field in the sensitive depth for the collection of the charge carriers produced by the incident radiation. The resulting charge was collected over a charge sensitive preamplifier coupled to a field effect transistor (FET) for signal shaping and amplification. The main amplifier further amplifies and shapes the signals.

Pulse shaping optimizes the signal to noise ratio and provides the shape of the pulse required by the pulse height analyser (PHA). The energy resolution was determined prior to any analysis so as to monitor the system performance using the full width at half maximum (FWHM) value.

4.6.3 Quantitative Analysis of Environmental Samples (QAES) program for quantitative analysis

The quantitative analysis of environmental samples (QAES), a modular program of the International Atomic Energy Agency (IAEA)'s Quantitative X-ray Analysis Software (QXAS) was first calibrated for quantitative analysis by way of three sub-routines of the program available for:

a) Quantitative analysis of unknown samples.

b) Performing calibration of the x-ray system.

c) Calculating energy distribution of primary x-rays

Sensitivity calibration involves determining the distribution of primary x-ray source from sub-routine (c) and intensity measurements of pure metal samples or analar compounds whose characteristic energies cover the analytical range of interest. Intensities of elements for compounds together with their areal densities were input to enable the program evaluate the sensitivities and the geometrical constants. The following standards were used for the calibration :

a) pure metal foils of molydenum (Mo), zinc (Zn), zirconium (Zr), iron (Fe), copper (Cu), lead (Pb), titanium (Ti) and tin (Sn).
b) thin film deposits of lead (Pb), uranium fluoride (UF_3), tungsten oxide (WO_2), titanium (Ti), molydenum (iv) oxide (MoO_2), gold (Au), copper (Cu) and dysprosium fluoride (DyF_3).
c) standard sample of Soil-7 (IAEA) certified standard reference material (CRM).

For each element the experimentally determined geometrical constants for the measured elements were compared with the theoretically determined value. The selected values of geometrical constants of the accepted elements were used to evaluate the average geometrical factor. The evaluation of sensitivities for other elements not measured in the calibration procedure were extrapolated. The goodness of the sensitivity calibration was verified by inspection of the variation coefficient of the geometrical factor *G*, calculated using the sensitivity values obtained.

4.7 Spectral data analysis

A Canberra S-100 PC based multi-channel analyser (MCA) was used for spectral data acquisition and storage. Both the coarse and fine loaded filters were irradiated for 60,000 seconds using ^{109}Cd source so as to give reasonable statistics. The loaded filters were placed on the sample holder such that the loaded side faced the source of radiation as per the recommended method (IAEA, 1996). Spectrum data analysis was done using the IAEA software, Analysis of X-rays by Iterative Least square fitting (AXIL). Quantitative analysis was done using Quantitative Analysis of Environmental Samples (QAES) software (Kump,1993) which relates the spectral intensities with the elemental concentrations based on the fundamental parameter technique (Kinyua, 1982., Sparks, 1975)).

4.8 Calculation of the elemental concentrations

Quantitative analysis depends upon the correlation of concentration of the element with observed fluorescence X-ray intensities. The correlation is represented by the basic equations derived using the fundamental parameters (Tertian and Claisse, 1982). The use of fundamental parameters is based on the following assumptions:-

a) a monochromatic radiation source is used to excite characteristic X-rays from the sample.

b) the sample is homogeneous, i.e, the density is well defined and constant throughout the sample volume.

c) a fixed geometry of the sample source and detector orientation must be maintained.

The use of fundamental parameters yields the following equation.

$$I_i = G_0 K_i(\rho_i d)\frac{1-e^{-a\rho d}}{a\rho d} \qquad \text{.....(14)}$$

where

I_i := fluorescent intensity in counts per second (c/s)

K_i = the relative excitation- detection efficiency in cm^2/g.

a = the combined absorption coefficient for primary and fluorescent X-rays in the sample.

ρ_0 *and* ρ_i = density of the sample and partial density of the element within the sample respectively (g/cm^3).

$\rho_i d$ = mass per unit area (g/cm^2) of the element *i* which is to be determined.

d = thickness of the sample (cm).

The last factor in the equation, i.e

$$\frac{1-e^{-a\rho d}}{a\rho d} = A_{corr}$$

is referred to as the absorption correction factor. It is responsible for the attenuation of the measured fluorescence intensity I_i. It depends strongly on the value of the product $(a\rho d)$. When $a\rho d$ is much smaller than 1, i.e, $a\rho d <<< 1$, then we deal with thin samples such as aerosols loaded on filters. Therefore $A_{corr} = 1$ for thin samples and equation (14) reduces to

$$I_i = G_0 K_i \rho_i d \ldots\ldots\ldots\ldots(15)$$

hence

$$\rho_i d = \frac{I_i}{G_0 K_i}\left(^{g}/_{cm^2}\right) \ldots\ldots\ldots\ldots(16)$$

therefore

$$M_i = \frac{I_i}{G_0 K_i} \cdot \frac{Area}{Volume} \ldots\ldots\ldots\ldots(17)$$

where

Area = *exposed area of the filter*(cm^2)

M_i = *mass of the element i* (g/m^3) *in the total exposed area of the filter.*

Volume = *volume of the air sampled in* m^3.

4.9 Sample preparation for analysis by Atomic Absorption spectrometry (AAS)

The filters were digested by boiling them gently in 20 millitres of high purity 70% nitric acid (Analar grade reagent) for 2 hours when the filter dissolved leaving small particles floating in the solution. This solution was then cooled to room temperature and 10 millitres of 70% perchloric acid added and again boiled gently until the particles dissolved. The solution was then cooled to room temperature and 5 millitres of distilled water added. The solution was then boiled gently for five minutes, cooled and then made up to 50 millitres in 1% nitric acid solution. Blank samples were prepared by digestion of the blank (i.e, unexposed) coarse and fine filters using the same procedure.

4.9.1 Standard solutions for calibration

Standard solutions for calibration of the spectrometer were prepared before analysis from 1000 ppm stock solutions (Analar reagents) prepared in 1M nitric acid solution. Standard solutions were prepared for lead (Pb), manganese (Mn), copper (Cu), nickel (Ni), iron (Fe) and zinc (Zn). The concentration range of the standards was as per the specifications of the spectrometer, that is (1-6)ppm (Shimadzu Corporation, 1991). The standards were then utilized for ploting the calibration curves for the various elements to be analysed. A typical calibration curve for one of the element (Fe) is shown in Fig 4.6.

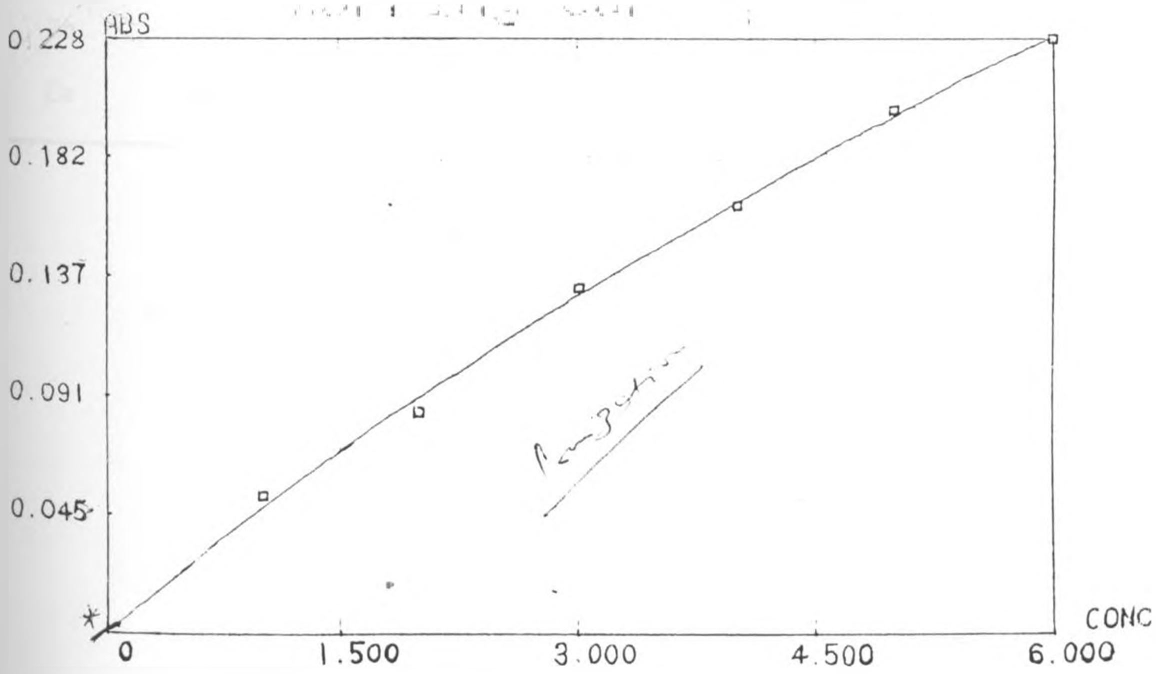


Fig 4.6: Calibration curve of Iron (Fe)

5.1 Quantitative analysis

Quantitative analysis was done by atomic absorption spectrometer Model AA-680 (Shimadzu Corporation, 1991) which uses a hallow cathode lamp with wavelength range of (190-900)nm. The AA-680 Model is composed of the spectrophotometer, the graphic printer, the gas control unit and the color graphic cathode ray tube (CRT) display and is capable of performing quantitative analysis based on atomic absorption and flame emission spectrometry. The operational parameters used during the analysis were as per the manufacturer's recommendations (Table 1) (Shimadzu Corporation, 1991).

Table 1: Operational parameters for the AA-680 Model

Element	Wavelength (nm)	HC Lamp current (mA)	Slit Width (nm)	Flame	Flow gas rate (L/min)	1% absorption concentration (ppm)
Fe	248.3	8	0.2	Air-CH_2CH_2	2.0	0.1
Mn	279.5	5	0.4	Air-CH_2CH_2	1.9	0.05
Pb	283.3	5	1.0	Air-CH_2CH_2	2.0	0.5
Zn	213.9	4	0.5	Air-CH_2CH_2	2.0	0.02
Cu	324.8	3	0.5	Air-CH_2CH_2	1.8	0.09

Chapter Five

5.0 Results and Discussion

5.1 Suspended particulate matter (SPM) levels for the month of May to November 1998

The values presented are the mean of samples collected per month for the period May to November 1998. The sampling height was 2.0 metres above the ground. Tables 2 and 3 shows the mean monthly values of coarse particles (2.0-10μm) and fine particles less than 2.0μm aerodynamic diameter.

Table 2: Mean monthly concentration in μg/m³ of coarse particulates for the period May to November 1998

Site	MAY	JUN	JUL	AUG	SEP	OCT	NOV
A	80.01	54.47	33.07	94.80	158.2	224.25	150
n=6	±12.3	±4.06	±22.65	±33.55	±3.70	±9.26	±46
B	20.00	99.42	61.70	66.83	179.04	146.30	88.20
n=6	±2.3	±34.32	±20.11	±62.40	±16.47	±54.90	±24.20
C	45.90	23.14	142.71	72.40	152.15	93.20	95.30
n=6	±3.95	±12.37	±46.59	±74.35	±21.43	±55.30	±20.80
D	39.63	41.38	191.34	155.61	162.10	233.85	123.60
n=6	±1.95	±22.41	±8.97	±4.82	±91	±28.5	±60.45
E	NS	79.88	74.16	38.70	41.73	96.70	43.00
n=6		±28.20	±45.09	±23.59	±38.80	±13.96	±24.10

NS= no sampling was done at this site for that month, n= number of determinations

Table 3: Mean monthly concentration in μg/m³ of fine particulates for the period May to November 1998 for the various sites.

Site	MAY	JUN	JUL	AUG	SEP	OCT	NOV
A	8.24	13.85	18.22	21.90	24.45	26.29	21.50
n=6	±3.21	±5.24	±3.94	±6.72	±10.96	±6.39	±9.40
B	42.40	21.52	20.09	13.84	31.58	17.05	24.60
n=6	±4.06	±6.78	±7.62	±8.12	±9.7	±7.76	±15.50
C	33.82	15.60	25.08	12.08	20.20	24.15	7.40
n=6	±5.01	±7.23	±0.065	±8.46	±11.6	±0.49	±3.10
D	14.41	20.63	36.06	16.73	24.25	35.70	19.40
n=6	±2.30	±4.68	±5.44	±14.20	±12.37	±20.1	±12.20
E	NS	6.44	28.80	11.98	17.88	14.38	17.80
n=6		±2.44	±0.125	±14.81	±10.25	±5.74	±5.30

NS= no sampling was done at this site for that month, n= number of determinations

Chapter Five

5.0 Results and Discussion

5.1 Suspended particulate matter (SPM) levels for the month of May to November 1998

The values presented are the mean of samples collected per month for the period May to November 1998. The sampling height was 2.0 metres above the ground. Tables 2 and 3 shows the mean monthly values of coarse particles (2.0-10μm) and fine particles less than 2.0μm aerodynamic diameter.

Table 2: Mean monthly concentration in μg/m³ of coarse particulates for the period May to November 1998

Site	MAY	JUN	JUL	AUG	SEP	OCT	NOV
A	80.01	54.47	33.07	94.80	158.2	224.25	150
n=6	±12.3	±4.06	±22.65	±33.55	±3.70	±9.26	±46
B	20.00	99.42	61.70	66.83	179.04	146.30	88.20
n=6	±2.3	±34.32	±20.11	±62.40	±16.47	±54.90	±24.20
C	45.90	23.14	142.71	72.40	152.15	93.20	95.30
n=6	±3.95	±12.37	±46.59	±74.35	±21.43	±55.30	±20.80
D	39.63	41.38	191.34	155.61	162.10	233.85	123.60
n=6	±1.95	±22.41	±8.97	±4.82	±91	±28.5	±60.45
E	NS	79.88	74.16	38.70	41.73	96.70	43.00
n=6		±28.20	±45.09	±23.59	±38.80	±13.96	±24.10

NS= no sampling was done at this site for that month, n= number of determinations

Table 3: Mean monthly concentration in μg/m³ of fine particulates for the period May to November 1998 for the various sites.

Site	MAY	JUN	JUL	AUG	SEP	OCT	NOV
A	8.24	13.85	18.22	21.90	24.45	26.29	21.50
n=6	±3.21	±5.24	±3.94	±6.72	±10.96	±6.39	±9.40
B	42.40	21.52	20.09	13.84	31.58	17.05	24.60
n=6	±4.06	±6.78	±7.62	±8.12	±9.7	±7.76	±15.50
C	33.82	15.60	25.08	12.08	20.20	24.15	7.40
n=6	±5.01	±7.23	±0.065	±8.46	±11.6	±0.49	±3.10
D	14.41	20.63	36.06	16.73	24.25	35.70	19.40
n=6	±2.30	±4.68	±5.44	±14.20	±12.37	±20.1	±12.20
E	NS	6.44	28.80	11.98	17.88	14.38	17.80
n=6		±2.44	±0.125	±14.81	±10.25	±5.74	±5.30

NS= no sampling was done at this site for that month, n= number of determinations

5.2 Trends of mean monthly suspended particulate matter (SPM) levels (coarse and fine) at two (2) metres above the ground for the various sites for the period May to November 1998.

Site A

At the start of the sampling exercise site A recorded high concentration for the coarse particulates (80 μg/m^3) than all the other sites (Fig 5.1). This reduced to an average value of 33.1μg/m^3 in July, then took an upward trend, recording a maximum (224.3 μg/m^3) in October. This period (September to October) was characterised by dry and dusty conditions, low humidity and high temperatures (Figs 5.4). For the fine particulates, lowest value recorded was in May (8.24 μg/m^3). This was followed by an upward trend with a maximum being recorded in October (26.3 μg/m^3) (Table 3 and Fig 5.2).

Site B

This site recorded the lowest value (20.0 μg/m^3) than the other sites for the coarse particulates at the start of the sampling exercise (Table 2 and Fig 5.1), this increased by a factor of five (5) in June. The low levels at the start of the sampling exercise could be due to the high levels of rainfall received in May (Fig 5.1) which washed away some of the particles. This reduced to an average of between 61.7 to 66.8 μg/m^3 in July and August before increasing again to a maximum of 179.0 μg/m^3 in September. The increase from August to September was by a factor of 3 (Fig 5.1). For the fine particulates, this site recorded the highest value of 42.4 μg/m^3 in May dropping to an average of between 20 to 21 μg/m^3 in June and July (Fig 5.2). Maximum value of 31.58 μg/m^3 was recorded in September.

Site C

This site recorded an average of 45.9 μg/m^3 at the start of the sampling exercise for the coarse filters, reducing to a minimum of 23.14 μg/m^3 in June (Table 2 and Fig 5.1). This was followed by an increase in July (142.71μg/m^3) by a factor of six (6). Maximum value

Fig 5.1: Variation of coarse particulate fraction levels with time for the various sampling sites

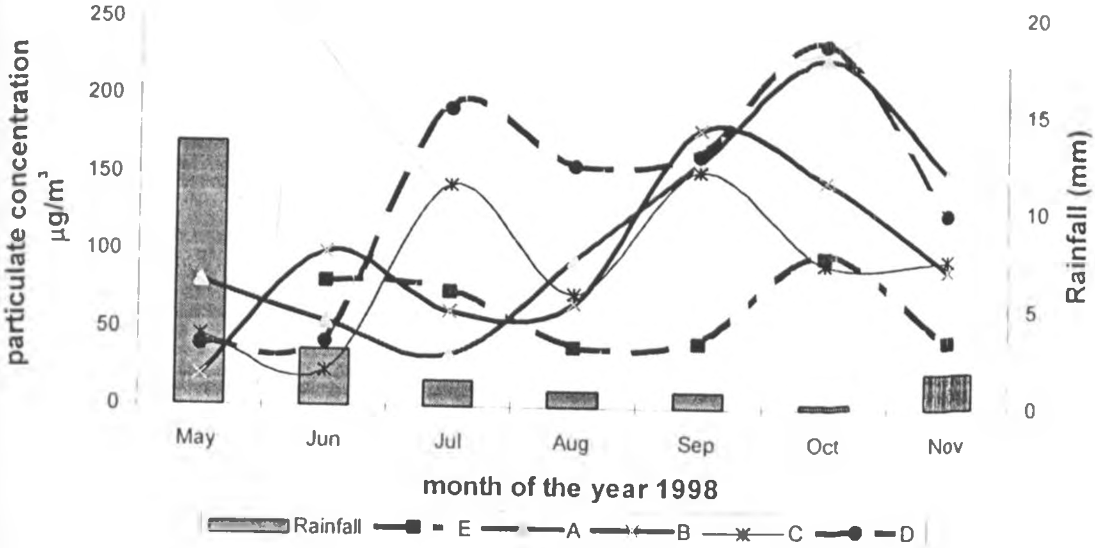
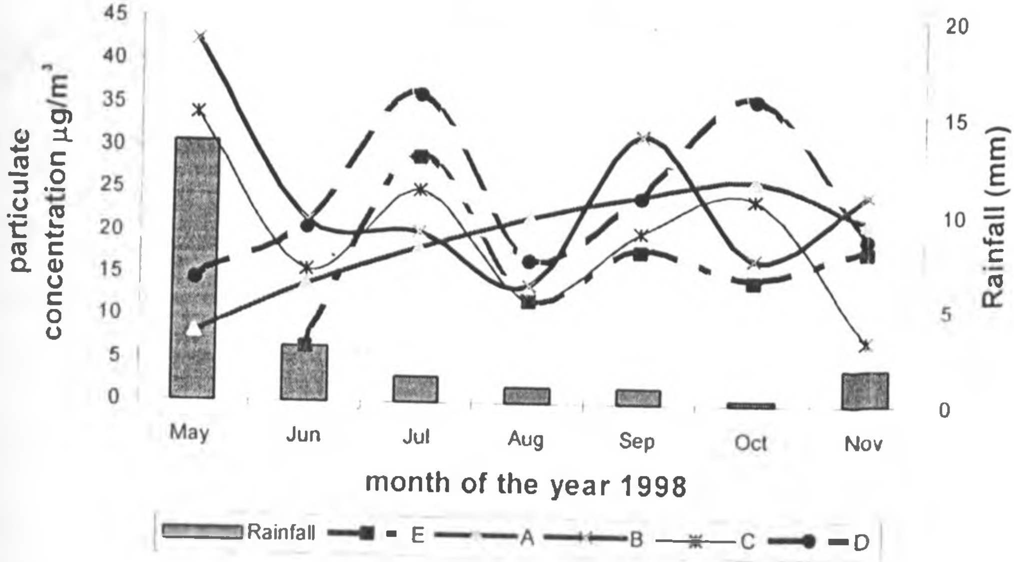


Fig 5.2: Variation of fine particulate fraction levels with time for the various sampling sites



of 152.15µg/m³ was recorded in September reducing to average values of between 93.2 to 95. µg/m³ in October and November. However, for the fine filters the highest value of 33.82 µg/m was recorded at the beginning of the sampling exercise (Table 3 and Fig 5.2) reducing to a average of 15.6 µg/m³ in June. This was followed by an increase of factor 1.6 in July reducing t

a minimum of 12.08 µg/m^3 in August. September and October recorded average values of between 20.2 to 24.15 µg/m^3.

Site D

This site recorded some of the highest levels for both coarse and fine particulates (Fig 5.1 and 5.2). Average values of between 39 to 41.38 µg/m^3 was recorded for the months of May to June for the coarse particulates. This was followed by an increase in July (191.3 µg/m^3) by a factor of 4.7 (Fig 5.1). Low average values of between 155.61 to 162.10 µg/m^3 was recorded for the month of August and September. This was followed by an increase to a maximum level of 233.85 µg/m^3 in October. For the fine particulates a similar trend was observed (Fig 5.2) with July (36.06 µg/m^3) and October (35.7 µg/m^3) recording the highest values.

Site E

The values recorded for the coarse filters ranged from 38.7 to 96.7 µg/m^3 for the entire period (Table 2 and Fig 5.1). Maximum values from 74.16 to 79.88 µg/m^3 were recorded in the period June to July and in October (96.7 µg/m^3). The fine particulates had a maximum in July (28.8 µg/m^3) reducing to average values of between 11.98 to 17.88 µg/m^3 for the rest of the months (Table 3 and Fig 5.2).

The SPM levels reflected the location of the sites in terms of the ground cover and surrounding activities. Site D which was nearest to an unpaved road and several children's playgrounds, recorded the highest mean monthly levels of between 155.6 to 233.9 µg/m^3 than all the other sites for the coarse particulates (Table 2 and Fig 5.1). Site E which was away from any road or footpath in a quiet area with no children's playgrounds nearby recorded low values, with most of the samples collected giving a mean monthly values of less than 100µg/m^3 for the period of May to November 1998 (Table 2 and Fig 5.1). It should be noted that the ground cover was mainly rock and the site was away from any road hence less soil dust. Site A which was located a minimum of 12.08 μg/m^3 in August. September and October recorded average values of between 20.2 to 24.15 μg/m^3.

Site D

This site recorded some of the highest levels for both coarse and fine particulates (Fig 5.1 and 5.2). Average values of between 39 to 41.38 μg/m^3 was recorded for the months of May to June for the coarse particulates. This was followed by an increase in July (191.3 μg/m^3) by a factor of 4.7 (Fig 5.1). Low average values of between 155.61 to 162.10 μg/m^3 was recorded for the month of August and September. This was followed by an increase to a maximum level of 233.85 μg/m^3 in October. For the fine particulates a similar trend was observed (Fig 5.2) with July (36.06 μg/m^3) and October (35.7 μg/m^3) recording the highest values.

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The values recorded for the coarse filters ranged from 38.7 to 96.7 μg/m^3 for the entire period (Table 2 and Fig 5.1). Maximum values from 74.16 to 79.88 μg/m^3 were recorded in the period June to July and in October (96.7 μg/m^3). The fine particulates had a maximum in July (28.8 μg/m^3) reducing to average values of between 11.98 to 17.88 μg/m^3 for the rest of the months (Table 3 and Fig 5.2).

The SPM levels reflected the location of the sites in terms of the ground cover and surrounding activities. Site D which was nearest to an unpaved road and several children's playgrounds, recorded the highest mean monthly levels of between 155.6 to 233.9 μg/m^3 than all the other sites for the coarse particulates (Table 2 and Fig 5.1). Site E which was away from any road or footpath in a quiet area with no children's playgrounds nearby recorded low values, with most of the samples collected giving a mean monthly values of less than 100μg/m^3 for the period of May to November 1998 (Table 2 and Fig 5.1). It should be noted that the ground cover was mainly rock and the site was away from any road hence less soil dust. Site A which was located about 10 metres away from an unpaved road recorded high levels for most of the months (Table 2 and Fig 5.1) than site B which was about 15 metres away from an unpaved road. Site C which was located on an open field at Olympic Primary school (Fig 4.1) recorded values comparable to site B and A. For the fine particulates, the levels did not reflect the location of the various sites in terms of the ground cover and activities surrounding them, the four sites A, B, C and D recorded comparable values for most of the months except May (Table 3 and Fig 5.2) when site A (8.24 $\mu g/m^3$) and site D (14.4 $\mu g/m^3$) recorded low levels. This could be due to their proximity to the road/footpath. Open fires (i.e, for cooking) were also prevalent near these sites. However, site E still recorded the lowest levels with most of the months recording less than 20 $\mu g/m^3$ except in July (Table 3 and Fig 5.2).

The SPM levels were found to follow a seasonal trend. Previous studies (Ngugi, 1983; Kimani, 1990) demonstrated similar findings, both established that maximum total suspended particulate matter (TSPM) values were recorded during the dry months while lower values occured during wet seasons. In this study highest values for the coarse particulates were observed in months of September and October 1998 (Table 2 and fig 5.1). These were months characterised by dry conditions, low humidity and high temperatures (Fig 5.1, 5.2 and 5.4). All the sites recorded their highest values, A:-158.2 to 224.3 $\mu g/m^3$, B:-146.3 to 179 $\mu g/m^3$, C:-93.2 to 152.2 $\mu g/m^3$, D:-162.1 to 233.9$\mu g/m^3$ and E:- 96.7$\mu g/m^3$ for the coarse particulates in these two months. This was attributed to the high level of soil dust during the dry weather conditions reported over the period. High levels were also observed for site B:- 61.7 to 99.4 $\mu g/m^3$, D:-155.6 to 191.3 $\mu g/m^3$ and E:- 74 to 79.9 $\mu g/m^3$ during the month of June, July and August (Table 2 and Fig 5.1) while high values for site A:- 94.8 $\mu g/m^3$ and C:- 72 to 142.7 $\mu g/m^3$ were observed in months of July and August. The months of June, July and August were characterised by low temperatures and high humidity (Fig 5.4). The high levels of SPM were attributed to the increased residential emissions from domestic heating using charcoal/wood and kerosine during the cold season. The fine particulate samples exhibited a similar trend for all the sites. Four of the sites A:- 24 to 26.3 µg/m^3, B:- 17 to 31.6 µg/m^3, C:- 20.2 to 24.2 µg/m^3 and D:- 24.3 to 35.7 µg/m^3 recorded their highest values in September and October (Table 3 and Fig 5.2).

The "Gent" stack filter unit sampler separates the particulates into two size ranges, the fine fraction of less than 2.0µm aerodynamic diameter ($PM_{2.0}$) and the coarse particulates between 2.0µm and 10µm (Maenhaut *et al*, 1992). The total SPM (PM_{10}) was calculated as the sum of fine and coarse mass concentrations.

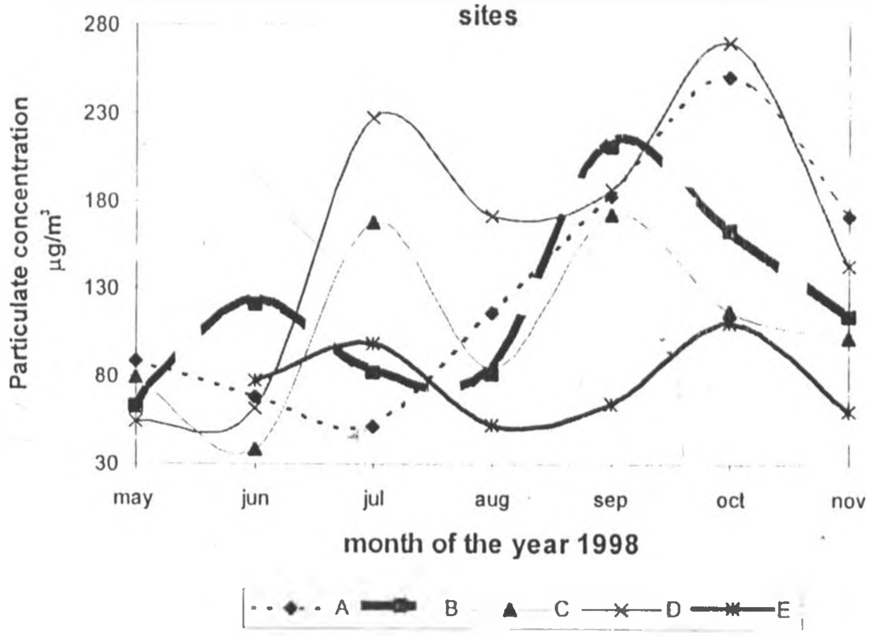
Table 4: Mean monthly PM_{10} concentrations in µg/m^3 for the period May to November 1998 for the various sites.

Site	May	Jun	Jul	Aug	Sep	Oct	Nov	Average
A	88.3	68.3	51.3	116.7	182.7	250.5	171.6	132.8±66.4
n=6	±10.4	±13.2	±26.5	±26.8	±14.6	±15.6	±51.7	n=42
B	62.4	120.9	81.8	80.7	210.6	163.3	114.6	119.2±48.4
n=6	±16.5	±58.1	±39.2	±70.5	±7.20	±49.6	±39.6	n=42
C	79.7	38.7	167.8	84.5	172.4	117.4	102.7	109±44.7
n=6	±20.5	±27.7	±66.0	±82.8	±33.0	±54.8	±33.7	n=42
D	54.1	62.0	227.4	171.3	186.4	269.6	143.0	159.1±74.1
n=6	±15.6	±25.1	±20.4	±19.0	±78.6	±48.6	±102.7	n=42
E	NS	77.8	99.0	52.2	64.4	111.1	60.8	77.6±21.1
N=6		±12.0	±63.9	±36.3	±38.7	±12.1	±32.2	n=36

NS= not sampling was done at this site for that month, n= number of determinations
PM_{10} and **$PM_{2.0}$** =particulate matter less than 10µm and 2.0µm aerodynamic diameter.

The total SPM (PM_{10}) values show a similar trend as observed for the coarse particulate fraction levels (Fig 5.1 and 5.3) for all the sites. Two peak levels were observed for each site. One occuring in the cold/humid period (June/July) with mean monthly values ranging from 38.7 to 227.4 µg/m^3 and in the dry period (September/October) with mean monthly values ranging from 64.4 to 269.6 µg/m^3. Compared to values (30-80 µg/m^3) obtained in a sub-urban site (Gatebe *et al.*, 1996), these values appear to be very high. This could be due to the nature of the ground cover in this area (bare ground with no vegetation cover), high population density and the accompanying high density housing unlike in the latter case, where there is vegetation cover and low density housing. In this study major contribution could be the resuspended dust and residential emissions. Height of sampling could also have contributed to the difference. While in this study sampling was at 2 metres, Gatebe *et al* (1996) sampled at 8 metres above the ground considerably reducing the effect of resuspended dust.

Fig 5.3: Variation of PM-10 levels with time for the various sampling sites



5.3 Variation of coarse particulate and fine particulate matter levels with weather conditions

Concentration of the coarse and fine particulates was found to vary with changes in weather conditions. This was done by considering concentrations of samples collected under different weather conditions. Figure 5.4 shows the mean monthly variation of humidity (%) and temperature (^{0}C) for the year 1998 (Kenya Meteorological Department).

5.3.1 Temperature

Other parameters being constant (i.e, rainfall and humidity), concentration of both coarse and fine particulates was found to increase with increased temperature. This is illustrated by considering both coarse particulate samples A285, A1810, A2811 collected at site A, B186, B286 collected at site B, E289, E1810, E3810 collected at site E and fine particle samples A245, A1410, A2411 collected at site A, B249, B3410, B2411 collected at site B.

Coarse particulates (site A)

Sample code	A285	A2811	A1810
Temperature(°C)	18.2	18.7	18.9
Rainfall (mm)	Nil	Nil	Nil
Humidity (%)	68.5	69	68.5
concentration(μg/m³)	67.71	104.1	230.8

Fine particulates (site A)

Sample code	A245	A2411	A1410
Temperature(°C)	18.2	18.7	18.9
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	68.5	69	68.5
Concentration(μg/m³)	11.45	30.1	30.9

Fine particulates (site B)

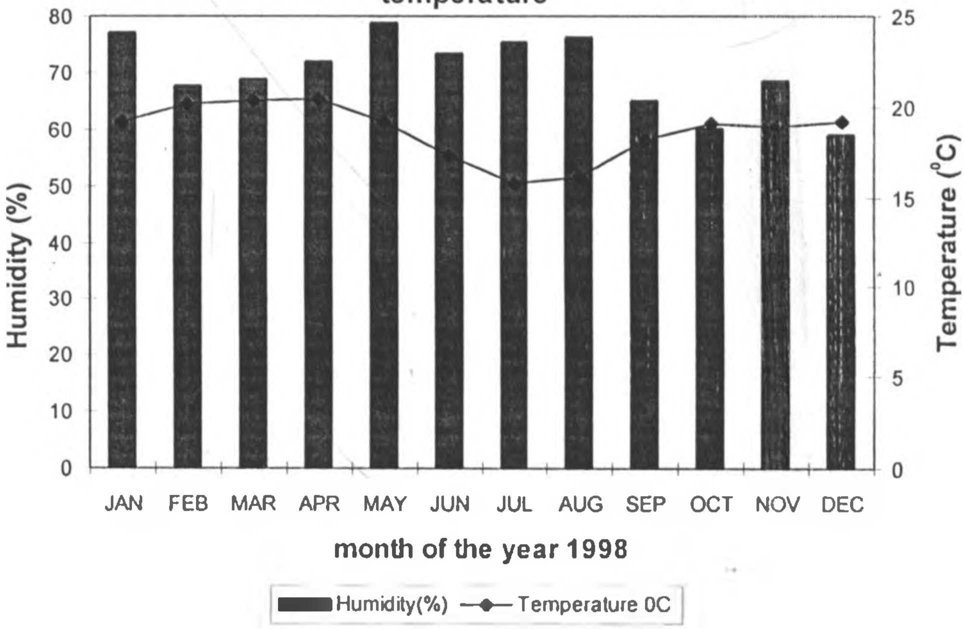
Sample code	B2411	B3410	B249
Temperature(°C)	16.7	17.85	17.95
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	58	59	58
Concentration(μg/m³)	7.90	11.40	38.3

Coarse particulates (site E)

Sample code	E289	E1810	E3810
Temperature(°C)	17.0	18.6	18.55
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	57	59	57
Concentration(μg/m³)	21.4	88.8	81.10

However no relationship could be established between the suspended particulate matter levels and temperature for site C and D for the samples collected. All the samples for these sites were collected at different humidity levels and rainfall conditions hence it was difficult to establish the trend with respect to temperature.

Fig 5.4: Mean monthly variation of humidity and temperature



5.3.2 Humidity

Temperature and rainfall being constant samples collected during high humidity levels recorded low suspended particulate matter levels. The SPM levels decreased with increase in humidity. This could be attributed to low levels of soil dust. This was detected for the coarse particle samples A2810, A1811, A2811 collected at site A, B188, B189, B289 collected at site B, C188, C289, C189 collected at site C, D189, D287, D188 collected at site D, E4810, E2810, E2811 collected at site E and fine particle samples B146, B1411, B4411 collected at site B, E247, E148, E248 collected at site E.

Coarse particulates (site A)

Sample code	A2810	A1811	A2811
Temperature(°C)	18.5	19.1	18.7
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	49	66	69
Concentration($\mu g/m^3$)	217.7	196.0	104.1

Coarse particulates (site B)

Sample code	B188	B189	B289
Temperature(⁰C)	17.45	17.95	17.95
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	71.5	66.5	58.0
Concentration(μg/m³)	111.0	172.4	170.8

Fine particulates (site B)

Sample code	B146	B1411	B4411
Temperature(⁰C)	18.9	18.8	19.0
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	70.5	66	63.5
Concentration(μg/m³)	14.7	17.9	30.4

Coarse particulates (site C)

Sample code	C188	C289	C189
Temperature(⁰C)	17.2	17.4	17.5
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	78.5	71.5	70.5
Concentration(μg/m³)	124.9	137.0	167.3

Coarse particulates (site D)

Sample code	D189	D287	D188
Temperature(⁰C)	15.9	15.9	15.5
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	50	72.5	75.5
Concentration(μg/m³)	226.4	200.3	159.0

Coarse particulates (site E)

Sample code	E4810	E2810	E2811
Temperature(⁰C)	20.1	19.4	20.2
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	52.5	60.5	64
Concentration(μg/m³)	109.6	107.3	74.4

Fine particulates (site E)

Sample code	E247	E148	E248
Temperature(⁰C)	16.0	15.4	16.1
Rainfall(mm)	Nil	Nil	Nil
Humidity(%)	68	74	75
Concentration(μg/m³)	24.7	22.5	1.5

However no such relationship could be detected for the fine particulate samples collected at sites A, C and D. Samples were collected at different temperature and rainfall levels.

5.3.3 Rainfall

Samples collected after a rainy day recorded low SPM levels as compared to similar samples collected at the same site with no rain having been received the previous day. This was attributed to the washing away of some of the particles. The effect is detected by considering samples collected at constant temperature. This is illustrated for coarse particle samples A247, A189 collected at site A; C285, C1811, C2810 collected at site C and fine particle samples A247, A149 collected at site A and samples B247, B149 collected at site B.

Coarse particulates (site A)

Sample code	A287	A189
Temperature(^{0}C)	17.8	17.4
Rainfall(mm)	38.6	Nil
Humidity(%)	68	65.5
Previous day weather conditions	Rainfall	Sunny, hot
Concentration(μg/m^3)	17.8	160.8

Fine particulates (site A)

Sample code	A247	A149
Temperature(^{0}C)	17.8	17.4
Rainfall(mm)	38.6	Nil
Humidity(%)	68	65.5
Previous day weather conditions	Rainfall	sunny, hot
Concentration(μg/m^3)	14.3	32.2

Fine particulates (site B)

Sample code	B247	B149
Temperature(^{0}C)	18	17.95
Rainfall(mm)	1.1	Nil
Humidity(%)	68	66.5
Previous day weather conditions	Drizzle	Sunny, hot
Concentration(μg/m^3)	12.5	36.2

Coarse particulates (site C)

Sample code	C285	C1811	C2810
Temperature(^{0}C)	19.7	20.1	19.7
Rainfall(mm)	11.0	3.8	Nil
Humidity(%)	78.5	69.5	45.5
Previous day weather conditions	Rainfall	Rainfall	sunny, hot
Concentration(μg/m^3)	41.95	116.1	132.3

Coarse particulate samples collected after a rainy day for sites B, D and E showed a similar trend but no such trend could be detected for the fine particulate samples collected at site D and E.

The weather conditions during sampling also determined the levels of suspended particulate matter collected. Samples collected during a rainy day recorded low SPM levels compared to similar samples collected with no rain. Coarse particle samples A289 collected at site A, B288 collected at site B, C186 collected at site C and fine particle samples C146 collected at site C, B246 collected at site B all recorded low SPM levels as compared to similar samples collected with no rain during the sampling exercise.

Coarse particulates (site A)

Sample code	A289	A1811
Temperature(^{0}C)	19.95	19.1
Rainfall(mm)	24.7	Nil
Humidity(%)	71	66
Weather conditions	Rainfall	Cold, cloudy
Concentration(μg/m^3)	155.6	196.0

Coarse particulates (site C)

Sample code	C186	C286
Temperature(^{0}C)	19.4	19.0
Rainfall(mm).	45.6	Nil
Humidity(%)	84	77.5
Weather conditions	Cloudy, showers	cloudy, cold
Concentration(μg/m^3)	10.8	35.5

Fine particulates (site C)

Sample code	C146	C246
Temperature(°C)	19.4	19.0
Rainfall(mm)	45.6	Nil
Humidity(%)	84	77.5
Weather conditions	Cloudy, showers	cloudy, cold
Concentration(μg/m^3)	8.4	22.8

Coarse particulates (site B)

Sample code	B286	B288
Temperature(°C)	18.3	18.4
Rainfall(mm)	Nil	13.5
Humidity(%)	71.5	94.5
Weather conditions	cloudy, cold	Showers, cloudy
Concentration(μg/m^3)	58.5	22.7

Fine particulates (site B)

Sample code	B246	B248
Temperature(°C)	18.3	18.4
Rainfall(mm)	Nil	13.5
Humidity(%)	71.5	94.5
Weather conditions	cloudy, cold	Showers, cloudy
Concentration(μg/m^3)	28.3	8.10

However no samples were collected on a rainy day for sites D and E, hence it was not possible to establish the effects for these sites.

Several studies have established that day to day changes in weather conditions affects the particulate levels in the atmosphere. Karue *et al* (1992) working on TSPM in a Kenyan urban area found the levels of samples collected to vary with the day's weather conditions (temperature, humidity and rainfall). They found that the TSPM collected increased with temperature and decreased with relative humidity. They also indicated that samples collected during a drizzle had low TSPM values indicating precipitation of the particles by the drizzle. Hien *et al* (1997) reported higher levels of TSPM during the dry season (107±7) μg/m^3 than in the rainy season

(7315) µg/m³ while Sacmo and Okita (1990) reported higher levels in winter (31-43) µg/m³ and spring (35.4-46.1) µg/m³ than in summer (16.7-21.0)µg/m³ for $PM_{8.0}$ samples collected in Sapporo (Japan).

5.4 Suspended particulate matter (SPM) values in μg/m³ at four (4) metres above the ground for the period December 1998 to May 1999.

The Tables 5 and 6 below shows the mean monthly values for the four sites B, C, D and E. The values presented are the mean of the samples collected per month. The PM_{10} values are presented in table 9.

Table 5: Mean monthly concentration in μg/m³ of coarse particulates for the period December 1998 to May 1999

Site	Dec'98	Feb'99	Mar'99	Apr'99	May'99
B	95.4	98.5	45.0	23.30	52.90
n=4	±42.6	±23.6	±44.9	±14.8	±21.1
C	45.3	128.9	68.95	13.90	55.15
n=4	±8.50	±56.5	±47.2	±14.2	±14.5
D	101.1	184.0	155.5	46.7	101.13
n=4	±46.5	±36.8	±109.5	±24.9	±28.4
E	53.1	28.2	70.2	29.0	39.35
n=4	±18.9	±15.0	±17.0	±10.5	±7.9

N= number of determinations

Table 6: Mean monthly concentration in μg/m³ of fine particulates for the period December 1998 to May 1999

Site	Dec'98	Feb'99	Mar'99	Apr'99	May'99
B	10.7	29.0	14.9	15.1	8.31
n=4	±4.9	±1.3	±4.5	±2.3	±6.9
C	17.5	20.5	16.55	8.85	7.97
n=4	±2.8	±1.2	±1.1	±1.8	±3.8
D	15.8	22.4	21.60	13.7	14.15
n=4	±2.9	±2.8	±19.6	±5.1	±6.5
E	6.5	23.70	14.4	21.45	18.51
n=4	±7.7	±0.3	±2.6	±14.8	±2.2

N= number of determinations

Trend similar to particulate loading obtained at 2.0 metres is observed for the sites B, C, D and E for both coarse and fine particulates. Site D recorded some of the highest levels (46.7-184.0 μg/m³) (Table 5) for the coarse particulates while Site E recorded lower values (28.2-70.2 μg/m³) (Fig 5.5) than all the other sites. Sites B, C and E recorded values less than 100 μg/m³ for most of the months while site D recorded values greater than 100μg/m³ for most of the months. However, these values were still lower than those collected at a height of 2.0 metres (Figs 5.1 and 5.5). This pointed to resuspension of dust being the main contributor to the particulates in the air. The highest value obtained at four (4) metres was 184 μg/m³ at site D as compared to 233.9 μg/m³ the highest obtained at two (2) metres height.

For the fine particulates, a slight reduction in particulate loading is observed. At two (2) metres sites B, C and D recorded values below 20 μg/m³ for most of the months. However at four (4) metres, values were mainly below 20 μg/m³ for most of the months (Table 3 and 6). The maximum recorded value was 29.0 μg/m³. Site E recorded comparable levels (6.44-28.8μg/m³) at both heights. It should be noted that this site was away from any playground or footpath/road, hence effect of resuspended dust at the lower height was minimal. The surface was mainly rocky hence less soil dust than the other sites.

Fig 5.5: Mean monthly variation of coarse particulate levels at four metres height for the various sites

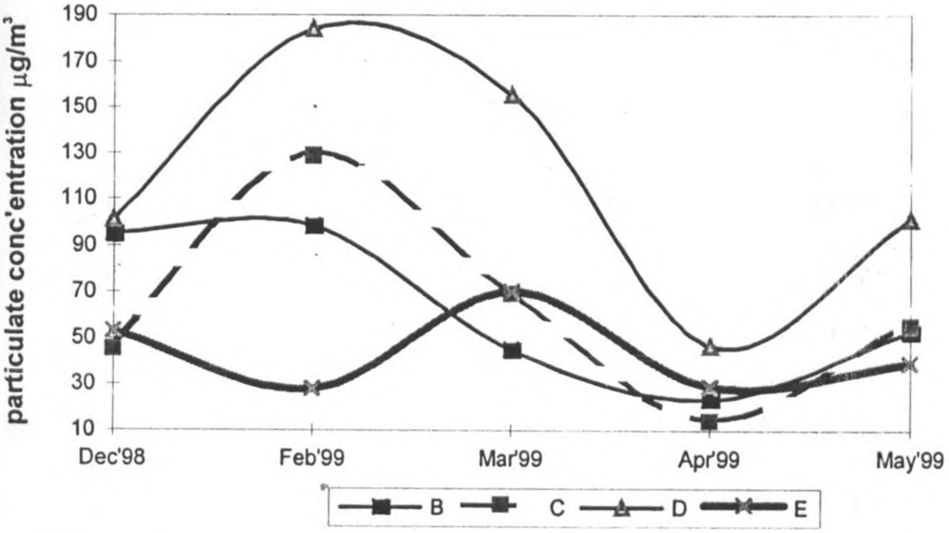


Fig 5.6: Mean monthly variation of fine particulate levels at four metres height for the various sites

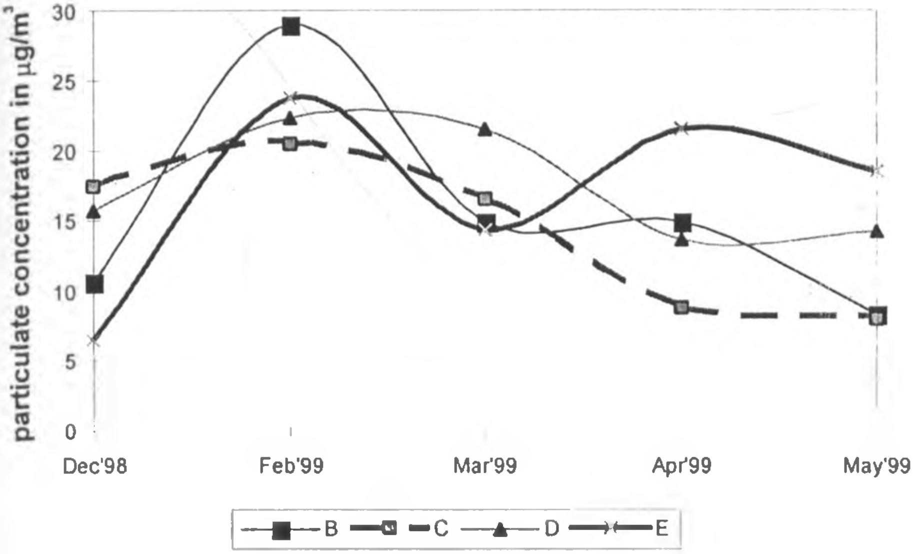


Table 7: Intercomparison of SPM concentration ranges (µg/m³) at heights of two (2) and four (4) metres above the ground for coarse particulate samples

Site	Two (2) metres	Four (4) metres
B	20.00-179.04	23.30-98.5
C	23.14-152.15	13.90-128.90
D	39.63-233.85	46.70-184.0
E	38.70-96.70	28.20-70.20

Table 8: Intercomparison of SPM concentration ranges (µg/m³) at heights of two (2) and four (4) metres above the ground for fine particulate samples

Site	Two (2) metres	Four (4) metres
B	13.84-42.40	8.31-29.00
C	7.40-33.82	7.97-20.50
D	14.41-36.06	13.70-22.40
E	6.44-28.80	6.50-23.70

For the coarse particulate fraction (Table 7) the sites showed a particulate loading reduction by factors ranging from 0.83 for site C to 0.55 for site B. It should be noted that sites B and D were located nearest to unpaved roads/footpath. The effect of resuspended dust could still account for the lower reduction in levels collected at this height than for other sites. For the fine particulate fraction reduction factors ranging from 0.82 for site E to 0.60

for site B were observed (Table 8). The fact that samples at the two heights were collected under different climatic conditions could also have contributed to the different levels observed. Transport of fine particulates of industrial origin by north easterlies prevalent in Nairobi could also have accounted for the levels at the higher height.

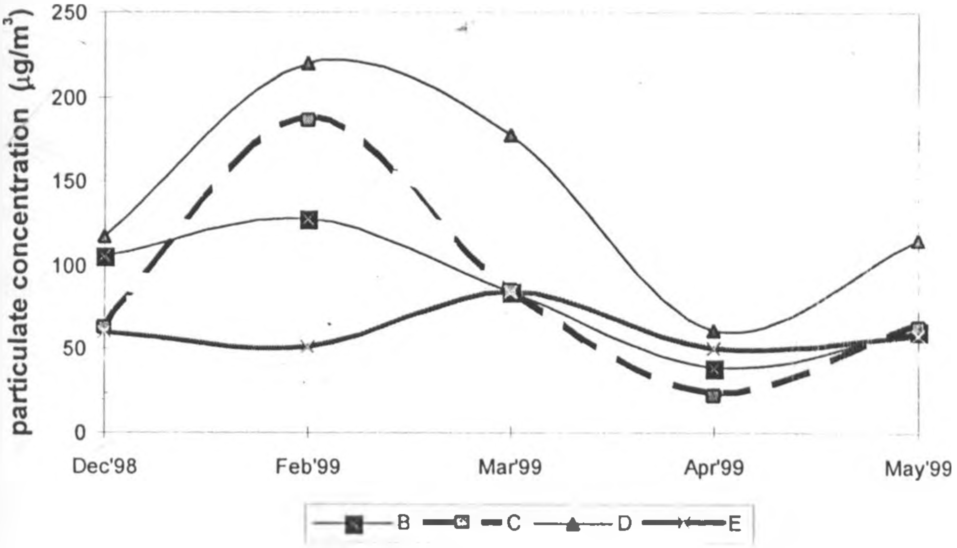
Table 9: Mean monthly PM_{10} values ($\mu g/m^3$) for the four sites for the period December 1998 to May 1999

Site	Dec'98	Feb'99	Mar'99	Apr'99	May'99	Average
B	106.1	127.5	84.8	38.4	61.2	83.6
n=4	±47.5	±25.0	±49.4	±12.6	±14.4	±31.6
						n=20
C	62.8	186.3	85.5	22.7	63.1	84.1
n=4	±16.0	±15.7	±48.2	±16.0	±18.4	±55.0
						n=20
D	116.8	220.1	177.0	60.9	115.3	138
n=4	±69.7	±20.6	±129.1	±29.3	±34.9	±55.1
						n=20
E	60.1	51.7	84.6	50.0	57.9	60.9
n=4	±19.5	±15.0	±19.5	±25.9	±10.1	±12.4
						n=20

n= number of determinations

The four sites B, C, D and E recorded lower PM_{10} values at the height of four (4) metres as compared to two (2) metres above the ground (Figs 5.3 and 5.7). At two (2) metres sites B, C and D had most of the months recording values greater than 100 $\mu g/m^3$. This reduced at four (4) metres with only site D recording more than 100 $\mu g/m^3$ for most of the months (Table 4 and 9). Site E recorded lower values for both heights for the entire period. Gatebe *et al* (1996) reported PM_{10} values ranging from 30 to 80 $\mu g/m^3$ collected at Kenya Meteorological Department headquarters (Nairobi) at a height of eight metres, which are quite low as compared to values obtained in this study (Table 4). The bare ground, high population density, houses constructed of mud and wood unlike in KMD could have contributed to the high levels of airborne soil dust realised in this area. Chih-Shan Li (1994) reported values ranging from 15 to 219 $\mu g/m^3$ for PM_{10} samples collected at Taipei urban area (Taiwan). These values are comparable to values obtained at two (2) metres height in this study. Reponen *et al* (1996) reported values ranging from 3.4 to 158.3μg/m^3 for urban sites and 2.1 to 74.2 μg/m^3 for sub-urban sites for PM$_{10}$ samples collected at four (4) metres height above the ground in the city of Kuopio (Finland). These values are comparable to values 60.9 to 138.0 μg/m^3 obtained at this height for some of the sites. Another study involving six cities in California's Joaquin Valley (SJV) (Show *et al.*, 1992) reported PM$_{10}$ annual averages ranging from 43 μg/m^3 in non-urban to 73 μg/m^3 in urban areas. Dockery *et al* (1992) reported lower values of PM$_{10}$ (27.6 μg/m^3) and PM$_{2.5}$ (17.7 μg/m^3) in St Louis in United States of America while Eastern Tennesse recorded mean values of 30μg/m^3 for PM$_{10}$ and 21.0μg/m^3 for PM$_2$.

Fig 5.7: Mean monthly variation of PM-10 levels at four metres height for the various sites



5.5 Office dustfall

The levels of dustfall from the various offices sampled for the period January to November 1998 are presented in the Table 10.

Table 10: Levels of office dustfall (μg/cm²/day) for the year 1998

Period sampled	Office(1)	Office(2)	Office(3)	Office(4)
Jan/Feb	0.375	1.300	NS	NS
Mar/April	0.490	0.920	2.386	NS
May	0.230	1.470	0.779	2.393
Jun	0.144	1.010	0.548	1.932
Jul	0.606	0.952	0.721	1.471
Aug	0.634	1.096	0.750	0.894
Sep	0.577	1.701	0.779	2.250
Oct/Nov	0.536	1.649	0.796	3.241
Average	0.449±0.182 n=8	1.262±0.314 n=8	0.966±0.632 n=7	2.030±0.807 n=6

NS = no sampling was done during this period , n= number of determinations

Dustfall for office (1) varied from 0.44 to 0.634μg/cm²/day while for office (2) they ranged from 0.920 to 1.649μg/cm²/day. These two offices show a small variation in the levels of dust recorded than the other offices for the entire period (Table10). It should be noted that these offices were located on the same same side of the office block. However the two offices show a difference in the values recorded with office (2) recording higher values. The sampling filters in office (2) were placed at a higher height and near the window than in office (1). This points to the window as the main entry of dust recorded in the two offices. It should be pointed out that the mobility (i.e, movement of people in and out) of offices (1), (2) and (4) was far less than in office (3). This indicates that most of the dust recorded was settling from the air coming in through the ventilation's rather than suspension of dust from the office floors. Several studies (Akhter *et al*, 1992., Fergusson *et al,* 1991., Diemel *et al*, 1981) have linked household dust to outdoor sources.

Office (4) which was the smallest, ventilated by a window and a door like office (1) and (2) recorded some of the highest values (Table 10). This could be due to the settling of dust in a small area. Office (3) which occupied a bigger space than all the other offices recorded higher values than office (1). It should be noted that the ventilation in this room included the door and an air conditioner which filtered the entering air. High mobility (i.e, people moving in and out) was noted for this office. This indicated that soil dust coming from outside and later airborne by various indoor activities contributed to most of the dust recorded in this office although entry of dust with the incoming air could not be ruled out. The dustfall does not seem to follow the seasonal trend with some of the highest values being recorded in May: Office (2):-1.470μg/cm^2/day, Office (3):-0.779μg/cm^2/day, Office (4):-2.393μg/cm^2/day (Table10) when highest amount of rainfall was received (Fig 5.1). The wet conditions makes surface dust (outdoor dust) to be dump and sticky making it more easy to stick on the shoes of people walking in and out of the various offices leading to high amounts being brought into the offices and later airborne by various indoor activities. Diemel *et al* (1981) sampled dustfall in 100 houses in Arnhem City, they recorded dustfall loadings ranging from (0.14 - 6.39 μg/cm^2/day) which are higher compared to this study. Fergusson *et al* (1985) observed mean dustfall loading of 0.098 μg/cm^2 from houses in Christchurch, NewZealand.

5.6 Elemental concentrations

5.6.1 Quality control

The experimental work started with the optimization of the X-ray fluorescence system. This included setting the optimum bias voltage, shaping time constant at which best detector resolution was obtained and optimum irradiation time for the loaded filters. The pulse shaping time was observed to vary with the resolution of the detector (Fig 5.8) with a maximum being attained at a shaping time constant of 6μs. The energy resolution (FWHM) at 5.9 kev MnKα peak varied from (160-180eV) for the entire period of analysis. Optimum irradiation time was found to be in the range of 50,000 to 60,000 seconds. The elemental sensitivity (c/s) of the detector was found to increase with increase in the atomic number of elements (Fig 5.9). A variation coefficient of 4.5% for the geometrical factor (G) was obtained which was an indication of a good sensitivity calibration.

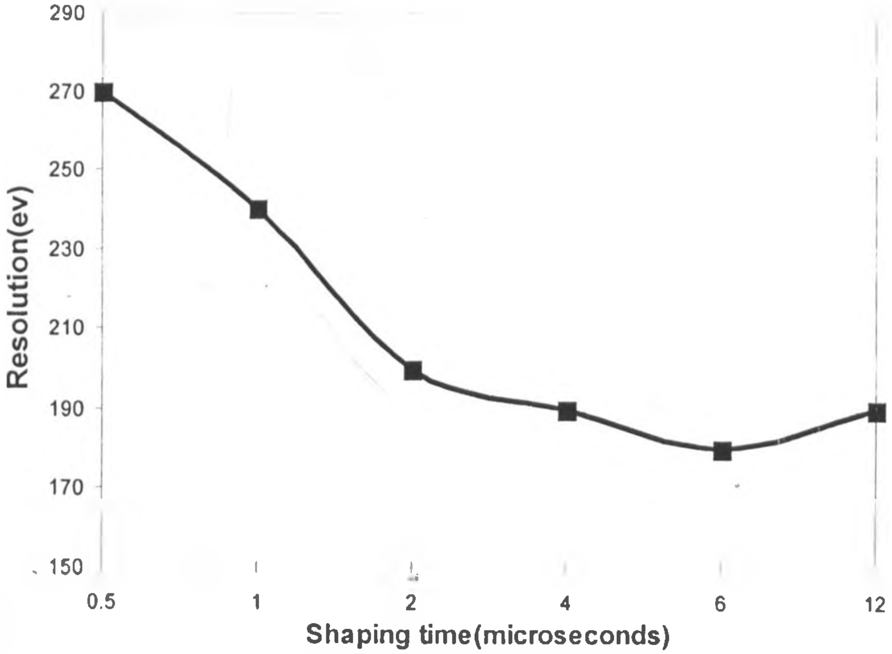


Fig 5.8: Variation of detector resolution with shaping time constant

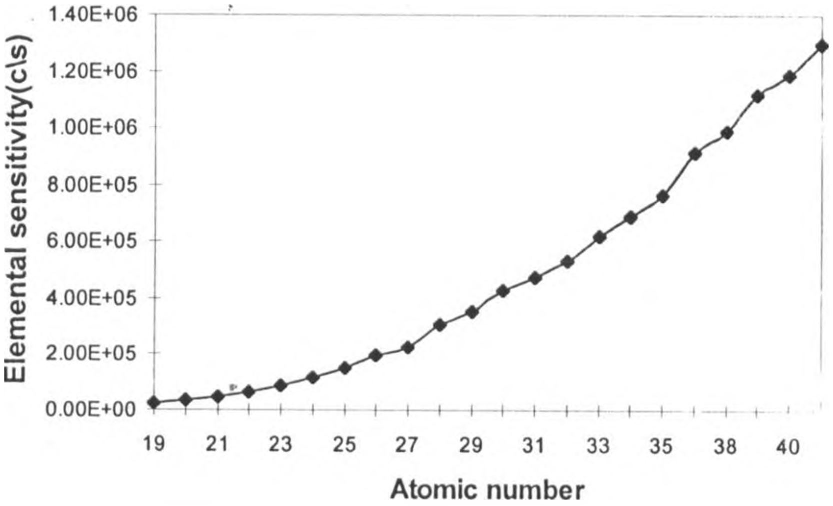


Fig 5.9: Variation of elemental sensitivity of the Si(Li) detector with atomic number

A Standard Reference Material (Urban Particulate Matter, SRM-1648) from the International Atomic Energy Agency (IAEA) was also analysed by both EDXRF and AAS together with the samples. The results do agree within 8 % of the certified values (Table 11 and 12). However, most elements show a negative deviation from the certified values, this could be due to loss of some of the elements with time. Loss during digestion procedures could also account for the negative deviation for samples analysed by AAS.

Table 11: Results of analysis of SRM-1648 by EDXRF(%)

Element	Concentration (%) n=3	Certified value (%)	Error (%)
K	1.11 ±0.024	1.05	+5.7
Cr	0.0371 ±0.0309	0.0403	-7.9
Fe	3.74 ±0.14	3.91	-4.4
Cu	0.0605 ±0.283	0.0609	-0.7
Zn	0.449 ±0.015	0.476	-5.6
Pb	0.605 ±0.013	0.655	-7.6

N=number of determinations

Table 12: Results of analysis of SRM-1648 by AAS

Element	Concentration(%) n=3	Certified value(%)	Error(%)
Cd	0.0076 ±0.00095	0.0075	+1.76
Fe	3.78 ±0.095	3.91	-3.23
Pb	0.627 ±0.034	0.655	-4.74
Zn	0.463 ±0.025	0.476	-2.64
Cu	0.060 ±0.005	0.0609	-1.52
Ni	0.0076 ±0.00095	0.0082	-6.91

N= number of determinations

Five of the samples analysed with XRF were digested and re-analysed with AAS. The results of EDXRF analysis were compared with the results of AAS analysis of the same set of samples. As can be seen in Table 13 and Figure 5.10 the consistency between the results shows good agreement between the two methods.

Table 13: Intercomparison of XRF and AAS (μg/m³)

Sample code	B381098		D18998		C28998		D14998		B18998	
	XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS
Fe	8.46	8.79	12.46	11.1	7.08	8.26	2.42	1.12	16.51	12.42
	±0.714	±0.618	±0.361	±0.208	±0.502	±0.305	±0.041	±0.032	±0.891	±0.604
Mn	0.866	0.818	0.905	0.973	0.555	0.536	BDL	0.147	1.29	0.994
	±0.029	±0.014	±0.132	±0.104	±0.042	±0.028		±0.021	±0.315	±0.114
Zn	0.317	0.219	0.302	0.267	0.278	0.179	0.125	0.162	0.305	0.249
	±0.038	±0.029	±0.026	±0.021	±0.016	±0.013	±0.014	±0.009	±0.027	±0.022
Cu	BDL	0.132	BDL	0.197	0.312	0.297	0.208	0.190	0.125	0.167
		±0.01		±0.012	±0.015	±0.011	±0.01	±0.005	±0.016	±0.013
Pb	0.186	0.108	0.128	0.177	0.015	0.107	0.193	0.183	0.519	0.433
	±0.008	±0.006	±0.014	±0.015	±0.003	±0.004	±0.016	±0.012	±0.043	±0.036

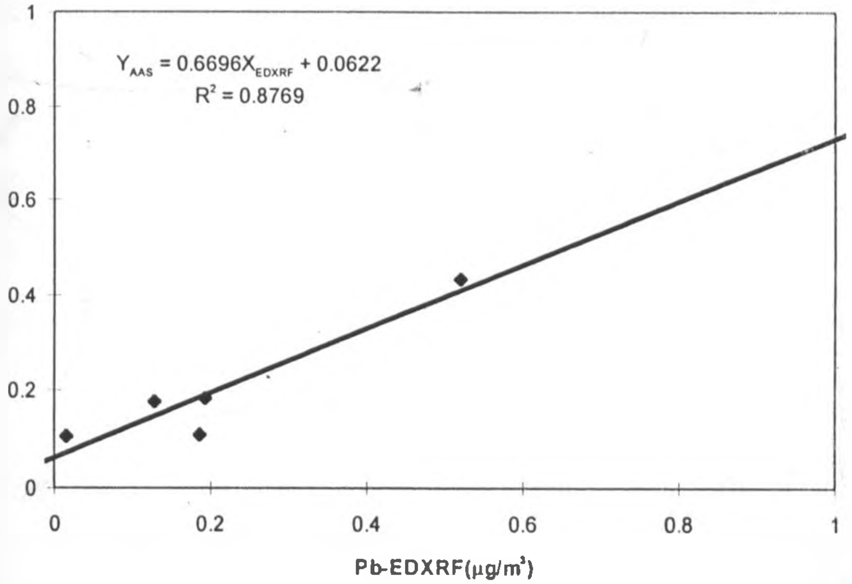


Fig 5.10: Comparison of Pb concentrations in five samples determined by AAS and EDXRF

5.6.2 Mean monthly elemental concentrations (μg/m³) at two (2) metres above the ground for the period May to November 1998

Elemental concentration results for samples collected from May to November 1998 for the sites A-E are presented in the Tables (14-23) below. The samples collected from May to July were analysed by Atomic Absorption Spectrophotometry (AAS) while those collected from August to May were analysed by Energy Dispersive X-ray Fluorescence (EDXRF).

The results are given in μg/m³. The trends for the elements manganese, iron, copper, zinc and lead are shown in Figures 5.11a-5.15a for the coarse particulates and 5.11b-5.15b for the fine particulates.

Table 14: Mean monthly elemental concentration (μg/m³) for the coarse particulate samples for site A for the period May to November 1998.

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	LDL	LDL	3.31 ±0.07	LDL
Ca	NA	NA	NA	2.16 ±1.23	7.49 ±0.88	7.20 ±0.28	6.05 ±0.53
Ti	NA	NA	NA	LDL	0.647 ±0.088	0.828 ±0.188	0.199 ±0.281
Mn	0.461 ±0.031	0.312 ±0.007	0.099 ±0.019	0.317 ±0.448	0.844 ±0.146	1.049 ±0.144	0.599 ±0.179
Fe	4.82 ±1.101	3.73 ±2.03	0.166 ±0.065	2.26 ±1.21	8.37 ±0.113	12.0 ±1.27	6.09 ±2.21
Cu	0.123 ±0.008	0.172 ±0.225	0.238 ±0.268	0.080 ±0.011	0.164 ±0.012	0.133 ±0.013	0.104 ±0.004
Zn	0.143 ±0.025	0.238 ±0.032	0.256 ±0.022	0.073 ±0.023	0.267 ±0.022	0.282 ±0.030	0.188 ±0.035
Pb	0.390 ±0.003	0.389 ±0.549	0.216 ±0.305	0.047 ±0.013	0.193 ±0.006	0.139 ±0.006	0.142 ±0.039
Br	NA	NA	NA	0.024 ±0.015	0.006 ±0.066	0.061 ±0.005	0.051 ±0.011
Zr	NA	NA	NA	0.0456 ±0.014	0.166 ±0.011	0.235 ±0.023	0.1165 ±0.055

NA -Not Analysed, LDL-low detection limits, n=6,number of determinations

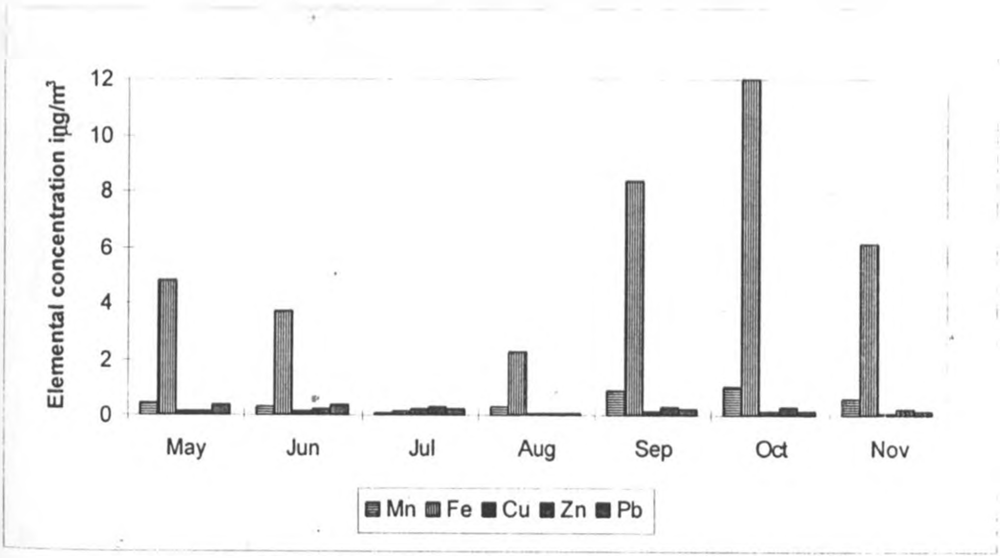


Fig 5.11 a: Mean monthly variation of Mn, Fe, Cu, Zn, and Pb for the coarse particulate samples for the period May to November 1998 for site A

Table 15: Mean monthly elemental concentration (µg/m³) for the fine particulate samples for site A for the period May to November 1998

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	LDL	LDL	2.435 ±0.431	LDL
Ca	NA	NA	NA	0.020 ±0.0054	9.13 ±2.50	5.21 ±0.35	8.02 ±0.42
Ti	NA	NA	NA	LDL	0.163 ±0.231	0.174 ±0.014	LDL
Mn	0.078 ±0.012	0.013 ±0.018	0.080 ±0.103	0.036 ±0.050	0.187 ±0.025	0.189 ±0.034	0.153 ±0.026
Fe	0.778 ±0.201	LDL	1.395 ±0.743	0.232 ±0.327	0.687 ±0.039	1.48 ±0.06	1.01 ±0.48
Cu	0.149 ±0.021	0.191 ±0.270	0.029 ±0.040	0.024 ±0.010	0.191 ±0.026	0.111 ±0.011	0.077 ±0.005
Zn	0.103 ±0.008	0.113 ±0.011	0.146 ±0.021	0.017 ±0.001	0.200 ±0.049	0.135 ±0.025	0.120 ±0.001
Pb	0.273 ±0.028	0.350 ±0.064	0.044 ±0.062	0.353 ±0.010	0.118 ±0.166	0.135 ±0.038	0.136 ±0.025
Br	NA	NA	NA	0.017 ±0.012	0.060 ±0.003	0.049 ±0.004	0.036 ±0.012
Zr	NA	NA	NA	0.007 ±0.002	0.018 ±0.001	0.027 ±0.007	0.018 ±0.003

NA -Not Analysed, LDL-low detection limits, n=6 number of determinations

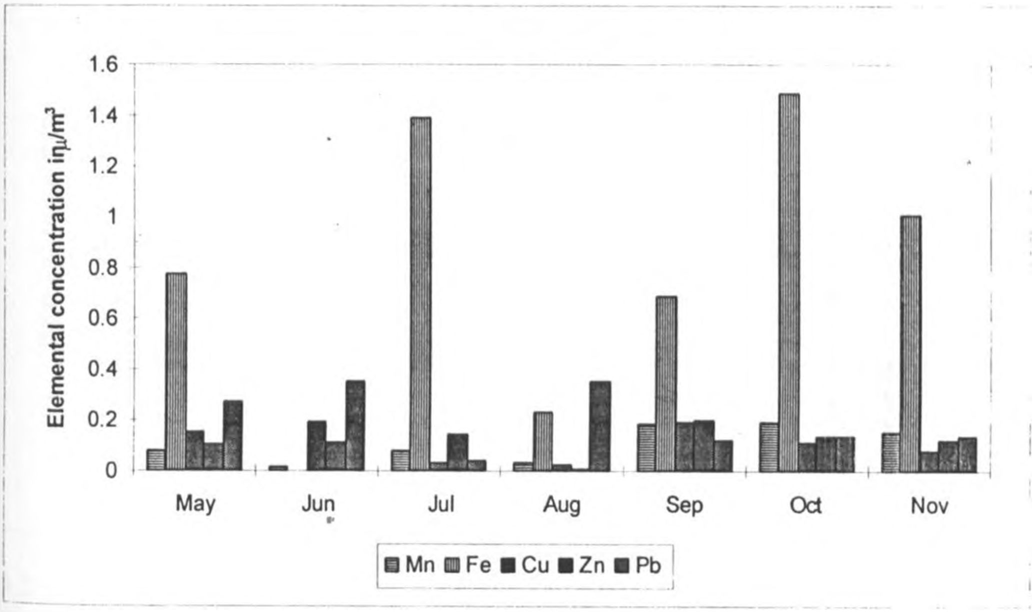


Fig 5.11 b: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the fine particulate samples for the period May to November 1998 for site A

Table 17: Mean monthly elemental concentration (μg/m³) for the fine particulate samples for site B for the period May to November 1998

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	LDL	4.08 ±0.021	3.03 ±0.064	LDL
Ca	NA	NA	NA	LDL	6.47 ±0.545	5.38 ±0.553	7.86 ±0.823
Ti	NA	NA	NA	0.868 ±0.053	0.250 ±0.142	LDL	LDL
Mn	0.032 ±0.001	0.010 ±0.014	0.072 ±0.030	0.207 ±0.008	0.142 ±0.059	0.116 ±0.042	0.151 ±0.002
Fe	0.502 ±0.103	0.726 ±0.155	0.389 ±0.110	0.918 ±0.809	0.721 ±0.187	0.627 ±0.292	0.558 ±0.351
Cu	LDL	0.065 ±0.009	0.135 ±0.191	0.083 ±0.002	0.171 ±0.011	0.110 ±0.018	0.091 ±0.005
Zn	0.101 ±0.002	0.114 ±0.025	0.136 ±0.002	0.122 ±0.003	0.144 ±0.023	0.115 ±0.020	0.108 ±0.015
Pb	0.325 ±0.126	0.430 ±0.420	0.125 ±0.176	0.228 ±0.080	0.144 ±0.009	0.099 ±0.020	0.131 ±0.006
Br	NA	NA	NA	LDL	0.051 ±0.005	0.038 ±0.012	0.034 ±0.010
Zr	NA	NA	NA	LDL	0.015 ±0.001	0.015 ±0.005	0.013 ±0.001

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

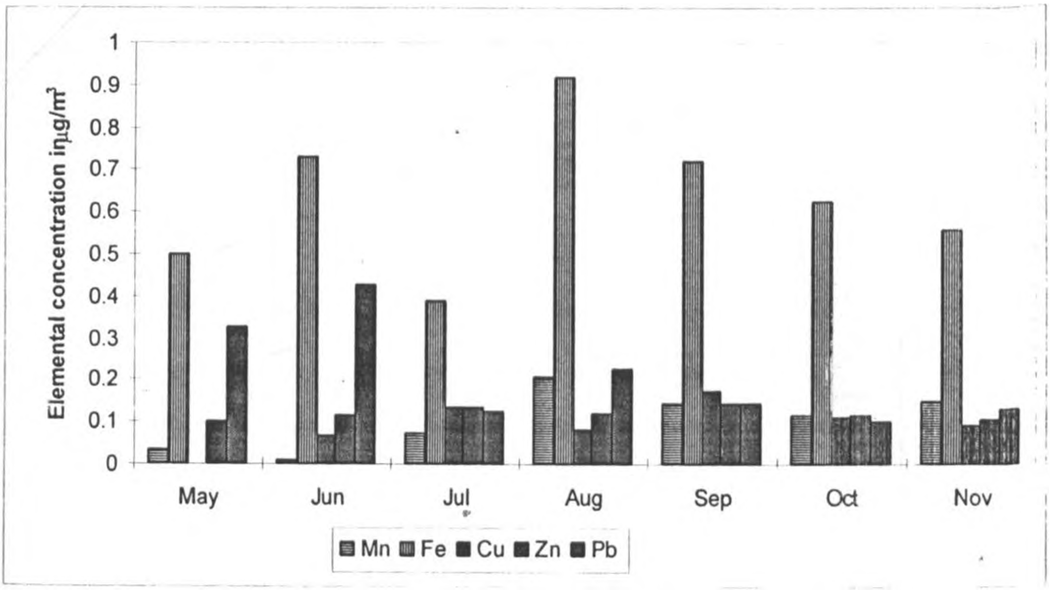


Fig 5.12 b: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the fine particulate samples for the period May to November 1998 for site B

Table 18: Mean monthly elemental concentration(μg/m³) for the coarse particulate samples for site C for the period May to November 1998

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	LDL	3.17 ±0.505	3.23 ±0.042	LDL
Ca	NA	NA	NA	8.14 ±0.007	7.75 ±0.636	5.98 ±0.767	6.55 ±0.536
Ti	NA	NA	NA	0.465 ±0.069	0.818 ±0.014	0.461 ±0.117	0.383 ±0.054
Mn	0.097 ±0.024	0.485 ±0.441	0.479 ±0.200	0.369 ±0.202	0.584 ±0.067	0.342 ±0.160	0.308 ±0.010
Fe	0.284 ±0.002	8.674 ±4.46	8.434 ±4.22	3.55 ±0..38	8.82 ±0.79	4.48 ±2.81	4.13 ±0.50
Cu	LDL	0.233 ±0.106	0.192 ±0.007	0.112 ±0.065	0.121 ±0.034	0.134 ±0.002	0.080 ±0.007
Zn	0.150 ±0.016	0.168 ±0.038	0.263 ±0.225	0.154 ±0.035	0.183 ±0.018	0.170 ±0.056	0.275 ±0.223
Pb	0.297 ±0.104	0.225 ±0.176	0.243 ±0.001	0.517 ±0.507	0.122 ±0.021	0.174 ±0.092	0.120 ±0.042
Br	NA	NA	NA	0.089 ±0.003	0.062 ±0.006	0.060 ±0.004	0.042 ±0.007
Zr	NA	NA	NA	0.027 ±0.001	0.187 ±0.002	0.094 ±0.061	0.075 ±0.007

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

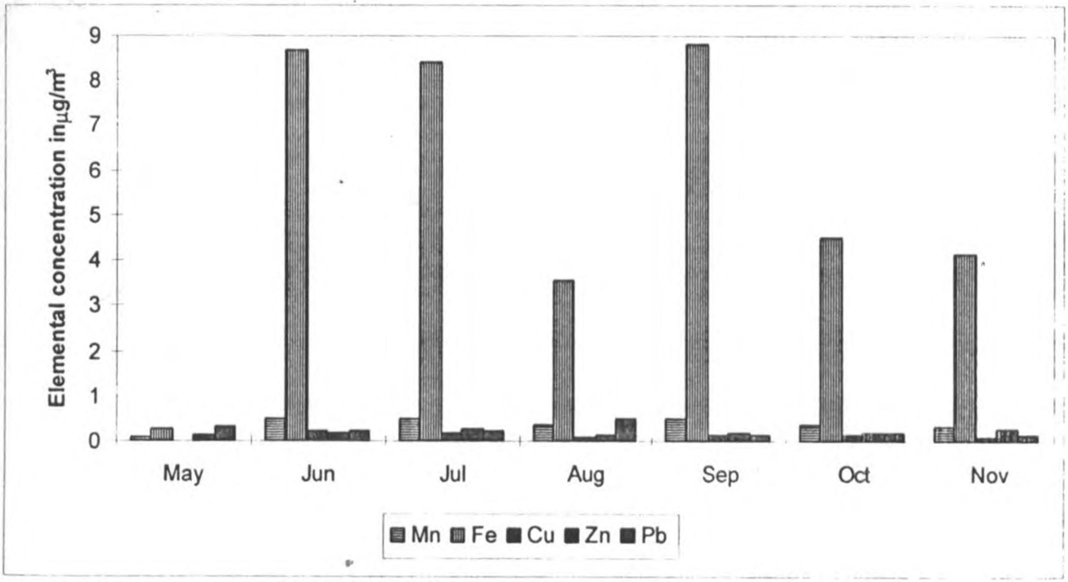


Fig 5.13 a: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the coarse particulate samples for the period May to November 1998 for site C

Table 19: Mean monthly elemental concentration (µg/m³) for the fine particulate samples for site C for the period of May to November 1998

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	LDL	LDL	2.25 ±0.325	LDL
Ca	NA	NA	NA	6.62 ±0.172	6.38 ±1.68	5.29 ±0.460	5.85 ±0.004
Mn	0.048 ±0.011	0.070 ±0.018	0.062 ±0.021	0.074 ±0.057	0.142 ±0.016	0.122 ±0.001	0.111 ±0.011
Fe	0.633 ±0.022	0.910 ±0.586	2.205 ±0.148	0.266 ±0.002	0.784 ±0.187	0.743 ±0.067	0.495 ±0.195
Cu	LDL	0.074 ±0.035	LDL	0.152 ±0.064	0.157 ±0.047	0.126 ±0.029	0.109 ±0.006
Zn	0.106 ±0.004	0.202 ±0.026	0.148 ±0.005	0.121 ±0.003	0.156 ±0.002	0.212 ±0.007	0.1034 ±0.046
Pb	0.258 ±0.023	0.214 ±0.011	0.376 ±0.285	0.263 ±0.141	0.192 ±0.019	0.118 ±0.021	0.120 ±0.021
Br	NA	NA	NA	0.067 ±0.005	0.056 ±0.014	0.051 ±0.001	0.026 ±0.004
Zr	NA	NA	NA	LDL	0.017 ±0.005	0.015 ±0.006	0.017 ±0.004

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

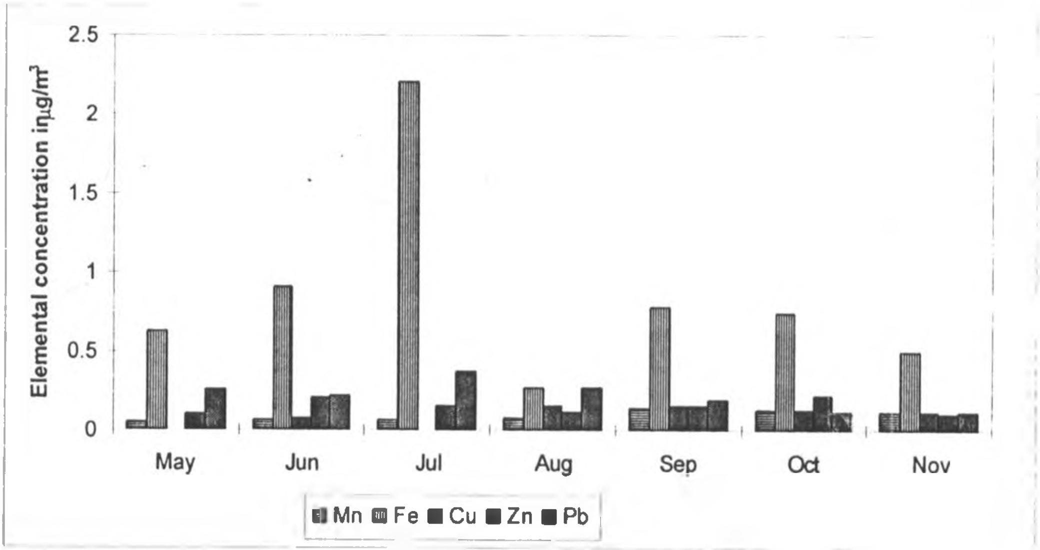


Fig 5.13 b: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the fine particulate samples for the period May to November 1998 for site C

Table 20: Mean monthly elemental concentration ($\mu g/m^3$) for the coarse particulate samples for site D for the period of May to November 1998

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	3.65 ±1.05	3.28 ±0.244	3.51 ±1.06	7.70 ±2.08
Ca	NA	NA	NA	8.38 ±0.306	7.495 ±1.803	8.935 ±0.262	6.384 ±0.202
Ti	NA	NA	NA	0.965 ±0.026	0.752 ±0.520	1.17 ±0.337	0.347 ±0.018
Mn	0.098 ±0.005	0.191 ±0.099	1.40 ±0.017	1.056 ±0.165	0.726 ±0.35	1.39 ±0.378	0.670 ±0.453
Fe	0.184 ±0.029	4.49 ±0.360	9.140 ±0.712	8.61 ±0.795	8.32 ±3.94	16.25 ±4.88	6.21 ±4.34
Cu	0.150 ±0.014	0.128 ±0.012	0.160 ±0.079	0.163 ±0.008	0.167 ±0.042	0.155 ±0.026	0.086 ±0.005
Zn	0.156 ±0.007	0.212 ±0.062	0.304 ±0.003	0.333 ±0.002	0.217 ±0.071	0.335 ±0.019	0.170 ±0.080
Pb	0.169 ±0.003	0.158 ±0.008	0.265 ±0.109	0.185 ±0.054	0.144 ±0.047	0.257 ±0.091	LDL
Br	NA	NA	NA	0.062 ±0.002	0.077 ±0.032	0.063 ±0.001	0.054 ±0.001
Zr	NA	NA	NA	0.130 ±0.024	0.141 ±0.086	0.252 ±0.066	0.086 ±0.056

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

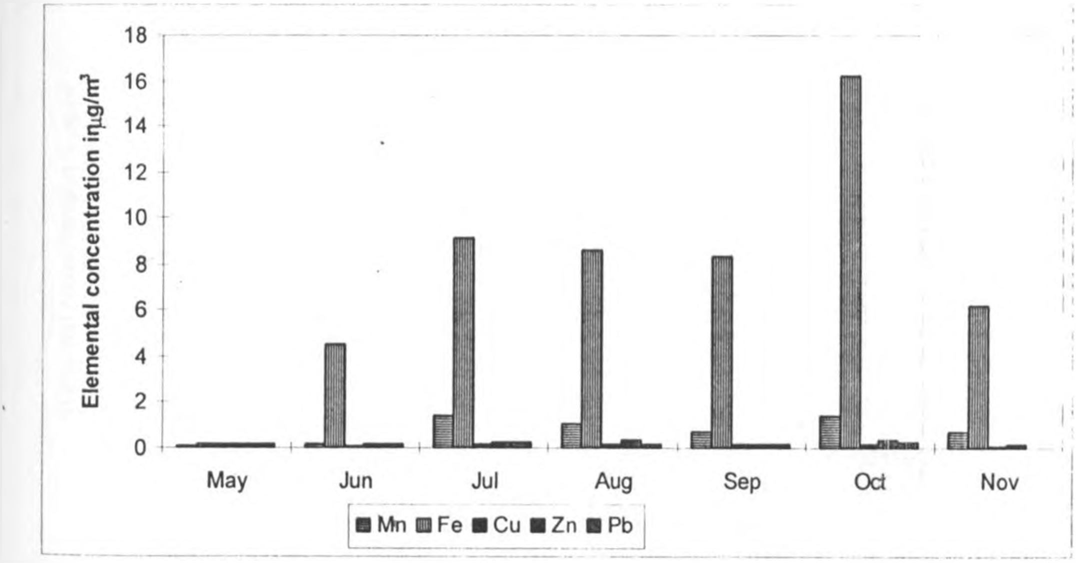


Fig 5.14 a: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the coarse particulate samples for the period May to November 1998 for site D

Table 21: Mean monthly elemental concentration (μg/m^3) for the fine particulate samples for site D for the period of May to November 1998

Element	May	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	NA	2.89 ±0.021	LDL	IDL	4.25 ±0.036
Ca	NA	NA	NA	6.63 ±1.21	6.19 ±1.55	5.77 ±0.502	6.61 ±1.30
Ti	NA	NA	NA	0.157 ±0.003	LDL	0.376 ±0.014	LDL
Mn	LDL	0.049 ±0.021	0.058 ±0.008	0.167 ±0.045	0.129 ±0.026	0.210 ±0.007	0.159 ±0.032
Fe	0.400 ±0.201	0.666 ±0.323	0.563 ±0.252	0.895 ±0.346	0.891 ±0.325	1.745 ±0.304	0.556 ±0.006
Cu	0.026 ±0.012	0.097 ±0.078	LDL	0.087 ±0.122	0.151 ±0.055	0.170 ±0.032	0.079 ±0.004
Zn	0.104 ±0.001	0.152 ±0.272	0.136 ±0.006	0.150 ±0.045	0.141 ±0.030	0.157 ±0.001	0.108 ±0.002
Pb	LDL	0.648 ±0.318	0.481 ±0.222	0.144 ±0.004	0.183 ±0.045	0.131 ±0.011	0.138 ±0.010
Br	NA	NA	NA	0.065 ±0.004	0.058 ±0.003	0.047 ±0.0091	0.040 ±0.005
Zr	NA	NA	NA	0.012 ±0.001	0.020 ±0.003	0.026 ±0.012	0.023 ±0.004

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

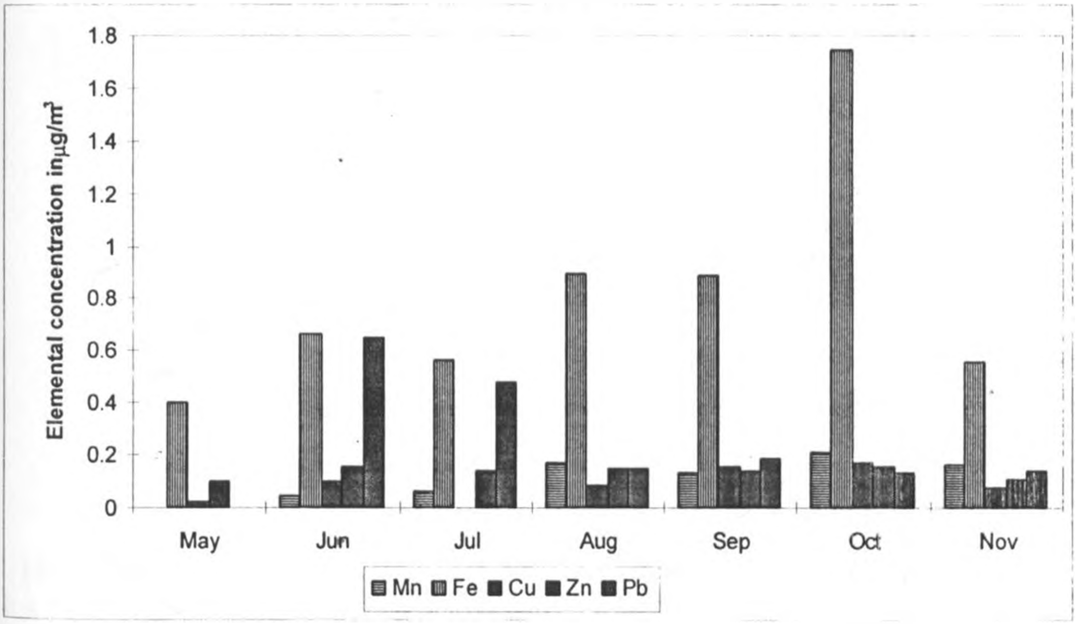


Fig 5.14 b: Mean monthly variation of Mn, Fe,Cu, Zn and Pb for the fine particulate samples for the period May to November 1998 for site D

Table 22: Mean monthly elemental concentration (μg/m³) for the coarse samples for site E for the period of May to November 1998

Element	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	3.39 ±0.504	3.83 ±0.799	LDL	LDL
Ca	NA	NA	7.09 ±0.323	6.69 ±1.06	6.29 ±0.327	8.15 ±0.408
Ti	NA	NA	0.692 ±0.045	0.667 ±0.064	0.302 ±0.101	LDL
Mn	0.660 ±0.024	0.675 ±0.505	0.379 ±0.028	0.301 ±0.166	0.430 ±0.017	0.149 ±0.094
Fe	4.30 ±0.122	4.704 ±1.52	3.99 ±0.509	2.21 ±2.13	4.48 ±0.163	1.22 ±1.07
Cu	0.086 ±0.015	0.110 ±0.035	0.240 ±0.108	0.170 ±0.015	0.126 ±0.022	0.280 ±0.355
Zn	0.112 ±0.018	0.130 ±0.031	0.172 ±0.048	0.157 ±0.029	0.163 ±0.020	0.125 ±0.018
Pb	0.509 ±0.203	0.722 ±0.127	0.396 ±0.335	0.128 ±0.029	0.145 ±0.035	0.123 ±0.019
Br	NA	NA	0.058 ±0.003	0.069 ±0.006	0.055 ±0.009	0.039 ±0.004
Zr	NA	NA	0.061 ±0.035	0.031 ±0.030	0.066 ±0.003	0.028 ±0.019

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

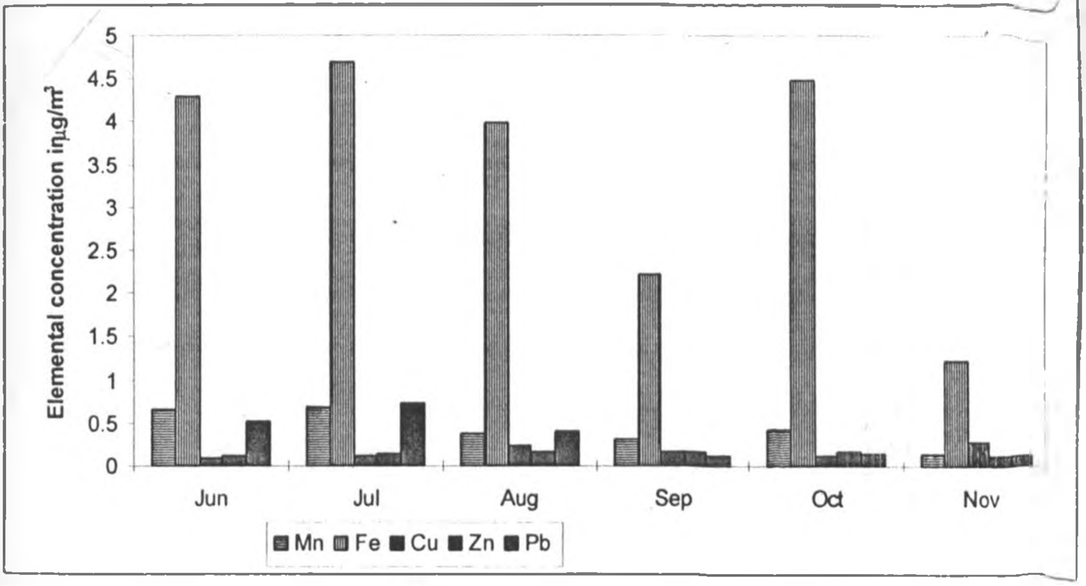


Fig 5.15 a: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the coarse partic samples for the period May to November 1998 for site E

Table 22: Mean monthly elemental concentration (μg/m³) for the coarse particulate samples for site E for the period of May to November 1998

Element	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	3.39 ±0.504	3.83 ±0.799	LDL	LDL
Ca	NA	NA	7.09 ±0.323	6.69 ±1.06	6.29 ±0.327	8.15 ±0.408
Ti	NA	NA	0.692 ±0.045	0.667 ±0.064	0.302 ±0.101	LDL
Mn	0.660 ±0.024	0.675 ±0.505	0.379 ±0.028	0.301 ±0.166	0.430 ±0.017	0.149 ±0.094
Fe	4.30 ±0.122	4.704 ±1.52	3.99 ±0.509	2.21 ±2.13	4.48 ±0.163	1.22 ±1.07
Cu	0.086 ±0.015	0.110 ±0.035	0.240 ±0.108	0.170 ±0.015	0.126 ±0.022	0.280 ±0.355
Zn	0.112 ±0.018	0.130 ±0.031	0.172 ±0.048	0.157 ±0.029	0.163 ±0.020	0.125 ±0.018
Pb	0.509 ±0.203	0.722 ±0.127	0.396 ±0.335	0.128 ±0.029	0.145 ±0.035	0.123 ±0.019
Br	NA	NA	0.058 ±0.003	0.069 ±0.006	0.055 ±0.009	0.039 ±0.004
Zr	NA	NA	0.061 ±0.035	0.031 ±0.030	0.066 ±0.003	0.028 ±0.019

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

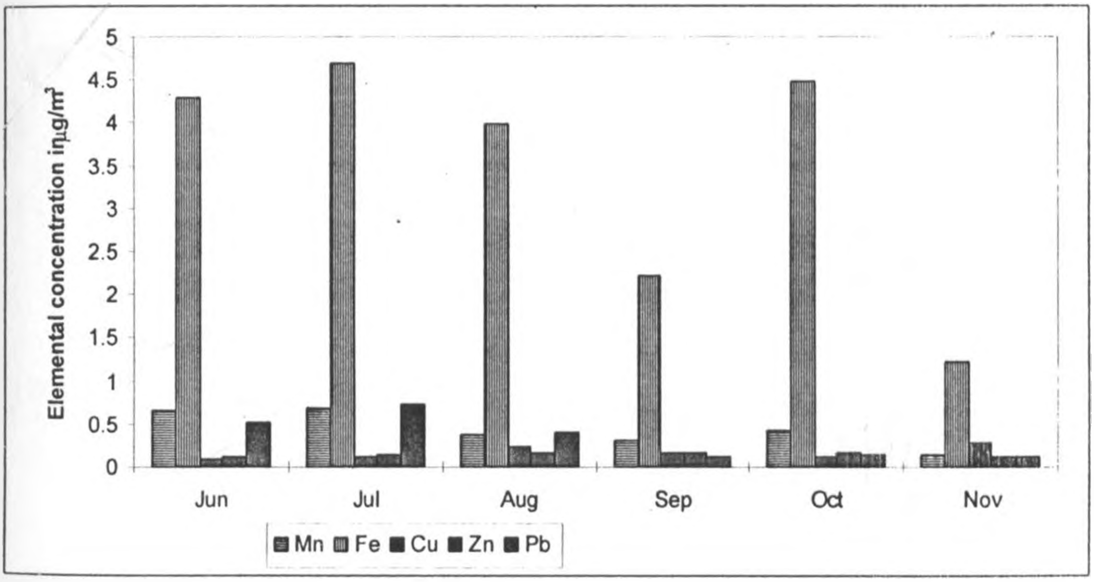


Fig 5.15 a: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the coarse particulate samples for the period May to November 1998 for site E

Table 23: Mean monthly elemental concentration (µg/m^3) for the fine particulate samples for site E for the period of May to November 1998

Element	Jun	Jul	Aug	Sep	Oct	Nov
Analytical technique	AAS	AAS	EDXRF	EDXRF	EDXRF	EDXRF
K	NA	NA	LDL	3.08 ±0.262	2.94 ±0.403	LDL
Ca	NA	NA	0.370 ±0.005	6.05 ±0.577	5.05 ±1.59	7.61 ±0.071
Ti	NA	NA	LDL	0.238 ±0.007	LDL	LDL
Mn	0.092 ±0.028	0.056 ±0.017	0.053 ±0.025	0.116 ±0.003	0.081 ±0.003	0.074 ±0.002
Fe	2.14 ±0.003	1.44 ±1.42	0.705 ±0.517	0.336 ±0.108	0.936 ±0.950	0.278 ±0.036
Cu	0.056 ±0.021	LDL	0.060 ±0.032	0.150 ±0.026	0.427 ±0.589	0.114 ±0.028
Zn	0.108 ±0.003	0.105 ±0.024	0.153 ±0.036	0.164 ±0.007	0.116 ±0.028	0.126 ±0.025
Pb	0.219 ±0.019	0.193 ±0.048	0.424 ±0.298	0.130 ±0.012	0.411 ±0.527	0.125 ±0.022
Br	NA	NA	0.049 ±0.026	0.056 ±0.014	0.079 ±0.090	0.035 ±0.006
Zr	NA	NA	0.050 ±0.004	LDL	0.036 ±0.045	0.020 ±0.012

NA-Not Analysed, LDL-lower detection limits, n=6, number of determinations

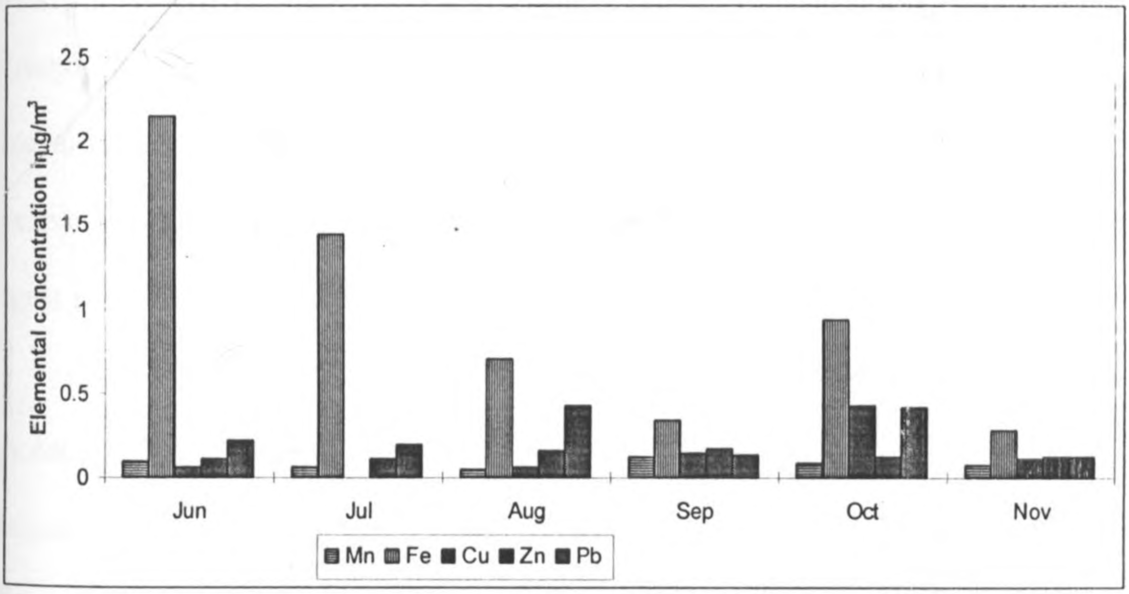


Fig 5.15 b: Mean monthly variation of Mn, Fe, Cu, Zn and Pb for the fine particulate samples for the period May to November 1998 for site E

5.6.3 Trends of mean monthly elemental concentration at two (2) metres above the ground by site for the period of May to November 1998.

Site A

Iron and manganese shows the same trend for the coarse particulate fraction (Table 14 and Fig 5.10a) with concentration levels as follows:- iron (0.166-12.0μg/m^3) and manganese (0.099-1.049μg/m^3). They show high values at the start of the sampling exercise decreasing to a minimum in July (iron: 0.166μg/m^3 and manganese: 0.099μg/m^3). This is followed by an upward trend for both elements with a maximum being recorded in October (iron: 12.0μg/m^3 and manganese: 1.049μg/m^3) (Fig 5.10a). This trend closely follows the variation of coarse particulate levels (Fig 5.1). For the fine particulate fraction, iron and manganese showed a similar trend (Table 15 and Fig 5.10b). However, the minimum values (iron: 0.232μg/m^3 and manganese: 0.0795μg/m^3 were observed in June while the highest values (iron: 1.485μg/m^3 and manganese: 0.189μg/m^3) were observed in October corresponding to the high levels of fine particulates (Fig 5.2). This suggests crustal origin for these elements. Lead shows high levels at the start of the sampling exercise recording maximum value (0.390μg/m^3) in May for the coarse and (0.350-0.353μg/m^3) in June and August for the fine particulates. The values decrease with increase in SPM towards October.

Copper and zinc exhibit the same trend for both the coarse and fine particulates, their concentration showing small variation through the entire period (Fig 5.10a and 5.10b). Their concentration were as follows:- copper (0.0802-0.238μg/m^3) in the coarse and (0.0237-0.191μg/m^3) in fine particulates, zinc (0.0727-0.282μg/m^3) for the coarse and(0.017-0.200μg/m^3) for the fine particulates (Table 14,15 and Figs 5.10a, 5.10b). This probably points to a similar source for these two elements.

Site B

Manganese and iron exhibit a similar trend for the entire period for both coarse and fine particulates (Fig 5.11a and 5.11b). Iron shows a similar trend as the SPM for both coarse and fine particulates (Fig 5.1). It recorded high levels in July (6.029μg/m^3) and September (10.28μg/m^3) corresponding to high SPM levels (Table 16 and Fig 5.11a). This probably points to a similar source for these elements which could be crustal dust. In the fine particulates iron shows a similar trend as the SPM with the concentration varying from 0.389μg/m^3 in July to 0.918μg/m^3 in August (Figs 5.2 and 5.11b). Manganese shows a close variation with SPM for the fine particulates in the months of May to June becoming negative towards November. Lead shows high values for the period May to August (Fig 5.11a and 5.11b) in both the fine and coarse particulates. For the coarse particulates lead shows a negative relation with SPM values with high levels (0.134-0.558μg/m^3) being recorded in the period May to August when SPM values were low (Fig 5.1 and 5.11a). This reduces to average values of 0.124 to 0.217μg/m^3 in the period September to November when high SPM values were recorded. However for the fine particulates lead shows a positive variation with the SPM which could be due to fine particulate fallout from the vehicular emissions from the nearby road (Fig 5.2 and 5.11b).

Copper and zinc exhibits a similar trend, showing little variation for the entire period for both fine and coarse particulates (Figs 5.11a and 5.11b). Copper concentration varied from 0.072 to 0.246μg/m^3 for the coarse and 0.065 to 0.171μg/m^3 for the fine particulates. Zinc concentrations varied from 0.128 to 0.271μg/m^3 for the coarse and 0.101 to 0.144μg/m^3 for the fine particulates (Table 16 and 17). A nearby metal works was suspected to be the main source of these two elements.

Site C

Iron and manganese shows a similar trend for the entire period in the coarse particulates (Fig 5.12a). Both show a close positive variation with SPM in the coarse particulates (Fig 5.12a and 5.1). Iron recorded maximum values in July (8.43μg/m^3) and September (8.82μg/m^3) which corresponded to maximum SPM values for the coarse particulates (Fig 5.12a). Manganese recorded a low value at the start of the sampling exercise in May (0.097μg/m^3) increasing with SPM to an average of 0.50μg/m^3 (Fig 5.12a and 5.1) for the rest of the period. In the fine particulates iron shows a positive variation with SPM (Fig 5.2 and 5.12b). However, higher values were recorded in the cold, humid and wet periods of May to August (Fig 5.4). This could indicate the increased residential emissions could be a probable source of iron in the fine particulates. Manganese shows a negative relationship with SPM from May to August recording low values (0.048-0.142μg/m^3). This could be due to less soil dust during the wet period. However, a positive relationship is observed for the period September to November (dry period) indicating soil dust could be a major contributor of the fine particulates. Lead exhibits a negative relationship with SPM (Fig 5.1 and 5.12a) for the coarse particulates for the entire period. Higher values (0.225-0.517μg/m^3) were observed within the period May to August when low SPM values were recorded (0.120-0.174μg/m^3) compared to values observed in the period of September to November when high SPM values were recorded. However, in the fine particulates, high values (0.214-0.376μg/m^3) were observed in the period May to August corresponding to the high SPM values observed (Fig 5.2 and 5.12b).

Copper and zinc levels show a similar trend in both the coarse and fine particulates (Fig 5.12a and 5.12b). Copper concentrations ranged from 0.080 to 0.233μg/m^3 for the coarse and 0.074 to 0.157μg/m^3 for the fine particulates. Zinc concentration varied from 0.150 to 0.275μg/m^3 for the coarse (Table18) and 0.106 to 0.212μg/m^3 for the fine particulates (Table19).

particulates (Fig 5.12a and 5.1). Iron recorded maximum values in July (8.43μg/m^3) and September (8.82μg/m^3) which corresponded to maximum SPM values for the coarse particulates (Fig 5.12a). Manganese recorded a low value at the start of the sampling exercise in May (0.097μg/m^3) increasing with SPM to an average of 0.50μg/m^3 (Fig 5.12a and 5.1) for the rest of the period. In the fine particulates iron shows a positive variation with SPM (Fig 5.2 and 5.12b). However, higher values were recorded in the cold, humid and wet periods of May to August (Fig 5.4). This could indicate the increased residential emissions could be a probable source of iron in the fine particulates. Manganese shows a negative relationship with SPM from May to August recording low values (0.048-0.142μg/m^3). This could be due to less soil dust during the wet period. However, a positive relationship is observed for the period September to November (dry period) indicating soil dust could be a major contributor of the fine particulates. Lead exhibits a negative relationship with SPM (Fig 5.1 and 5.12a) for the coarse particulates for the entire period. Higher values (0.225-0.517μg/m^3) were observed within the period May to August when low SPM values were recorded (0.120-0.174μg/m^3) compared to values observed in the period of September to November when high SPM values were recorded. However, in the fine particulates, high values (0.214-0.376μg/m^3) were observed in the period May to August corresponding to the high SPM values observed (Fig 5.2 and 5.12b).

Copper and zinc levels show a similar trend in both the coarse and fine particulates (Fig 5.12a and 5.12b). Copper concentrations ranged from 0.080 to 0.233μg/m^3 for the coarse and 0.074 to 0.157μg/m^3 for the fine particulates. Zinc concentration varied from 0.150 to 0.275μg/m^3 for the coarse (Table18) and 0.106 to 0.212μg/m^3 for the fine particulates (Table19).

Site D

This site recorded the highest mean monthly values for both iron (16.25μg/m^3) and manganese (1.40μg/m^3) than all the other sites for the coarse particulates (Table 20 and Fig 5.13a). This corresponds to the high values of SPM obtained for the coarse particulates (Fig 5.1). Manganese recorded low levels (0.098-0.191μg/m^3) in May to June corresponding to low values of SPM collected. This increased by a factor of seven (7) in July coinciding with increase of SPM by a factor of five (5) (Fig 5.1). Values above 0.600μg/m^3 (Fig 5.13a) were observed for the rest of the period with a maximum (1.39μg/m^3) being observed in October corresponding to the highest SPM value (233.9μg/m^3) (Fig 5.1). Iron shows a similar trend with concentration levels closely varying with SPM for the entire period (Fig 5.1 and 5.13a). In the fine particulates Fe exhibits a similar trend with the highest value (1.75μg/m^3) being recorded in October corresponding to the highest SPM value (Fig 5.2). Manganese recorded low values (0.049-0.058μg/m^3) for the period May to July increasing by a factor of three (3) in August. Lead shows small variation (0.144-0.265μg/m^3) over the entire period for the coarse particulates (Fig 5.13b). However, high values (0.481-0.648μg/m^3) were observed between June and July (Fig 5.13b) in the fine particulates reducing by a factor of 4.6 in August.

Copper and zinc show a similar trend with small variation over the entire period for both fine and coarse particulates (Fig 5.13a and 5.13b). Maximum values were observed in the period September to October for both fine and coarse particulates.

Site E

Iron and manganese exhibits the same trend in the coarse particles, showing similar variation with the SPM levels (Fig 5.1 and 5.14a). High values (4.3-4.704μg\m^3) were observed in the coarse particulates for iron in June and July (Table 22). This reduced to an average of 2.21μg/m^3 in September corresponding to a drop in SPM values (38.7- 41.7μg/m^3) (Fig 5.1). Manganese recorded highest values (0.675μg/m^3) in July and (0.43 μg/m^3) in October corresponding to maximum levels of SPM observed (Fig 5.1).

In the fine particulates iron show a negative relationship with SPM values at the start of the sampling exercise becoming positive towards November (Fig 5.1 and 5.14a). The highest value was observed in June (2.14μg/m^3) when lowest SPM value (6.44μg/m^3) was recorded. This decreased further with increase in SPM in July. Manganese exhibits a similar trend as iron (Fig 5.14b). High values (0.092μg/m^3) in June when low SPM value was observed (Fig 5.2). Lead shows high values (0.396-0.722μgm^3) in the period June to August for the coarse particulates (Fig 5.14a). This reduced in September by a factor of three (3). In the fine particulates high values were recorded in August (0.424μg/m^3) and October (0.411μg/m^3) (Fig 5.14b).

Copper and zinc show a similar trend in the coarse particulates, with a small variation in concentration over the entire period (Fig 5.14a). Concentration for copper in the fine particulates ranged from 0.056 to 0.427μg/m^3 with the maximum value (0.427 μg/m^3) being observed in October (Fig 5.14b). Zinc concentrations varied from 0.105 to 0.164μgm^3 for the entire period (Table 23 and Fig 5.14b).

5.6.4 Mean elemental concentration in μg/m^3 for samples collected at two (2) metres above the ground for the period of May to November 1998

The mean elemental concentration in μg/m^3 for the elements analysed for the various sites have been calculated for the period May to November 1998 (Table 24 and 25). In the coarse particulate fraction high concentrations (0.381 -7.80μg/m^3) for elements potassium, calcium, titanium, manganese and iron were observed for all the sites as compared to (0.029 -0.337μg/m^3) observed for copper, zinc, bromine, lead and zirconium. The levels of potassium, calcium, titanium, manganese and iron observed tended to reflect the location and activities near the site. Sites A, C and D all near a road/footpath recorded the highest levels for calcium, titanium and iron (Table 24). Site A and D recorded highest levels for potassium, this could possibly be attrbuted to ashdust from the frequent cooking fires nearby. A similar trend was observed in the fine particulate fraction for all the sites as compared to that observed for copper, zinc, bromine, lead and zirconium (0.011 - 0.250μg/m^3). Site A and C recorded highest levels for potassium (Table 25) which could be attributed to fine ash particle fallout form the frequent wood/charcoal fires nearby.

Table 24. Mean elemental concentrations ($\mu g/m^3$) for coarse particulate samples collected at two (2) metres above the ground for the period May to November 1998 for the various sites.

Site	SPM	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
A	113.5	3.31	5.185	0.419	0.526	6.025	0.135	0.197	0.211	0.029	0.129
n=42	(62.1)	(0.071)	(3.51)	(0.384)	(0.331)	(5.01)	(0.071)	(0.097)	(0.139)	(0.031)	(0.098)
B	94.5	1.435	6.967	0.387	0.543	5.070	0.119	0.191	0.315	0.059	0.066
n=42	(53.7)	(1.68)	(2.14)	(0.293)	(0.347)	(3.35)	(0.066)	(0.056)	(0.209)	(0.017)	(0.05)
C	89.26	1.600	7.104	0.532	0.381	5.480	0.125	0.195	0.243	0.063	0.096
n=42	(47.3)	(1.85)	(1.01)	(0.195)	(0.158)	(3.26)	(0.075)	(0.052)	(0.137)	(0.019)	(0.067)
D	135.4	4.533	7.799	0.809	0.790	5.148	0.144	0.247	0.168	0.064	0.152
n=42	(73.1)	(2.12)	(1.11)	(0.353)	(0.526)	(4.190	(0.029)	(0.076)	(0.088)	(0.009)	(0.071)
E	62.4	1.804	7.054	0.415	0.432	3.485	0.169	0.143	0.337	0.055	0.046
n=36	(24.4)	(2.09)	(0.80)	(0.3290	(0.206)	(1.43)	(0.077)	(0.024)	(0.248)	(0.013)	(0.02)

N=number of determinations

Table 25: Mean elemental concentration ($\mu g/m^3$) for fine particulate samples collected at two (2) metres above the ground for the period May to November 1998 for the various sites.

Site	SPM	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
A	19.3	2.44	5.591	0.169	0.105	1.23	0.107	0.117	0.201	0.037	0.016
n=42	(6.4)	(0.431)	(4.07)	(0.009)	(0.072)	(1.25)	(0.076)	(0.06)	(0.123)	(0.026)	(0.011)
B	24.4	1.775	4.928	0.280	0.100	0.991	0.075	0.106	0.165	0.031	0.011
n=42	(9.7)	(2.09)	(3.439)	(0.410	(0.076)	(0.898	(0.070)	(0.048)	(0.134)	(0.021)	(0.007)
C	19.8	2.250	6.033	LDL	0.090	0.862	0.089	0.150	0.220	0.050	0..012
n=42	(8.9)	(0.325)	(0.593)		(0.035)	(0.628)	(0.065)	(0.044)	(0.090)	(0.011)	(0.008)
D	23.9	1.785	6.298	0.133	0.110	1.102	0.087	0.135	0.246	0.053	0.020
n=42	(8.7)	(2.14)	(0.410)	(0.178)	(0.076)	(0.703)	(0.061)	(0.021)	(0.230)	(0.011)	(0.006)
E	16.2	1.503	4.770	0.238	0.079	0.973	0.135	0.129	0.250	0.055	0.027
n=36	(7.5)	(1.736)	(3.117)	(0.007)	(0.024)	(0.714)	(0.153	(0.025)	(0.135)	(0.019)	(0.021)

N=number of determinations

5.7 Correlation factors

To determine the possible sources of the elements analysed over the entire period for both the fine and coarse particulate concentrations, the interelement correlations were calculated (Pearson product-moment). The resulting correlation matrices for the various sites are presented in the tables (26-35)

5.7.1 Interelement correlation matrices for the sites A-E for the period May to November 1998.

Table 26: Coarse particulates (site A)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.017	1.000									
Ca	0.819	0.482	1.000								
Ti	0.905	0.353	0.621	1.000							
Mn	0.859	0.302	0.903	0.871	1.000						
Fe	0.400	0.194	0.886	0.852	0.992	1.000					
Cu	-0.310	0.803	0.087	0.073	-0.301	-0.333	1.000				
Zn	0.386	0.452	0.098	0.078	0.425	0.450	0.690	1.000			
Pb	-0.622	0.691	0.095	0.473	-0.260	-0.160	0.380	0.192	1.000		
Br	-0.562	-0.792	0.164	0.066	0.310	0.404	-0.295	0.181	-0.635	1.000	
Zr	0.979	0.213	0.877	0.868	0.968	0.971	0.752	0.953	0.694	0.384	1.00

Table 27: Fine particulates (site A)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Z
TSP	1.000										
K	0.815	1.000									
Ca	0.231	-0.062	1.000								
Ti	0.954	-0.531	-0.473	1.000							
Mn	0.649	0.446	0.866	0.755	1.000						
Fe	-0.541	0.081	0.471	-0.473	0.453	1.000					
Cu	-0.246	0.101	0.802	-0.854	-0.334	0.325	1.000				
Zn	-0.213	0.183	0.915	-0.791	0.454	0.651	0.528	1.000			
Pb	-0.445	-0.304	-0.931	0.610	-0.982	-0.752	-0.783	-0.930	1.000		
Br	-0.712	0.315	0.824	-0.894	0.935	0.548	0.472	0.980	-0.484	1.000	
Zr	0.704	0.692	0.673	0.645	0.962	0.931	0.583	0.075	-0.892	0.076	1.0

5.7 Correlation factors

To determine the possible sources of the elements analysed over the entire period for both the fine and coarse particulate concentrations, the interelement correlations were calculated (Pearson product-moment). The resulting correlation matrices for the various sites are presented in the tables (26-35)

5.7.1 Interelement correlation matrices for the sites A-E for the period May to November 1998.

Table 26: Coarse particulates (site A)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.017	1.000									
Ca	0.819	0.482	1.000								
Ti	0.905	0.353	0.621	1.000							
Mn	0.859	0.302	0.903	0.871	1.000						
Fe	0.400	0.194	0.886	0.852	0.992	1.000					
Cu	-0.310	0.803	0.087	0.073	-0.301	-0.333	1.000				
Zn	0.386	0.452	0.098	0.078	0.425	0.450	0.690	1.000			
Pb	-0.622	0.691	0.095	0.473	-0.260	-0.160	0.380	0.192	1.000		
Br	-0.562	-0.792	0.164	0.066	0.310	0.404	-0.295	0.181	-0.635	1.000	
Zr	0.979	0.213	0.877	0.868	0.968	0.971	0.752	0.953	0.694	0.384	1.000

Table 27: Fine particulates (site A)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.815	1.000									
Ca	0.231	-0.062	1.000								
Ti	0.954	-0.531	-0.473	1.000							
Mn	0.649	0.446	0.866	0.755	1.000						
Fe	-0.541	0.081	0.471	-0.473	0.453	1.000					
Cu	-0.246	0.101	0.802	-0.854	-0.334	0.325	1.000				
Zn	-0.213	0.183	0.915	-0.791	0.454	0.651	0.528	1.000			
Pb	-0.445	-0.304	-0.931	0.610	-0.982	-0.752	-0.783	-0.930	1.000		
Br	-0.712	0.315	0.824	-0.894	0.935	0.548	0.472	0.980	-0.484	1.000	
Zr	0.704	0.692	0.673	0.645	0.962	0.931	0.583	0.075	-0.892	0.076	1.000

Table 28: Coarse particulates (site B)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.979	1.000									
Ca	0.482	0.331	1.000								
Ti	0.949	0.981	0.412	1.000							
Mn	0.865	0.862	-0.101	0.834	1.000						
Fe	0.915	0.991	0.395	0.976	0.831	1.000					
Cu	0.179	0.946	0.623	0.971	0.354	0.521	1.000				
Zn	0.658	0.992	0.192	0.973	0.834	0.973	0.892	1.000			
Pb	-0.415	-0.423	-0.901	-0.474	0.096	-0.471	-0.642	-0.261	1.000		
Br	-0.479	0.594	-0.301	0.563	0.910	0.555	0.423	0.711	0.431	1.000	
Zr	0.866	0.802	0.631	0.822	0.393	0.834	0.867	0.694	-0.841	0.011	1.000

Table 29: Fine particulates (site B)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.515	1.000									
Ca	0.737	0.332	1.000								
Ti	0.453	0.601	0.942	1.000							
Mn	0.529	-0.153	0.933	0.875	1.000						
Fe	0.779	0.938	0.401	0.582	-0.111	1.000					
Cu	-0.067	0.242	-0.071	-0.092	0.403	0.863	1.000				
Zn	-0.717	-0.482	-0.811	0.023	0.900	-0.321	0.192	1.000			
Pb	-0.496	0.093	0.012	-0.873	-0.512	0.041	-0.312	-0.671	1.000		
Br	-0.798	-0.763	-0.861	-0.941	-0.682	-0.814	0.418	-0.753	0.971	1.000	
Zr	0.629	0.631	0.752	0.913	0.815	0.465	0.022	0.088	-0.764	-0.793	1.000

Table 30: Coarse particulates (site C)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.690	1.000									
Ca	0.148	-0.291	1.000								
Ti	0.899	0.624	0.486	1.000							
Mn	0.631	0.556	0.557	0.985	1.000						
Fe	0.826	0.567	0.283	0.864	0.955	1.000					
Cu	-0.325	0.801	-0.023	0.433	0.388	0.314	1.000				
Zn	-0.070	-0.401	-0.401	-0.361	-0.342	-0.121	0.170	1.000			
Pb	-0.367	-0.510	0.012	-0.253	-0.215	-0.514	0.101	-0.574	1.000		
Br	-0.340	-0.141	0.072	0.101	0.121	-0.194	0.457	-0.842	0.913	1.000	
Zr	0.984	0.754	0.078	0.893	0.865	0.982	0.334	-0.041	-0.667	-0.345	1.000

Table 31: Fine particulates (site C)

	TSP	K	Ca	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000									
K	0.718	1.000								
Ca	0.098	-0.842	1.000							
Mn	0.637	0.538	-0.381	1.000						
Fe	0.865	0.477	-0.512	0.964	1.000					
Cu	-0.608	-0.301	0.731	-0.032	-0.012	1.000				
Zn	0.099	0.891	-0.615	0.293	0.224	0.172	1.000			
Pb	0.081	-0.533	0.103	-0.573	-0.581	-0.623	-0.341	1.000		
Br	0.040	-0.101	0.622	-0.304	-0.211	0.456	0.188	0.867	1.000	
Zr	0.570	0.202	-0.566	0.898	0.819	-0.454	0.261	-0.821	-0.701	1.000

Table 32: Coarse particulates (site D)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	-0.642	1.000									
Ca	0.851	-0.821	1.000								
Ti	0.870	-0.852	0.998	1.000							
Mn	0.957	-0.542	0.921	0.911	1.000						
Fe	0.924	-0.544	0.833	0.837	0.923	1.000					
Cu	0.366	-0.948	0.803	0.836	0.367	0.290	1.000				
Zn	0.773	-0.712	0.976	0.951	0.862	0.742	0.563	1.000			
Pb	0.695	-0.841	0.992	0.963	0.523	0.452	0.812	0.721	1.000		
Br	0.260	-0.851	0.411	0.463	0.007	0.201	0.483	0.244	0.483	1.000	
Zr	0.999	-0.681	0.876	0.894	0.892	0.982	0.645	0.763	-0.798	0.381	1.000

Table 33: Fine particulates (site D)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	-0.758	1.000									
Ca	-0.981	0.831	1.000								
Ti	0.725	-0.392	-0.782	1.000							
Mn	0.293	-0.140	-0.523	0.345	1.000						
Fe	-0.162	-0.721	-0.894	0.512	0.786	1.000					
Cu	0.164	-0.945	-0.964	0.675	0.294	0.793	1.000				
Zn	0.470	-0.793	-0.594	-0.044	0.433	0.684	0.563	1.000			
Pb	0.308	-0.411	0.034	-0.091	-0.855	-0.343	0.245	0.024	1.000		
Br	-0.335	-0.352	0.188	-0.723	-0.313	-0.025	0.020	0.349	0.460	1.000	
Zr	0.725	-0.472	-0.873	0.974	0.557	0.718	0.745	0.162	-0.255	-0.644	1.000

Table 34: Coarse particulates (site E)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	-0.609	1.000									
Ca	-0.612	-0.261	1.000								
Ti	-0.276	0.982	-0.236	1.000							
Mn	0.646	0.201	-0.891	0.256	1.000						
Fe	0.696	0.032	-0.753	0.125	0.965	1.000					
Cu	-0.793	-0.061	0.952	0.021	-0.041	0.103	1.000				
Zn	0.217	0.532	-0.808	0.593	0.511	0.863	0.701	1.000			
Pb	0.263	0.453	-0.033	0.601	0.413	0.512	0.291	0.333	1.000		
Br	-0.021	0.682	-0.871	0.623	0.694	0.473	-0.772	-0.773	0.100	1.000	
Zr	0.603	-0.201	-0.592	-0.101	0.862	0.966	-0.453	0.707	0.492	0.220	1.000

Table 35: Fine particulates (site E)

	TSP	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
TSP	1.000										
K	0.266	1.000									
Ca	0.925	0.300	1.000								
Ti	0.552	-0.622	-0.274	1.000							
Mn	-0.291	0.801	0.633	-0.877	1.000						
Fe	-0.243	0.222	-0.567	0.499	-0.411	1.000					
Cu	-0.202	0.672	0.143	0.155	0.245	-0.263	1.000				
Zn	-0.132	0.062	-0.356	-0.722	0.294	-0.411	-0.012	1.000			
Pb	-0.366	-0.051	-0.783	0.572	-0.633	0.101	0.366	0.025	1.000		
Br	-0.307	0.763	-0.166	-0.043	0.223	0.800	0.872	-0.274	0.593	1.000	
Zr	0.927	-0.452	0.811	0.772	-0.898	0.764	0.071	-0.261	0.352	0.233	1.000

In site *A*, calcium, titanium, manganese and zirconium had high positive correlations (0.819 - 0.979) with SPM in the coarse particulate range while copper, zinc, lead, bromine, iron and potassium showed low correlations (-0.622 - 0.400) (Table 26). For the fine particulates the situation is similar except for calcium which now shows low correlations (0.231) (Table 27). Manganese, titanium, calcium, and zirconium in the coarse particulates show high correlations with each other (0.851 - 0.971) which may suggest similar source, example crustal dust. In the fine particulates copper, calcium,and zinc showed high correlation with each other (0.528 - 0.915). Bromine also exhibits a high correlations (0.548 - 0.980) with zinc, calcium, manganese and iron. In both the coarse and fine particulate samples bromine and lead show negative correlations (-0.635 – -0.484) which may point to different sources. This could also be due to the distance of the suspected source (i.e, the busy langata road) from this site. Displacement reactions of bromine over the distance could have reduced the correlation. Other sources not related to motor vehicles could also have played a role in determining the airborne concentrations of bromine and lead.

For site *B,* elements potassium, titanium, zinc, zirconium show high positive correlations (0.658 - 0.979) (Table 28) with SPM in the coarse particulate range which may suggest crustal dust as the main source while calcium, copper, lead, and bromine had low correlations(-0.479 – 0.482).

For the fine particulates a similar trend is exhibited except for zinc which shows high negative correlation (-0.717) (Table 29) with SPM. The high positive correlations of zinc and iron with SPM in the coarse particulate range (0.973) could point to possible contamination of surface soil dust by fine particle fallout from a metal works near this site. High positive correlations between the elements potassium, calcium, titanium, manganese, iron, zirconium and SPM for both the coarse (0.631 - 0.976) and fine (0.515 - 0.942) particulates was observed suggesting crustal dust to be the main component of SPM in this site. This could be due to the road near the site which is usually dusty during dry conditions. Bromine and lead showed high positive correlation (0.971) with each other in the fine particulate range. This could point to a possible similar source for this elements which could have been vehicular emissions from the road nearby.

Two groups of elements are evident in site *C*, potassium, titanium, iron, zirconium and manganese which show high positive correlations (0.631 - 0.984) with SPM (Table 30) in the coarse particulate range while copper, zinc, lead, calcium and bromine show high positive correlations with SPM (0.570 - 0.865) in the fine range (Table 31). Bromine and lead are highly correlated with each other (0.867 - 0.913) in both the fine and coarse particulates. This site was near a trading centre pointing to vehicular emissions as the most probable source of these elements. The low positive correlation of calcium (0.098 - 0.148) with SPM in both the fine and coarse particulate range pointed to possible anthropogenic source. This could probably be emissions from the frequently burning urban refuse near the site

In site *D*, seven elements (calcium, zinc, lead, iron, manganese, titanium, and zirconium) of the ten (10) elements analysed showed high positive correlation (0.695 - 0.999) with SPM in the coarse particulate range (Table 32) while for the fine particulates only zirconium and titanium had high positive correlation (0.725) (Table 33). Potassium shows poor correlation with SPM in both fine (-0.758) and coarse (-0.642) particulates. This could probably point to anthropogenic source for this element near the site. High correlations observed between iron, copper and zinc (0.684 - 0.793) in the fine particulates may point to a similar source. This could probably be attributed to possible contamination of the surface soil dust by fine particle fallout from metal works nearby which is later airborne.

High positive correlation between lead (0.695) and SPM in the coarse particulates indicated possible soil contamination by fine lead fallout from automobile exhausts in the nearby busy traffic road (Kibera drive) (Fig 4.1). Moderate positive correlation (0.460 - 0.483) between bromine and lead was observed both in the fine and coarse particulates.

For site *E*, only manganese, iron and zirconium showed high positive correlations (0.603 - 0.696) with SPM in the coarse particulates (Table 34) while for the fine particulates calcium, titanium and zirconium were highly correlated (0.552 - 0.927) with SPM (Table 35). Bromine and lead were poorly correlated (0.100) with each other in the coarse particulates but in the fine particulates they were highly correlated (0.593). This pointed to possible similar source for these elements in the fine range, e.g. vehicular emissions.

5.8 Enrichment factors

The enrichment factor is given as a ratio between elemental levels in the air and in the earth's crust. The factor demonstrates the enrichment of an element in the air relative to it's concentration arising purely from resuspension of crustal material and hence a measure a of pollutant, as opposed to natural sources (Harrison., *et al;* 1982). In this study, Iron (Fe) was used as the reference element (Mason and Moore, 1982) and the formulae below (Eqn 18) was used for the calculations.

$$E.F = \frac{\left(X/_{Fe}\right)_{air}}{\left(X/_{Fe}\right)_{crust}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

where

$E.F$ = *Enrichment factor*

X = *concentration of trace element of interest*

Fe = *concentration of iron*

The mean enrichment factors for samples collected at two (2) metres above the ground from various sites for the period May to November 1998 are presented in tables 36 and 37.

Table 36: Enrichment factors for the coarse particulate samples collected at two (2) metres above the ground

Sites	A	B	C	D	E
K(25,900)	0.3	0.5	0.6	1.7	1.0
Ca(36,300)	1.2	1.9	1.8	2.1	2.8
Ti(4,400)	0.8	0.9	1.1	1.8	1.4
Mn(1000)	4.4	5.4	3.5	7.7	6.2
Fe(50,000)	1.0	1.0	1.0	1.0	1.0
Cu(70)	16.0	16.8	16.3	20.0	34.6
Zn(132)	12.4	14.3	13.5	18.2	15.5
Pb(16)	109.4	194.2	138.6	102	302.2
Br(1.6)	152.5	361.8	360.4	388.5	495.9
Zr(220)	4.9	5.8	3.9	6.7	3.0

Crustal amounts in ppm shown in parenthesis (Mason, 1966)

Table 37: Enrichment factors for the fine particulate samples collected at two (2) metres above the ground

Sites	A	B	C	D	E
K(25,900)	1.0	3.5	1.3	3.1	3.0
Ca(36,300)	6.3	6.9	9.6	7.9	6.8
Ti(4,400)	0.8	3.2	-	1.4	0.7
Mn(1000)	4.3	5.0	5.2	5.0	4.0
Fe(50,000)	1.0	1.0	1.0	1.0	1.0
Cu(170)	25.6	22.1	30.5	23.2	40.7
Zn(132)	36.1	40.4	65.8	46.5	50.1
Pb(16)	512.8	521.5	797.7	698.5	804.2
Br(1.6)	1488.6	965.3	1812.0	1491.2	1756.8
Zr(220)	2.92	2.4	3.3	4.2	6.2

Crustal amounts in ppm shown in parenthesis(Mason, 1966).

Two groups of elements are evident. Those with low enrichment factors: potassium: (0.265 - 3.459), calcium: (1.185 - 9.637), titanium: (0.695 - 3.206), manganese: (3.476 - 7.673), zirconium: (2.43 - 6.710) which may suggest crustal origin and high enrichment factors, copper: (16.00 - 40.66), zinc: (12.385 - 68.80), lead: (101.98 - 804.2), bromine: (152.49 - 1812.0) in both the fine and coarse particulates (Table 36 and 37). Bromine and lead show more enrichment in site E than all other sites in the coarse particulate samples indicating possible transport of particulates from other areas since no road was near this site. Zinc is more enriched in site D than the rest of the sites in the coarse particulates, this could be due to the effect of fine particle fallout from the nearby metal works. The four elements (copper, zinc, lead and bromine) are more enriched in the fine particulates for all the sites hinting at possible anthropogenic sources. Calcium however shows marginal enrichment (6.28 - 9.637) in the fine particulates for all the sites. This could be as a result of fine particulates from the frequent wood/charcoal fires used for cooking in the open and burning of refuse in the area (Kroger *et al*, 1994).

5.9 Mean elemental concentration in μg/m^3 for samples collected at four (4) metres above the ground for the period December 1998 to May 1999.

The mean elemental concentration in μg/m^3 for the elements analysed for the four sites B, C, D and E are presented in the Tables 38 and 39. A similar pattern of elemental concentration is observed as at two (2) metres height (Table 24 and 25) High levels (0.233 - 6.29 μg/m^3) for elements potassium, calcium, titanium, manganese and iron were observed as compared to (0.036 - 0.222 μg/m^3) for copper, zinc, lead, bromine and zirconium in the coarse particulate fraction. A similar concentration profile is observed in the fine particulate fraction in all the sites with high concentrations being observed for elements calcium, titanium, manganese and iron as compared to copper, zinc, lead, bromine and zirconium (Table 39). Sites B, C and D recorded the highest concentrations for calcium, titanium, manganese and iron for both coarse and fine particulate fractions. This probably points to resuspended soil dust as a significant contributor of these elements at this height. It should be noted that potassium was not detected in the fine particulate fraction for the sites, which may suggest coarse particles from resuspended soil dust to be the main source. Large standard deviations were noted for the particulate concentrations, which is indication of the large variation in concentration of the samples collected under different conditions, i.e, weather conditions. Example sample B18499 recorded 12.8μg/m^3 as compared to B28299 level of 115.3 μg/m^3 for coarse particulate samples at site B. This was also noted for elements iron and manganese with mean monthly variations of (2.31 -6.29 μg/m^3) and (0.277 - 0.656 μg/m^3) respectively(Table 42 and 43) being observed for the coarse particulate fraction. Iron also showed a large variation (Table 43) in the fine particulate fraction (0.326 - 0.818 μg/m^3).

Table 38: Mean elemental concentrations($\mu g/m^3$) for coarse particulate samples collected at four (4) metres above the ground.

Site	SPM	K	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
B	63.02	3.83	1.97	0.445	0.558	4.59	0.117	0.165	0.222	0.054	0.067
n=20	(32.83)	(1.18)	(0.497)	(0.117)	(0.258)	(2.31)	(0.029)	(0.031)	(0.038)	(0.017)	(0.023)
C	62.43	LDL	1.66	0.448	0.351	3.66	0.100	0.150	0.169	0.051	0.075
n=20	(42.31)		(0.258)	(0.210)	(0.219)	(2.84)	(0.013)	(0.059)	(0.060)	(0.006)	(0.068)
D	117.68	4.75	1.83	0.541	0.656	6.29	0.095	0.163	0.120	0.047	0.095
n=20	(53.42)	(0.071)	(0.453)	(0.215)	(0.3690	(3.67)	(0.031)	(0.071)	(0.015)	(0.008)	(0.057)
E	43.97	LDL	1.55	0.233	0.277	2.31	0.104	0.118	0.142	0.045	0.036
n=20	(17.79)		(0.298)	(0.016)	(0.085)	(0.796)	(0.023)	(0.030)	(0.063)	(0.006)	(0.011)

n=number of determinations

Table 39: Mean elemental concentration ($\mu g\backslash m^3$) for fine particulate samples collected at four (4) metres above the ground

Site	SPM	Ca	Ti	Mn	Fe	Cu	Zn	Pb	Br	Zr
B	15.58	1.65	0.245	0.135	0.643	0.115	0.116	0.225	0.031	0.022
n=20	(8.03)	(0.380)	(0.064)	(0.039)	(0.264)	(0.034)	(0.028)	(0.073)	(0.006)	(0.013)
C	14.28	1.48	0.222	0.107	0.393	0.088	0.081	0.168	0.033	0.012
n=20	(5.56)	(0.184)	(0.071)	(0.0220	(0.211)	(0.020)	(0.029)	(0.083)	(0.006)	(0.002)
D	17.54	1.62	LDL	0.192	0.818	0.094	0.113	0.162	0.034	0.018
n=20	(4.15)	(0.372)		(0.080)	(0.378)	(0.013)	(0.019)	(0.0570	(0.004)	(0.013)
E	16.92	1.45	LDL	0.111	0.326	0.104	0.107	0.205	0.032	0.013
n=20	(6.79)	(0.262)		(0.049)	(0.078)	(0.026)	0.029)	(0.109)	(0.008)	(0.002)

LDL=lower detection limits, n=number of determinations

5.9.1 Enrichment factors

The mean enrichment factors for samples collected at four (4) metres above the ground for the period December 1998 to May 1999 are presented in tables 40 and 41 below.

Table 40: Enrichment factors for the coarse particulate samples collected at four (4) metres above the ground

Sites	B	C	D	E
K(25,900)	1.6	ND	1.5	ND
Ca(36,300)	0 .6	0.6	0.4	0.9
Ti(4,400)	1.1	1.4	1.0	1.1
Mn(1000)	6.1	4.8	5.1	6.0
Fe(50,000)	1.0	1.0	1.0	1.0
Cu(70)	18.2	19.5	10.8	32.1
Zn(132)	13.6	15.5	9.8	19.3
Pb(16)	151.1	144.3	59.4	192.0
Br(1.6)	367.7	435.5	234.5	604
Zr(220)	3.3	4.6	3.4	3.5

Crustal amounts in ppm shown in parenthesis (Mason, 1966)
ND-Not detected

Table 41: Enrichment factors for the fine particulate samples collected at four (4) metres above the ground

Sites	B	C	D	E
Ca(36,300)	3.5	5.2	2.7	6.1
Ti(4,400)	4.3	6.4	ND	ND
Mn(1000)	10.5	13.6	11.8	17.0
Fe(50,000)	1.0	1.0	1.0	1.0
Cu(70)	127.7	160.7	82.3	228.3
Zn(132)	68.6	77.9	52.1	124.6
Pb(16)	1093.5	1335.9	618.9	1967.0
Br(1.6)	1526.0	2592.2	1310.4	3038.7
Zr(220)	7.9	6.8	4.9	9.2

Crustal amounts in ppm shown in parenthesis (Mason, 1966)
ND-Not detected

A similar trend for enrichment factors as observed for samples collected at two (2) metres is evident (Table 36 and 37). Potassium, calcium, titanium, manganese and zirconium show low enrichment factors (Table 40 and 41) both in the coarse and fine particulates, while copper, zinc, lead and bromine show high enrichment factors. However copper, zinc, lead and bromine appear to be more enriched in the fine particulate range than in the coarse. Manganese show marginal enrichment (10.48-17.02) (Table 41) in the fine particulates for all the sites indicating possible anthropogenic source in the fine range. Higher enrichment

Table 42: Intercomparison of elemental concentration (μg/m³) ranges at heights of two (2) metres and four (4) metres above the ground for the coarse particulate samples

Element	Two (2) metres	Four (4) metres
K	1.435 –4.533 (1.804)	*3.83 - 4.75 (4.29)
Ca	5.185 –7.104 (7.054)	1.55 - 1.97 (1.745)
Ti	0.387 –0.809 (0.419)	0.233-0.541 (0.447)
Mn	0.381 –0.790 (0.526)	0.277 -0.656 (0.455)
Fe	3.485 –6.025 (5.148)	2.31 -6.29 (4.125)
Cu	0.119 –0.169 (0.135)	0.095 -0.117 (0.102)
Zn	0.143 –0.247 (0.195)	0.118 -0.165 (0.157)
Pb	0.168 –0.337 (0.243)	0.120 -0.222 (0.156)
Br	0.029 –0.064 (0.059)	0.045 -0.054 (0.049)
Zr	0.046 –0.152 (0.096)	0.036 -0.095 (0.071)

(Median value shown in parenthesis) * Potassium could not be used for intercomparison because it was only detected in two of the five months sampled at only two of the four sites.

The elements calcium, titanium, and zirconium associated with crustal dust showed reduction in concentration by higher factors (calcium: 0.288, titanium: 0.636, zirconium: 0.704) except for manganese and iron (manganese: 0.779 and iron: 0.854) at the height of four (4) metres than for the elements copper, zinc and bromine associated with anthropogenic origin. Reduction factors for these elements were as follows: copper: 0.745, zinc: 0.746 and bromine: 0.844) (Table 42). However lead showed a reduction in concentration by a factor (0.687) comparable to that of calcium, titanium and zirconium.

Table 43: Intercomparison of mean elemental concentration (μg/m³) ranges at heights of two (2) metres and four (4) metres above the ground for the fine particulate samples

Element	Two (2) metres	Four (4) metres
K	1.503 -2.25 (1.78)	LDL
Ca	4.77 -6.298 (5.481)	1.45 -1.65 (1.550)
Ti	0.133 -0.280 (0.238)	0.222 -0.245 (0.234)
Mn	0.079 -0.110 (0.095)	0.107 -0.192 (0.123)
Fe	0.862 -1.102 (0.982)	0.326 -0.818 (0.518)
Cu	0.075 -0.135 (0.088)	0.088 -0.115 (0.099)
Zn	0.106 -0.150 (0.132)	0.081 -0.116 (0.110)
Pb	0.165 -0.250 (0.233)	0.162 -0.225 (0.187)
Br	0.031 -0.055 (0.052)	0.031 -0.034 (0.033)
Zr	0.011 -0.027 (0.016)	0.012 -0.022 (0.016)

(Median value shown in parenthesis)

For the fine particulate samples calcium, bromine and iron showed high reduction of concentration at the height of four (4) metres. Potassium was not detected for all the sites at this height. Calcium reduction factors ranged from (0.262 - 0.303), iron: (0.378 - 0.742) and bromine: (0.618) (Table 43). For the rest of the elements (titanium, copper, zinc, lead, and zirconium) the concentrations at the two heights remained in the same range. Their reduction factors varied from 0.773 to 0.900. However, manganese showed some increase in concentration at the height of four (4) metres in the fine particulate fraction which could point to a source outside this area. It should be appreciated that the samples at the two heights were collected under different climatic conditions which could also have contributed to the variations observed.

5.9.3 Mean bromine/lead ratios for the various sites

The table 44 below shows the mean bromine/lead ratios observed for coarse and fine particulate samples collected at two (2) and four (4) metres height.

Table 44 Mean bromine/lead ratios observed for the various sites

Coarse particulate fraction		
Site	Two (2) metres	Four (4) metres
A	0.335± 0.184 n=8	NS
B	0.300± 0.112 n=12	0.261± 0.058 n=20
C	0.344± 0.119 n=8	0.327± 0.050 n=20
D	0.372± 0.121 n=8	0.387± 0.072 n=20
E	0.345± 0.141 n=14	0.324± 0.077 n=20

Fine particulate fraction		
Site	Two (2) metres	Four (4) metres
A	0.296±0.167 n=8	NS

B	0.333± 0.053 n=12	0.148± 0.035 n=20
C	0.299± 0.081 n=8	0.205± 0.074 n=20
D	0.354± 0.061 n=8	0.229± 0.058 n=20
E	0.252± 0.118 n=14	0.184± 0.066 n=20

NS=not sampled, n=number of determinations

Site D had some of the highest bromine/lead ratios at both heights in both coarse and fine particulate fractions. The ratios were 0.372 at two (2) and 0.387 at four (4) metres height for coarse particulate fraction (Table 44). For the fine particulate fraction the ratios were 0.354 at two (2) and 0.229 at four (4) metres height. It should be noted that this site was nearest to the suspected source of both elements (i.e, the vehicular emissions from the nearby kibera drive road)

At both heights higher bromine/lead ratios were observed in the coarse particulate fraction than in the fine particulate fraction (Table 44). Higher bromine/lead ratios were also observed at the lower height for both particulate fractions. This may suggest vapourization of bromine near the ground level (probably due to heating from the warm surface) meaning more of the bromine may be in the vapour phase at the higher height, hence the lower concentrations detected.

5.9.4 Intercomparison of mean elemental concentrations (μg/m^3) observed in various studies

The Tables 45 and 46 below shows the mean elemental concentration values (μg/m^3) observed in various studies for coarse particulate and fine particulate fractions respectively.

Values observed in this study are higher for most of the elements analysed than those observed at KMD, a suburban site except for lead, bromine and copper in both coarse and fine particulate fraction (tables 45 and 46). The higher levels for elements, calcium, titanium, manganese, zirconium, potassium and zinc observed in this study could be due to the high levels of soil dust observed in this area unlike in KMD. KMD is less populated, has more vegetation cover on the ground and the fact that samples were collected eight (8) metres above the ground could account for the lower levels observed. Higher levels of bromine and lead observed in KMD could be due to proximity to a major highway.

Elemental concentrations obtained in this study for the coarse particulate fraction are higher compared to studies done in Goteberg (Sweden), Damascus (Syria) and Boston (U.S.A.) (Table 45 and 46). For the fine particulate fraction the values are still higher except for bromine and lead observed in Boston (U.S.A.). It should also be appreciated that all this studies were carried out in different geographical areas with different sorroundings and pollution sources. This would directly or indirectly reflect the elemental levels observed.

Table 45 Mean elemental concentration (μg\m³) observed for the coarse particulate fraction

	Coarse particulate fraction					
Element	Nairobi (Kibera)1	Nairobi (Kibera)2	Nairobi (KMD)3	Sweden (Goteberg)4	Syria (Damascus)5	U.S.A. (Boston)6
K	2.54	--------	---------	0.073	0.380	0.112
Ca	6.82	1.75	0.091-3.975	0.061	4.300	0.214
Ti	0.512	0.417	---------	-------	0.097	0.026
Mn	0.534	0.461	0.004-0.089	0.001	0.017	0.0058
Fe	5.04	4.21	0.232-1.580	0.039	0.860	0.281
Cu	0.138	0.104	0.130-1.174	0.0011	0.004	0.0104
Zn	0.195	0.149	0.007-0.049	0.0065	0.012	0.0122
Pb	0.255	0.163	0.031-0.465	0.0025	0.023	0.076
Br	0.054	0.049	0.007-0.060	0.0045	0.009	0.0257
Zr	0.098	0.068	----------	--------	------	--------

the high levels of soil dust observed in this area unlike in KMD. KMD is less populated, has more vegetation cover on the ground and the fact that samples were collected eight (8) metres above the ground could account for the lower levels observed. Higher levels of bromine and lead observed in KMD could be due to proximity to a major highway.

Elemental concentrations obtained in this study for the coarse particulate fraction are higher compared to studies done in Goteberg (Sweden), Damascus (Syria) and Boston (U.S.A.) (Table 45 and 46). For the fine particulate fraction the values are still higher except for bromine and lead observed in Boston (U.S.A.). It should also be appreciated that all this studies were carried out in different geographical areas with different sorroundings and pollution sources. This would directly or indirectly reflect the elemental levels observed.

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	Coarse particulate fraction					
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K	2.54	--------	---------	0.073	0.380	0.112
Ca	6.82	1.75	0.091-3.975	0.061	4.300	0.214
Ti	0.512	0.417	---------	-------	0.097	0.026
Mn	0.534	0.461	0.004-0.089	0.001	0.017	0.0058
Fe	5.04	4.21	0.232-1.580	0.039	0.860	0.281
Cu	0.138	0.104	0.130-1.174	0.0011	0.004	0.0104
Zn	0.195	0.149	0.007-0.049	0.0065	0.012	0.0122
Pb	0.255	0.163	0.031-0.465	0.0025	0.023	0.076
Br	0.054	0.049	0.007-0.060	0.0045	0.009	0.0257
Zr	0.098	0.068	----------	--------	------	--------

Table 46 Mean elemental concentration (µg\m^3) observed for the fine particulate fraction

	Coarse particulate fraction					
Element	Nairobi (Kibera)1	Nairobi (Kibera)2	Nairobi (KMD)3	Sweden (Goteberg)4	Syria (Damascus)5	U.S.A. (Boston)6
K	1.951	------	-------	0.060	0.161	0.0762
Ca	5.52	1.55	0.033-4.150	0.017	0.310	0.0419
Ti	0.205	0.234	-------	-------	0.014	-------
Mn	0.097	0.136	0.001-0.034	0.001	0.0049	0.0036
Fe	1.032	0.545	0.094-0.360	0.014	0.138	0.075
Cu	0.099	0.100	0.007-0.069	0.001	------	0.016
Zn	0.127	0.104	0.008-0.072	0.011	0.0086	0.027
Pb	0.216	0.190	0.055-0.419	0.0076	0.045	0.326
Br	0.045	0.033	0.008-0.098	0.0028	-------	0.086
Zr	0.017	0.016	--------	--------	--------	--------

(1)-Kibera (Nairobi)-situated three (3) kilometres from city centre, samples were collected at a height of two (2) metres above the ground.

(2)-Kibera (Nairobi)- samples were collected at a height of four (4) metres above the ground.

(3)- Kenya meteorological department headquarters, is located to the northwest of the city centre, five kilometres away, in a suburban area. The site was near a major highway. The samples were collected at a height of eight (8) metres above the ground (Gatebe *et al,* 1996).

(4)- sampling was done on the Swedish west coast. The site was located close to the open sea, surrounded by fields, rocks and small groups of trees with no disturbing sources of anthropogenic particulate pollution in the immediate vicinity (Foltescu *et al,* 1994).

(5)- samples were collected in the Zabadani valley, forty (40) kilometres northwest of Damascus. The major source of airborne partculate was most probably desert soil dispersion. Other sources included anthropogenic emissions from industries, waste burning and automobiles (Cornille *et al,* 1990).

(6)- sampling was done in a high school field located in a suburban neighborhood. Sources of pollution were suspected to be residential/ industrial oil combustion (George *et al,* 1985)

5.10 Detection limits for the EDXRF system

The lower detection limits (LDL) (μg/m^3) for the various elements (Table 47) have been calculated for the EDXRF using the following equation (Nguyen *et al*, 1997):-

$$Det\ \ Lim = \frac{3.C}{N_p}\sqrt{N_B} \quad \ldots\ldots(19)$$

where

C is the concentration of the element in μg/m^3.

N_p is the net peak area for the element.

N_B is the net background area under the element peak.

Table 47 Lower detection limits for EDXRF

Element	LDL (μg/m^3)
K	1.388± 0.214
Ca	0.829± 0.099
Ti	0.279± 0.031
Mn	0.0621± 0.001
Fe	0.0502± 0.002
Cu	0.0407± 0.014
Zn	0.0246± 0.0036
Br	0.0158± 0.004
Zr	0.00629± 0.0076
Pb	0.0240± 0.0111

5.11 Acute respiratory incidences(ARI) point prevalence for the year 1998.

The results of ARI point prevalence for the year 1998 are shown in the Table 48 below.

***Table 48: Distribution of the children contacted and the percentage of the ARI episodes per month for the year 1998.**

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
No of children	724	754	781	808	836	857	661	624	651	621	661	64
No of contacts 1	23.2	36.6	30.7	36.1	41.5	37.1	36.9	37.5	35.9	28.7	28.6	21
2	5.7	9.0	9.4	13.7	16.4	22.5	17.1	6.6	13.4	13.5	15.6	8.
3									4.0	5.0	4.1	2.
4									2.0	1.8	0.3	-
Total %	29.9	45.6	40.1	49.8	57.9	59.6	54.0	44.1	55.3	49.0	48.6	31

*KEMR\JICA ARI project progress report.
No of contacts= the % refers to the number of children with ARI at each contact.

The point prevalence of ARI ranged between 29.9% in January to 59.6% in June. The total number of children who were under continuous surveillance throughout the study period of one (1) year (January - December 1998) were 146 and the average ARI incidence was 8.49±4.01 episodes per child per year (KEMRI/JICA, 1998/99).

The ARI point prevalence showed a seasonal variation, with both the cold and the dry season having high point prevalence (Fig 5.4 and Table 48). However, the cold period (May to August) (Fig 5.4) had higher prevalence (44.1 - 59.6%) than the dry period (September to December) whose point prevalence ranged from (31.9-55.3%). It should be recalled that some of the highest total SPM levels were recorded during these two periods (Fig 5.3).

5.11.1 Regressional analysis

Monthly mean ARI incidences were regressed on total SPM (PM_{10}) and fine particulate levels for the two sites B and E which were located within the ARI study boundaries (Fig 4.1). A linear regression model involving the two variables was used (Axum, 1993). Total SPM and fine particulate values for the period May to December 1998 were used in the regression. Analysis of variance (ANOVA) was done by Axum graphic software (Axum, 1993).

***Table 48: Distribution of the children contacted and the percentage of the ARI episodes per month for the year 1998.**

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
No of children	724	754	781	808	836	857	661	624	651	621	661	646
No of contacts 1	23.2	36.6	30.7	36.1	41.5	37.1	36.9	37.5	35.9	28.7	28.6	21.7
2	5.7	9.0	9.4	13.7	16.4	22.5	17.1	6.6	13.4	13.5	15.6	8.2
3									4.0	5.0	4.1	2.0
4									2.0	1.8	0.3	-
Total %	29.9	45.6	40.1	49.8	57.9	59.6	54.0	44.1	55.3	49.0	48.6	31.9

*KEMR\JICA ARI project progress report.

No of contacts= the % refers to the number of children with ARI at each contact.

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The Tables 49 - 52 below shows the results of regression analysis for sites B and E for both total SPM and fine particulate values.

Table 49 Regression analysis of variance for site B (total SPM)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Explained variation (Regression)	6.7	1	6.7	0.072
Unexplained variation (Residual)	558	6	93.01	
Total	564.7	7		

Table 50 Regression analysis of variance for site B (fine particulate levels)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Explained variation (Regression)	287.3	1	287.3	5.93
Unexplained variation (Residual)	284.8	6	47.4	
Total	564	7		

Table 51 Regression analysis of variance for site E (total SPM)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Explained variation (Regression)	75.1	1	76.1	0.898
Unexplained variation (Residual)	423.94	5	84.79	
Total	494.6	6		

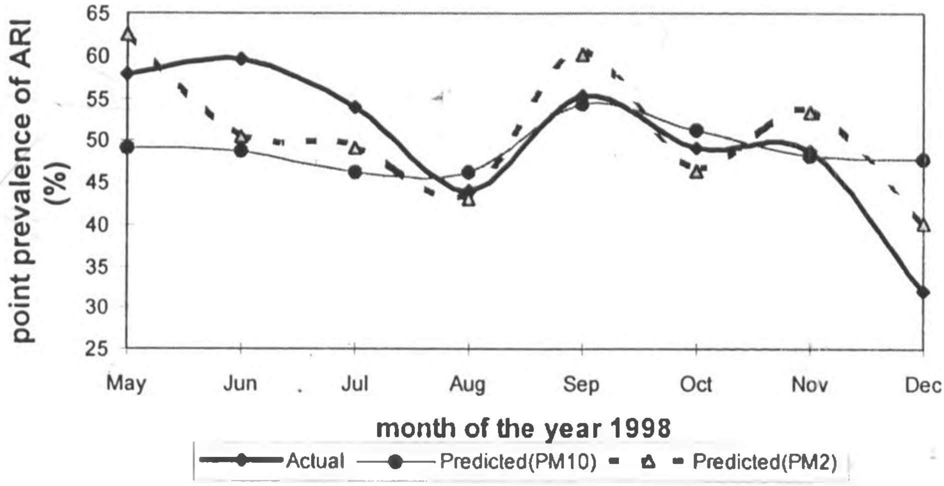
Table 52 Regression analysis of variance for site E (fine particulate levels)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Explained variation (Regression)	65.8	1	65.8	0.767
Unexplained variation (Residual)	429.2	5	85.8	
Total	494.6	6		

For both sites only small and insignificant associations were detected for both total SPM and fine particulate levels. This can be seen from the small F values obtained in the analysis of variance except for fine particulate levels for site B which was high although still non-significant at both P=1 and P=5 level.

For both sites B and E only (1-15)% of the variation of the ARI incidences could be explained by the variation of the PM_{10} and fine particulate levels, however for site B, PM_{10} accounted for 50.95% of the total variation of the ARI incidences. A positive variation is observed between predicted cases of ARI (with respect to fine particulate levels -PM_2) for the period July to December (Fig 5.16)

Fig 5.16: Actual and predicted cases of ARI with respect to PM_{10} and fine particulate levels (PM_2) at site B



Several research workers have reported significant positive associations between PM_{15}, PM_{10}, $PM_{2.5}$ and total suspended particulates (TSP) with respiratory morbidity. Dockery *et al* (1989), reported positive association between rates of chronic cough, bronchitis and chest illness in children, with several measures of particulate pollution (TSP, PM_{15} and $PM_{2.5}$). In another study by Pope (1989), in Utah valley (USA), an association between elevated PM_{10} levels and hospital admissions for pneumonia, pleurisy, bronchitis and asthma was observed. The association was found to be stronger with children's admissions than with adults.

Table 53 Actual and predicted cases of ARI for Site B and E with respect to total SPM and fine particulate levels from May through December 1998.

	Site B				Site E			
	PM$_{10}$		PM$_{2\ 0}$		PM$_{10}$		PM$_{2\ 0}$	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
May	57.9	49.0	57.9	62.4	NS	NS	NS	NS
Jun	59.6	48.6	59.6	50.4	59.6	48.6	59.6	45.3
Jul	54.0	46.2	54.0	49.1	54.0	51.9	54.0	54.9
Aug	44.1	46.1	44.1	43.1	44.1	44.7	44.1	47.7
Sep	55.3	54.3	55.3	60.1	55.3	46.5	55.3	50.2
Oct	49.0	51.3	49.0	46.3	49.0	53.8	49.0	48.7
Nov	48.6	48.2	48.6	53.4	48.6	45.9	48.6	50.2
Dec	31.9	47.7	31.9	40.2	31.9	45.7	31.9	45.4

Chapter Six

6.0 Conclusion and Recommendations

6.1 Conclusion

The mean PM_{10} values varied from (77.6 - 159.1 µg/m^3) for samples collected at a height of two (2) metres and (60.9 - 138 µg/m^3) at four (4) metres above the ground. For the samples collected at the two (2) metres height, 66% exceeded the WHO 24 hour guideline of 70 µg/m^3 (WHO, 1987) while at four (4) metres height, only 50% of the samples exceeded this limit. This was probably due to the high levels of resuspended soil dust at two (2) metres height. These values are higher than previous data (30 - 80µg/m^3) reported for a sub-urban site in Nairobi. The SPM data obtained in this work is lower than that reported in urban sites in Asia (15 - 219 µg/m^3) and higher than that reported in urban and sub-urban sites in United States of America (1 - 97 µg/m^3) and Europe (2.1 - 74.2 µg/m^3). The SPM levels also varied with the weather conditions. The levels of particulate matter were found to increase with temperature, while low values were registered during high humidity. Samples collected after a rainy day and during a drizzle recorded low SPM values (10.8 - 22.7 µg/m^3) for coarse particles, (8.10 - 14.3 µg/m^3) for fine particles. This was probably due to the washing away of some of the particulate matter. Mean monthly values showed a strong seasonal trend with the highest values being observed in the cold (51.3 - 227.4 µg/m^3) and dry (60.8 - 269.6 µg/m^3) seasons. This was probably due to the high levels of soil dust during the dry season and increased residential emissions from the domestic heating (mainly wood/charcoal and kerosine fuels) during the cold season.

For samples collected at two (2) metres height, higher values (0.046 - 7.11 µg/m^3) were observed in the coarse particulate fraction for elements calcium, potassium, iron, titanium and manganese which are associated with crustal dust. The elements copper, zinc, bromine and lead which are associated with anthropogenic origin had lower levels (0.029 - 0.337 μg/m^3). Most of the highest concentrations were observed in the dry period (September - October). For most of the sites calcium, titanium, zirconium, potassium, iron and manganese showed high correlations (0.612 - 0.984) with the suspended particulate matter (SPM) in the coarse particle fraction suggesting soil dust to be the major source. For some of the sites potassium and calcium also registered low correlations (-0.642 - 0.482) with SPM. This pointed to other possible sources for these elements apart from soil dust, e.g, burning of urban refuse and residential emissions. Copper, zinc, bromine and lead had low correlations (–0.793 - 0.386) with SPM in the coarse particle fraction indicating possible anthropogenic sources. However lead and zinc registered high correlations (0.658 - 0.773) with SPM in the coarse particle fraction for some of the sites which may suggest possible soil contamination by fine particle fallout from anthropogenic sources, example motor vehicle exhausts and metal works in the area.

Lower concentrations were observed for elements calcium, iron, titanium, manganese and zirconium (0.036 - 6.29 μg/m^3) in the coarse particulate fraction for samples collected at four (4) metres height than at two (2) metres. The elements copper, zinc and lead also registered lower levels (0.095 - 0.222 μg/m^3) at this height. However bromine registered a slight increase in concentration at four (4) metres height. The elements calcium, titanium and zirconium showed reduction in concentration by higher factors (0.288 - 0.704) than for copper, zinc, and bromine (0.745 - 1.2) in the coarse particle fraction. This pointed to resuspended soil dust at two (2) metres height as being responsible for the high levels observed for these elements in the coarse particle fraction. However, lead showed reduction in concentration by a factor (0.687) comparable to that of calcium, titanium and zirconium.

For the fine particulate samples collected at two (2) metres height, the elements potassium, calcium, titanium and iron still registered higher values (0.133 - 6.3 $\mu g/m^3$) than most of the other elements. Potassium, calcium, titanium, manganese and iron showed both high (0.515 - 0.925) and low (-0.981 - 0.453) correlations with SPM at different sites. This may suggest various sources for these elements in the fine particle fraction (e.g, soil dust, residential emissions and metal/welding works in the area). Zirconium registered high correlations (0.570 - 0.927) with SPM in all the sites.

Levels for most elements for samples collected at four (4) metres height remained in the same range as observed at two (2) metres except for calcium, bromine and iron. Higher reduction factors were observed for calcium (0.262 - 0.303), bromine (0.618) and iron (0.378 - 0.742) than for titanium, copper, zinc, lead and zirconium (0.773-0.900). Manganese registered an increase in concentration at this height.

Low enrichment factors were observed at both heights for potassium (0.265 -1.699), calcium (0.401 - 9.637), titanium (0.790 - 6.42), manganese (3.476 - 17.02) and zirconium (2.43 - 9.24) suggesting soil dust to be the main origin. However marginal enrichment for calcium (6.28 - 9.64) in the fine particle samples at two (2) and manganese (10.48 - 17.02) at four (4) metres height were observed hinting at other possible sources apart from soil dust. The high enrichment factors observed for copper (10.77 - 228.3), zinc (12.39 - 124.6), lead (59.37 - 1967.0) and bromine (152.49 - 3038.7) at both heights suggested anthropogenic activites (i.e, industrial operations, automobile exhausts and residential emissions) to be the major contributors.

Pb levels varied from 0.412 to 0.587$\mu g/m^3$ for PM_{10} samples collected at two (2) metres and 0.282 to 0.447 $\mu g/m^3$ at four (4) metres height respectively. The levels were below WHO guidelines (0.5 -1$\mu g/m^3$) (WHO, 1987). Bromine/lead ratios varying from

0.137 to 0.392 were observed at both heights hinting at vehicular emissions as the major sources of these elements at some of the sites. At both heights higher bromine/lead ratios were observed in the coarse particulate fraction than in the fine particulate fraction. Higher bromine/lead ratios were also observed at the lower height for both particle fractions. This suggested more of the bromine existed in the vapour phase at the higher level.

Elemental concentrations in this study were found to be higher by factors ranging from 1.3 to 6.0 for most elements (calcium, potassium, titanium, manganese, iron, zinc and zirconium) except for copper, bromine and lead than previous reported case for a sub-urban site in Nairobi. Compared to studies in other parts of the world (Europe and Asia) data from this study was found to be higher.

The average Acute Respiratory Infections (ARI) incidences was 8.49±4.01 episodes per child per year. The ARI incidences point prevalence showed a seasonal trend with both the cold and dry seasons having high point prevalence. However the cold period (May to August) had higher prevalence (44.1 - 59.6%) than the dry period (September to December) whose point prevalence ranged from 31.9 to 55.3%. It should be noted that some of the highest total SPM and fine particulate levels were recorded during these two periods. Regressional analysis of monthly mean ARI incidences of children under five (5) years of age on total SPM and the fine particulate levels showed no significant correlation. At the two sites only (1 - 15%) of the variation of ARI incidences could be explained by the variation of the total SPM (PM$_{10}$) and fine particulate levels (PM$_{2.0}$). No significant correlation could be established between the acute respiratory infections and the particulate levels, this could be due to the short sampling period and also the highly fluctuating number of children under surveillance.

Dustfall sampled in a typical working office environment varied from 0.449 to 2.03 μg/cm^2/day. The levels of dustfall sampled in the various offices were found to depend on the position of the filter in the room (near windows, doors and height from floor), opening of windows, doors, and floor sweeping.

6.1 Recommendations

Some features prevalent in this area contribute to the high levels of PM_{10} recorded, these features lead to the generation of soil dust and particulates in general in one way or the other. These include:-

a) the high population density.

b) fallout of soil particles from the mud walled houses.

c) unpaved roads and footpaths.

d) burning of refuse.

e) extensive use of biomass fuels, i.e, wood and charcoal.

To reduce the high level of generation of soil dust and other particulates, the population should be encouraged to :-

- use more environmental friendly building materials such as timber and cementing of the mud walls to reduce soil particle fallout.
- plant vegetation cover such as grass on the bare children's playgrounds.
- urban refuse collection should be improved to reduce the incidences of refuse burning.
- efforts should be made to pave the roads and footpaths in the area.

Vehicular emissions continue to be the major source of lead and bromine in the air of our urban centres. This is due to the use of leaded gasoline. The following is recommended :-

- research work should be undertaken to establish the ambient lead and bromine levels in the air of the country's major urban centres and areas near the major highways.

- extensive studies should be initiated to determine the levels of lead in the blood of urban populations of major urban centres to assess the impact of the pollutant.
- efforts should be initiated towards phasing out the use of leaded gasoline in the country. Introduction of unleaded gasoline has been found to significantly reduce the blood lead levels of urban population. Introduction of unleaded gasoline in Mexico city in 1990 (World resources, 1998) led to reduction of mean blood lead level concentrations in school children from 16.5 to 11.14 μg/dl in 1992. Also a decrease of 14.5 to 2.8 μg/dl was observed in United States of America (World Resources, 1998).
- Studies should be initiated to characterise the organic constituents of the suspended particulate matter (SPM).

Although no significant correlations were detected between the PM_{10}, levels and Acute Respiratory Infections (ARI) incidences of children under five years of age, this should not be used as a yardstick to dismiss the high pollution levels in the area. Epidemiological case studies (Dockery *et al,* 1989; Pope, 1989; Dockery *et al,*1995; Dockery *et al,*1992) done in United States of America and some European countries have established strong associations between PM_{10} levels and respiratory morbidity and mortality. It is therefore necessary to carry out more extensive epidemiological case studies throughout the country especially in those communities living near the industrial areas.

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Appendix(a)

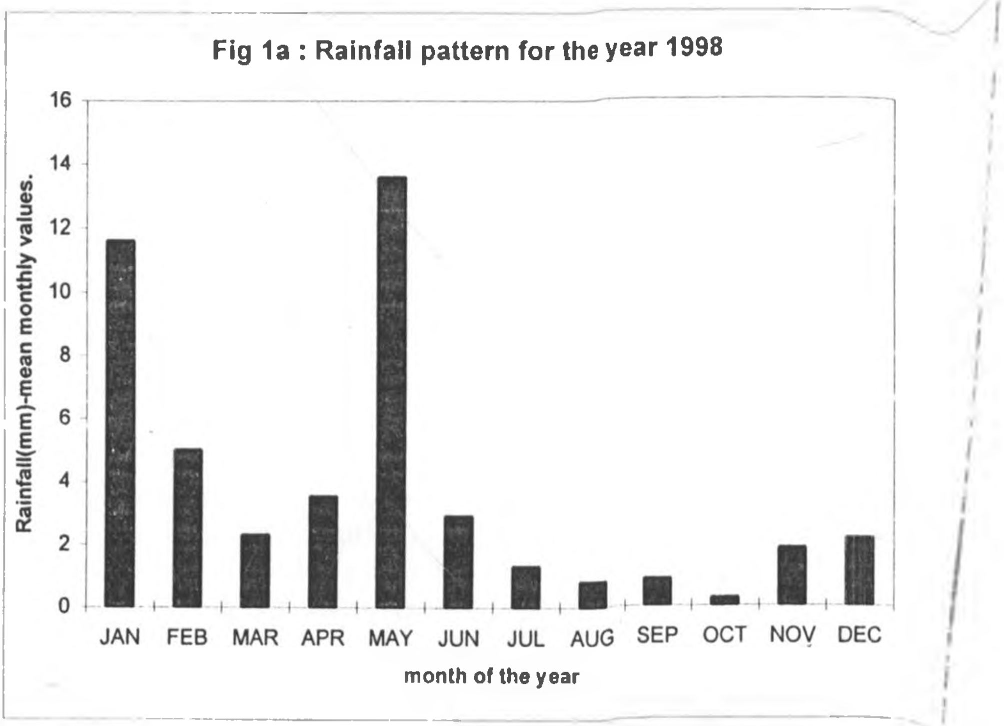
Fig 1a : Rainfall pattern for the year 1998

Source: Kenya Meteorological Society-Dagoretti Station

Table 1a: World Health Organization(WHO) air quality guideline values

Pollutant	Averaging time	Maximum limit value($\mu g/m^3$)
Sulphur dioxide (SO_2)	1 hour	500
	24 hours	125
	Year	50
Nitrogen Dioxide (NO_2)	1 hour	200
	24 hours	--
	Year	40
Ozone(O_3)	1 hour	150-200
	8 hours	120
Carbon Monoxide(CO)	1 hour	30,000
	8 hours	10,000
Black Smoke(BS)	24 hours	50
	Year	--
PM_{10}	24 hours	70
Lead	Year	0.5-1.0

Source: Bjarne Sivertsen (2000), Understanding air Quality Measurements, Norwegian Institut for Air Research (NILU: TR 4/200)

Appendix (b.1)

Heavy Metals analysis of fine and Coarse Suspended Particulate Matter (SPM) and monitoring of Acute Respiratory Infections (ARI) in Kibera, Nairobi, Kenya

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Abstract

High population density, industrialization and increased vehicle use have led to considerable deterioration of air quality in most urban centres. The most obvious air pollutant is the increased load of suspended particulate matter now shown to have some adverse health effects mostly associated with particles in the size range of about 10µm and below. In this work, measurements of SPM and ARI monitoring in Kibera have been done. The study was aimed at determining levels of SPM and its correlation to ARI, levels of heavy metals and the influence of the weather. Samples (PM_{10}) were collected by way of "Gent" sampler, weighed and analysed for heavy metals by Energy Dispersive X-ray Fluorescence (EDXRF) and Atomic Absorption Spectrometry (AAS) system. The study of the ARI was mainly concentrated in the Makina area within Kibera. The children under study (n=1231) were visited twice a month by a team of officers from the Kenya Medical Research Institute (KEMRI). They were all under five years of age and 146 presented themselves continuously for one year. They all lived within ¼ mile of the air sampling stations (n=2). The data on the health status of the children was elicited by the use of a questionnaire administered to the mother plus a physical examination by the doctor. The information gathered concerned the child's health status since the last visit (i.e., 14 days recall period), date and duration of the sickness. Results of analysis by gravimetric, EDXRF and AAS of coarse (2 -10µm EAD) and fine (≤2µm EAD) particulate samples are as follows. The mean PM_{10} values varied from (77.6 -159.1µg m^{-3}) while mean monthly values showed a strong seasonal trend with the highest values being observed in the cold (51.3 - 227.4µg m^{-3}) and dry (60.8 -269.6µg m^{-3}) seasons. Ten elements (K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Br and Zr) were measured from the suspended particulate matter. In the coarse particulate fraction, Cu, Zn, Br and Pb registered lower levels (0.029 - 0.337µg m^{-3}) than Ca, Ti, Zr, K, Fe and Mn (0.381-7.80µg m^{-3}). High enrichments were observed for Cu (16.0 - 40.66), Zn (12.39 - 68.8), Pb (101.98 - 804.2) and Br (152.9 - 1812.0) in both fine and coarse particulate fractions. Major contributors of the SPM are the emissions from residential, urban refuse burning, industrial (cottage) operations and vehicles. Regression analysis of mean monthly ARI incidences of children and PM_{10} particulate levels showed no significant correlation (= 0.05).

Keywords: Suspended particulate matter (SPM), heavy metals, Energy Dispersive X-ray Fluorescence, Atomic Absorption Spectroscopy, acute respiratory infection (ARI), EAD-Equivalent aerodynamic diameter

- A paper presented during the 5th Kenya Meteorological Society Workshop held in Mombasa, Kenya between 4th to 8th September 2000

Appendix (b.2)

Elemental composition of fine and coarse particulate matter samples collected in a suburban setting in Nairobi, Kenya

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Abstract

High population density, industrialization and increased vehicle use have led to considerable deterioration of air quality in most urban centres. The most obvious air pollutant is the increased load of suspended particulate matter which is known to have some adverse health effect on human. Health effects are mostly associated with particles in the size range of about 10μm and below. Results of analysis by gravimetric, EDXRF and AAS of coarse (2-10μm EAD) and fine (≤2μm EAD) particulate samples collected in a suburban setting in Nairobi are presented. The mean PM_{10} values varied from (77.6 -159.1μg m^{-3}). Mean monthly values showed a strong seasonal trend with the highest values being observed in the cold (51.3 -227.4μg m^{-3}) and dry (60.8 - 269.6μg m^{-3}) seasons. Ten elements (K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Br and Zr) were measured from the suspended particulate matter. In the coarse particulate fraction Cu, Zn, Br and Pb registered lower levels (0.029 - 0.337μg m^{-3}) than Ca, Ti, Zr, K, Fe and Mn (0.381-7.80μg m^{-3}), elements associated with crustal origin. High enrichments were observed for Cu (16.0 -40.66), Zn (12.39 -68.8), Pb(101.98 -804.2) and Br(152.9 - 1812.0) in both fine and coarse particulate fractions suggesting major contributors being residential emissions, urban refuse burning, industrial operations and vehicular emissions. Regressional analysis of mean monthly ARI incidences of children under five years of age on PM_{10} particulate levels showed no significant correlation

Keywords: Suspended particulate matter, Energy Dispersive X-ray Fluorescence (EDXRF), Atomic Absorption Spectroscopy(AAS), sub-urban, acute respiratory infections(ARI)

-A paper ready for submission to an international journal

Appendix (b.3)

Elemental composition of suspended particulate matter collected at two different heights above the ground in a sub-urban site in Kenya

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Abstract

Suspended particulate matter samples were collected in a sub-urban area in Nairobi over a 12 month period at two different heights above ground using a "Gent" SFU sampler. A total of 126 sets of duplicate fine and coarse particulate matter samples were collected. The samples were analysed by energy dispersive x-ray fluorescence (EDXRF) and atomic absorption spectroscopy (AAS) for up to 10 elements. It was found that 66% of the samples collected at two metres and 50% of the samples collected at four metres height exceeded the WHO 24 guideline of 70μg m^{-3}. Reduction in concentration of between 30 to 74 % for Ca, Ti, Zr and Fe were observed both in coarse and fine particulate matter fractions at the higher height. The elements Cu, Zn, Pb and Br represented 0.5 to 1.1 % of the total coarse particulate matter at both heights. Higher proportions of 1.5 to 3.5 % were observed at both heights in the fine particulate matter fraction. High enrichment factors were observed for Cu (10.8 - 228.3), Zn (12.4 - 124.6), Pb (59.4 - 1967) and Br (152.5 - 3038.7) at both heights suggesting anthropogenic activities such as industrial, urban refuse burning, residential and vehicular emissions could be the major contributors. Pb and Br were mainly from the vehicular emissions as indicated by the strong correlations (r > 0.593) and the Br/Pb ratios (0.307 to 0.339).

Keywords: Sub-urban, Energy Dispersive X-Ray Fluorescence(EDXRF), Atomic Absorption Spectroscopy(AAS), Enrichment factors, Heavy metals.

-A paper ready for submisssion to an international journal