UNIVERSITY OF GHANA, LEGON

CHARACTERIZATION AND SOURCES OF AIR PARTICULATE MATTER AT KWABENYA, NEAR ACCRA, GHANA

BY

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This thesis is submitted to the University of Ghana, Legon in partial fulfillment of the requirement for the award of PhD Physics degree.

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DECLARATION

Candidate's Declaration

I hereby declare that except for the references to other peoples work, which have been duly cited, this thesis is the result of my own research and that it has neither in part nor whole been presented for the award of any degree elsewhere.

.....

CANDIDATE: INNOCENT JOY KWAME ABOH

DATE: 12th May 2009

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with guidelines on supervision of thesis laid down by the University of Ghana.

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THESIS RELATED PUBLICATIONS

Part of the work presented in this thesis appears in the following publications and presented as posters at International Conferences.

Publications

1. Identification of Aerosol Particle sources in semi-rural area of Kwabenya, near Accra, Ghana by EDXRF - **Innocent Joy Kwame Aboh**, Dag Henriksson, Jens Laursen, Magnus Lundin, Francis Gormon Ofosu, Niels Pind, Eva Selin Lindgren and Tomas Wahnstrom,X-rays Spectrometry, Vol38, pp. 348, (2009)

2. Possible Sources of Atmospheric Aerosol during 2005/06 Harmattan Season at Kwabenya, Ghana - **I. J. K. Aboh** and F. G. Ofosu, Journal of Applied Science and Technology (JAST), Vol 13 No.1 & 2, pp. 55, 2008

3. Levels and sources of particulate lead in air at Kwabenya, near Accra - F. G. Ofosu and **I. J. Kwame Aboh**, Journal of Ghana Science Association, Vol. 10 No. 1, pp. 1, (2008)

Poster Presentations

1. Identification of Aerosol Particle Source in Semi-rural area of Kwabenya, near Accra, Ghana - ***Innocent Joy Kwame Aboh***, *Dag Henriksson1, Jens Laursen, Magnus Lundin, Francis Gormon Ofosu, Niels Pind, Eva Selin Lindgren and Tomas Wahnström* (Poster presented at EXRS2008, *Cavtat, Dubrovnik, Croatia, June 16-20, 2008)*

2. Characteristics and source assignment of aerosol particles in a semi-urban area in Ghana during the Harmattan season using EDXRF analysis - ***Innocent Joy Kwame Aboh***, *Dag Henriksson1, Jens Laursen, Magnus Lundin, Francis Gormon Ofosu, Niels Pind, Eva Selin Lindgren and Tomas Wahnström* (Poster presented at *EUROanalysisXIV Conference, Antwerp, Belgium, 9-14 September 2007)*

Articles submitted for publication

1. Determination of mass, element and black carbon concentrations in 2005/06 Harmattan aerosol at Kwabenya – (near Accra)– Ghana – **I. J. Kwame Aboh** and F. G. Ofosu (Paper presented to Journal Ghana Science Association - 2008)

2. Seasonal Variation of Suspended Particulate Matter at Kwabenya, near Accra – F. G. Ofosu and **I. J. Kwame Aboh** (Paper presented to Journal of Applied Science and Technology - 2008)

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ABSTRACT

Gravimetric, reflectometric and elemental analyses have been carried out on airborne particulate matter sampled in a semi-rural area of Kwabenya, near Accra-Ghana. The PM_{10} aerosols were sampled using a Gent sampler, size segregating the aerosol into coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) fractions. The data and derived information were generated from 216 days of sampling spanning a period of about 14 months, 28th December 2005 to 12th February 2007. The particulate matter (PM) at Kwabenya was dominated by the coarse particulates and showed low levels during the Rainy season and high levels during the Harmattan period. The levels measured during the 2006/07 Harmattan were very high. The mass concentration for the measuring period were in the following ranges; coarse ($PM_{10-2.5}$) fraction (0.16 - 1794.01 $\mu g/m^3$); $PM_{2.5}$ (fine) fraction (0.50 - 430.23 $\mu g/m^3$) and PM_{10} (0.87 $\mu g/m^3$ to 2064.89 $\mu g/m^3$). Additional information about the ambient air was obtained through the subsequent determination of elemental concentration using energy dispersive x-ray fluorescence (EDXRF) analysis and black carbon (BC) concentration through the "black smoke method". The elements identified and quantified with the Quantitative X-ray Analysis System (QXAS) package software were: Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr and Pb in the coarse fraction. The following elements were identified and quantified in the fine fraction: Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr and Pb. Validation of the quantitative methods with the standard reference filter SRM2783 gave very good agreement (within ±15%) for most elements analysed except for Ni (±43%)which was very close to the detection limit. The elemental concentrations in the two fractions vary from season to season. Using simple correlation analysis some elements correlate, the elemental correlations also vary

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from season to season, for example during the Harmattan S, Cl, V, Br and Sr correlated very well but during the Rainy season S did not correlate with V and Br. This could serve as possible source indicators. The BC concentration in the fine fraction (ranging from 0.01 to 5.97 μgm^{-3}) was generally higher than in the coarse fraction and comparable to data from some developed countries. A receptor model using principal component and regression analysis was used to identify sources contributing to the air particulate matter at Kwabenya. The species used in the model were mass, BC and elemental concentrations. The following major sources were identified in the coarse aerosol: Soil/Dust, Biomass/LDT and Sea aerosol. In the fine aerosol the following sources were identified: Soil/Dust, Biomass/LDT and some industrial sources. The contribution of the sources to the PM load varied from season to season, There was very good agreement between the experimental and model data (mass, BC and elemental concentrations). Comparing the data with WHO limit (50 μgm^{-3} for 24-hour mean) and Ghana EPA guideline limit (70 μgm^{-3} for 24 hours) for PM_{10}, a total of 185 and 130 days respectively out of 216 days had values above these limits. For $PM_{2.5}$ a total of 60 days had values exceeding the WHO limit (25 μgm^{-3} for 24-hour mean). The levels of S, Ni and Pb were also comparable to industralised countries. There is the need for some mitigation measures to curb the emission of these elements and fine BC.

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To God be the Glory for all the great things He has done!

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DEDICATION

This thesis is dedicated to my wife – Mrs. Joyce A. S. Aboh

and my children – Dzidefo, Makafui and Sedem

To God be the Glory!

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 OVERVIEW

Particles exist in the environment as suspensions in air and are commonly called aerosol. Hinds[1] and Colbeck[2] define aerosol as suspension of solid or liquid particles in a gaseous medium (air). The aerosol particles have a very wide size range from molecular clusters of 0.001μm to fog and dust particles as large as a few hundred micrometers.[2-4]

Pollution is defined in the Tenth Report of the Royal Commission on Environmental Pollution as: "*The introduction by Man into the environment of substances or energy liable to cause hazard to human health, harm to living resources and ecological systems, damage to structure or amenity or interference with legitimate use of the environment*".[5] Air pollution is the emitting of solid, liquid and gaseous material into the air environment. The emissions can originate from stationary or mobile sources and can sometimes involve some chemical or/and physical transformations before eventually being returned to surfaces such as the soil, plants, trees, monuments, buildings, etc.

It is generally perceived that air pollution is one of the most vexing problems facing industrialized and developing countries because these microscopic particles are present everywhere in our environment. All things, both living and non-living, are exposed in varying degrees to air pollution. The degree of exposure depends on the location and activities (industrial, domestic, vehicular, etc) taking place.

The ubiquitous nature of aerosol particles exerts an important influence on the hydrological and climatic system. For example, aerosol particles are found in both the

troposphere and the stratosphere and affect climate through scattering, transmission and absorption of radiation.[6] Studies have shown that a layer of small particles is always located in the stratosphere at altitude centered around 25 km at the equator and 17 km at the poles.[7] Aerosol particles provide surfaces for heterogeneous chemical reactions which can influence gas-phase chemistry in the troposphere.[8] Aircraft exhaust particles in the upper atmosphere are source of ice and cloud nuclei. Biomass burning, especially in the tropics, leads to significant perturbations of tropospheric aerosol loading in these regions, and could be leading to changes in cloud behaviour.

The origin of the particles could be from natural processes (e.g. sea spray, dust, etc) or from man-made processes known as anthropogenic processes (vehicle emissions, emission from industries, waste incineration, etc). From the definition of air pollution above, chemicals such as sulphur dioxide from volcanoes or methane from the decay of natural vegetation are not air pollutants, but sulphur dioxide from coal burning or methane from rice growing are air pollutants. However, human activities disturb natural systems hence the line distinguishing between the natural and anthropogenic processes become increasingly blurred. For example, radon – a radioactive gas is a hazard in some types of geographical formation and the radon exposure by mining in those formations increases exposure levels, which is air pollution. It is estimated that anthropogenic sources account for more than 30% of the aerosol particles measured by mass and are mainly small size or "fine" (PM< 2.5μm) particles.[9] For example the anthropogenic component of sulphate, which is essential for cloud formation, exceeds 60% of total sulphate particles over urban areas.[10] Natural sources are usually of the larger aerodynamic diameter (coarse particle mode) and include dust storm, sea spray, bush and forest burning.

Aerosol particles in the atmosphere are caused by a wide range of sources and have diverse compositions and characteristics. As a result, the effects of aerosol particles on the environment and humans are many and varied. Some of the effect could just be a nuisance like dust deposited on a clean surface to serious climatic effect like environmental degradation, acid rains, impact on climate, impact on human and animal health.

1.1.2 HEALTH EFFECTS

For many centuries aerosol particles have been recognised for their potentially negative impact on human health and ecosystems. Already in the Hippocratic Corpus (c. 400 B.C) medical links between health and air quality were mentioned.[11] The Romans complained of foul air in ancient Rome. With the introduction of coal in London in the 13th century, regulations were introduced to reduce smoke problems. In the 17th century, John Graunt, a fellow of the Royal Society concluded that the high death rate in London was partly as a result of coal burning. Awareness of the effects soot deposited on buildings had been noticed over 200 years ago and it was speculated that it had the same effect on the respiratory organs. In Italy, Bernardino Ramazzini catalogued many occupational risks of air pollution in *De Morbis Artificium*.[12] In 1713, Linné and his colleagues described silicosis in Swedish miners.[13] However, it was not until the second half of the 20th century that more typical air pollution as experienced today have forced scientists, politicians and decision makers to take note and put in place the necessary remedial actions.

Since the famous smog incident in 1952 in London, resulting in about 4000 excess deaths, it has been recognised that the negative influence on human health caused by aerosol particles had been grossly under-estimated. These negative effects of airborne particles have also been observed in the work environment. Epidemiological studies in

several countries have shown conclusively that there is a direct link between particulate air pollution and adverse health effects. Both indoor and outdoor particulate air pollution are responsible for these adverse health effects. The physical properties of aerosols affect the transport and deposition of the particles in the human respiratory system, whilst the chemical composition and the physical properties determine their impact on health. For two to three decades environmental authorities in developed countries have been active in sampling and analysing particles with (aerodynamic) diameters smaller than 10 micrometers, PM_{10}. Studies during the last ten years indicate, however that the very smallest particles are even more hazardous to health, and smaller particles $PM_{2.5}$, $PM_{1.0}$ and even nanoparticles have been more extensively studied.[14-19] Fine carbon or fly ash particles have been suspected to increase the respiratory toxicity of coexisting acidic air pollutants, by concentrating acid on their surfaces and so delivering it efficiently to the lower respiratory tract.[20] The number of death from air pollution is estimated to be more than 3 million/year, with about 1 million/year in cities and 2 million/year in rural settings. The largest contributor to the rural death toll is biomass fuel burning, as a source of domestic energy, from indoor pollution.[9,21] The causes of death are not only related to lung injuries but also to cancers and cardiovascular diseases. The increased awareness has lead to regulatory legislation regarding emissions and concentration levels of particulate matter (PM) in many countries all over the world. In general, the "finer" or smaller the aerosol particle the more hazardous it is due to the size and morphology. Thus small particles:

- can easily be transported over long distances far away from their sources
- can easily be inhaled and deposited in the lower part of the human respiratory tract

- have larger surface area per unit mass and hence higher ability to absorb gas molecules and transport them to any part of the respiratory system to catalyze chemical and biochemical reactions
- consist of a large soluble fraction.[9]

In fact, the American Academy of Pediatrics in a statement issued before the Clean Air Scientific Advisory Committee of the United States Environmental Agency (USEPA) on April 7th 2005 stated *"Research has firmly established that exposure to high levels of particulate matter impacts the ability of children's lungs to grow. The adverse effects of air pollution on the development of lung function is seen in boys and girls, regardless of history of asthma, suggesting that most children are susceptible to chronic effect of breathing particulate air pollutants. When this damage occurs, it is irreversible, and reduced lung function is a strong risk factor for future health consequences as an adult. Particulate matter air pollution is also linked to other adverse respiratory health effects in infants and children, such as asthma exacerbations, chronic cough, and bronchitis symptoms".* [22] Other researchers had confirmed these assertions and had gone on to show that low-birth weight, preterm births and infant mortality are increased in communities with high levels of particulate air pollutions.[23-25]

Ingestion of aerosol particles that have initially deposited on crop or soil and inhalation of air are the two main ways in which aerosol particles enter the human body. It has been shown that aerosol particles with diameter less that 2.5 μm have more serious influence on the occurrence of respiratory diseases.[26-29] Lead in aerosol has been implicated in the impairment of the development of children.[30] Some of the aerosol inhaled may contain radioactive nuclides, attached to very small particles, which are quickly transported to the

lower lung where the attached radionuclides could cause cancer.[31] Increased morbidity and mortality due to chronic diseases have also been attributed to aerosol particles. [32-34]

1.1.3 EFFECT ON CLIMATE

Aerosol particles can affect the atmospheric radiation budget by either absorbing and/or scattering of solar radiation. For example, soot particles are known to have a high absorption for solar radiation. This absorption of solar radiation by aerosol particles leads to heating of the atmosphere while scattering of solar radiation results in cooling of the atmosphere. The main processes that determine the overall state of the climate system are heating by incoming solar radiation and cooling by outgoing long-wave (infrared) terrestrial radiation.[35-37] This heating or cooling of the atmosphere can result in perturbation of the radiation balance of the troposphere known as radiative forcing.[38,39] Radiative forcing is the change in the balance between radiation coming into the atmosphere and radiation going out. A positive radiative forcing tends on average to warm the surface of the Earth, and negative forcing tends on average to cool the surface. Aerosol particles contribute significantly to radiative forcing of climate.[35,40-43] Black particles are most effective in absorbing solar radiation, hence black carbon (BC) in aerosol particles has been suggested to be the second most important component of global warming.[44] The 1997-1998 severe El Nino induced droughts in Indonesia, Mexico and Central America have been linked to high biomass burning around the world.[45]

1.1.4 EFFECT ON FORESTS AND VEGETATION

It is a well known fact that forests and vegetation play an important role in the environment. For example, through photosynthesis forest and vegetation are sources of oxygen, help in preventing soil erosion, and provide food and shelter for animals. Therefore, any damage to the forest and vegetation could pose serious problems to human

beings, animals and the whole environment. Heavy metals in aerosol particles have been suspected to cause damage, since the beginning of the twentieth century, to the forest and vegetation. In 1912 Hedgecock documented that heavy metal aerosol particles from a nearby copper smelter were partially responsible for devastation of a large area (approximately 47,000 acres) in Tennessee.[46] The partial destruction of forest and vegetation in other parts of the world by particle emission has also been reported by other researchers.[47-49] This damage ranges from damage to leaves and other parts of the tree to the more catastrophic destruction of the whole vegetation.

1.1.5 MEASURES FOR ADDRESSING AIR POLLUTION IN GHANA

Most developed countries have recognized the adverse effects posed by aerosol particles, especially on human health, and this has resulted in increased routine monitoring of atmospheric particles.[50] In contrast however, there is almost no routine monitoring of aerosols in developing countries, especially in Africa (except for South Africa). Hence data on concentrations as well as characteristics of particulate matter are almost non-existent in developing countries most of which are in the Southern hemisphere.[51,52] To understand fully how aerosol particles behave under different climatic conditions there is the need to characterize aerosol particles in many different places including the developing countries, especially those near the equator. Such characterization would not only assist the developing countries to comply with international conventions and standards but would form an informed-basis for setting appropriate standards for the developing countries themselves as pertains in the developed countries.

1.2 CURRENT AIR POLLUTION STATUS IN GHANA

1.2.1 SOME ACTIVITIES CONTRIBUTING TO AIR POLLUTION

1.2.1.1 INTRODUCTION

In 1980's Ghana undertook major economic reforms with the assistance of the World Bank and the International Monetary Fund (IMF) which resulted in the expansion and growth of the economy. Following the economic recovery programme there has been an increase in industrial activities in the country. The activities that have seen growth are in the areas of mining, road and housing Construction, plastic manufacturing, transport, metallurgical (steel and aluminium) reprocessing and fabrication, agricultural and other industrial concerns that depend mainly on chemicals (fertilizers, insecticides, pesticides, pharmaceutical, textiles, etc). The main industrial activities in the country are mining, agriculture, and manufacturing listed in order of capacity.

All these industrial activities contribute towards atmospheric pollution in the form of gaseous pollutants, coarse and fine airborne particulate matter and solid waste. In addition there are the annual bush fires, sea spray, automobile exhaust gases, etc. These pollutants have their effect on human health, physical materials, the ecosystem and climate but unfortunately no known data is available in terms of their social and economic cost.

The Government has made it a general requirement by law, for new businesses to provide an environmental impact assessment (EIA) and for the existing ones to provide environmental management plan (EMP). National environmental standards to serve as a guideline for compliance have also been introduced. For some specific sources however, additional legislation have been put in place to control to some extent their emissions.

1.2.1.2 ENERGY AND INDUSTRIALIZATION

Ghana Poverty Reduction Strategy (GPRS) document is the country's developmental plan aimed at the attainment of middle-income level (GDP > US$1000) by the year 2015. This vision envisages the almost tripling of the current GDP, which currently is US$420 (2004), in ten years. To achieve this will require the establishment of more industries with electrical power consumption expected to increase as much as six to nine times the current installed capacity of 1600 MW. The Power crisis of 1998 has also shifted power generation from hydro to thermal power, which involves the combustion of high volumes of crude oil. Hence to be able to meet this enormous anticipated increase, more thermal plants would have to be built. Ghana has at present two thermal plants supporting the hydroelectric-generation, at Aboadze near Takoradi.

Except for mining all other industries are located in the urban areas and lack of proper zoning procedures give rise to the situation whereby industries are inter-mixed with residential areas. With the growth of industries, one can envisage high pollution levels beyond the already existing levels of which little efforts are being made towards its mitigation. A great number of the manufacturing industries are located at Tema near Accra and more than 90% of the country's industries are in the Southern part of the country.

Most of the energy for everyday domestic use in Ghana and the rest of sub-Saharan Africa are derived from biomass burning (fuel wood and charcoal) and in places in the urban areas some people go to the extreme of using worn-out vehicle tires as fuel. Biomass burning accounts for about 70% of total energy consumption in Africa.[53,54] The annual bush fires that occur during the dry season, when temperatures are low, also

coincide with high demand of fuel wood and charcoal period contributing large amounts of soot and ash particles into the atmosphere.[55]

The industrial processes, the energy processes and the bush fires all release toxic elements and gases, some of which interacts with rain water to cause acid precipitation which has its far reaching ecological effects.

1.2.1.3 MINING

Arsenopyrite gold ore deposits are the predominant gold deposits in the country.[56] The extraction processes require high temperature roasting releasing arsenic, antimony and other heavy metals into the atmosphere. Since these activities occur in the forest zones the pollutants, carried down by rainwater affect the forest and hence crop cultivation. Vast areas have been affected by acid rain. The acid rains also pollute waters that flow into rivers, which are used for human consumption.

1.2.1.4 VEHICULAR EMISSION

Ghana, it is currently estimated, has vehicular population growth rate of more than 70,000 vehicles per annum with more than 65% concentrated in the Accra-Tema Metropolitan Area. Like most African countries, the vehicles are concentrated on only a small fraction of the road network.[57] Most of the vehicles are second-hand without catalytic converters. Automobile emission is becoming a serious problem, especially in the cities and is the main focus of the country's environmental authorities.

The Government of Ghana has approved a Legislation Instrument L.I. 1732 [Petroleum (amendment) Regulation 2003] banning the production, importation, storage, sale and use of leaded gasoline in the country with effect from 1st January 2004. Consequently, Methylcyclopentadienyl Manganese Tricarbonyl (MMT) - a manganese-based gasoline

anti-knock additive, has been in use in Ghana since January 2004 in unleaded Gasoline production. MMT is used in some countries including the United States, Canada and China. But there is a serious controversy about MMT use in some other countries especially in the European Union. The addition of MMT to gasoline supply has raised concern about public health risks associated with the inevitable increase in the environmental levels of manganese. In fact, several studies have reported that manganese causes significant health hazard in heavily air polluted areas.[58-60]

Combustion of unleaded gasoline in internal combustion engines causes the emission of various compounds such as carbon monoxide, carbon dioxide, hydrocarbons and other organic compounds. When MMT-containing fuel is combusted, small quantities of manganese compounds are emitted in the automotive exhaust along with carbon monoxide, carbon dioxide and other gaseous compounds. The amount of manganese emitted, the manufacturer's claim, is very small because only a few parts per million of manganese are added to the unleaded fuel and only a small percentage of this is emitted.

Manganese is an element that is essential to maintaining good health. It is also a natural component of the soil and is found in food, water and air. Adverse health effects of manganese have been associated with organic Manganese compounds (pesticides) and inorganic manganese.[61-63] However, exposure to high concentrations of airborne manganese for prolonged periods of time can produce adverse health effects affecting primarily the nervous system leading to slower visual reaction time, poorer hand steadiness, and impaired eye-hand coordination.[64,65] Some researchers have long recognized a relationship between manganese intoxication and Parkinsonism.[66-68]

1.2.1.5 STREET DUST, SOIL AND DESERT SAND

A lot of dust, about 900 – 1500 million tons, enters the atmosphere each year from natural soil dust. Dust is easily blown away by the wind and can travel over thousands kilometers. For example, Sahara dust has been found by satellite images to reach the Western Hermisphere and even the Arctic. The Sahara desert is regarded as the largest dust source in the world.[69] Also dusts originating from China have caused haze in California in the USA. When dust passes over polluted areas they can be coated with sulphur due to chemical process on their surfaces.[70] These particles can then serve as giant cloud condensation nuclei (CCN), which may enhance the collision and coalescence of droplets and therefore increase warm precipitation formation and decrease the clouds albedo.[71] This in effect means enhanced rainfall but this has been disproved by some researchers showing that it rather reduces rainfall.[72] For a country like Ghana, which is under threat from the downward movement of the Sahara, this could pose a lot of problem for rainfall patterns which have been decreasing over the years.

In the urban areas of Ghana, a large quantity of construction sand and gravel is needed to support the rapid expansion of the towns and construction of roads and other infrastructure. These are brought in from the surrounding rural areas in haulage trucks moving on unpaved roads trapping a lot of mud which are then deposited on the paved roads. In addition, the status of the road network whereby several roads are unpaved plays a significant role in the entrainment of dust; particles, which are suspended by vehicular movement on paved and unpaved roads. This is a major contributor to fugitive dust emissions.[73] Most of the "sand winning" as it is termed is done in unplanned and illegal manner with serious damage to the environment and the surrounding air quality. There is also a lot of construction sand and gravel processing plants whose processes

involve gravel transportation, crushing, screening, storage and hauling. The operations of these plants also generate high concentration of dust into the atmosphere.

The harmattan, a dry desert wind from the Sahara, blows from the northeast from December to March, lowering the humidity and creating hot days and cool nights in the north. In the southern part of the country, the effects of the harmattan are felt in January and February. It has been shown by Baumbach *et al*[53] that in Lagos-Nigeria the particle concentration more than doubled during the dry season when the northly harmattan wind from the Sahara are prevalent.

1.2.1.6 SEA SPRAY

Ghana has 537-kilometer (334-mi.) coastline which is mostly a low, sandy shore backed by plains and scrub and intersected by several rivers and streams. Common salt is produced in commercial quantities along the coast of Ghana near Accra (at Ada). Half of the country lies less than 152 meters (500 ft.) above sea level, and the highest point is 883 meters (2,900 ft.). The general wind direction is North-East in the Southern part of the country and depth of penetration of the coastal wind is high, sometimes covering more than two-thirds of the country.

The marine aerosol comprises two distinct aerosol types:

The first, being the primary sea-salt aerosol produced by mechanical disruption of the ocean surface. The sea-salt aerosol is produced at the ocean surface by the bursting of air bubbles resulting from entrapment of air induced by wind stress that are subsequently dechlorinated by acidic materials, when the Cl^- is replaced by the SO_4^{2-} or NO_3^-. This process is especially evident in the coastal atmosphere and has been regarded as the major global source for gaseous chlorine in the atmosphere.[74,75] This dechlorination process is

highly corrosive and has had a major impact on the materials used in Ghana for infrastructure development. Metallic materials such as vehicles, electronic appliances, and telephone and streetlight poles have not been spared by this corrosive nature of the sea spray.

The second is the formation of secondary aerosol, primary in the form of non-sea salt sulphate and organic species formed by gas-to-particle conversion processes.

1.2.2. ISSUES

1.2.2.1 URBANISATION

The world's urban population is growing very rapidly and by the United Nations estimations the total population growth between 2000 and 2030 will take place in the cities of the less developed countries.[76] In Ghana, from the 2000 Housing and Population Census more than 20% (about 4 million people) of the countries population live in the Accra-Tema Metropolitan area and its environs.

The urban areas are the commercial hub of the country, more and more young people are drawn to the cities looking for new jobs and new opportunities. The physical properties of the urban areas in Ghana, like in the rest of the world, are divided between highly developed affluent areas and less developed slump areas.[77,78] The city limits/boundary are continuously being moved as a result of the creation of satellite settlements, without the most basic of infrastructure, that are being absorbed. The economic crises of the African region have also fueled the migration of people to the urban areas since the 1970s. This demographic change has confronted city authorities with the task of providing the urban population with the necessary infrastructure such as housing, portable water, efficient solid and liquid waste disposal systems, etc.[79]

The increasing urbanization of developing countries, like Ghana, has in it attendant problems that lead to poor health and the degeneration of the urban environment.[80] Construction boom and other drastic changes to both land use and the atmosphere above compared to the surrounding rural areas are brought about by urbanisation.[81] This inadvertently modifies both the climate and air quality as the urban area grows. Cities by nature are concentrations of human activity; hence they are subjected to the highest levels of pollution and pollution impact.[82]

Though most developed countries have long placed the improvement of air quality on their development agenda, the opposite is the case in sub-Saharan Africa where most city authorities are unable to keep pace with development and urbanization, and therefore lack pollution control measures. The lack of capacity, both capital and human, in sub-Saharan Africa together with expected population growth means that the situation can only get worse.[83]

1.2.2.2 CLIMATE

The climate of a place influences the type of activities that take place and hence have an impact on the levels of particulate pollution. The climate of Ghana is tropical and humid (relative humidity 55% - 85%), but temperatures vary with season and elevation. There are two main raining seasons in Ghana (April to July and from September to November) except in the north of the country where there is only one (starts April and lasts until September). Annual rainfall ranges from about 1,100 mm in the north to about 2,500 mm in the southwest.

During the harmattan period, there is an increase in particulate matter levels which are closely linked to the increased atmospheric stability that usually coincide with the dry

season and the absence of precipitation and effective ventilation.[84-86] This is also enhanced by the absence of leaves and vegetation which acts as filters during the rainy seasons, coupled with the minimal washout effect of rains during this period. These seasonal variations have been shown to be more visible in tropical climate than temperate regions.[87]

In most areas the highest temperatures occur in March (average high about 32 °C) and the lowest in August (average low about 21 °C). The variation in both annually and daily temperature are quite small. It is comparatively dry along southeast coast, hot and humid in southwest, and hot and dry in the north.

1.2.2.3 INCREASED PUBLIC ENVIRONMENTAL AWARENESS

Environmental awareness is on the increase in the country and leading to frequent social agitations on environmental issues. In 1999 the Accra Metropolitan Authority with the assistance of the British Government started the construction of an ultra modern landfill site for domestic and industrial waste at Kwabenya, near Accra after a thorough environmental impact assessment. This landfill project has been brought to a standstill because of environmental pollution concerns raised by residents around the area. Recently, residents of Juapong and Aflao in the Volta Region took to the streets in demonstrations against the Juapong Textile Company and the West African Cement Company respectively for polluting their air environment. The people living in the Mining areas have had series of demonstrations against surface mining as a result of the "perceived" environmental (including air) pollution. On June 15, 2005 a demonstration by the Chiefs and people of Prestea, a mining town in the Western Region, against surface mining in the area, resulted in the Police firing live bullets into the crowd injuring eight seriously including an eleven year old boy who had his lip blown off.[88] These

agitations do not augur well for Ghana's vision of accelerated industrial growth and a prime destination for foreign investments. The best way these agitations can be stemmed is to do systematic and continuous air quality monitoring and generate the necessary scientific data to allay the concerns of the public.

1.2.3 TRENDS IN MONITORING

Not much air pollution studies have been done in Ghana in particular and Africa in general.[51,52] The following modest activities have however been carried out in the country in the field of air pollution:

- Air Quality Management in Takoradi Thermal Power Station
- Biomonitoring of Air Pollution using lichens
- Air pollution monitoring of Kpone and Tema Oil Refinery

In addition to these projects the Environmental Protection Agency (EPA) has a number of mobile stations, which they use to measure NOx, SOx and TSP but not on regular and sustained basis. The **Fig. 1-1** shows PM_{10} concentration in roadside ambient air monitored by the EPA.

1.2.3.1 AIR QUALITY MONITORING AND MANAGEMENT AT THE TAKORADI THERMAL POWER STATION

The Volta River Authority (VRA) is in charge of the generation, transmission, distribution of power for industrial and domestic use in Ghana and selling of electricity to Togo and Benin. Until 1997 power generation was 95% hydro from the Akosombo dam built in 1961. Increased demand coupled with the decreasing water level in the lake has compelled VRA to produce only 45% of Ghana's power requirement from hydro and 55% from the Takoradi Thermal Plant.

The thermal plant is 330 MW combined cycle plant, consisting of two 100 MW combustion turbine generator with associated heat recovery steam generators. Currently, the plant is using light crude oil. The combustion of this fuel results in the emission of various air pollutants, such as:

- Oxides of Nitrogen (NOx)
- Sulphur Dioxide (SO_2)
- Carbon Dioxide (CO_2)
- Carbon Monoxide (CO)
- Particulate Matter (PM_{10} and $PM_{2.5}$)

CO_2, CO, and the particulate matter are the direct products of the combustion whereas NOx, and SO_2 are dependent on the nitrogen and sulphur contents of the oil. To mitigate the harmful effect of these atmospheric emissions the plant design incorporated a modelled stack height that improves the dilution and dispersion of the flue gas. This help to distribute the impact of the emitted pollutant over a wide ground surface area and reduces the average ground level concentration and the impact on vegetation.

The concentration of fuel bound nitrogen content for the light crude oil imported is limited to 120mg/l to minimize NOx emission. SO_2 is controlled by limiting the fuel total sulphur content to 0.2% by weight to ensure that SO_2 emissions fall within acceptable guidelines set by Ghana EPA.

Ambient air is monitored at three locations:

- Aboadze, the nearest community in the prevalent wind direction
- Beposo, the point of maximum out fall of airborne plant emissions
- The Western fence of the plant as control or background monitoring station

Results of some of the monitoring work done is given in **Figures 1-2** and **1-3**.

1.2.3.2 BIOMONITORING OF AIR POLLUTION USING LICHENS

Two species of Lichens (*Paramedia* and *Lecanora*) in the *Crutose* family were identified and used in the arseno-pyrites gold mining area of Ghana (Obuasi and Prestea) and the Tema/Doryim area, which is the hub of Ghana's industries to monitor the deposition of heavy metals from air pollution. Akim Oda and Sameraboi, two rural farming communities where the same lichens were identified were also used as the control. The results of this work, as shown in **Table 1-1**, showed that the mining and the industrial areas had higher elemental concentration values than the farming communities suggesting clearly that these two places were polluted. [89,90]

1.2.3.3 AIR POLLUTION MONITORING OF KPONE AND TEMA OIL REFINERY

The Tema Oil Refinery in 2003, as a result of persistent accusations by the citizens of Kpone, a fishing community east of the refinery and the Tema industrial area, requested the Ghana Atomic Energy Commission to undertake air monitoring at both Kpone and its plants. **Fig. 1-4** shows the spectra of selected aerosol filters from Kpone and the Tema Oil Refinery. The result is shown in **Table 1-2**. The elemental concentrations of most elements in the PM_{10} samples were consistently higher for Kpone than at the Tema Oil Refinery. However, the values for $PM_{2.5}$ showed consistently lower values for Kpone than the Refinery. Since most of the elements identified were not precursors from fuel combustion it was concluded that the operations of the refinery were not responsible for the air pollution complains of Kpone, but other sources.

FIGURE 1-1: PM_{10} CONCENTRATION IN AMBIENT AIR AT SOME ROADSIDES IN ACCRA

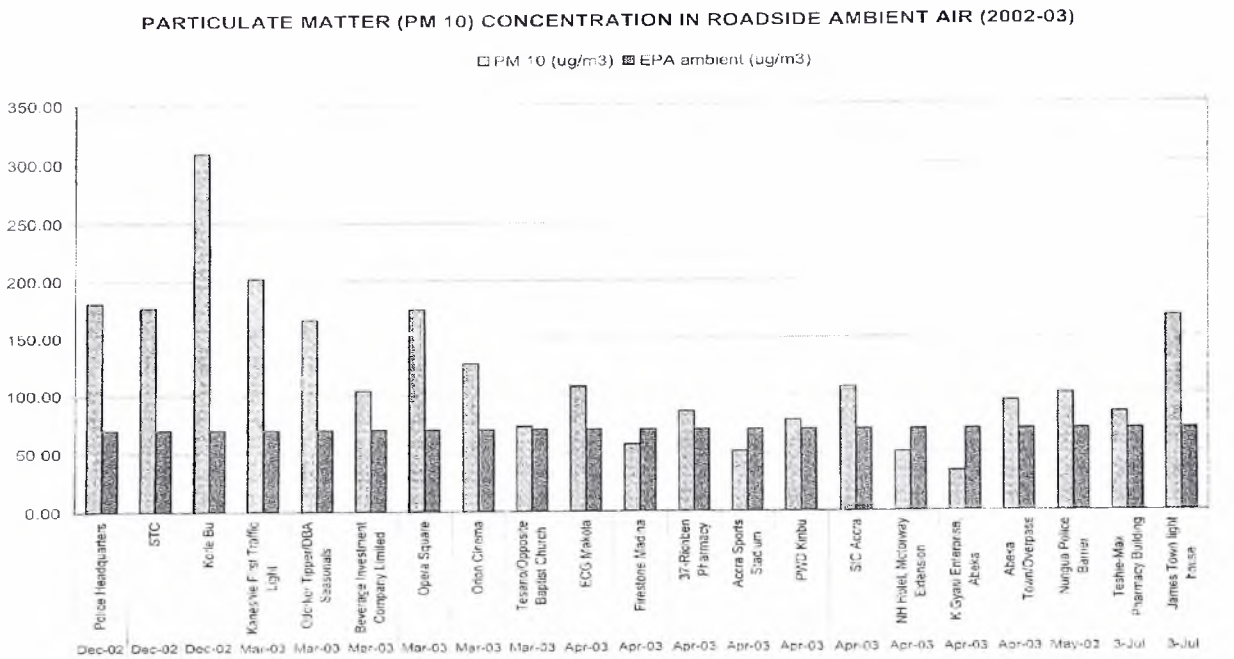


FIGURE 1-2 : AMBIENT NO_X CONCENTRATION(ppm)

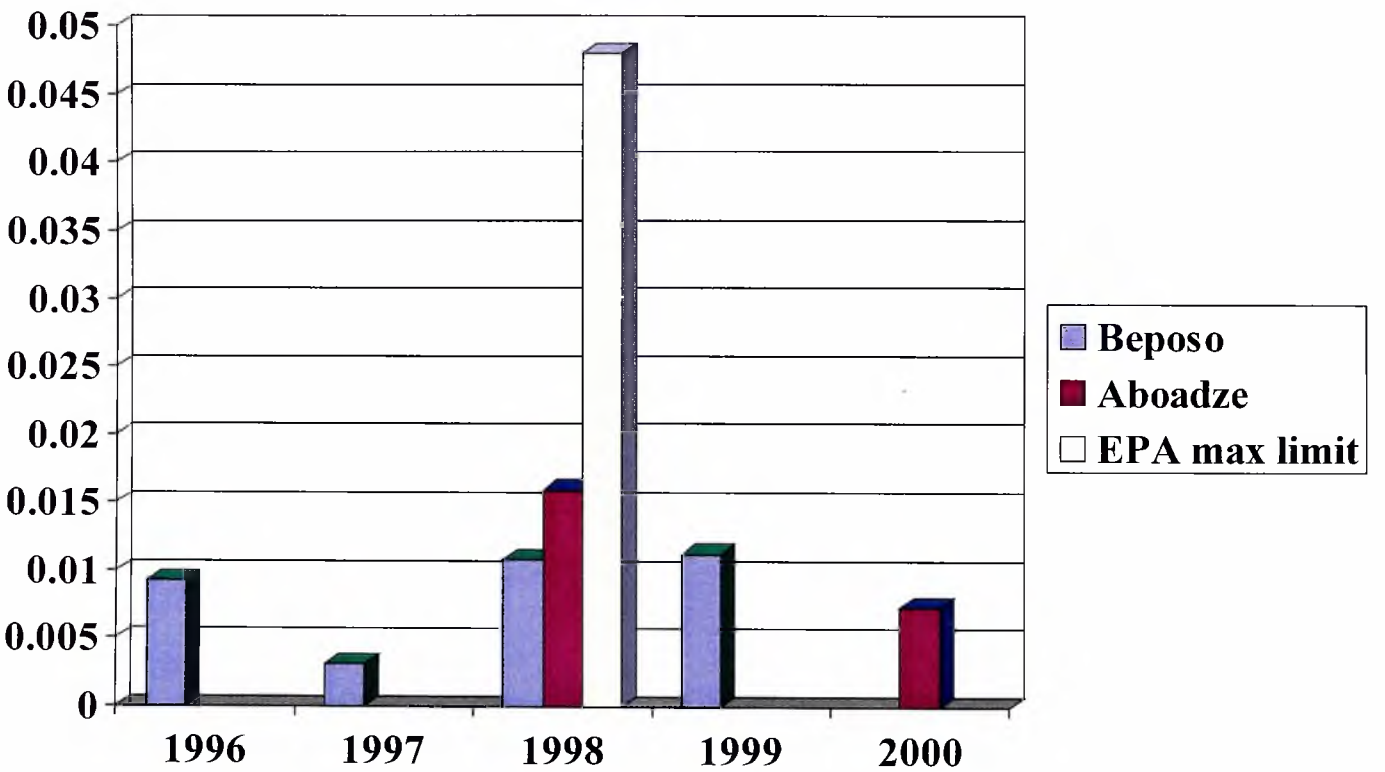


FIGURE 1-3: AMBIENT SO_2 CONCENTRATION (PPM)

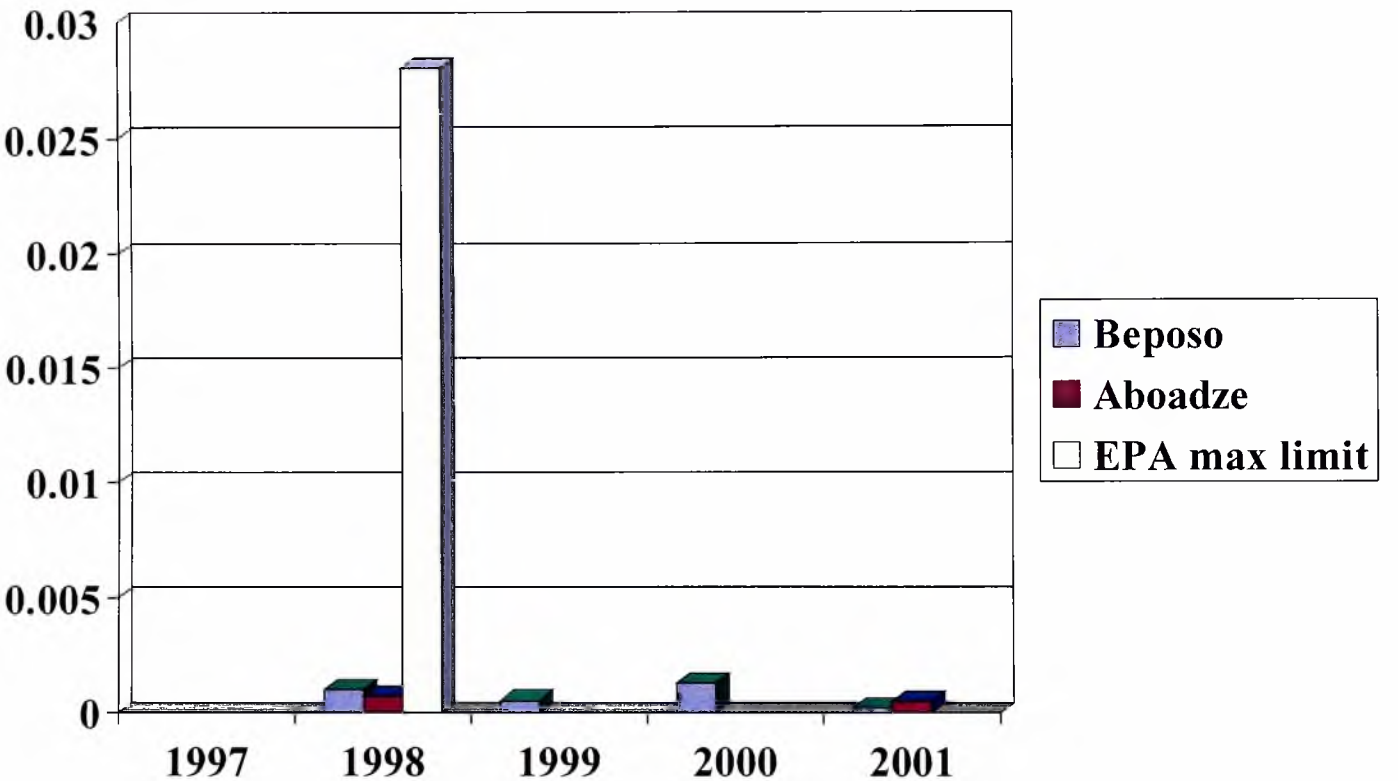


TABLE 1-1: MEAN CONCENTRATIONS OF ELEMENTS IN THE TWO LICHEN SPECIES

	Mean Value (µg/g)				
Element	**Obuasi**	**Prestea**	**Tema/Doryim**	**Samreboi**	**Akim Tafo**
Al	17260	7510	8010	1350	2070
As	110	73.2	0.8	1.84	0.8
Ba	650	110	156	204	190
Br	8.2	5.7	10.4	5.6	5.2
Ca	6860	14380	17190	26090	21640
Ce	9.6	3.2	10.4	0.5	2.6
Co	4.6	3.5	4.4	3.9	5.0
Cr	68.9	19.7	28.6	6.3	4.3
Cl	390	461	592	390	303
Dy	1.2	0.8	0.8	0.7	-
Fe	18730	4410	7530	1340	1150
Ga	66.6	45.0	-	-	-
Hf	2.0	0.8	2.4	0.3	1.1
Hg	1.5	6.1	-	0.9	2.2
I	305	13.2	19.0	4.5	8.6
K	3926	4750	3840	2800	3740
La	5.5	2.3	5.8	2.0	1.5
Mg	5750	6000	4780	5230	6025
Mn	106	198	275	440	635
Na	1960	1248	765	360	170
Rb	15.1	13.7	13.7	8.1	11.3
Sb	4.5	1.9	0.7	0.1	0.4
Sc	3.4	1.5	1.8	0.8	0.4
Sm	1.1	0.4	1.1	0.1	0.2
Th	1.6	0.6	1.2	0.2	0.4
Ti	2270	715	1187	235	222
U	0.8	0.2	-	-	-
V	42.3	12.6	18.5	1.9	1.9
W	3.9	1.9	-	-	-
Zn	157	118	115	112	62

FIGURE 1-4: PIXE SPECTRA OF SOME SELECTED AEROSOL-LOADED FILTER SAMPLE

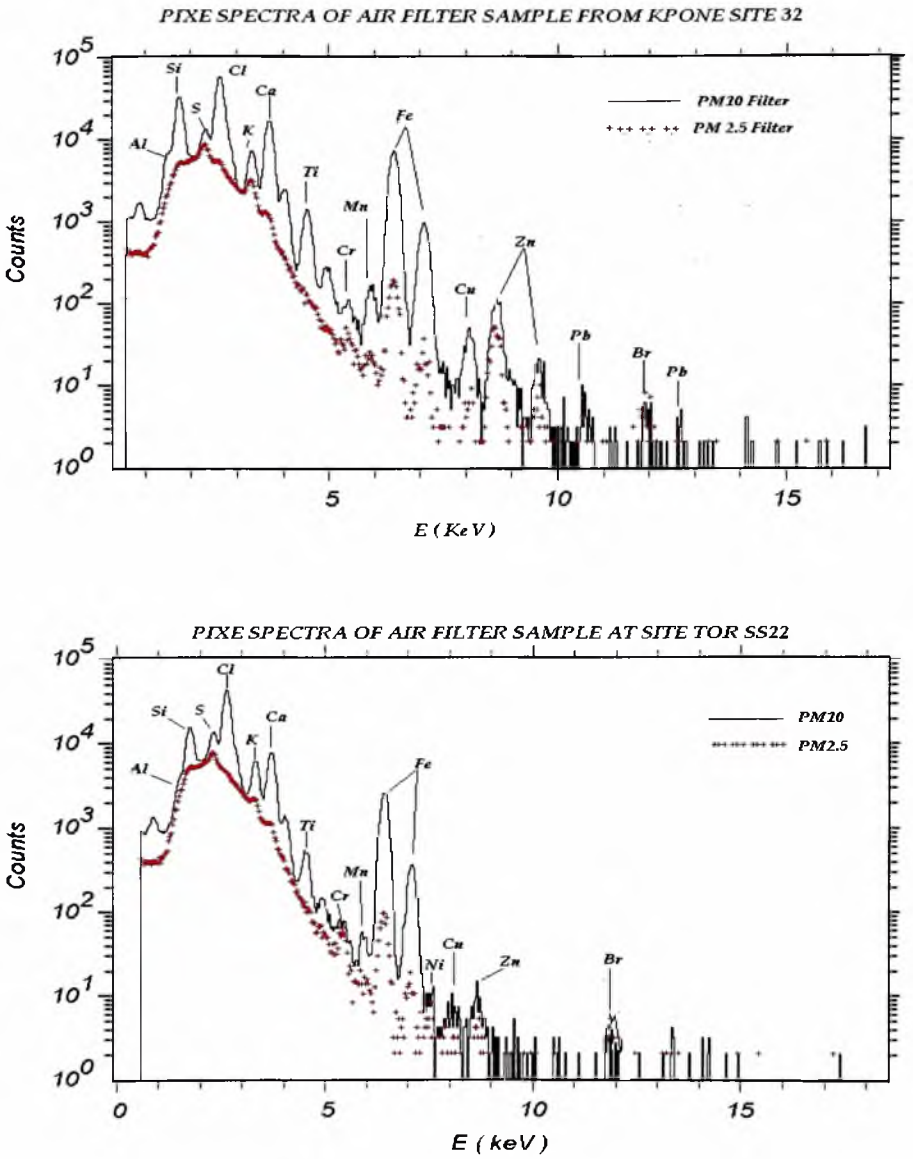


TABLE 1-2: AVERAGE CONCENTRATION OF ELEMENTS IN AIR PARTICULATE MATTER AT KPONE AND TEMA OIL REFINERY IN GHANA

	KPONE		Tema Oil Refinery	
	PM10	PM2.5	PM10	PM2.5
Element	(ng/cm^2)		(ng/cm^2)	
Al	1541	464	434	2171
Si	2913	512	977	5669
P	111	351	88	107
S	416	466	313	470
Cl	2482	231	1384	3242
K	323	171	488	541
Ca	974	54	351	1424
Ti	121	-	51	168
Cr	6	5	8	-
Mn	24	6	14	28
Fe	1919	58	696	2239
Ni	-	-	8	-
Cu	205	2	46	-
Zn	84	47	124	16
Br	-	18	-	-

1.2.4 CHALLENGES

A great deal of research and studies have been carried out on soil, water and vegetation pollution studies in Ghana. Air pollution however has had little attention and is only now being looked at as a result of the shift from hydro power generation (95% in 1997 to 45% in 2003). As the country begins to industrialize on a large scale, it is in a unique position to implement regulations and thus avoid many of the problems that have occurred in the northern hemisphere.

Current activities are mostly based on gravimetric analysis for TSP, very little of elemental characterization, and virtually no post data evaluation (source identification or source apportionment). Very little data available on background levels due

particularly to lack of access to mains supply for powering the samplers in rural "unpolluted" areas. Use of petrol-driven generators introduces additional on-site pollution that is sometimes picked up when wind direction changes. This has also contributed to data generated so far not put to optimum use.

The current national capacity to monitor and enforce environmental standards, particularly in air quality standard, is rather weak. This is due essentially to inadequate number of well-trained personnel in atmospheric sciences, and lack of appropriate equipment for monitoring and assessment.

It will be more appropriate for proper studies to be carried out at this time when Ghana has switched from leaded petrol to unleaded petrol (from January 2004). Currently, non-vehicular air pollution levels are low in most parts of the country, except in the mining areas, and much can be done to control the situation. With the expected growth of industries and human population in the future, the conditions will be so critical that a substantial portion of the national budget will be required to fight and control air pollution effects.

1.3 OBJECTIVE OF THE THESIS

Despite the measures taken to address these serious environmental challenges, there exist gaps regarding adequate baseline data upon which impact can be assessed. These gaps which are very pronounced due to lack of scientific data in air quality in the country can only be filled by field measurements, laboratory analysis and air pollution modelling. Secondly, the data generated would also assist the industries and the regulatory authorities to take the necessary action, to repair or forestall any pollution threat by their operations.

1.3.1 GENERAL OBJECTIVE

The overall objective of the thesis is to carry out research and monitor the relevant variables used to describe air quality, with a view to establishing a baseline data upon which impact may occur. It also seeks to establish the origin and characteristics of size-segregated aerosols for $PM_{2.5}$ (fine) and $PM_{10-2.5}$ (coarse) over Kwabenya, near Accra with special emphasis placed on the influence of major sources like traffic emissions, bush fires and biomass burning, soil, sea spray and major industrial emissions. This will be assessed by a combination of field measurements, chemical/physical analysis using mainly nuclear analytical techniques, and receptor modelling.

1.3.2 SPECIFIC OBJECTIVES

The Specific objectives are:

- To establish mass concentrations of $PM_{2.5}$, $PM_{10-2.5}$ and PM_{10} over Kswabenya, near Accra.
- To analyse heavy metals and other elements in the particulate matter using EDXRF and other methods for chemical characterisation of the aerosol, e.g. black carbon.
- To establish source signatures and relate variations in particle concentrations to the influence of strong sources
- To determine anthropogenic (man made) and natural contributions to air quality over Kwabenya
- To relate particle concentrations to available climatic parameters (temperature, wind direction and speed, humidity/rainfall and air pressure)
- To model atmospheric pollution (receptor model) using data generated.

CHAPTER 2

AEROSOL PARTICLES AND SAMPLING INSTRUMENTS

2.1. PARTICLE FORMATION

One of the most important physical parameters in the analysis of aerosol particles is the particle size. The others are particle shape and density. Many aerosol particle properties depend on the size, since it influences the transportation, deposition and migration of the aerosol through the environment. Whereas coarse particles result mainly from mechanical processes, fine particles are formed mainly by chemical reactions and by the coagulation of even smaller species including molecules in the vapour state.

While small liquid particles and some solid particles formed by condensation are almost always spherical, most solid aerosol particles usually have complex shapes.[1] For example, soil particles may be flaky and metallurgical fume may be aggregate chains formed from condensed droplets. They have varying densities, hence for comparison to be made between air particulates in aerosol studies the concept of an "equivalent diameter" is used. This is the diameter of the sphere that would have the same value of a particular property as that of an irregular shaped particle. The most commonly used equivalent diameter is the aerodynamic diameter, defined as the diameter of a sphere of unit density ($1 g/cm^3$) which has the same terminal settling velocity in air as the particle under consideration.[1,91]

For this work, unless otherwise stated, the diameter refers to the aerodynamic diameter. Airborne particles cover a wide size range (**Fig. 2-1**). Hence atmospheric aerosol particles size distribution varies from place to place depending on the sources emitting them and the meteorological parameters prevailing at that place. However,

the most important aerosol particles which have serious health, climatic and environmental effects are those smaller than 10μm in diameter.[91,92]

Aerosol particles once in the atmosphere can have their size, number and chemical composition changed by several mechanisms until they are ultimately removed from the atmosphere. The atmospheric aerosol size distribution is normally multi-modal in shape reflecting the different formation mechanisms of primary and secondary (formed through gas-to-particle conversion processes) aerosol and have a wide size range.[94] There are three different types of particle size distributions, namely - number, diameter and mass. Normally, fresh particle size distribution shows at least three groups of particles. These are nucleation mode, accumulation mode and coarse mode (**Fig. 2-2**). Their respective mass median aerodynamic diameter (MMAD) size distributions are: <0.1 μm, 0.1-2 μm and >2 μm. In general, the nucleation and accumulation mode particles constitute the fine particles and there is comparatively little mass exchange between the fine and coarse particle modes, hence they exist together in the atmosphere as two chemically distinct aerosols. They have different chemical compositions, sources and lifetime in the atmosphere.

2.1.1 NUCLEATION MODE PARTICLES

Nuclei mode (also known as Aitken mode) particles, are particles with a mass median aerodynamic diameter less than 0.1 micrometer (MMAD <0.1 μm). These are formed by the condensation of hot vapours from combustion processes and by nucleation processes in the atmosphere.[10,96] Studies of atmospheric Aitken particles suggest that carbon (C) and sulphur (S) are the main components, with a mass ratio of C/S of approximately 3:1. This links the formation of this mode of particles mainly to the cycles of S and hydrocarbons.[97] When a vapour becomes increasingly supersaturated,

molecules accumulate into clusters (embryo); formed due to the attractive Van der Waals' forces without the assistance of condensation nuclei or ions.[98] This type of nucleation is known as homogeneous nucleation or self-nucleation.

The formation of new particles via homogeneous nucleation, though rare, is commonly believed to happen in relatively clean environment, where the condensation of nucleating species onto pre-existing aerosol particles is highly inefficient.[99] But this is not a limiting factor, since significant production of H_2SO_4-H_2O particles is also possible in more polluted air, but it requires both cool and humid conditions combined with relatively high concentration of sulfuric acid vapour. When a vapour becomes increasingly supersaturated, leading to continuous formation of molecular clusters, these clusters are unstable and continuously disintegrate. In super saturated vapour, the cluster concentration increases to the point where they collide with one another frequently in a process similar to coagulation except that here the "agglomerates" disintegrate immediately they are formed.

In photochemical smog, certain gas phase reactions are promoted by ultraviolet light and form low-vapour-pressure reaction products. These products exist at high super-saturation, because of their low vapour pressure, and can form particles by homogeneous nucleation. The homogeneous nucleation rate increases with the following:

i. decreasing ambient temperature
ii. higher relative humidity
iii. decreasing surface tension, and
iv. lower equilibrium vapour pressure of the nucleating species (or gases).

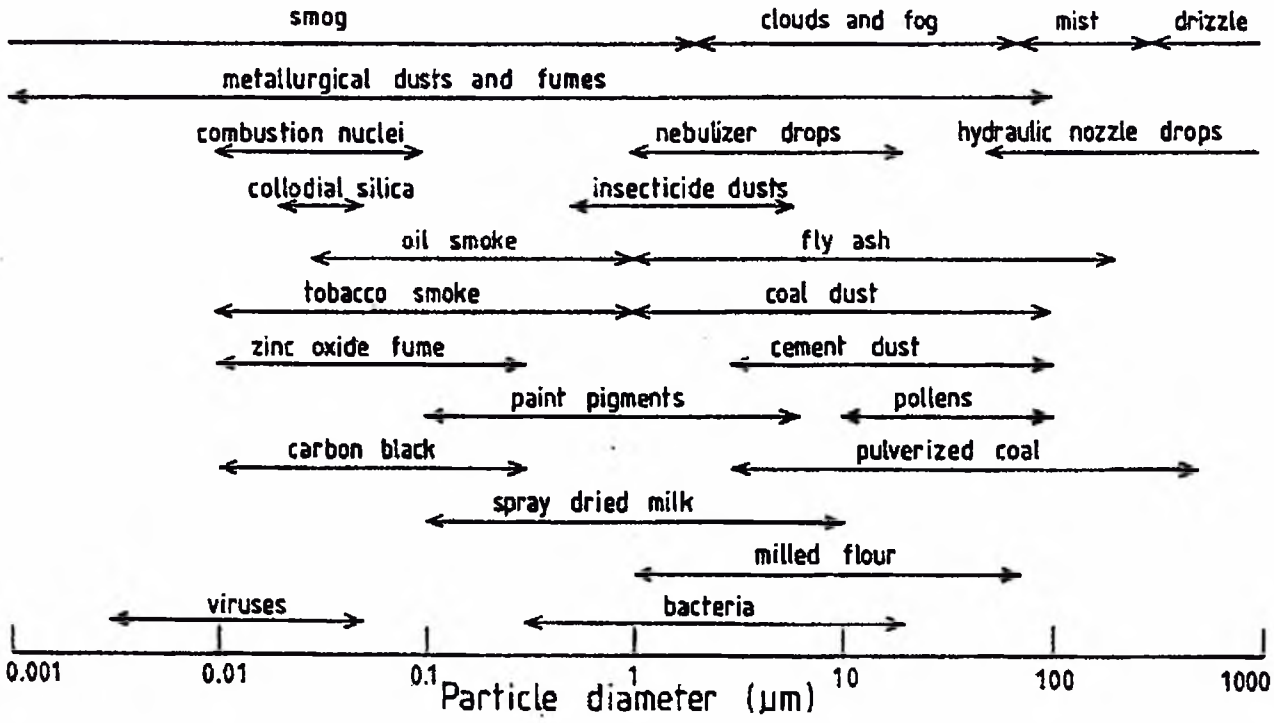


FIGURE 2-1: SIZE RANGE OF AEROSOL PARTICLES (FROM COLBECK[2])

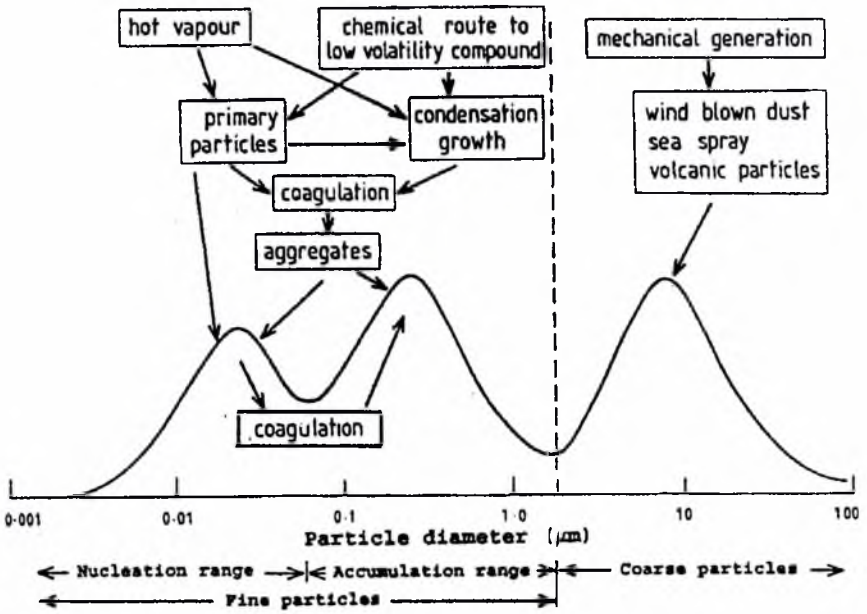


FIGURE 2-2: IDEALISED TRIMODAL SIZE DISTRIBUTION OF FRESH PARTICLES, SHOWING GENERAL RELATIONSHIPS BETWEEN THE THREE COMMON SIZE RANGES AND THEIR FORMATION MECHANISMS IN THE ATMOSPHERE. (FROM COLLS[95] WITH SLIGHT MODIFICATIONS)

In contrast, heterogeneous nucleation occurs in areas where other nuclei, particles or ions from pre-existing aerosol, are present. Here the process of particle formation (nucleation) is complemented by heterogeneous condensation on other nuclei (particles or ions) present in the condensable vapour system. The best known example of this is the formation of cloud droplets by water condensation onto hygroscopic aerosol particles (Cloud Condensation Nuclei (CCN)). In the atmosphere the following are the major components of fine particles: sulphates, nitrates and carbonaceous compounds, indicating that the fine particle material is mainly derived from atmospheric chemical reactions. The precursors which aid the formation of these components of the fine particles are SO_2 and other S-containing gases, NO_x and other N-containing gases and organic vapours. The fine particles formed by gas-to-particle

conversion (GPC) are known as secondary aerosols.[8,100] In the presence of solar radiation GPC is highly enhanced. Although some directly emitted particles are found in the fine particle mode, secondary particles formed from gases dominate the fine particle mass.

2.1.2. ACCUMULATION MODE PARTICLES

Accumulation mode particles, with an MMAD in the range 0.1 – 1 μm, are formed from coagulation of nuclei mode particles, because of their small size and high concentration especially near the source. Hence nuclei mode particles have relatively short lifetime. As the name suggests, particles accumulate in this mode because the removal mechanisms for the nuclei mode particles are weak. The particles in the accumulation mode also coagulate too slowly to reach the coarse-particle mode where they can be removed by sedimentation. They can however be removed by rainout or washout. It has been found that carbonaceous particles exist mainly in the accumulation mode.[101] Accumulation mode particles typically (though not generally true in all cases) have longer atmospheric life time (i.e. days to weeks) than coarse mode particles, and tend to be rather uniformly dispersed across an urban area or large geographical regions. The size range of the accumulation mode includes the wavelengths of visible light, and these particles account for most of the visibility effects of atmospheric aerosol.

Fog and cloud droplets play an important role in the accumulation mode formation processes and under conditions of high humidity, there exist two sub-modes: a condensation mode with MMAD of 0.2 – 0.3μm and a droplet mode with MMAD of 0.5 – 0.8μm. The droplets are formed by the growth of hygroscopic condensation-mode particles. This process may be facilitated by chemical reactions in the droplet.

2.1.3 COARSE MODE PARTICLES

Coarse mode aerosol particles originate chiefly from the disintegration of larger pieces of matter. Mineral pollutants constitute one source of coarse particulates in air and many of the large particles in atmospheric dust, particularly in rural areas, originate as soil or rock and consequently their elemental concentrations of Al, Ca, Si and O are similar to the earth crust. Sources of large coarse particles include natural ones such as sand storms, large salt particles from sea spray and human activities such as from agriculture, surface mining, stone grinding and crushing in quarries. Human activities result in particles of the topsoil and rocks being picked up by the wind. The particles readily settle out or impact on surfaces, because of their large size. Hence their lifetime in the atmosphere is only a few hours or days depending on the prevailing meteorological conditions.

2.2 PARTICLE TRANSPORT

In between emission and removal, aerosol particles are transported in the atmosphere. The source-transport-sink sequence determines the residence (life) time of the particle in the atmosphere. This motion of particles in air is dependent on the aerodynamic diameter of the particles.[102]

2.2.1 RESIDENCE TIME

Particles at the smaller end of the size range undergo a continuous change in size and composition and are constantly loosing their entity. Nucleation mode particles have residence time less than one day because they undergo rapid coagulation. Particles larger than 10μm diameter are efficiently scavenged by sedimentation and washout. Intermediate-size particles are mainly incorporated into cloud droplet. For this type of particles a great difference between residence time and altitude is observed. In the lower troposphere the residence time is about a week and in the stratosphere the order

of months to even years.[98] Due to the absence of clouds in the stratosphere the removal by precipitation is not possible.

2.2.2 PARTICLE MOTION

In steady conditions the motion of aerosol particle is typically a result of the action of two forces, a constant external force such as gravity and the resistance of the gas to particle motion. For example in still air, a particle undergoing gravitational settling can be shown to be settling with a velocity proportional to the square of the diameter. Hence gravitational settling is very important for large or coarse particles. Due to this rapid depletion by gravitational sedimentation, coarse particles (and particles larger than 10μm) are mainly present in the atmosphere close to their sources.[2]

One parameter that is very useful for the analysis of complex particle motion is the particle relaxation time (τ). The relaxation time is proportional to the square of the diameter and inversely proportional to the viscosity of the gaseous medium.[1,101] It characterizes the time required for a particle to adjust or "relax" its velocity to new conditions in the atmosphere. The relaxation time is analogous to the characteristic acceleration for a car, such as the "0 to 100" (km/h) time. It depends on the mass and mobility of the particle and is not affected by the nature and magnitude of the external forces acting on it. Hence large particles have long (large) relaxation times.

A particle injected into a moving gas with an initial velocity υ_{x0} relative to the gas, in the absence of external force, would be progressively pulled by resistance force exerted by the gas medium until the particle has the same velocity as the medium. The distance traveled by the particle relative to the gas medium before it catches up with the flow is known as the particle stopping distance, S or inertial range. The stopping

distance, S_x, is related to the relaxation time,τ, and the particle initial velocity relative to the gas by

$$s_x = v_{x0}\tau \qquad \ldots 2.1$$

On a displacement scale, the stopping distance represents a measure of a particle's effective initial momentum, which is diminished to zero by air friction over a distance equal to the stopping distance.

Relaxation time τ = mB, where m is the particle mass and B is the particle mobility, hence the stopping distance can be expressed in terms of particle mobility and its initial momentum by

$$s_x = Bmv_{x0} \qquad \ldots 2.2$$

The stopping distance represents the distance a particle will travel in still air if an external force acting on the particle were turned off. It is very important when considering how particles behave within moving air that is changing direction, e.g. when a particle moves in an airstream that is abruptly turned 90°. **Eqn. 2.1** shows that, for the same initial velocity, a larger particle will have a larger stopping distance. The velocity of the air and the size of the particle influences the stopping distance in changing wind direction, and would determine whether the particle remains airborne (follow the airstream) or not (exit the airstream trajectory). As illustrated in **Fig. 2-3**, larger particles and particles with higher air velocity are not able to follow the movement of airstream as it changes direction. Hence they are removed from the airstream.

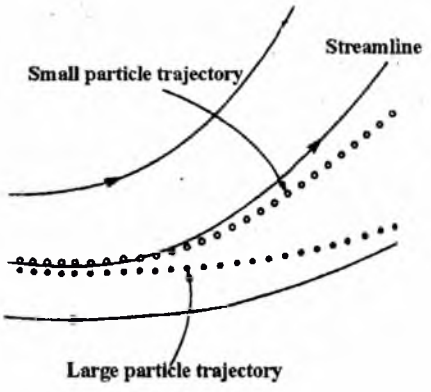


FIGURE 2-3: DIAGRAM ILLUSTRATING THE CONCEPT OF PARTICLE INERTIA (FROM MARK[102] WITH SLIGHT MODIFICATIONS)

2.3. PARTICLE DEPOSITION MECHANISMS

Atmospheric aerosols are complex with respect to particle size, shape, chemical composition, concentration, etc. Once the aerosol particles are emitted into the atmosphere, their size distribution is modified by physical and chemical mechanisms. Dry and wet removal are such physical mechanisms. Coagulation, caused by Brownian motion of particles, or by external forces acting between particles, is another. Condensation and evaporation processes change both the size and the composition of the particles depending on the local temperature and relative humidity. Heterogeneous chemical reactions on and inside aerosol particles result primarily in changes of the chemical composition and may lead to change in particle size. Coagulation, condensation/evaporation and heterogeneous reactions are not considered as deposition mechanisms since they mainly remove particles from certain size ranges to others. This could however aid the deposition mechanisms as the particle size grows (as the particle size becomes larger).

Aerosol particles emitted into the atmosphere are ultimately removed from the atmosphere by deposition onto some surfaces. Surfaces like buildings, water, human body and respiratory system, soil and vegetation are some examples. A mass flux from the atmosphere to the earth's surface occurs by two processes: dry deposition and wet deposition. These processes transfer pollutants to the ecosystem and are responsible for the many negative environmental effects.

2.3.1. DRY DEPOSITION

Dry deposition is defined as the continuous transport of particulate and gaseous matter from the atmosphere directly onto surfaces, not associated with precipitation. The mechanisms involved are:

1. Gravitational settling (of predominantly coarse particles) – this is the process by which the particles are transported to a surface by the force of gravity, all particles are subjected to this process but in varying degree due to their mass.
2. Turbulent exchange of (predominantly) fine particles and gases to the surface.
3. Diffusion – particles are deposited on a surface after being brought in contact with the surface by Brownian diffusion. Since Brownian diffusion increases with decreasing size, deposition by diffusion is mainly important for gases and sub-micron particles.[103]
4. Interception – this takes place when a particle, following the streamlines of a flow around an obstacle, is of a size sufficiently large such that its surface and that of the obstacle come into contact (geometricical effect of large particles).
5. Inertial Impaction – this takes place when a particle because of its inertia, is unable to adjust to the abruptly changing streamlines near an object.

6. Biological mechanisms – biological cell/organism can attract and absorb onto their surfaces some particulates and gases. For example, gases can be transferred to surfaces of vegetation through stomata and leaf cuticles.

Though all the mechanism listed above play an important role in dry deposition, the most important mechanisms are sedimentation, impaction, interception and diffusion. Diffusion is an important removal mechanism for nucleation mode particles while inertial impaction, interception, and gravitational settling are important removal mechanisms for coarse mode particles. These removal mechanisms are least efficient for accumulation mode particles, thus the particles are caused to accumulate in this mode, hence the name.[104]

The factors that govern dry deposition are the airborne concentrations, the atmospheric movements and the ability of the underlying surface to absorb and/or capture the species that come in contact with it. For trace gases the uptake at the surface is dependent on the reactivity and solubility of the species and the type of surface. Generally, the nature of the surface does not have a strong influence on the dry deposition flux of coarse particles but is more complex for fine particles.

Dry deposition has a strong diurnal cycle, because the mechanisms involved are meteorological and sometimes biological. The dry deposition of fine particles (and gases) is more significant during the daytime because it is mainly controlled by turbulent exchange (with the surface) which is more efficient during the day.

2.3.2 WET DEPOSITION

Wet deposition is the process by which particles and gases are removed from the atmosphere and are subsequently delivered to the earth's surface during precipitation

events. It involves uptake into the cloud droplets (rainout) and uptake into precipitation elements (washout). It is important to note that only rainout leading to subsequent precipitation is regarded as wet deposition. Most of the uptake into clouds do not produce wet deposition, since most of the cloud never precipitate. Wet deposition is not receptor surface dependent.

There are many mechanisms that contribute to wet deposition, among these are the capture of small particles by cloud droplets (coalescence) and water condensation onto particles (nucleation scavenging). If the particles contain water soluble salts, their ability to form droplet is enhanced. In the washout process, only a fraction of the particles in the path of a falling rain drop will collide with it. The remainder, and particularly the fine particles, may be swept in the streamline around the rain drop. For this reason large particles are known to be more efficiently removed than small particles.

2.4. AEROSOL SAMPLING INSTRUMENTS

2.4.1. GENERAL CONSIDERATIONS

The choice of an aerosol sampling instrument depends on the substance to be measured, the properties it has, and the information to be gained from the measured values. Measurements can be carried out where the particles are formed to determine emissions or at receptor location to determine air quality (**Fig. 2-4**). The primary aim of measurements is to determine concentrations of air pollutants but the mass flow rates are also very important to determine the dilution effect of the emissions.

The main aim of all aerosol sampling is to collect representative samples for analysis. These samples must accurately reflect the airborne particles in both concentration and size distribution. Isokinetic sampling is a procedure to ensure that a representative

sample of aerosol enters the inlet of a sampling tube when sampling from a moving aerosol stream. Sampling is said to be isokenetic when the inlet axis of the sampler, is aligned parallel to the gas streamlines and the gas velocity (U) entering the probe head is equal to the free-stream velocity (U_0)approaching the inlet (**Fig. 2-5**). In this type of scenario there is no particle loss at the inlet, regardless of particle size or inertia. But there is no guarantee that there will not be particle loss between inlet and the collector (e.g. filter), it guarantees only the concentration and size distribution of the aerosol entering the tube is the same as that in the flowing stream.

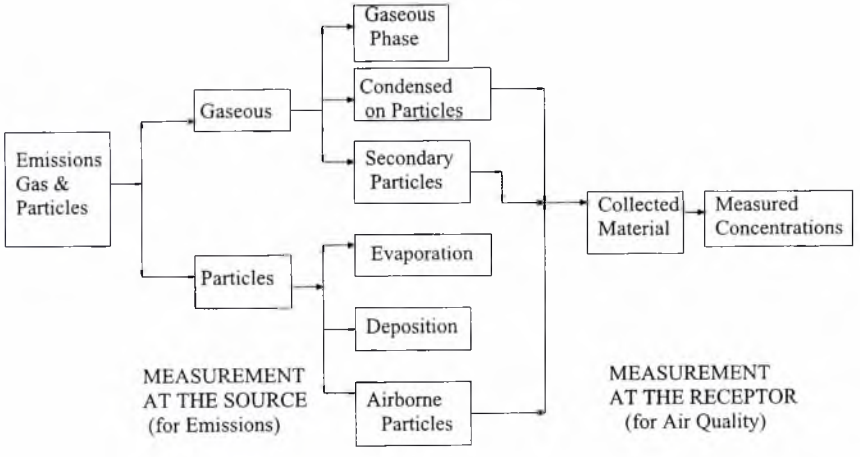


FIGURE 2-4: SCHEMATIC DIAGRAM OUTLINING EMISSION, TRANSPORT, TRANSFORMATION AND SAMPLING OF AIRBORNE POLLUTANTS

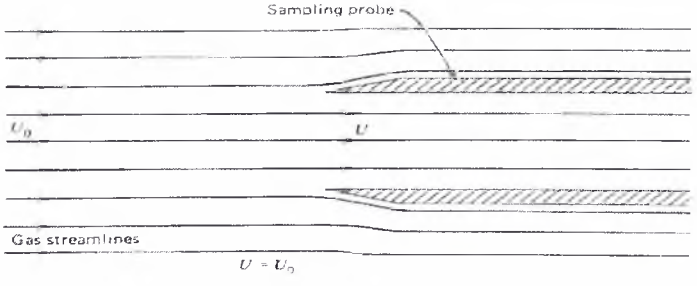


FIGURE 2-5 – ISOKINETIC SAMPLING (FROM HINDS[1])

Anisokinetic sampling is a failure to sample isokinetically, and may result in the distortion of particle size distribution and a biased estimate of the concentration. These effects arise because of particle inertia in the region of curved streamlines near the inlet. The sample may contain excess or deficiency of large particles depending on the conditions.

Fig. 2-6 below shows the three possible scenarios of anisokinetic sampling. In **Fig. 2-6(a)** the probe is not aligned to the gas flow streamlines; here the concentration will be underestimated because most of the heavy particles would be lost because of inertia. In **Fig. 2-6(b)** the velocity in the probe exceeds the stream velocity, this is known as superisokinetic sampling, here some particles with high inertia in the volume sampled cannot follow the converging streamlines to enter the probe and are lost from the sample. Thus the concentration would be underestimated. In **Fig 2-6(c)**, the stream velocity exceeds the velocity in the probe, subisokinetic sampling. Here some heavy particles which were not initially in the flow will enter because of the slow velocity in the probe hence the concentration would be over-estimated.

In aerosol sampling technology it is very important to distinguish between integrated (discontinuous) and continuous measuring methods. The continuous sampling instruments measure the temporal profile of the measured quantity. Integrated or discontinuous sampling instruments provide the measured quantities as a mean value over a sampling period. It is advisable therefore that in the use of integrated sampling instruments to have some knowledge of the profile of the air pollutants to be measured. This would lead to setting of sensible sampling periods.

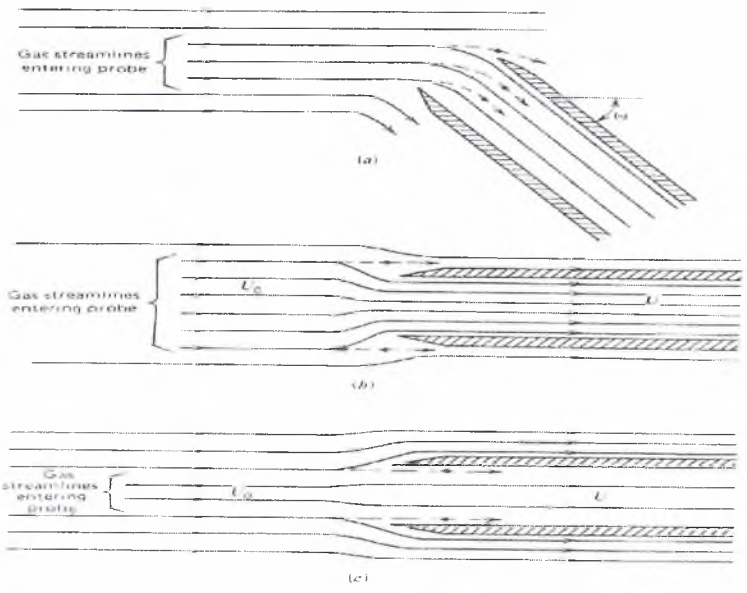


FIGURE 2-6 – ANISOKINETIC SAMPLING (FROM HINDS[1]),
(a) MISALIGNMENT
(b) SUPERISOKINETIC SAMPLING, $U>U_0$,
(c) SUBISOKINETIC SAMPLING, $U<U_0$

Aerosol sampling instruments often require the drawing of ambient air through some type of filter material. This is achieved using a pump or a known volume of ambient air is pulled through a filter so as to collect the particles on the filter. The filter is then removed and taken to the laboratory to determine the gain in the filter mass due to particle collection. Ambient PM is calculated on the basis of the gain in filter mass, divided by the product of sampling period and sampling flowrate. Using appropriate analytical techniques, its chemical components can also be determined. The ambient air stream is processed on its way to the filter so that only particles of some predetermined aerodynamic characteristics are allowed to reach the filter. This is one of the most highly developed measurement principles that apply to the quantification of the wide variety of chemical components in suspended particles.[92,105] When the filter is impregnated with an absorbing solution, or when the filter material has

specific gas-absorbing properties, quantitative measures of gases as a well as particle phases are possible.[3] The filter characteristics will govern the efficiency of particle collection. The chemical analysis to be done on the filter cannot be separated from the filter material used and the methods used to obtain the samples. Different methods are available to fractionate the sample stream on the basis of particle size.[92] They include direct impaction, virtual impaction and cyclonic flow.

2.4.2. INTEGRATED (DISCONTINUOUS) SAMPLING INSTRUMENTS

2.4.2.1. IMPACTORS

Impaction is one of the removal modes that is extensively applied in collection and measurement of aerosol particles. It has been thoroughly analysed, both experimentally and theoretically.[1] It was first used in the early fifties for collecting dust for the evaluation of the occupational environment.

All inertial impactors operate on basically the same principle, i.e. an aerosol is passed through a nozzle and the output airstream directed against a flat plate (**Fig. 2-7**). The plate called an impaction plate deflects the flow to form an abrupt 90° bend in the streamlines. Particles whose inertia exceeds a certain value are unable to follow the streamlines and impact (collide) on the flat plate. The smaller particles, with lower inertia, continue to follow the streamlines and avoid the impaction plates. They therefore remain airborne and flow out of the impactor. Hence the impactor separates aerosol particles into two size ranges; particles larger than a certain aerodynamic size are removed from the air stream, and those smaller than that size remain airborne and pass through the impactor.

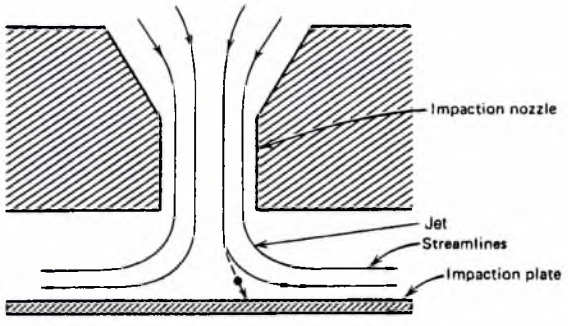


FIGURE 2-7: CROSS-SECTIONAL VIEW OF AN IMPACTOR (FROM HINDS[1])

Dichotomous Virtual Impactor

The dichotomous virtual impactor is based on the principle of inertial impaction. It is called "virtual" because the impaction plate is replaced by a collector probe so as to prevent the particles from bouncing off and overloading of the collectors. Here aerosol particles below a specified aerodynamic diameter are drawn through a size-selective inlet and accelerated through an impactor nozzle (**Fig. 2-8**). After passing through the nozzle, the airflow is divided into minor flow and major flow. The large particles have sufficient inertia that when the airstream in which they are being transported is rapidly forced to change direction, the particles will separate from the airstream. The separated particles impact on a "virtual impaction surface". They are then carried by the minor flow onto a filter at the surface. This creates the divergence of the flow. The smaller particles move with the diverted stream. These are carried radially away from the jet axis by the major air flow. The separation is not caused by the interaction of the collected particles with the impaction surface. The separated particle streams are available for collection by standard filter media. In most cases, the cut-off between the large and small particles is such that the particles are divided into coarse and fine particles.

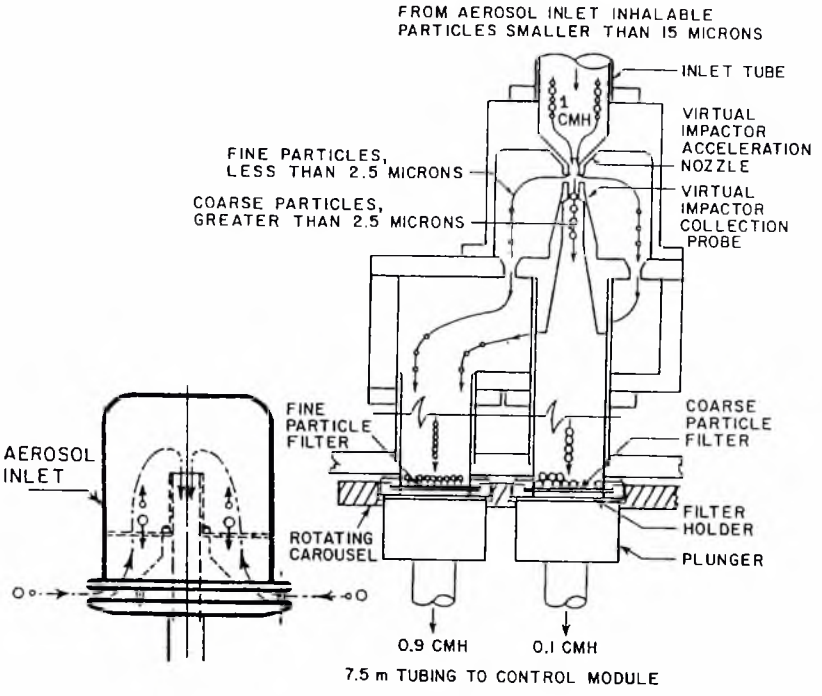


FIGURE 2-8: DICHOTOMOUS PARTICLE SAMPLER FOR SEPARATING AIRBORNE PARTICULATE MATTER INTO TWO SIZE FRACTIONS (FROM IAEA[107])

The initial problems of the inlet size cut-off being dependent on wind speed[106] and the failure of nozzle concentricity leading to loss of large particles (> 3μm)[107] have been resolved. Improvements have been made in the design of new inlets to improve the separation and also address the wind dependency of the previous design.[108]

Cascade Impactors

This is also based on the principle of impaction like the dichotomous virtual impactors. However, here the virtual impactors are replaced by a series of real impaction surfaces and there is only one air flow stream through all the impaction surfaces making it look like operating a number of impactors in series. The concept of the cascade impactor is shown in **Fig. 2-9**. The impactor is designed so that the airstream carrying the entrained aerosol particles are forced to change direction

rapidly. The particles with mass and/or velocity above a certain threshold would detach from the streamline and impact on the collection surface.

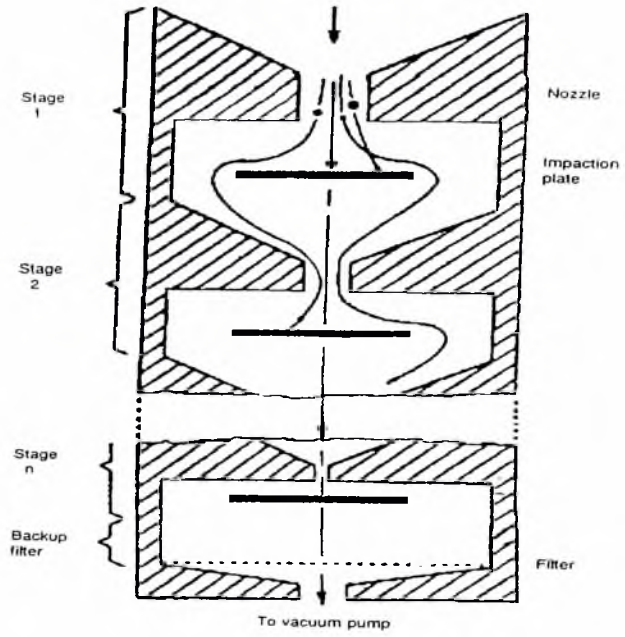


FIGURE 2-9 – A SCHEMATIC DIAGRAM OF A CASCADE IMPACTOR

The impactor plates are arranged in order of decreasing cut-off size with the largest cut-off size impactor at the top and each separate impactor is referred to as an impactor stage. To achieve the different cut-offs with the same flow through all the stages, the nozzle size is decreased at each stage. By the principle of continuity of flow, decreasing the nozzle size while the flow rate is constant results in an increase in the flow velocity through the nozzle. The increase in the flow velocity results in a lower cut-off diameter.

With the casacade impactor it is possible to obtain detailed information on the size distribution of the airborne particles and their constituents. There has been considerable use of cascade impactors that provide multiple samples in various size ranges with particles collected in each stage of the impactor.[107] Although usually only

small amounts of mass are collected because of the large number of stages, the samples are suitable for instrumental analysis such as NAA and EDXRF. The samplers can be single or multiple jet devices that collect air over a wide range of flow rates.

One major practical difficulty with impactors is the bounce of particles after collision with the collector surface. It is therefore necessary to exert care and effort towards minimizing the problems reviewed by some researchers in order to yield proper size-segregated samples.[109] Coatings have often been applied to lower bounce in conventional multistage impactor.[110]

2.4.2.2. CYCLONES

The cyclone also known as cyclone collector or cyclone separator has been in use over 100 years and is still one of the most widely used of all the industrial gas-cleaning devices. The main reason is that it is inexpensive, have no moving parts and it can be constructed to withstand very harsh operating conditions depending on the material used in the construction.[111-115] Typically, an aerosol enters tangentially near the top (**Fig. 2-10**) and is forced into a downward spiral simply because of the cyclone's shape and the tangential entry. Cyclones use inertia to remove particles from the aerosol. The cyclone imparts centrifugal force on the aerosol stream, usually within a conical shaped chamber. Cyclones operate by creating a double vortex inside the cyclone body. The incoming gas is forced into circular motion down the cyclone near the inner surface of the tube. At the bottom of the cyclone, the gas turns and spirals up through the center of the tube and out of the top of the cyclone.[116]

Particles in the aerosol are forced towards the cyclone walls by the centrifugal force of the spinning gas but are opposed by the fluid drag force of the gas traveling through and out of the cyclone. For large particles, inertial momentum overcomes the fluid drag force so that the particles reach the cyclone walls and are collected. For small particles, the fluid drag force overwhelms the inertial momentum and causes these particles to leave the cyclone walls with the existing gas. Gravity also causes the larger particles that reach the cyclone walls to travel down into a bottom hopper. While they rely on the same separation mechanism as momentum separators, cyclones are more effective because they have a more complex gas flow pattern.[116]

This type of technology is part of the group of air pollution controls collectively referred to as "precleaners". They are oftentimes used to reduce the inlet loading of particulate matter (PM) to downstream collection devices by removing larger and abrasive particles. The partially clean airstream is then passed to a more expensive final control devices such as fabric filters or electrostatic precipitators (ESP). Hence they are used to control PM, and primarily PM greater than 10 micrometers (μm) in aerodynamic diameter. However, there are high efficiency cyclones designed to be effective for PM < 10 μm or < 2.5 μm (PM_{10} and $PM_{2.5}$).

The collection efficiency of cyclones varies as a function of particles size and cyclone design. Cyclone efficiency generally increases with:

- particle size and/or density
- inlet duct velocity
- cyclone body length
- number of gas revolutions in the cyclone
- ratio of cyclone body diameter to gas exit diameter

- dust loading
- smoothness of the cyclone inner wall

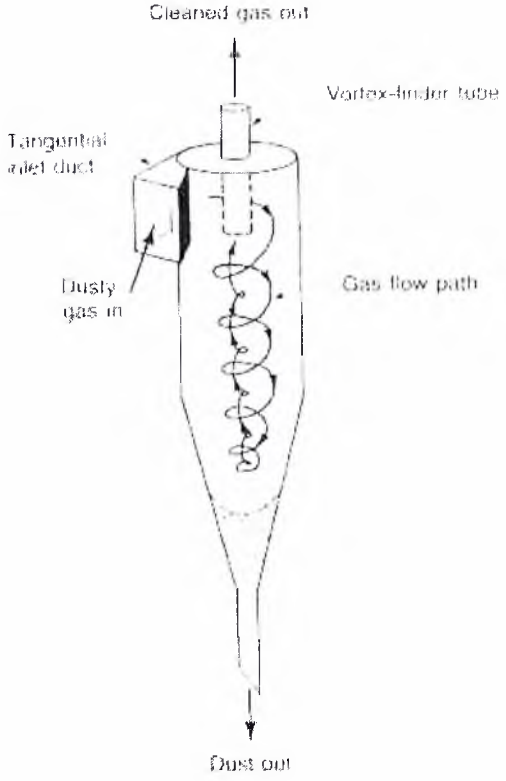


FIGURE 2-10: SCHEMATIC DIAGRAM OF A CYCLONE

Cyclone efficiency will decrease with increases in:

- gas velocity
- body diameter
- gas exit diameter
- gas inlet duct area
- gas density

A common factor contributing to decreased control efficiencies in cyclones is leakage of air into dust outlet.[117]

There are three classifications of cyclone control efficiencies, i.e., conventional, high efficiency, and high-throughput. Higher efficiency range cyclones are designed to achieve higher control of smaller particles than conventional cyclones. Higher efficiency cyclones come with higher pressure drops, which is a limiting factor in cyclone design. [111,112,118] High throughput cyclones are only guaranteed to remove particles greater than 20 μm, although collection of smaller particles does occur to some extent. The control efficiency of the various classifications is given in **Table 2-1**.

TABLE 2-1: CONTROL EFFICIENCY RANGES FOR THE THREE CYCLONE CLASSIFICATION AND TYPE OF AEROSOL[119]

	% Efficiency		
Type of Aerosol	**Conventional**	**High Efficiency**	**High Throughput**
TSP	70 - 90	80 - 90	80 - 90
PM10	30 - 90	60 - 95	10 - 40
PM2.5	0-40	20 - 70	0 - 10

2.4.3. DIRECT-READING INSTRUMENTS

The direct reading instruments (usually referred to as survey instruments) are those that can measure the mass concentration *in situ*. Generally, the direct-reading instruments are less accurate than the integrated samplers, but more convenient because their speed of operation allows monitoring and assessment, in space or time, of changing concentrations. Because of their time-sensitive data, they are very useful in source identification and control, short term compliance monitoring, emergency response, forensic investigations and numerical modeling. Some of the direct-reading

mass concentration measuring instruments are Tapered Element Oscillating Microbalance (TEOM) , Piezobalance and Beta gauge methods among others.

In addition to direct-reading mass concentration measuring methods there are other instruments such as optical particle counters, electric mobility analyzers, condensation nuclei counters and photometers. These are all based on some characteristics of the aerosol which is measured and related to either the number of particles or the mass. Of interest to this thesis are the direct-reading instruments measuring mass concentration.

The direct-reading instruments require a sensitive means of determining the mass of the particles collected *in situ*. The main problem associated with the direct-reading instrument is how to remove free water and standardize the sampling procedure. This is achieved by heating the air stream and filter. This heating procedure is likely to volatise some particles from the air stream and filter. To overcome this potential for volatisation, some researchers have reduced the operating temperatures from 50°C to 40° C and further consideration is being given reduce the temperature to 30° C.[120] In addition to the above limitations of the direct-reading instrument methods, there are performance limitations due to some or all of the following factors: humidity, gas adsorption, and particle collection efficiency.

2.4.4. SAMPLING OF GASES

There are gas analyzers with sufficient sensitivity and speed of response to give a continuous measurement of the pollutant concentration as the sample is delivered to them. Many other techniques simply capture the pollutant, or a chemical derived from it, from the sample for later quantitative analysis in the laboratory by conventional methods such as titration and spectrophotometry. The technique for gas pollutant

measurement is that a specific chemical reaction should occur between the gas and the captive absorbed molecules retain all the gas from the sample air. There are different methods; among them are bubblers, impregnated filters, diffusion tubes and denuder tubes.

There are two distinct group of gas air pollution samplers – Passive samplers (automatic samplers) and active samplers (non-automatic samplers). The non-passive samplers are generally cheaper and easier to install and maintain but do not give as good accuracy or resolution as passive methods.

The most commonly used passive sampler is the diffusion tube. This provides a simple and inexpensive method of screening air quality in an area, to give a general indication of average pollution concentration over a period of weeks or months. The sampler consists of a small plastic tube open at one-end and an absorbent packed at the other. The absorbent used depends on the pollutant gas to be monitored; nitrogen dioxide being the most common, then benzene, sulphur dioxide and ozone. Tubes are usually exposed for two to four weeks then sent to the laboratory for analysis. The main advantage is the low cost which permits sampling at a number of points in the area of interest; this is very useful in highlighting "hotspots" of high concentration where detailed studies may be needed.

Active samplers can be divided into two groups; namely, the non- or semi-automatic and the automatic (continuous analyzers). Non – or semi-automatic sampler methods collect pollutants either by physical or chemical means for subsequent analysis in a laboratory. Typically, a known volume of air is pumped through a collector such as a filter or a chemical solution for a known period of time, which is then removed for

analysis. Examples are sulphur dioxide or smoke bubblers. On the other hand the automatic samplers produce high-resolution measurements for pollutants such as ozone, oxides of nitrogen, sulphur dioxide and carbon monoxide. Hydrocarbons can also be measured, but are limited by cost. Because the data are analyzed on-line and in real-time, it is especially useful for monitoring pollution episodes (e.g. heavy traffic emissions). In order to ensure that the data produced are accurate and reliable, strict maintenance, operational and quality assurance/control procedures are required and must be rigidly followed if the results are to be relied on.

There are other methods that involve adsorption of the gas molecules by intermolecular forces to the surfaces of a solid collecting substrate and subsequently stripping them off by heating to appropriate temperatures or solvent extraction and delivered into a gas chromatograph or an equivalent analysis system. Also there is condensation trapping at liquid oxygen temperature (-183° C) so that volatiles condense out but the air itself passes through unchanged.

2.5. FILTERS

The material on which the aerosol sample is collected is very important if any meaningful results are to be obtained from the analysis. The material should be able to retain the particles, without coming off very easily, but must permit air flow readily through it. The sample collected should be provided in a manner that would make it easy to analyze both for mass concentration and chemical composition. Fibrous and porous membrane filters are the most commonly and important filter types used in aerosol sampling.

2.5.1 FIBROUS FILTERS

Fibrous filters consist of a mat of randomly positioned fibers that have been pressed together, and often with a binding material, so that most are perpendicular to the direction of the airflow. Aerosol particles are removed by these types of filters when they collide and attach to the surface of the fibers and not as microscopic sieves in which only particles smaller than the pore size can get through, as in the case of liquid filtration.

These types of filters have porosity from 70 to greater than 99% and range in size from submicrometer to 100 μm. Glass fiber, quartz and cellulose (paper) are the most common types. They have lower pressure drops across them and are well suited for high volume sampling. High-efficiency filters have a low air velocity through them. Thus to obtain a large filter area in an element of convenient size the filter materials are pleated. The glass and quartz fiber filters have a high retention of particles with sizes above 0.3 μm.

Glass fiber filters have very high capacity but one major draw back is its ability to convert sulphur dioxide to sulphate hence increase the PM load in situ. This is not a problem with quartz fiber or paper filters. The glass fiber filters have very high blank values for a lot of elements and therefore they are unsuitable for trace element analysis especially with nuclear analytical techniques. The quartz fiber filter, though better than glass fiber for blanks, still have high blank values and therefore are equally unsuitable for trace element analysis. The penetration of particles into the filter mat of fibrous filters is not uniform thus they are not useful for EDXRF analysis. Though cellulose filters can be used for ambient monitoring, there are problems associated

with maintaining the same humidity for the exposed and unexposed filters. This has led to very limited use.

2.5.2 POROUS MEMBRANE FILTER

Porous membrane filters are made from cellulose esters, sintered metals, polyvinyl chloride and/or Teflon and other plastics. They have a different structure from the fibrous filters, with less porosity, between 50 – 90%, than the fibrous filters. Gas flow through the filter follows an irregular path through the complex pore structure. When aerosol is drawn through the filter, particles are deposited on the structural elements that form the pores. Membrane filters have high efficiency, even of particles smaller than the manufacturer's stated pore sizes which are based on liquid filtration, and a greater resistance to airflow and higher pressure drop than other types of filters.

For trace element analysis using nuclear analytical techniques, as in this work, the membrane filters are better suited. The filters commonly used are polycarbonate (e.g. Nuclepore) and polytetrafluoroehylene (PTFE) popularly known as Teflon. A number of tests have been carried out on the efficiency of membrane filters and it has been found that the collection efficiency depends on pore size, especially with the Nuclepore filters.[121-123] For example, it was observed that the 0.8 μm Nuclepore filter had only 72% efficiency for submicron particles observed with condensation nuclei counter.[37]

One problem that is associated with these filters is the loss of coarse particles from the filter in handling and transport from sampling site to the laboratory which has been noticed by a number of researchers. Dzubay and Barbour[124] have suggested the use of oil coating on the filters to prevent such shake-off effects. The coating should also be applied to the blank samples that are analysed as part of the analytical process.

CHAPTER 3

ANALYTICAL TECHNIQUES AS APPLIED TO AEROSOLS

3.1 INTRODUCTION

Historically, people detected aerosol particulates with their lungs, their noses and their eyes. Discomfort from smoke inhalation near cooking fires surely resulted in people moving upwind. The most common indicator of pollution, however, has been smoke and/or visible clouds due to the ability of the clouds to scatter light as a result of pollutant gases and particulates.[125] High correlation observed among black smoke from chimneys, reduced visibility, black deposits on buildings and clothing, and respiratory distress in the 14th century England led to the first recorded air pollution regulation by a royal decree.[126] Though the measurement method was crude, and many of the health consequences may have been caused by invisible SO_2 gas, the regulatory decision was correct.

One of the most common approaches for determining the composition of atmospheric aerosols involves the analysis of deposits collected on filter substrate. While filter sampling is inexpensive compared to online measurements, it requires manual operations and the number of filters that must be analyzed before any meaningful deductions can be made is large (usually > 30). Gravimetric analysis is used almost exclusively to obtain mass measurements of filters in a laboratory environment. Gravimetry determines the net mass by weighing the filter before and after sampling with a microgram sensitive balance in a temperature- and relative humidity-controlled environment. The main problem that arises here is interference from electrostatic charges which induce non-gravimetric forces between the filter and the balance.[127] The charge is usually removed from most filters by exposing it to low-level

radioactive sources prior to weighing. Accurate gravimetric analysis requires the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapour and other gases. Liquid water associated with particle deposits is effectively removed by equilibration at low temperature and relative humidity. Some particles may however volatize if they are exposed to ambient air for more than a day or two.[128,129]

No matter how much air is drawn through a filter, and despite occasionally high particle loadings in the atmosphere, the amount of sample available for chemical analysis is very small. The typical mass loading on a low- to medium volume sampler is less than 5 mg and many of the chemical species of interest that must be measured are less than 1 μg in the deposit.

While most of the current air particulate standards are based on mass concentration, there is need to know the chemical composition so as to determine the biological effect as well as the sources emitting these particles. The essence of any analytical method in environmental science is to make measurements in order to attain a specified goal. Hence the sampling and analytical methodology must be appropriate. Therefore in this work and for any analysis, there is the need to find the qualitative nature of the sample and the quantity or concentrations present so as to make informed decisions. There are three main factors to consider in any analytical technique and this is especially critical in analysis of aerosol particles, where the mass of the deposits collected is very small:

- Specificity: In determining the presence of an element, with what certainty is the presence determined?

- Sensitivity: Given the presence of an element, what is the change in the detected element per unit change in concentration?
- Detection limit: What is the smallest amount of concentration or amount that can be ascertained?

In addition, how will the sample be presented; is there a need for sample preparation?

Elemental concentrations in atmospheric aerosol reflect the processes generating them. Therefore, elemental and/or chemical composition analysis of atmospheric aerosols is very useful to detect the sources of aerosols. The ultimate goal of any aerosol measurement and analysis is to determine the particle sources and where appropriate study physical and chemical processes occurring in the particles during their life time (atmospheric transportation).

There are many analytical techniques available for the determination of elemental composition of materials (i.e. aerosol particulates). Some of the methods used in aerosol chemical (or species) determination includes among others; inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma auger electron spectroscopy (ICP-AES), inductively coupled plasma optical emission spectrometry (ICP-OES), gas chromatography – mass spectrometer (GC-MS), instrumental neutron activation analysis (INAA), energy dispersive x-ray fluorescence (EDXRF), micro-X-ray energy dispersive fluorescence analysis (μ-EDXRF), proton induced x-ray emission (PIXE), total reflection x-ray fluorescence (TXRF), thermo-optical and light scattering methods (for total, organic and black carbon [BC]).[130-137] In particular, advances in electronics have led to the development of a wide variety of instrumental methods to be used with the older classical chemical procedures. Most of the instrumental techniques use "comparator" instead of "absolute methods". In

general, the equipment required may be rather expensive, but their convenience, sensitivity, accuracy and precision make them attractive. These instruments have changed the face of both qualitative and quantitative analysis.

A variety of spectrometric techniques depend on the electromagnetic spectrum emitted or absorbed by the sample being analysed. The spectra are characteristic of the elements or chemical compounds present in the sample. The analysis is made by comparing results from samples with those obtained from calibration standards under identical conditions. The key component of these types of instrumentation is devices to isolate a chosen discrete energy or a range of energies (or wavelengths) for measurement.

The energies (or wavelengths) emitted or absorbed by elements and chemical compounds of analytical interest range from gamma- and x-ray regions (<100 Å or 10^{-8}m) through the ultraviolet and visible regions to the infrared (7000 Å). There is no single spectrometer that can span this wide range which is about 1 – 150,000 eV. Hence instruments that are versatile in terms of good performance over a wide range of applications are preferred. X-ray spectrometers, especially X-ray Fluorescence (XRF) and electron probe analysis systems, belong to this category and are currently used world wide.

3.2. X-RAYS

3.2.1 X-RAY FLUORESCENCE ANALYSIS

X-rays are part of the electromagnetic spectrum with wavelength ~10^{-5} to ~100Å produced by the deceleration of high energy electrons and/or by electron transitions in the inner orbits of atoms. X-rays have the following general properties:

- Occur as continuous spectra

- Occur as characteristic line spectra
- Occur as characteristic band spectra
- Produce characteristic absorption spectra
- Propagate without transfer of matter
- Are unaffected by electric and magnetic fields
- Are invisible and hence undetected by the human senses

There are three main interactions of x-rays with matter, namely – Photoelectric absorption, Compton scattering and Pair production. Depending on the material, when X-rays interact with matter a fraction might pass through the sample, a fraction might be absorbed in the sample and produces fluorescent radiation, and a fraction is scattered. Scattering can occur with or without loss of energy. When there is loss of energy it is known as Compton scatter, and without loss of energy is known as Rayleigh scatter.

When x-rays of intensity, I_0, pass through a material of finite thickness, d, and density, ρ, the transmitted intensity of photons which have not suffered interactions, I, in the material is given by the Beer-Lambert law

$$I = I_0 e^{-\mu \rho d} \qquad \ldots 3\text{-}1$$

where

μ is the mass attenuation coefficient, which is energy dependent. Thus μ is composed of three major components:

$$\mu(E) = \tau(E) + \sigma_{coh}(E) + \sigma_{inc}(E) \qquad \ldots 3\text{-}2$$

where

$\tau(E)$ is the photoelectric mass absorption coefficient

$\sigma_{coh}(E)$ is total coherent mass scattering coefficient

$\sigma_{inc}(E)$ is total incoherent mass scattering coefficient

Pair production is only possible when the energy of the photons is greater than 1.02 MeV and as such not important for x-ray photon interactions. These three main processes depend on the thickness of the sample (d), density (ρ) and composition of the material and the incident x-rays energy (E_0).

Photoelectric absorption occurs when the atom (or sample) being irradiated completely absorbs the x-ray photons. Electrons in the inner shell of the atom (sample) can be expelled by x-ray photons or electrons with sufficient energy. For example if the ejection takes place in the K-shell, a hole is created in the K-shell making the atom unstable with a higher energy. An electron from a higher orbit will fill the hole created in the K-shell. The excess energy is emitted as x-rays and when this happens, it is seen as a line in a spectrum. The energy of the emitted x-rays depends on the difference in energy of the shell with the initial hole and the energy of the electron that fills the hole. Each atom has its specific energy levels, so the emitted radiation is characteristic for that atom. Different holes can be produced in the atom, hence an atom emits more than just one energy (or line). The emitted line(s) is/are characteristic and serve as a fingerprint of the element.

For an electron to be removed from an atom, the x-ray must have a higher energy than the binding energy of the electron. If an electron is removed, the incoming radiation is absorbed, the higher the absorption the higher the fluorescence. Hence the process is known as X-ray Fluorescence (XRF). For very high energies very few photons are

able to interact with the atom to eject electrons as most of the energy just passes through.

X-ray fluorescence (XRF) is an analytical technique used to determine chemical composition of all kinds of material and have been in use around 1910.[138] The sample/material could be solid, liquid, powder, filters and in other forms. XRF also used to measure thickness and composition of layers and coatings. The main advantages are that it is fast, accurate and non-destructive and usually requires little or no sample preparation. Currently the application of XRF is very wide and diverse and includes among others the food, plastic, metal, cement, oil and mining industries. It is also applied in mineralogy, geology, pharmacy, medicine and research. It is also used extensively in environmental analysis of soil, water, air, vegetation and waste.

X-ray fluorescence has been used to quantify elements from atomic number 11 (Na) to 92 (U). In aerosols, it has been used to detect and quantify elements from Na to La, Au, Hg, Tl, Pb and U. In addition to its multi-elemental nature, another advantage is that sample preparation is generally not necessary. Most importantly, the filters remain intact after analysis and can be analyzed using other techniques to give additional information. To achieve greater sensitivity and efficiency for low Z elements like Na, Mg, Al, and Si the filter is placed in a vacuum. This can also result in the evaporation of volatile compounds but can be minimized by the introduction of helium atmosphere.

Basically, XRF spectrometer systems consist of a source (of x-ray or generator), a sample holder and a detection system (detector). The spectrometer systems are generally divided into two main groups: energy dispersive (EDXRF) and wavelength

dispersive (WDXRF). The difference between the EDXRF and WDXRF is found mainly in the detection system. The EDXRF detector detects and measures different characteristic energies emitted from the sample. On the other hand, the WDXRF detector uses an analyzing crystal to disperse the various wavelengths similar to a prism dispersing different colours in different directions. Although WDXRF, generally, displays a higher sensitivity for low-atomic number elements than EDXRF but it requires higher excitation power. This higher excitation energy may produce excessive sample heating, causing the filter to brittle and potential degradation of the filter material. EDXRF applies 100 to 1000 times lower excitation energy and hence avoids sample damages.

In this work only the EDXRF system has been used. Generally, the source irradiates a sample and a detector measures the radiation coming from the sample. X-ray tubes and Si(Li) detectors was used in this work as the source and detector respectively.

3.2.2 EDXRF SPECTROMETRY

When characteristic x-rays produced from a sample are incident on the detector, in this work a semiconductor detector, it interacts with the detector material. The x-ray energies produce ionization in the detector. The total ionization produced by each energy photon entering the detector is converted to voltage signals with amplitude proportional to the energy of the incident photons.[139] The detector signals can then be processed by a pulse processor unit and a multi channel analyzer to obtain a spectrum of the sample. The position of the peak in the spectrum corresponds to the energy of the x-ray photon from which it is coming and the net area under each peak in the spectrum is used in the elemental quantification of the sample.

There are three very important properties of detectors that are taken into consideration before they are used in x-ray fluorescence analysis namely;

- Resolution - The ability of the detector to differentiate between different photon energies. Higher resolution detector is one that has the best ability to differentiate between two very close photon energies.
- Sensitivity - How efficiently the incoming photons are counted. Therefore high sensitivity implies that the number of pulses being recorded against the number of incoming photons is very high.
- Dispersion - The ability of the detector to separate x-rays with different energies, a high dispersion implies that different energies are well separated.

The fluoresced characteristic x-rays produced by the sample is used for both the qualitative and quantitative analysis. Though the fluoresced characteristic x-rays are generated as a result of photoelectric interactions, the scattering (both coherent and incoherent) of the excitation energy generates a background that interferes with the analysis of the characteristic x-rays. The intensity of the measured signal depends on a number of factors: the

- Energy of incident x-rays for monochromatic excitation or energies of incident x-rays for polychromatic excitation
- Detector efficiency
- Fluorescence yield of sample
- Attenuation of photons by sample (depends on sample thickness)
- Attenuation of photons in air (depends on the source-sample-detector distances)

- Inter-element effects (the measurement of the element of interest may not depend only on its concentration but also on the concentration of other elements present)
- The number of atoms of the element of interest in the sample.

In this work monochromatic excitation was used and will be the only excitation discussed.

For monochromatic excitation, the characteristic (fluorescent) x-rays which are emitted by an element i in a thin layer dx at a depth x within a sample is given by[140]

$$dI_i = I_0 G \csc\varphi_1 \tau_i(\rho d)_i \{1 - (1/J_i)\} w_i f_i \varepsilon \, e^{-\mu_0 x\rho \csc\varphi_1} e^{\mu_i x\rho \csc\varphi_2} dx \qquad \ldots 3\text{-}3$$

where

I_0, I_i – intensity of primary and fluorescent radiation respectively (photons/second)

τ_i – photoelectric mass absorption coefficient at the incident energy, E_0, (cm^2/g)

J_i – the ratio (jump ratio) between the photoelectric mass absorption coefficient at the top and bottom of the absorption edge of the element of interest

W_i – fluorescent yield of the element for interest

f_i – fraction of the energy E_i with respect to total x-rays energy emitted

μ_0, μ_i – mass absorption coefficients of the sample to primary, E_0, and fluorescent, E_i, radiation respectively

ε_i – efficiency of the detector for x-rays of energy E_i

φ_1, φ_2 – angle between sample surface and primary/fluorescent radiation respectively

G – geometric factor

ρ_i – density of element i within sample

ρ – density of the sample

By integrating **Equation 3-3** for a specimen of thickness d (i.e. between $x = 0$ and $x = d$), and multiplying the numerator and the denominator by d, the following general equation is obtained:

$$I_i = I_0 G \csc\varphi_1 \tau_i \{1 - (1/J_i)\} w_i f_i \varepsilon_i (\rho d)_i (\rho d) \{1 - e^{-\bar{a}_{i,s}\rho d_1}\} / \bar{a}_{i,s}\rho d \quad \ldots 3\text{-}4$$

where $\bar{a} = \mu_0 \csc \varphi_1 + \mu_i \csc \varphi_2$ ... 3-5

For very thick samples, the exponential term in **Eqn 3-4** decreases rapidly with increasing thickness d of the sample layer. This infinitely thick sample layer is often reached in practice where solids and bulky materials are analyzed.[56] Under such conditions, **Eqn 4** can be written as

$$I_i = \frac{G_0 K_i (\rho d)_i}{\bar{a}} \quad \ldots 3\text{-}6$$

where

$\bar{a} = \mu_0 + \mu_i$ for $\varphi_1 = \varphi_2 = 90^\circ$

$G_0 = I_0 G$

and $K_i = \{1 - (1/J_i)\} w_i f_i \varepsilon_i$

a constant that involves all the fundamental parameters

Eqn 3-2 can be further written as

$$I_i = G_0 K_i (\rho d)_i A_{corr} \quad \ldots 3\text{-}7$$

where $A_{corr} = \{1 - e^{-\overline{a_{i,s}} \rho d_1}\} / \bar{a}_{i,s} \rho d \quad \ldots 3\text{-}8$

For a sufficiently thin sample, **Eqn 3-4** can be approximated by the expansion of the exponential term, as:

$\exp(-x) \approx 1 - x$, and becomes

$$I_i = G_0 K_i (\rho d)_i \quad \ldots 3\text{-}9$$

But

$$S_i = G_0 K_i \quad \ldots 3\text{-}10$$

where S_i is the Sensitivity of the spectrometer.

The sensitivity value depends on a number of experimental factors and the characteristics of the sample and is independent of the physical nature of the sample. Hence the sensitivity can be obtained by simply calibrating the equipment with standards samples of known mass per unit area.

From **Eqns 3-9** and **3-10** we get

$$I_i = S_i (\rho d)_i \quad \ldots 3\text{-}11$$

Hence for "thin" samples there is a linear relationship between the fluorescent x-ray intensity (I_i) and the concentration $(\rho d)_i$.

Aerosol samples collected on membrane filters can be regarded as thin samples, because the x-ray attenuation by the filter material can be neglected, since the particulates are deposited on the surface of the filter. For very low filter loadings, e.g.

less than 100 μgcm^{-2}, the net measured intensity is proportional to the mass per unit area of the analyte.

Aerosol particulates however show significant effects of the sizes and compositions of individual particles. These effects result from the absorption of both the incident and fluorescence x-ray radiation within the particles. This self-absorption effect can be very significant in x-rays from light (low *Z*) elements. It has been shown that this can occur within the individual coarse particles, which are collected on the surface of the filter or in fine particles collected in absorbing layer which is at least partly within the volume of the filter.[141] This can be reduced if the aerosol is size segregated. For example, the fine particle mode aerosol can be the result of gas to particle conversion and coagulation, so that a reasonable amount of similarity in composition among particles is expected. But this is not the case for the coarse particulates which are generated from mechanical processes and can be diverse in composition.

3.3 THE BLACK CARBON REFLECTOMETER

Black carbon (also known as elemental carbon) and organic carbon (OC) have been found to be a significant cause of light extinction[142-145] and a major chemical constituent of atmospheric aerosol (TSP, $PM_{2.5}$, PM_{10}).[143,146,147] Three classes of carbon are commonly measured in aerosol samples collected on quartz-fiber filters. These are organic (volatilized or non-light absorbing carbon), elemental or light absorbing carbon and carbonate carbon. Carbon dioxide (CO_2) measurement evolved upon acidification however can be used to determine carbonate carbon (K_2CO_3, Na_2CO_3, $MgCO_3$, $CaCO_3$).[148]

Elemental or black carbon (EC or BC) generally refers to particles that appear black and are sometimes called "soot" or "graphitic carbon". BC is more useful when

consideration is being given to visibility reduction or light absorbing carbon, though other organic carbon also absorbs light (e.g. motor oil, asphalt, tar, coffee). For source apportionment by receptor models, several consistent but distinct fractions of carbon in both source and receptor samples are preferred regardless of their light absorbing or chemical properties.[149]

Carbon is very abundant in suspended particles, hence simple and reliable methods are needed to quantify it in aerosols. Methods that are able to distinguish between BC and OC are preferable because these species differ in origin, atmospheric chemistry and optical properties. One such method was developed by Gagel[150] and is known as the "black smoke method". A light source (high-performance LED with maximum emission at 650 nm) shines on the aerosol filter and the reflected light is measured by photo-diodes located in a black housing. The Reflectometer is calibrated by the manufacturer. Measuring the reflected light emitted by a white filter and a totally black filter, enables the calibration parameter of the manufacturer's to be used.

The output voltage is converted to a measure of blackness known as "black smoke number", RZ. This is determined from the three output voltages obtained (from the aerosol filter to be evaluated, the totally white filter and the totally black filter). The equation relating the output voltage to the black smoke number is:

$$RZ = RZ_{max}(U_{RZ0} - U_{RZ})/(U_{RZ0} - U_{RZmax}) \qquad \ldots 3\text{-}12$$

where

U_{RZ0} = output voltage with blank (white) filter (which is set to 8.0 V according to the instructions manual)

U_{RZmax} = output voltage with totally black filter (set to 0.4 V)

U_{RZ} = output voltage with actual filter to be evaluated

Provided that a thin layer of aerosol particles is collected on the filter ("single dust layer"), there is a simple relationship between the mass concentration of BC collected on the filter, C_R and the RZ. This relation is given by:

$$C_R = - (RM_1/V) \ln(1 - (RZ - RZ_0)/(kRZ_{max})) \quad \ldots 3\text{-}13$$

where

C_R = the black carbon concentration

V = the sampled air volume

RM_1 = the black carbon mass in a single dust layer on the filter

RZ_0 = the black smoke number for a white (blank) filter

RZ = the black smoke number for the actual filter

RZ_{max} = the black smoke number for a black filter

k is calibration constant.

3.4 OTHER ANALYTICAL TECHNIQUES

The techniques mentioned above are commonly applied methods to aerosols and they are used to generate very important results in terms of mass, elements and BC. However, other aerosol analytical techniques such as neutron activation analysis are also applied to aerosol. Neutron Activation Analysis (NAA) is a very powerful technique for the non-destructive multi-elemental determination of many trace elements and has been applied to aerosol by many of researchers.[151-155] It was first proposed as an analytical tool in the late 1930's.[156-159] It was discovered that samples containing certain rare earth elements become highly radioactive after exposure to neutrons. In general, the technique involves the bombardment of a sample with particles (such as neutrons) or radiations. A nuclear reaction will occur if the energy of the radiations or particles exceeds the threshold energy. Stable isotopes in the

sample may be converted to radionuclides, which then undergo radioactive decay, a process accompanied by the emission of gamma-radiation (γ-rays). The detection of radiation can be used to identify and quantify the elements present in the sample.

New analytical techniques are also being continuously created that provide specific measurements and for example, organic compounds, mineral compounds, particle shape and isotopic abundance in particles sampled onto filter. Some of these measurements have also been used to relate aerosols concentrations to their sources.

Electron microscopy has been used, for example, to study the size, morphology and concentration data.[160,161] Elements have been identified in single particles using Electron probe microanalysis (EPMA).[162] X-ray diffraction (XRD) has been used to identify compounds in crystalline structures including silica, mineral dusts and asbestos.[163-166]

Isotope Dilution Mass Spectrometry and Accelerator Mass Spectrometry have been used to measure isotopic ratios[167-175]and isotopic concentrations[176-179]respectively for pollution source identification. For example, ^{14}C is present in emissions from vegetative burning but absent in emissions from fossil fuel combustion, hence by using accelerator mass spectrometry the isotopic concentration of ^{14}C can be measured with a very high sensitivity.

Other analytical techniques such as Raman Spectroscopy, Laser Microprobe Mass Spectrometry (LMMS), Fourier Transform Infrared (FTIR) Spectrometry, Electron Spectroscopy for Chemical Analysis (ESCA), Scanning Electron Microscopy (SEM), Light Microscopy, etc have all been applied to examine, identify and/or quantify aerosol samples.

CHAPTER 4

EXPERIMENTAL METHODS, ANALYSIS AND RESULTS

4.1 SELECTION OF STUDY AREA

Monitoring of pollution levels, and hence air particulates, in the atmosphere is of fundamental importance because it enables us to measure the extent to which pollution is actually occurring and how efforts to mitigate it are working, if any. This is not an easy task in urban and semi-urban areas because the air quality is the result of a complex interaction between natural and anthropogenic environmental conditions.[180] The urban and semi-urban air pollution is a serious environmental problem because of its varying and irregular distribution of sources. Urban areas are small densely populated area and over this small area are mixed development comprising industries, real estate and in some cases, like in Ghana, agricultural industry.[181] Site selection in any monitoring programme is a very important and crucial and a lot of consideration has to be given to it. For a strong source or few strong sources, air monitoring sites are not determined qualitatively but quantitatively using atmospheric dispersion models.[181-186] In Ghana, as in this work, we do not know where the sources are and other parameters using dispersion model for site selection was not feasible. It was therefore critical that whatever site that was selected can produce samples that are representative of conditions prevailing in that environment at the time of sampling. Site selection requires the need to:

- Identify the purpose to be served by monitoring
- Identify the monitoring site type that will best serve the purpose
- Identify the general location where the site is placed
- Identify specific monitoring sites

The sampling position at the sampling site is also very important.

There are several functions that a monitoring station can serve and hence there are a number of criteria for the location of a sampler.[182] For example two important criteria are:

- Determination of the effect of source emission changes on air quality
- Assessment of the effective dose level to the population.

These two reasons will certainly not lead to the same sampling location and hence it is the object of the study that provides a rational and systematic means of sighting the monitoring station. A number of issues must be taken into account in site selection since it is not always possible to optimise measurements for all air pollutants at any one location.

Monitoring sites are usually classified according to the type of environment in which they are located or the pollutant source. The site description reflects the influence of either the particular pollutant source or the overall land use. Typical monitoring location type includes:

- Urban centre – an urban location representative of typical population exposure in towns and city centre
- Urban background – an urban location distanced from sources and therefore broadly representative of city-wide background conditions (e.g. urban residential area)
- Suburban – a location type situated in a residential area on the outskirt of a town or city
- Roadside – a site sampling within 1 – 5 m of a busy road
- Kerbside – a site sampling within 1 m of a busy road

- Industrial – an area where industrial sources make an important contribution to the total pollution burden
- Rural – an open countryside location, in an area of low population density distance as far as possible from roads, polluted and industrial areas
- Other – any special source-oriented or location category covering monitoring undertaken in relation to specific emission sources such as power stations, carparks, airports, tunnels, etc.

In Ghana, no sustained air particulate monitoring has been undertaken to guide this work. Lack of adequate equipment to do multi-site sampling and the need to have a general view of the air quality were the main guiding principles that influenced the site selection. The need to locate the site away from any major source coupled with the need to avoid local anthropogenic and soil derived contaminations as a result of re-suspension of dust were also considered. The sampling was done in a semi-urban area and the following are some of the additional issues considered:

- Site accessibility – the sampling site must be accessible for site visits but must be free from public interference
- Security of the sampler – the sampler was placed in an environment where nobody could temper or vandalise it.
- Access to utilities – the sampler was located at a point where it could be connected to power source. This is to prevent the use of generators which will contribute to the sample.
- Site visibility – The site was very visible alerting people of the measurement to prevent any mishap.

- Aerodynamic clearance/sheltering – the site chosen allows for free airflow around the sampling inlet to ensure representative sampling thus preventing the sampling of stagnant air or highly sheltered microenvironment.
- Local air trajectories – the location so selected was about 20 km from Accra City Centre in the North-East direction which is on a major air trajectory from the Gulf of Guinea.

In order for future health impact assessment, the sampling height selected is 1.6 m; this height is in the breathing level of the average Ghanaian. The sampling was done at the Ghana Atomic Energy Commission, precisely at the Radiation Technology Centre. The coordinates of the sampling site are 5˚40'35.0 N, 0˚11'12.0 W. This is in the North-East of the Accra City Centre with coordinates of 5˚35'00 N, 0˚13'08.0 W.

4.2 EXPERIMENTAL PROCEDURES

4.2.1 SAMPLING AND GRAVIMETRY

The aerosol particles were collected using the GENT sampler. The GENT sampler consists of a compact vacuum pump system that is controlled by a timer and connected to the stacked filter head unit (SFU) as shown in **Fig. 4-1**. The filter head unit is based on sequential filtration through two filters with different pore sizes. The SFU has a pre-impaction stage that acts as a PM_{10} inlet. The SFU is connected to the pumping system via flexible Poly-flow tubing which was less than 20 m (the manufacturer's recommendation is that it should be less than 100 m). The GENT sampler is used to collect particles in the two size fractions, fine (aerodynamic diameter, $d_a<2.5$ μm) and coarse ($2.5<d_a<10$ μm) on Nuclepore track etched polycarbonate filter. The air inlet is at a height of 1.6 m above the ground and the total

airflow through the filters was 1 m^3h^{-1}(16-17 litres per minute (lpm)). A sampling time of approximately 24 hours was used in this work.

A filter diameter of 47 mm was used; the coarse fraction has a nominal pore size of 8 μm and the fine fraction 0.4 μm. The coarse filters are pre-coated (by the manufacturer) with Apiezon Type L grease to provide a tacky surface to prevent particle rebound and consequently prevent sample loss. The fine filters are however not coated with Apiezon.

Loading of stacked filter unit with the pre-weighed Nuclepore filters is done in a dust-free environment. **Fig. 4-2** show the SFU cassette unit loaded with filters and capped to be sent to the sampling site. More than two stacked filter units were used; hence when one SFU with the exposed filters was changed, it was replaced with another preloaded SFU.

The coarse filter is placed in the top part of the filter cassette so that the air flow will pass through it before getting to the fine filter as shown in **Fig. 4-3**. The filter holders are tightened with a special PVC wrench set attached to the sampler. This is very important since any air leak will affect the loaded mass on the filter.

The samples were collected during the period 27th December 2005 – 12th February 2007. The sampling time was approximately 24 hours. The filters were conditioned for 72 hours, before and after sampling in a temperature and humidity control weighing room. Unannounced and planned load shedding made the sampling very irregular creating gaps in the data.

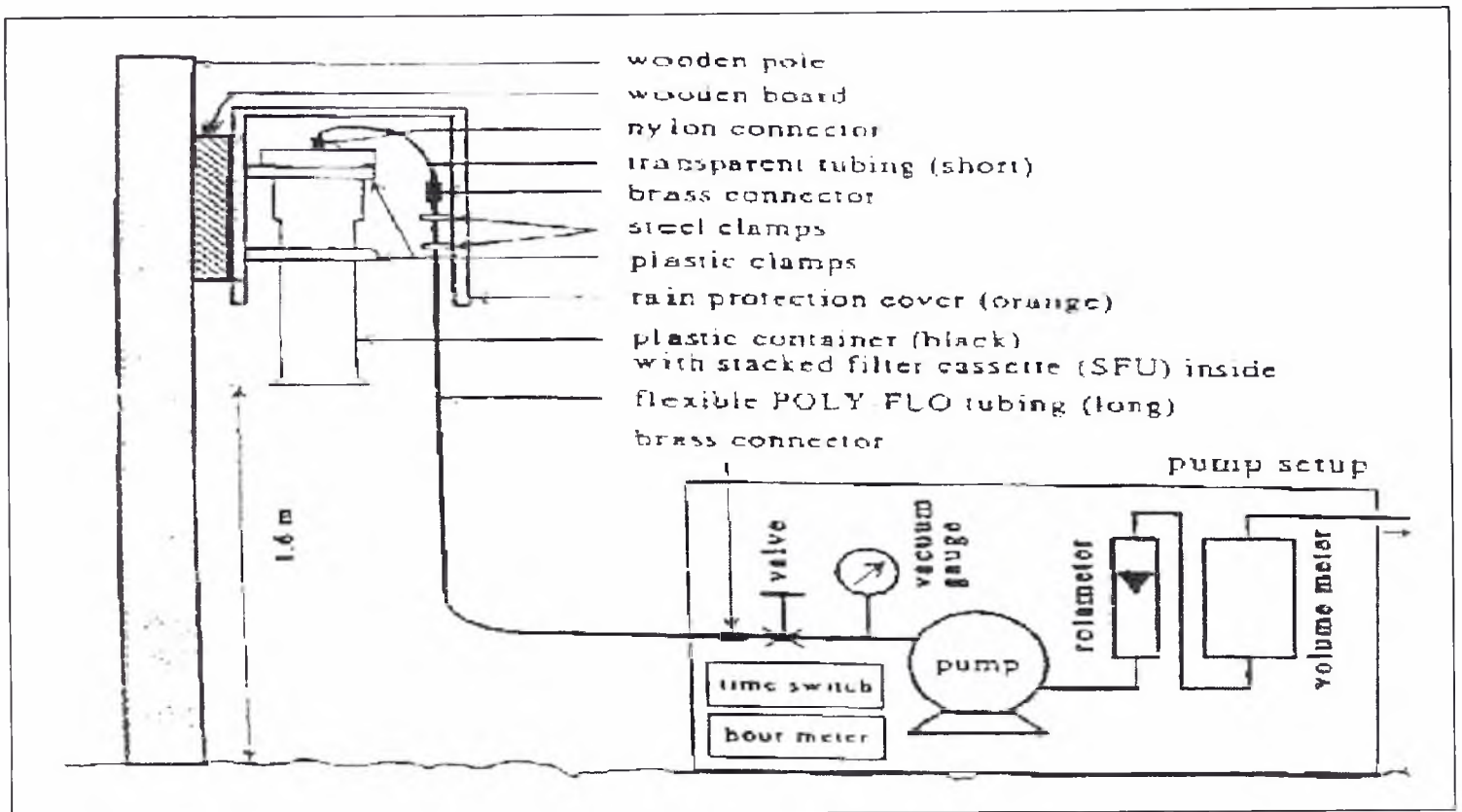


FIGURE 4-1: SCHEMATIC DIAGRAM OF THE GENT SAMPLER USED

FIGURE 4-2 TWO STAGE STACK FILTER CASSETTE UNIT (SFU) LOADED WITH FILTERS AND CAPPED

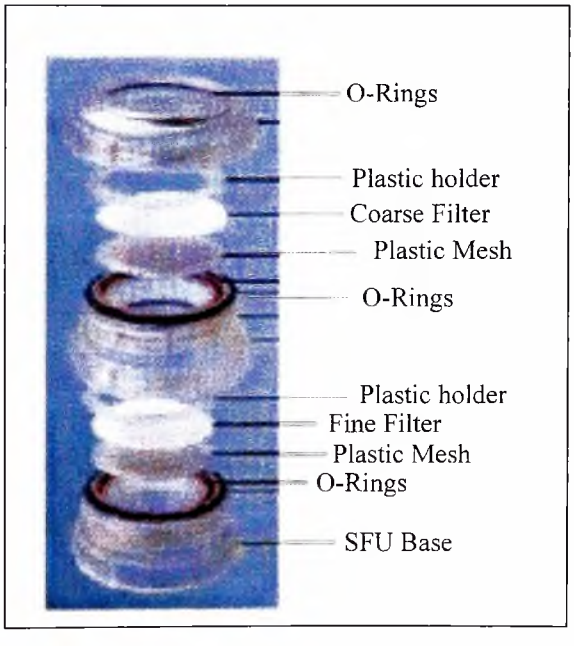


FIGURE 4-3 SCHEMATIC DIAGRAM OF SFU

Gravimetric analysis determines the net mass by weighing the filter before and after sampling. The measured mass concentration was calculated in μgm^{-3} as follows:

$$MC = \frac{LM - IM}{VT} \quad \ldots 4\text{-}1$$

where

MC = mass concentration (μgm^{-3})

LM = loaded filter mass (μg)

IM = initial filter mass (μg)

V = volume flow rate in m^3h^{-1}

T = sampling time (h)

For practical purposes the PM_{10} mass concentration was calculated from

PM_{10} = Coarse fraction ($PM_{10\text{-}2.5}$) + Fine fraction ($PM_{2.5}$) ... 4-2

A Sartorious MC-5 microbalance with readability of 0.001 mg was used for the mass measurement after static on the filter was removed using a Po-210 source. The total mass of particulate matter collected on the filters varied from day to day as shown by **Fig. 4-4** and **4-5**. The calculated daily PM10 mass concentration is presented in **Fig. 4-6**. Mean monthly mass concentration for Coarse ($PM_{10\text{-}2.5}$), Fine ($PM_{2.5}$) and PM_{10} aerosol are shown in **Fig. 4-7**.

4.2.2 BLACK CARBON DETERMINATION

The black carbon analyzer used in this work has been described in Chapter 3. The Gagel method[150] was used for the analysis. The daily black carbon (BC) concentration in the coarse and fine size fractions are shown in **Fig. 4-8**. The percentage BC to Mass Concentration is given in **Fig. 4-9**.

FIGURE 4-4: COARSE MASS CONCENTRATION DURING THE INVESTIGATION PERIOD

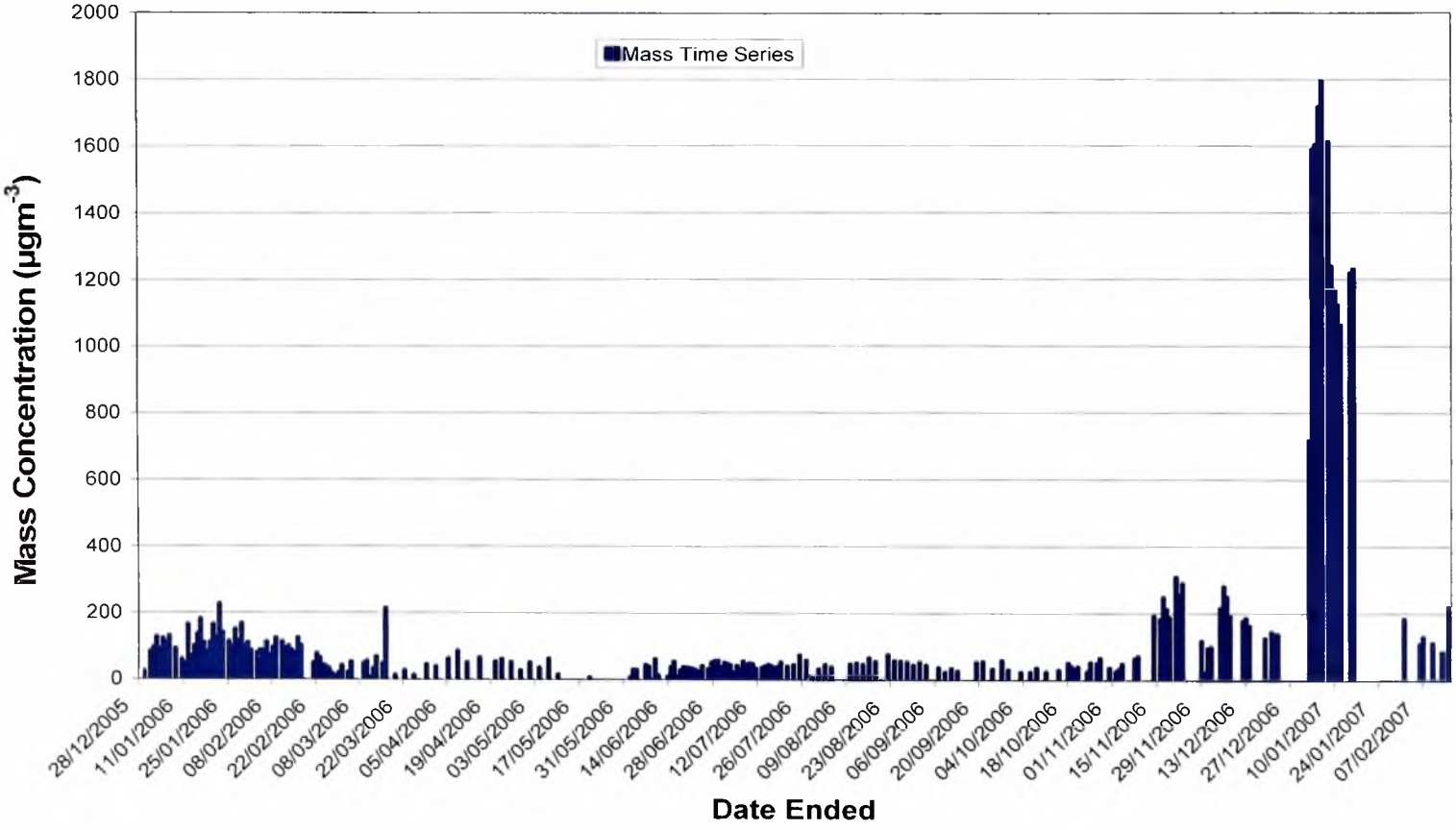


FIGURE 4-5: FINE MASS CONCENTRATION DURING THE INVESTIGATION PERIOD

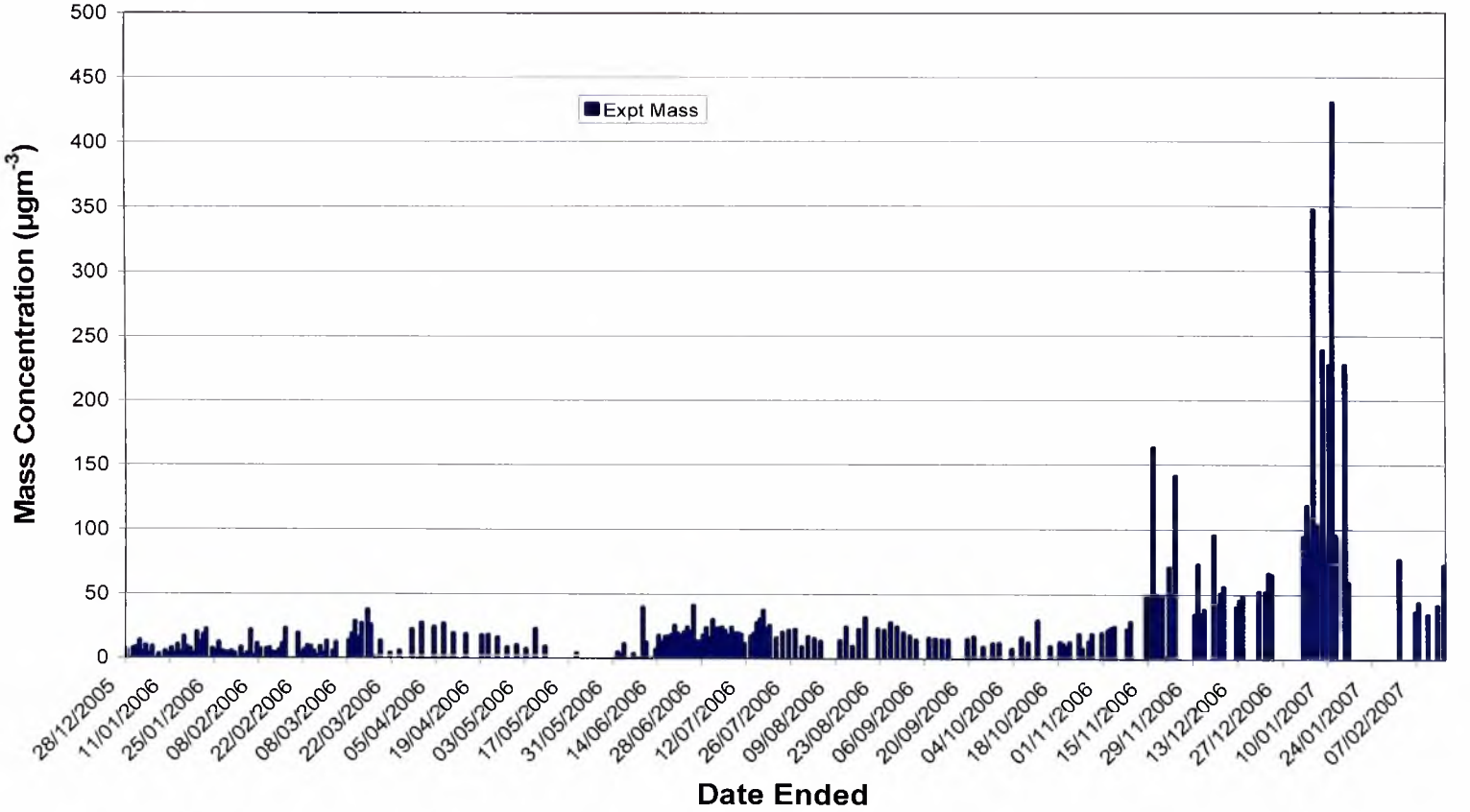


FIGURE 4-6: PM_{10} MASS CONCENTRATION DURING THE INVESTIGATION PERIOD

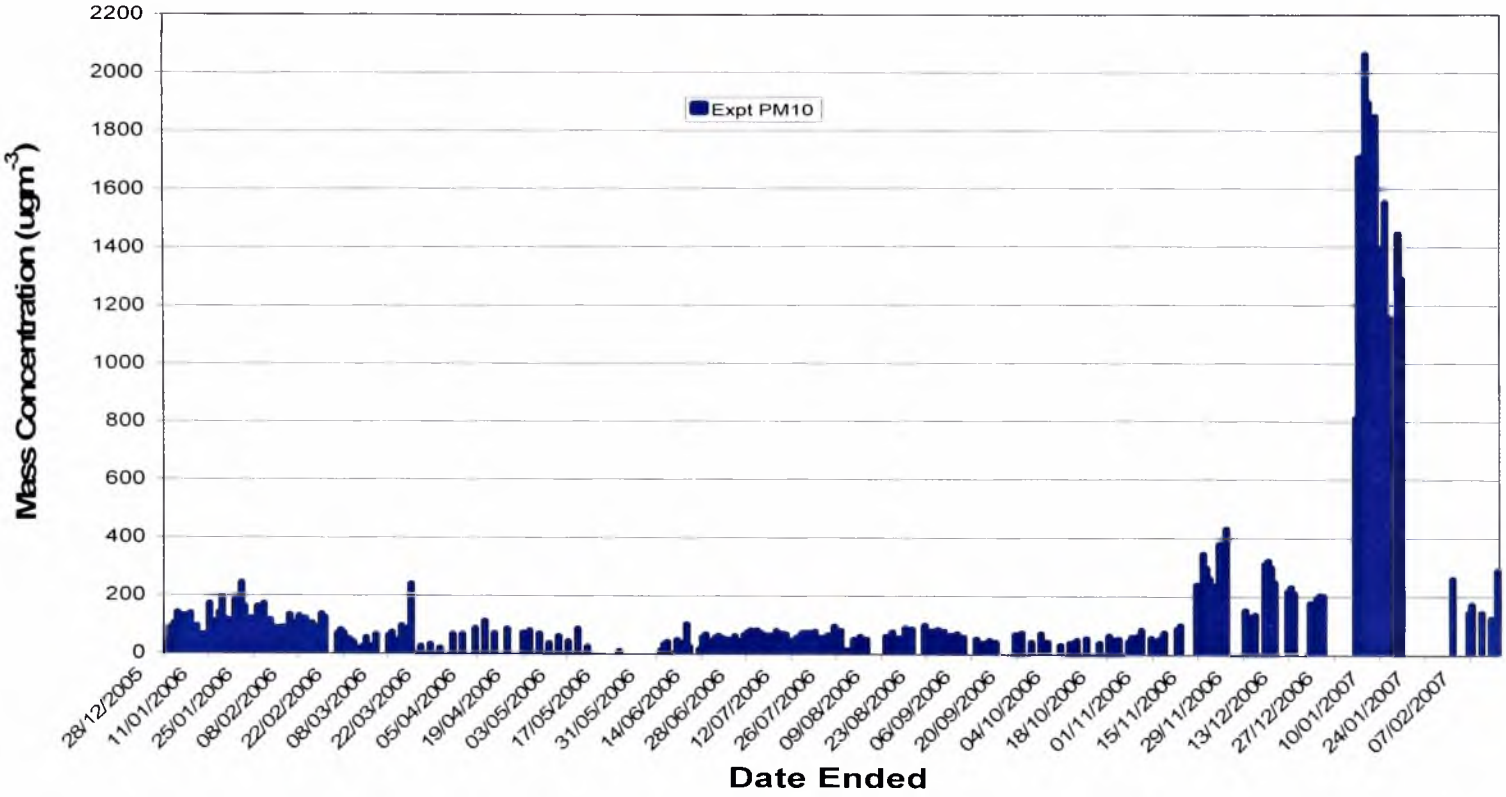


FIGURE 4-7: MEAN MONTHLY FINE, COARSE AND PM_{10} MASS CONCENTRATION

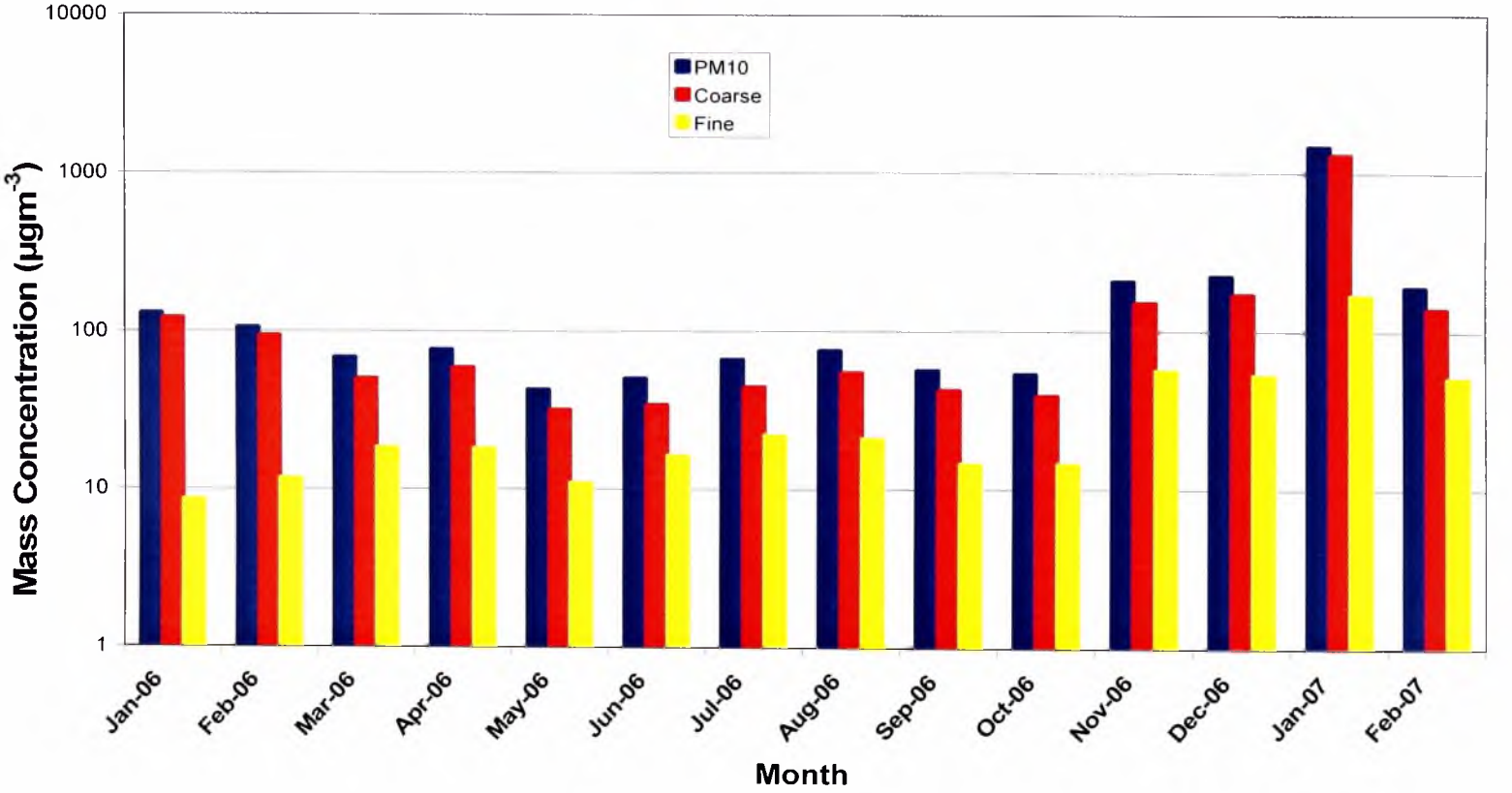


FIGURE 4-8: BLACK CARBON CONCENTRATION DURING THE INVESTIGATION PERIOD

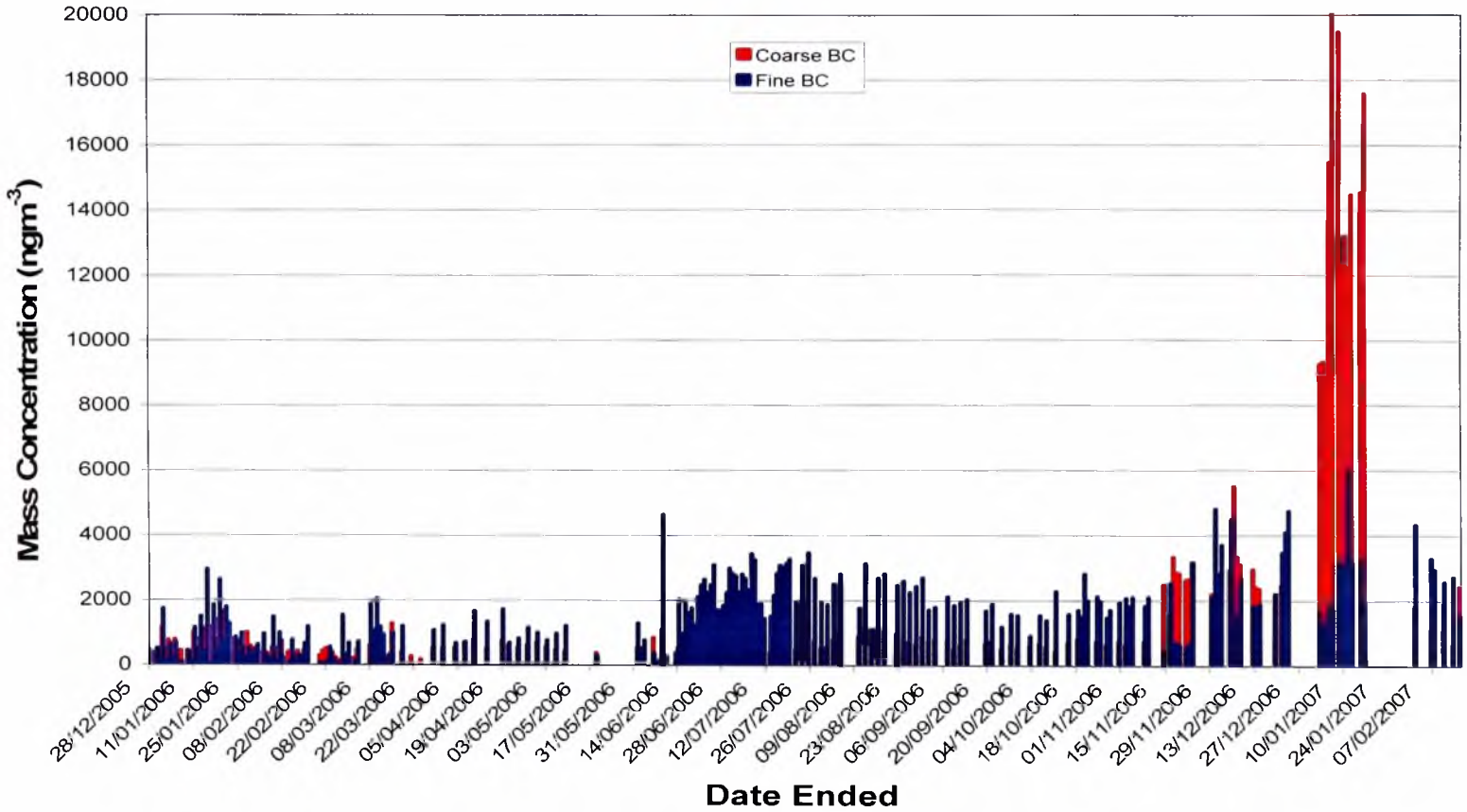
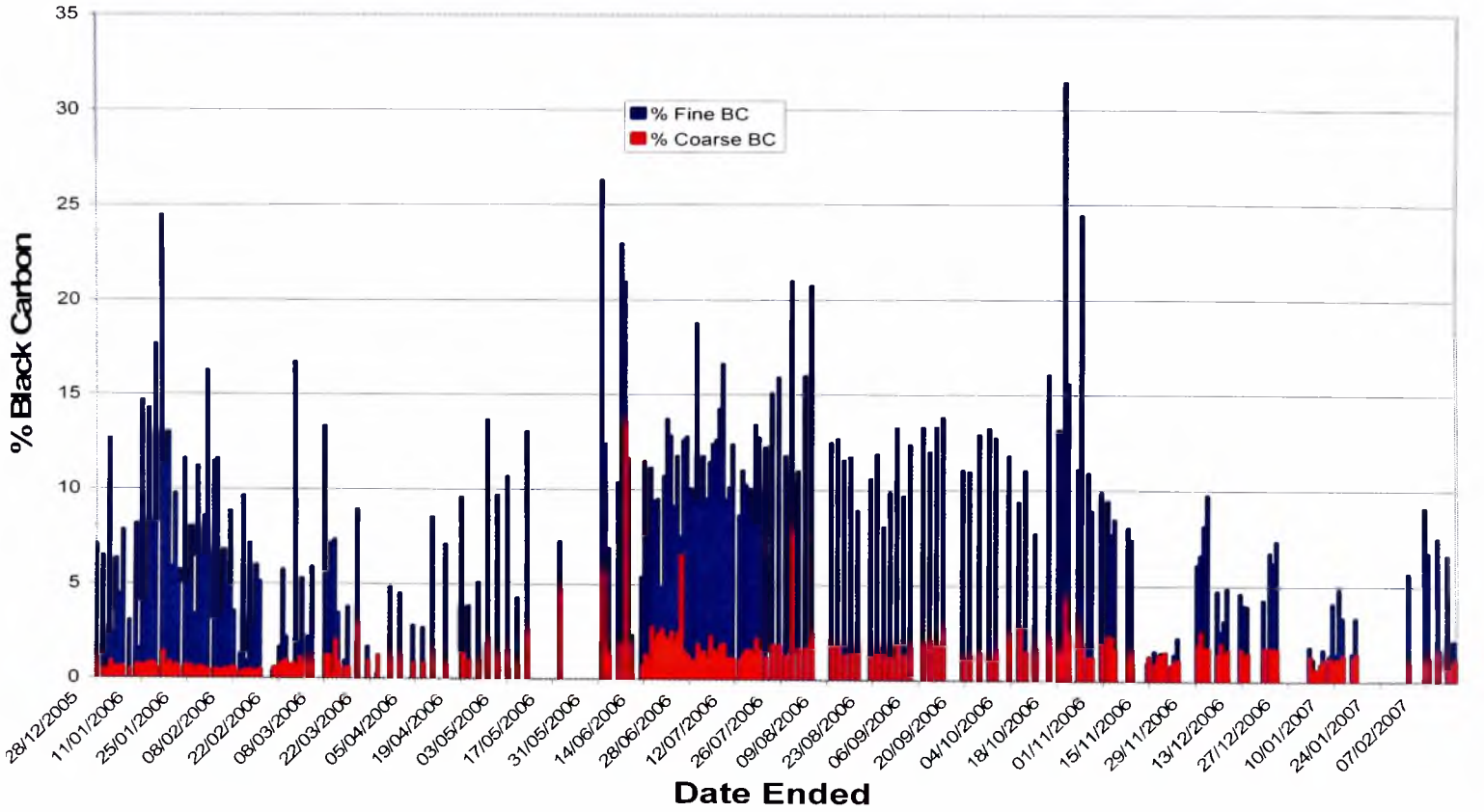


FIGURE 4-9: PERCENTAGE BLACK CARBON CONCENTRATION DURING THE INVESTIGATION PERIOD

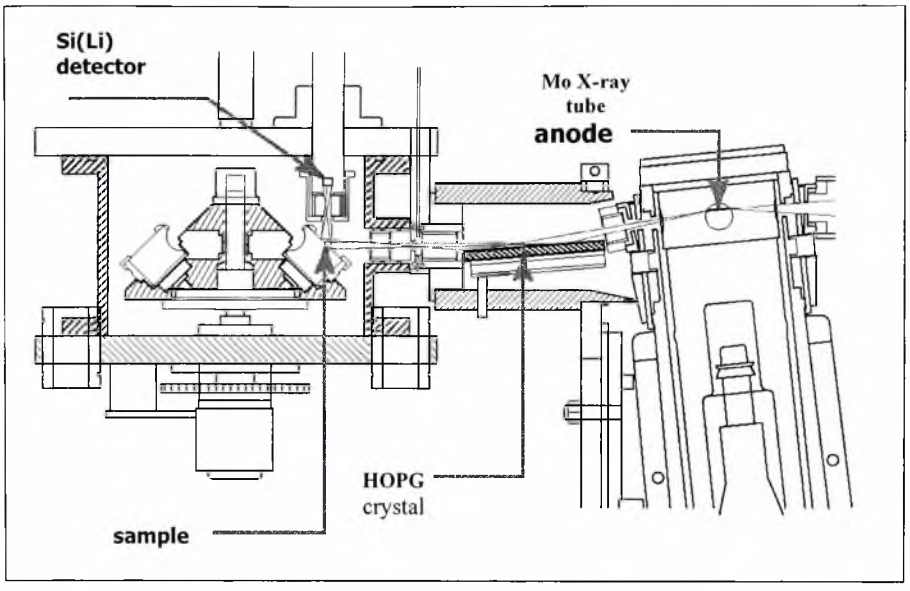


4.2.3 ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS (EDXRF)

The general principle of EDXRF analysis has been described in Chapter 3. The EDXRF spectrometer at the Royal Veterinary and Agricultural University of Denmark was used in the study.[187] The spectrometer is a compact, flexible and sensitive unit, using a high power Mo X-ray tube. The primary beam was monochromatized by a Highly Oriented Pyrolytic Graphite (HOPG) crystal of dimension 5x25x75 mm. Using 90° irradiation geometry a vertical/horizontal reference system is maintained. The detector is a Kevex *SuperDry* Peltier cooled Si(Li) detector. The detector has an active area 20 mm^2 and a 5 μm Be window. The multi-stage peltier module cools the detector crystal and its assembly below -95 °C to maintain the energy resolution at 146 eV (FWHM of Mn Kα). The vacuum in the cryostat is maintained by an ion pump with an internal water-cooled heat exchanger to transfer the heat to the ambient air.

The filters to be analysed were mounted onto a standard *Spectro* cup and placed in the evacuated cylindrical aluminium irradiation chamber. A PC-controlled conical shaped exchangeable eight position sample holder for the mounted filters. The X-ray tube was operated at a voltage of 40 kV and a current of 40 mA in the measurements. The live time of each spectrum was 2000 s. The geometry of the spectrometer is shown in **Figure 4-10.** Since the irradiation chamber is evacuated, elements down to Al can be detected, analysed and quantified. The spectrometer was calibrated using thin film material from NIST (NBS SRM 1832) and the X-ray fluorescence spectra were fitted with AXIL software.[188,189] The evaluation model used for quantification of the elements was the fundamental parameters approach[190] in the QXAS package.[191]

Figure 4-10: A SKETCH OF THE EDXRF SPECTROMETER



When the fundamental parameter approach is applied to air filters, the EDXRF intensity **Eqn 3-4** in Chapter 3 reduces to

$$I_i = G_o \varepsilon \ (E_i) K_i(E_o) C_i \qquad \ldots 4.3$$

where

I_i = measured net intensity of analyte i

C_i = concentration of the analyte i

G_o = the instrumental constant

ε = detector efficiency

K_i = product of all the fundamental parameters of the analyte i

E_o, E_i = excitation energy and analyte energy respectively

This equation neglects matrix correction because the air filters can be assumed to be thin samples. Hence a linear relationship is expected and equation 4.3 can be re-arranged to obtain

$$C_i = M_i I_i \quad \ldots 4.4$$

where M_i = Calibration factor

The quantification system was validated using NIST Standard Reference Material SRM 2783. **Table 4.1** shows analysis of the standard reference material.

TABLE 4-1: VALIDATION OF EDXRF SPECTROMETER USING SRM2783

ng/cm^2 Element	Experimental	Certified	Ratio Expt/Certified
Al	1793 ± 300	2330 ± 53	0.77
Si	6506 ± 420	5884 ± 160	1.11
K	496 ± 31	530 ± 52	0.94
Ca	1274 ± 70	1325 ± 170	0.96
Ti	140 ± 10	150 ± 24	0.93
Cr	13 ± 3	14 ± 3	0.93
Mn	35 ± 3	32 ± 2	1.09
Fe	2564 ± 138	2661 ± 160	0.96
Ni	10 ± 2	7 ± 2	1.43
Cu	41 ± 3	41 ± 4	1.00
Zn	135 ± 7	180 ± 13	0.75
Rb	2.0 ± 0.6	2.0 ± 0.6	1.00
Pb	34 ± 2	32 ± 6	1.06

The elemental concentrations determined by the AXIL programme are given in ng/cm^2. **Eqn 4-1** was used to express the value in ng/m^3. The minimum detection limits for the spectrometer are shown in **Table 4-2**.

TABLE 4-2: MINIMUM DETECTION LIMIT FOR PARTICULATE MATTER ON NUCLEPORE FILTERS WITH THE EDXRF SPECTROMETER

Element	DL (ng/cm^2)[a]	DL (ng/m^3)[b]
Al	436	228
Si	218	114
S	80	42
Cl	53	28
K	20	11
Ca	13	6.8
Ti	7.7	4
V	6	3.2
Cr	4.5	2.4
Mn	3.6	1.9
Fe	2.3	1.2
Co	1.9	1
Ni	1.3	0.7
Cu	1.2	0.6
Zn	1.1	0.6
Br	0.7	0.3
Rb	0.7	0.4
Sr	1	0.5
Pb	1.7	0.9

(a)DL is calculated as 3 times the square root of background concentration (3σ). Mo Ka: 17.44 keV, V=40 kV, I=40mA, collection time 2000 s.
(b)DL for particle concentration is calculated for a sampling of 24 m^3.

The statistical analysis for the measurements is given in **Tables 4-3** and **4-4** for coarse and fine fractions respectively. The number of filters contributing to the data set is given as counts together with the mean, standard deviation (Std Dev.), median, minimum and maximum values. It should be noted that the standard deviations listed in the tables, (Std Dev), are not "true" deviations which express fluctuations in experimental conditions for the analytical methods. Instead, they are combinations of these and the variations that occur due to changing weather conditions and human activities from one day to another. The median, minimum, maximum and St. Dev may

give better information on the extent of influence of these extreme conditions. The true Standard deviations for measurements on the same standard sample on this instrument are in the order of about 10 % (Selin Lindgren; 2006).[190]

Fig. 4-11 and **4-12** show the daily variations in the elemental concentration of some selected elements for coarse and fine fractions respectively.

TABLE 4-3: CONCENTRATION COARSE PM - ELEMENTS, BC AND MASS (28th December 2005 – 12 February 2007)

Element/ ng/m³	# of Days	Mean	StDev	Median	Min	Max
13 Al	201	3828.56	8707.43	1405.39	363.96	52309.42
14 Si	213	13540.01	33808.86	4286.64	118.63	233707.50
16 S	211	522.36	555.15	346.20	42.29	3425.45
17 Cl	213	1458.22	1210.71	1064.24	26.75	6981.94
19 K	213	1414.46	3290.09	467.99	12.08	24135.81
20 Ca	213	2203.30	5992.61	588.88	23.62	49899.12
22 Ti	213	398.75	971.19	128.18	4.21	7413.49
23 V	101	22.17	37.38	10.84	3.11	233.23
24 Cr	171	7.46	8.52	4.94	1.65	70.18
25 Mn	211	76.09	194.58	23.13	2.63	1644.17
26 Fe	216	3604.38	8521.80	1307.18	2.52	67143.01
27 Co	67	12.74	19.29	7.72	2.04	120.46
28 Ni	173	6.85	10.79	3.24	1.55	64.08
29 Cu	198	8.01	12.56	4.37	0.50	89.71
30 Zn	213	18.63	33.81	8.10	1.10	210.55
34 Se	23	0.54	0.13	0.53	0.27	1.06
35 Br	215	8.77	12.26	5.72	0.70	84.58
37 Rb	209	6.79	17.11	1.84	0.49	137.12
38 Sr	211	20.10	56.38	5.07	0.57	495.94
82 Pb	204	6.72	11.89	2.77	0.53	78.94
BC(µg/m³)	216	1.647	3.235	0.708	0.002	20.028
Mass (µg/m³)	216	151.142	308.035	57.040	0.160	1794.006

Table 4-4: CONCENTRATION OF FINE PM - ELEMENTS, BC and MASS (28th December 2005 – 12 February 2007)

Element/ ng/m³	# of Days	Mean	StDev	Median	Min	Max
Al	83	780.32	1031.55	374.31	49.16	6601.87
Si	177	1370.86	2843.47	374.54	70.27	22310.09
S	214	395.92	292.07	325.43	32.62	1252.09
K	214	329.82	305.84	230.56	17.44	2283.64
Ca	205	119.87	287.92	34.80	7.02	2702.69
Ti	181	32.63	59.55	11.86	2.67	465.19
Mn	185	6.81	10.63	3.24	0.99	84.58
Fe	216	246.27	456.51	96.20	2.07	3909.44
Ni	171	3.24	2.76	2.26	1.09	18.80
Cu	173	4.03	3.88	2.91	0.25	37.22
Zn	204	5.69	5.42	4.59	0.52	45.61
Br	215	5.07	3.56	4.13	0.79	17.13
Rb	130	1.38	1.35	1.06	0.18	9.40
Sr	84	2.81	4.19	1.08	0.33	23.49
Pb	169	2.38	1.66	2.00	0.49	10.02
BC (µg/m³)	216	1.646	1.133	1.681	0.010	5.968
Mass (µg/m³)	216	30.267	48.968	18.029	0.495	430.23

4.3 METEOROLOGICAL DATA

About 100 m from the sampling site, the Ghana Atomic Energy Commission has a mini weather station. The station measures the following parameters; maximum relative humidity, solar radiation, precipitation, minimum and maximum temperature with a resolution of 24 hours (daily). Unfortunately the station did not have the capability to measure wind speed and direction which is critical in determining the air pollution source directions. **Fig. 4-13** shows the monthly variation of particulate mass with total precipitation.

FIGURE 4-11: DAILY VARIATION OF SOME SELECTED COARSE PM ELEMENTS DURING THE INVESTIGATION PERIOD

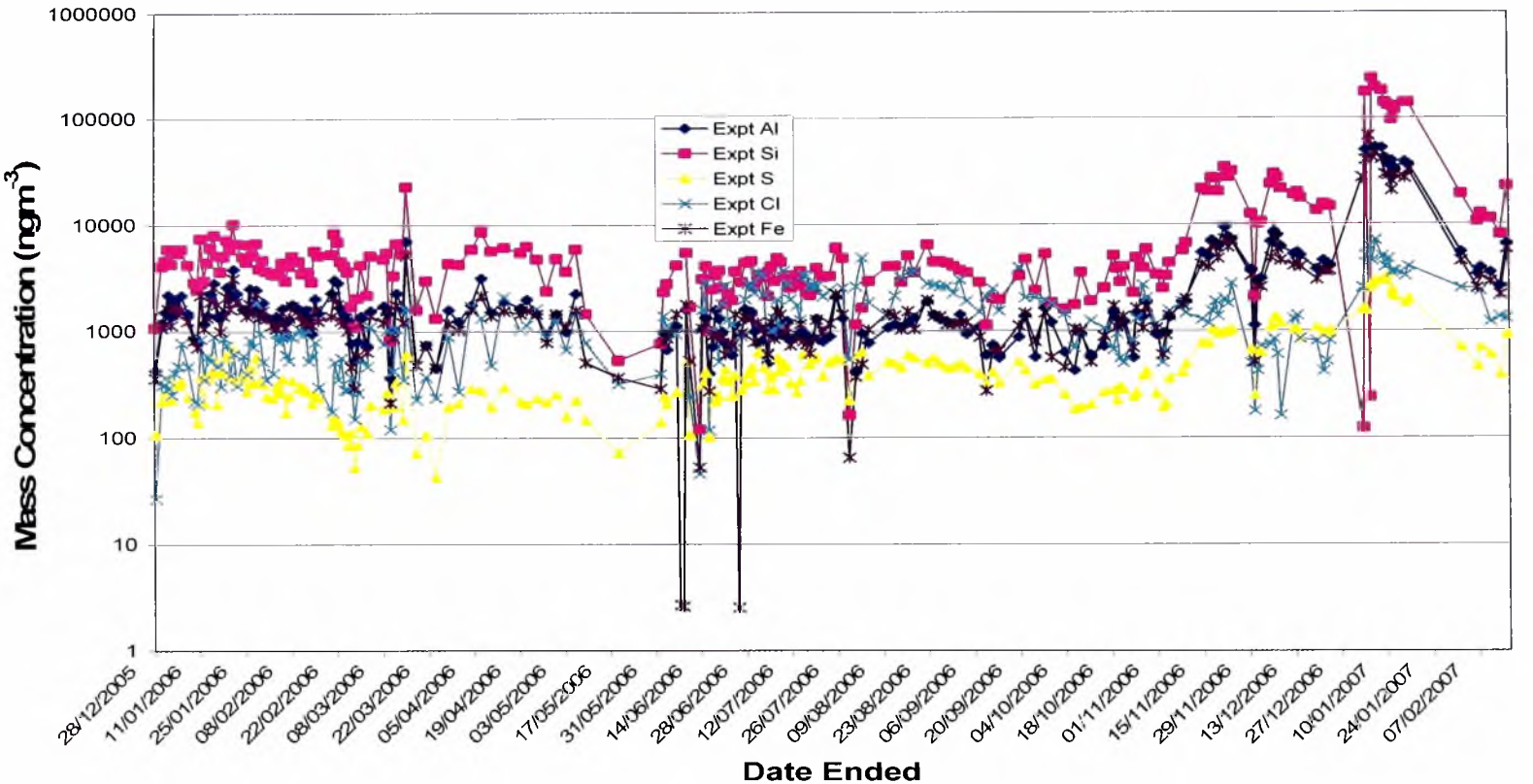


FIGURE 4-12: DAILY VARIATION OF SOME SELECTED FINE PM ELEMENTS DURING THE INVESTIGATION PERIOD

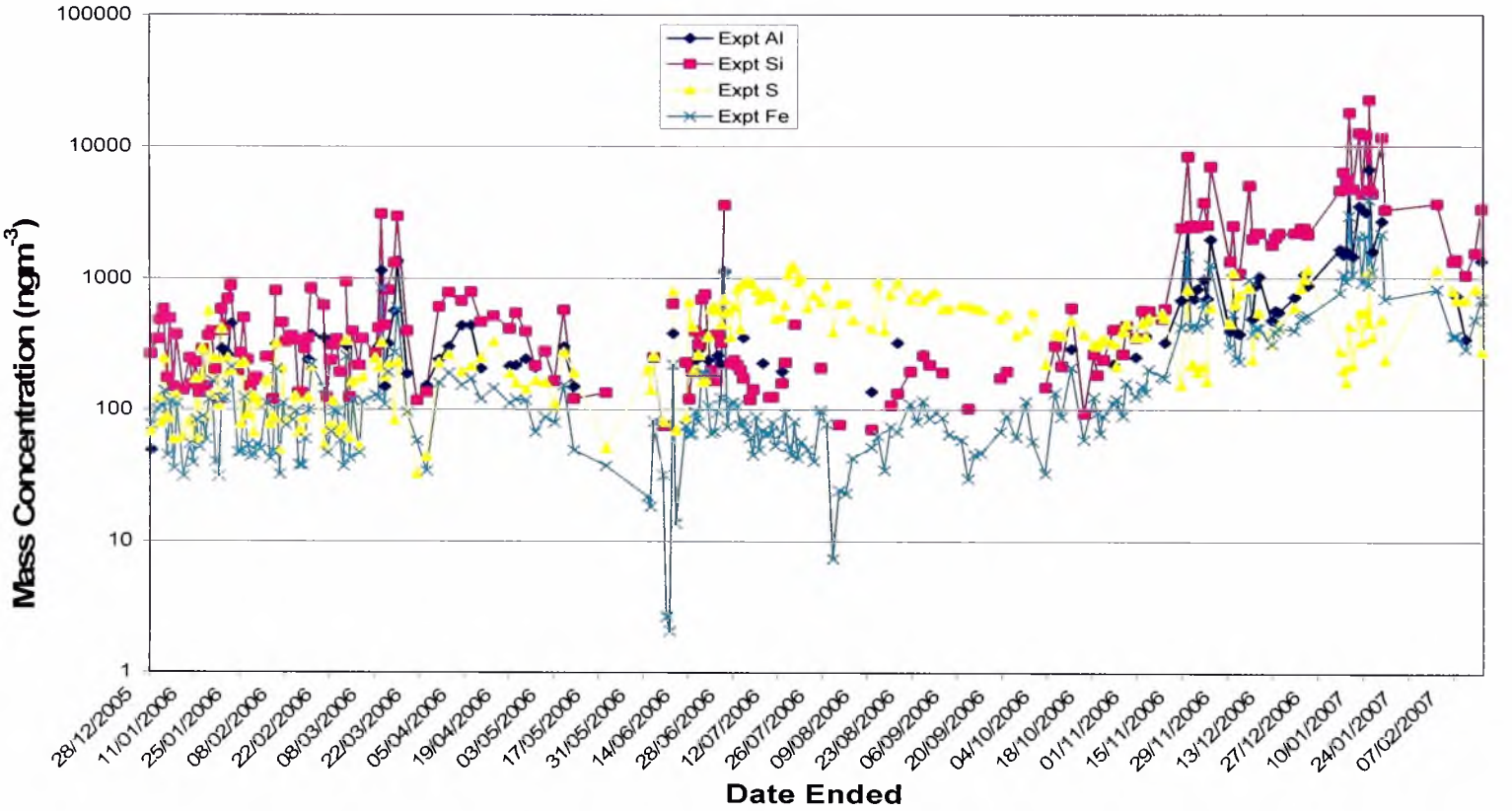
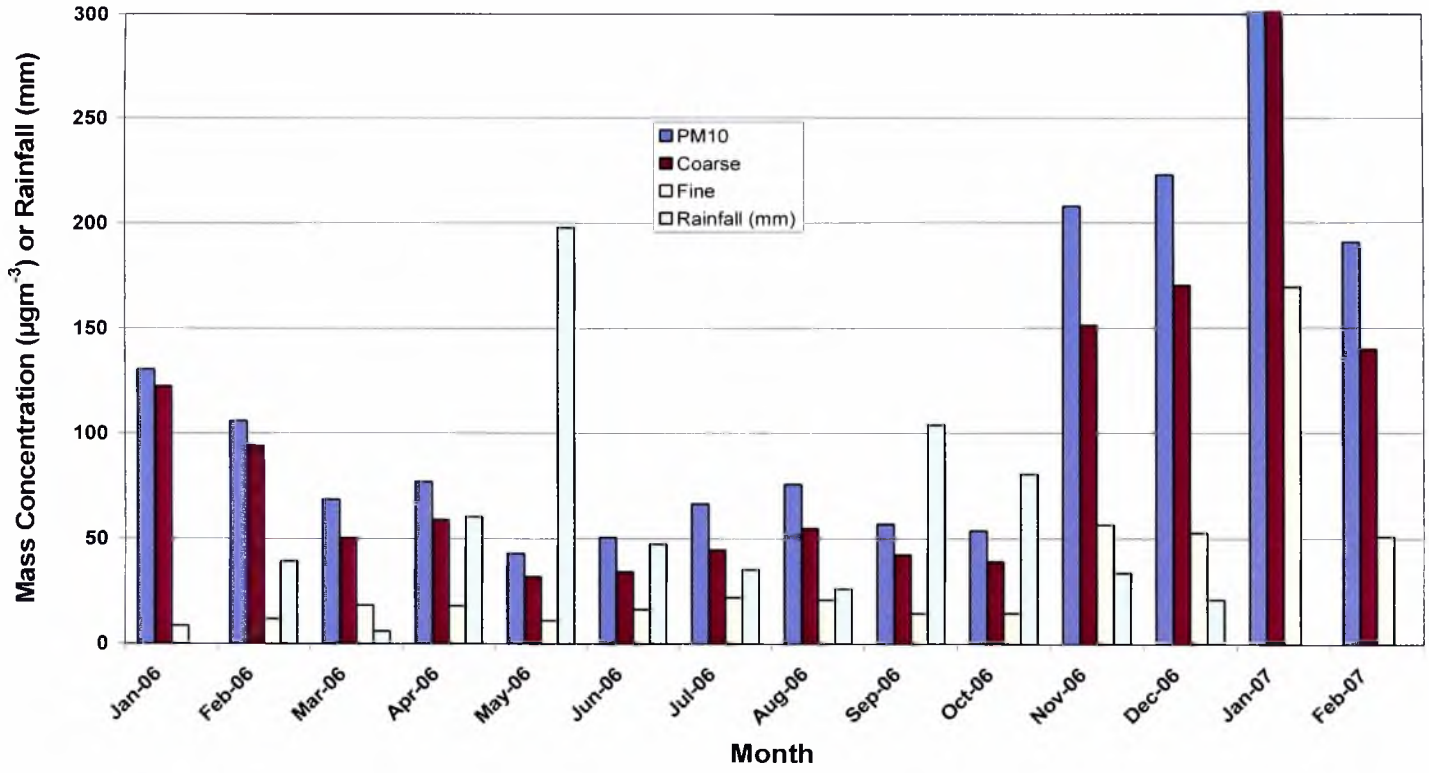


FIGURE 4-13: MONTHLY VARIATION OF PM WITH TOTAL PRECIPITATION



NB: *January 2007 coarse and PM10 values have been truncated to show the other monthly variations in detail, the real values are 1302.1 and 1471.4 µgm-3 respective*

CHAPTER 5

AIR POLLUTION AND RECEPTOR MODELING

5.1 OVERVIEW OF AIR POLLUTION MODELLING

Modeling of air pollution has become a very important tool for regulatory purposes, policy-making and research applications. Due to the high cost of air pollution monitoring, measurements combined with modeling have become a very efficient method in air pollution research. For effective management strategies to be developed for improving air quality, an understanding of the relationship between pollutant sources and their impact at a receptor site is required. Hence the need to identify the sources emitting the air pollutants, the amount of pollutants they are emitting and the physical and chemical transformations taking place during the dispersion.

Zannetti[192] classified air pollution models according to the basic characteristics of the model. This classification includes:

- Eulerian models – solve numerically atmospheric diffusion equation
- Gaussian models – in which the concentration distribution is Gaussian in both the horizontal and vertical directions
- Lagrangian models – which either consider processes in moving air mass to stimulate dispersion process
- Semi-empirical models – which are based on semi-empirical or statistical methods and seek to analyse the relationships of air quality and atmospheric measurements or to forecast air pollution episodes

- Receptor models – which consider the observed concentrations at a receptor point and attempt to apportion the contributions from various sources.

Broadly, there are three main air quality models, namely dispersion models, statistical models and receptor models.

5.1.1 DISPERSION MODELS

Atmospheric dispersion models describe the turbulent diffusion processes in the atmosphere and are mainly used for a wide variety of purposes such as:[193]

- Establishing a source-receptor relationships;
- Evaluating the contribution to concentrations from various sources
- Estimating the distribution of spatial concentration and population exposure to pollution
- Optimizing emission reduction strategies and analyzing emission scenarios
- Predicting the concentrations over time
- Analyzing the representativity measurement of stations
- As tools for research

All the above cannot be accomplished using only air quality measurements. Hence these models require meteorological and geographical information in addition to source and emission data. There are some limitations such as inaccuracy in estimation of the input data, deficiencies in modeling the physical and chemical phenomena. To minimize these, the models have to be subjected to continual quality control and assurance procedures. In addition, a high quality data base and continuous evaluation of the model is needed.

The dispersion models are usually classified as:

- Local – time scale less than a few minutes
- Local to Regional – several hours
- Regional to Continental – several days
- Continental to Global – weeks or more

Dispersion models on the local scale are usually used for quantification of the concentrations of pollutants that can cause adverse health effects and deposition of air pollutants and its influence. Models based on Gaussian concentration are widely used and mainly for regulatory purpose.

Regional scale models are mainly used for policy-making or research purposes. They are used for quantifying deposition and concentrations of elements such as sulfur, nitrogen compound and other compound such as photo-oxidants (e.g. ozone). They are also used for heavy metal, persistent organic pollutants (POP) and radioactive and hazardous materials air quality episodes.

Continental scale models, also known as long-range transport has the same aim and purpose as the regional scale models. In the continental scale however, it is very important to take into account parameters of the atmospheric boundary layer and the relevant weather conditions over the modeling period.

5.1.2. STATISTICAL MODELS

These types of models do not explicitly cover the dispersion and chemical transformation of air pollutants in the atmosphere. Statistical model can be of several types, including

rapid assessment and empirical models. The main aim of these types of models is to summarise the key results from detailed models of air pollutants in the form of graphs and look-up chart. Some statistical models also use the relationship between measured quality and parameters related to weather and emissions. When these are integrated with inventory techniques these models could be used to study the following types of situations:

- The impact of emissions from an individual point source on short-term air quality at a critical receptor and/or at a known distance from the source
- The impact of the emissions from an individual point source on the long-term average air quality in the vicinity
- The impact of area source emission, such as road traffic and bush burning related emissions, on the long-term average air quality of an urban area.

These types of models require extensive database of historical air quality measurement and meteorological data to formulate the model. In the Netherlands[194] such a model for ozone monitoring is in use. The model requires the maximum concentration of the measuring sites of the previous day, statistics from the past and the maximum temperature of the previous day and the forecast temperature, both as averages for the Netherlands to forecast the ozone level for the next three days.

5.1.3 RECEPTOR MODELS

Receptor models focus on the behaviour of the ambient environment at site (normally called a receptor) as opposed to source-oriented models which focus on transport, dilution and transformations from the source to the sampling or receptor site. The

fundamental principle of receptor modeling is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of contaminants in the atmosphere.[195] Airborne pollutants in the atmosphere form a very complex system, hence mathematical or statistical methods are used to identify and apportion the sources.

Chemical characteristics such as elemental concentration or shape of particles in a series of particle samples at the receptor can be used to resolve the main sources. To obtain a data set for receptor analysis, the normal approach is to analyse a large number of chemical constituents such as elemental, organic or gaseous concentration in the air samples. Elemental tracers are used in most receptor modeling but elements alone are not always sufficient to distinguish emitting source. For example, when leaded motor fuel was in use, lead and bromine were the main markers of road traffic pollution, but with the ban on leaded fuel these elements are disappearing as makers of road traffic pollution. Though current receptor models are focusing on chemical compositions, elemental concentrations are still being used. The elemental concentration if combined with other measurements such as BC, mass and chemical compositions are better in resolving the sources.

Several approaches have been successfully applied to receptor modeling.[196-199] Receptor models can be divided into two main groups; chemical mass balance and multivariate methods. Data from measuring site and potential sources are used in chemical mass balance method thus allowing, in principle, calculation of proportions of various known sources sampled at the receptor (measuring) site. The multivariate methods, e.g. target transformation factor analysis and principal component analysis with multiple linear

regression analysis, usually use only chemical composition data to ascertain the number of sources, the chemical composition of their emissions and their relative contributions to the measured concentrations. Because the source apportionment is based on statistical methods, these methods require a large sample dataset, the more the better.

Chemical mass balance requires that the composition of all the contributing sources be known, but this is not often the case since it is not practicable since the emissions are difficult to recognize and sample. Secondly the analytical technique cannot measure all the species in the source or the source composition fail to contain all the species observed in the samples. Using the multivariate models these problems can be overcome. It is also the only method available when there is no source information.

5.2 RECEPTOR MODELING USED IN THIS WORK

Most multivariate receptor models, as in this work, first apply principal component analysis (PCA) to the data set. PCA describes a system by determining a minimum set of vectors that span the data space to be interpreted. A new set of variables are found as linear combinations of the measured variables so that the observed variations in the system can be reproduced by a smaller number of these causal factors. PCA has been widely used in studies of airborne particulate matter composition data since the early 1980s.[200] PCA is generally available in most computer package for statistical analysis for examples SPSS and NCSS.

The model assumes a linear model relating experimental measured variables and the source profile matrix

$$\mathbf{C} = \mathbf{P} \cdot \mathbf{S} \qquad \ldots 5\text{-}1$$

where

C is the data matrix of dimension **i**,**k** and units are ng/m^3

P is the source profile matrix of distinct sources of dimension **i**,**j** and units are $ng/\mu g_{source}$

S is the source contribution matrix of dimension **j**,**k** and units ng_s/m^3

Equation 5-1 can be generalised as:

$$\mathbf{c}_{m,n} = \Sigma_l \, \mathbf{p}_{m,l} \, \mathbf{s}_{l,n} \qquad 5\text{-}2$$

where

$\mathbf{c}_{m,n}$ is the measured concentration of variable **m** in observation number **n**

$\mathbf{p}_{m,l}$ is the modelled concentration of variable **m** in source **l**

$\mathbf{s}_{l,n}$ is the modelled contribution to source **l** in observation number **n**

PCA can be performed only on set of samples in which the various sources contribute different amounts of particles to each sample; the mass balance is a matrix equation of the form:

$$\mathbf{Z} = \mathbf{L} \cdot \mathbf{F} \qquad \ldots 5\text{-}3$$

where

Z is sampling matrix

L is factor loading matrix and

F is factor score matrix respectively.

In a PCA analysis, the data are normalised by subtracting a mean value $\langle \mathbf{c_m} \rangle$ and dividing by the standard deviation, σ_m

$$\mathbf{z_{m,n}} = (\mathbf{c_{m,n}} - \langle \mathbf{c_m} \rangle)/\sigma_m \qquad \ldots 5\text{-}4$$

where a row, **m**, in **Z** corresponds to the autoscaled values of the variable, **m**, in **C**.

In this case each standardised value has a mean value of zero and a standard deviation of 1. Hence the values of **Z** are autoscaled concentrations and **L** gives the contributions to the measured variables from the factors identified. The factor scores **F** show the daily contributions from the different factors (sources).

To rescale **L** and **F** to the physical meaningful matrices **P** and **S,** a 'tracer' sample with sample number n+1, having all the variables set to zero is included in the data set.[129,190] PCA is used to determine the score matrix **F** in which the rows are treated as autoscaled values of the row in the source matrix.

The sample mass which was determined by gravimetric analysis is then used in a mass balance calculation to transform the scaled scores into unscaled source matrix. This was achieved by regression of the transformed values on the mass variable of the coarse. The source matrix of the particulate matter (i.e coarse particles) values must be related to the experimental mass value, C_{cs} by the relation:

$$\mathbf{C_{cs,n}} = \Sigma_m \mathbf{s_{m,n}} = \sigma_m(\mathbf{f_{m,n}} - \mathbf{f_{m,n+1}}) \qquad \ldots 5\text{-}5$$

where $\mathbf{s_{m,n}}$ and $\mathbf{f_{m,n}}$ are the source, **S** and autoscaled variable in **F** respectively for variable **m** in observation **n**..

The coefficients σ_m are found by regression of $(f_{m,n} - f_{m,n+1})$ on $C_{cs,n}$. The elements in the source matrix describe the daily variation of the PM (coarse PM as in this example) mass-variable of the source in ng/m^3. The source profile matrix is then calculated from:

$$\mathbf{P = CS^T (SS^T)^{-1}} \qquad \ldots 5\text{-}6$$

This was repeated for the fine fraction ($PM_{2.5}$).

There exists a set of natural physical constraints in order to obtain physical meaningful results:

- The predicted source compositions must be non-negative; a source cannot have a negative percentage of an element. Hence all negative values of **S** and **L** must be truncated to zero.
- The predicted source compositions to the aerosol must all be non-negative; source cannot emit a negative mass.
- The sum of the predicted elemental mass contributions for each source must be less or equal to the total measured mass for each element.

The accuracy of the model is determined by how good the experimental data can be reproduced by the model.

5.3 RESULTS OF THE RECEPTOR MODEL

The species used in receptor model are mass, BC, elemental concentrations. In the PCA analysis, several runs were made. The number of factors was varied and varimax as well as promax rotations were performed. It was assumed that the pollution sources will be independent of each other and because varimax gave the most consistent results it was the

rotation that was used in the factor analysis. It was found that the same factors appeared in the analysis even if some variables were omitted, although the factor loadings for the different elements varied slightly.

TABLE 5-1: CONCENTRATION OF COARSE PM - ELEMENTS, BC AND MASS (28TH DECEMBER 2005 – 31 MARCH 2006)

Element/ ($ng/m^{3)}$	# of Days	Mean	StDev	Median	Min	Max
Al	68	1672.25	936.16	1510.35	363.96	7044.23
Si	69	4771.18	2847.20	4449.88	819.19	22834.64
S	68	265.58	137.69	251.98	42.29	684.55
Cl	69	573.55	340.60	511.87	26.75	1861.36
K	69	480.89	243.34	439.50	72.91	1657.06
Ca	69	647.50	415.33	615.47	102.76	3444.44
Ti	69	151.03	79.10	140.13	23.54	574.79
V	51	11.83	4.67	10.91	3.11	24.27
Cr	55	6.29	2.94	6.11	1.79	14.87
Mn	69	27.53	14.69	27.37	4.02	106.16
Fe	69	1377.56	700.99	1277.82	211.83	5177.45
Co	48	8.32	3.09	8.07	2.19	17.35
Ni	26	3.28	1.13	3.15	1.82	7.77
Cu	51	3.18	1.42	3.17	0.50	10.36
Zn	69	8.29	6.86	6.86	1.72	53.94
Br	68	2.90	1.35	2.86	0.70	9.49
Rb	69	2.22	1.15	2.13	0.53	7.77
Sr	69	5.66	3.47	5.65	0.57	28.48
Pb	65	2.80	1.34	2.63	0.53	6.45
BC ($\mu g/m^3$)	69	0.57	0.33	0.50	0.01	1.69
Mass ($\mu g/m^3$)	69	88.66	48.25	89.59	8.64	228.17

When the whole data spanning 14 months were used in the model, the fit between the experimental and the model was not very good. This could be attributed to the varying sources and source strength which are seasonal dependent. The data was therefore divided into three, according to the seasons – Harmattan (December 2005 – March 2006), Raining (April 2006– October 2006) and Harmattan (November 2006 – February 2007).

Tables 5-1 to 5-6 give the statistical analysis for the measurements when the dataset was divided according to the classifications above. The number of filters contributing to the data set is given as number of days together with the mean, standard deviation (Std Dev.), median, minimum and maximum values.

TABLE 5-2: CONCENTRATION OF FINE PM - ELEMENTS, BC AND MASS (28TH DECEMBER 2005 – 31 MARCH 2006)

Element/ng/m^3	# of Days	Mean	StDev	Median	Min	Max
Al	20	381.51	318.54	301.80	49.16	1352.40
Si	65	448.36	521.82	327.65	117.55	3078.72
S	69	145.95	99.20	116.38	32.62	567.04
K	69	144.04	99.48	116.07	17.44	462.73
Ca	68	46.22	60.68	32.80	8.48	415.62
Ti	56	14.59	15.61	10.90	3.17	98.74
Mn	48	3.54	2.79	2.68	1.14	16.65
Fe	69	112.59	121.84	88.28	31.20	847.32
Ni	24	2.22	0.62	2.13	1.48	4.32
Cu	26	2.42	0.67	2.23	0.25	4.02
Zn	60	2.17	1.32	2.00	0.52	7.46
Br	68	2.00	1.01	1.69	0.79	5.42
Rb	16	0.73	0.37	0.61	0.18	1.72
Sr	15	1.17	0.98	0.97	0.33	3.45
Pb	29	1.29	0.57	1.18	0.51	2.87
BC (µg/m^3)	69	0.70	0.66	0.52	0.01	2.96
Mass (µg/m^3)	69	10.59	7.72	7.91	2.03	37.84

TABLE 5-3: CONCENTRATION OF COARSE PM - ELEMENTS, BC AND MASS (4TH APRIL – 31 OCTOBER 2006)

Element/ng/m^3	# of Days	Mean	StDev	Median	Min	Max
Al	90	1128.45	456.63	1052.18	400.98	3185.81
Si	97	3423.89	1530.08	3350.16	118.63	8581.07
S	96	360.40	140.21	339.55	71.09	662.47
Cl	97	1790.63	988.34	1753.71	45.58	4900.17
K	97	418.90	168.14	413.50	12.08	1432.84
Ca	97	482.38	186.97	471.09	23.62	1048.34
Ti	97	94.12	44.18	88.14	4.21	247.06
V	23	5.14	1.13	4.80	3.64	7.43
Cr	79	4.27	2.00	3.73	1.65	13.98
Mn	96	17.34	6.61	16.82	2.63	37.84
Fe	100	1023.49	460.57	1034.55	2.52	2212.74
Ni	100	3.17	0.80	3.16	1.55	6.44
Cu	100	4.48	1.00	4.32	2.52	7.93
Zn	97	8.14	4.03	7.57	1.10	36.47
Se	18	0.50	0.07	0.53	0.27	0.56
Br	100	6.23	1.76	6.12	2.01	12.01
Rb	93	1.44	0.57	1.55	0.49	3.20
Sr	96	4.14	1.41	4.13	0.99	8.90
Pb	93	2.77	1.53	2.52	0.66	8.46
BC (µg/m^3)	100	0.67	0.24	0.68	0.04	1.46
Mass (µg/m^3)	100	42.81	16.56	42.58	0.16	87.84

TABLE 5-4: CONCENTRATION OF FINE PM ELEMENTS, BC AND MASS (4TH APRIL – 31 OCTOBER 2006)

Element/ ng/m^3	# of Days	Mean	StDev	Median	Min	Max
Al	27	294.73	184.51	243.82	136.44	1128.73
Si	65	333.84	445.18	222.42	70.27	3578.00
S	98	513.26	275.76	493.77	50.85	1252.09
K	98	293.45	181.06	249.16	21.14	744.58
Ca	90	33.62	51.54	24.11	7.02	494.39
Ti	78	10.07	10.69	7.70	2.67	91.63
Mn	91	3.20	1.97	2.76	0.99	18.12
Fe	100	91.21	109.38	75.58	2.07	1087.95
Ni	100	2.30	0.58	2.14	1.09	4.98
Cu	100	2.94	0.85	2.68	1.71	7.90
Zn	97	5.78	3.12	5.52	0.99	25.90
Br	100	6.47	3.51	5.76	1.04	17.13
Rb	69	0.96	0.49	1.01	0.37	2.14
Sr	23	0.67	0.63	0.53	0.37	3.52
Pb	95	2.15	1.15	2.04	0.49	6.87
BC (µg/m^3)	100	1.92	0.86	1.90	0.10	4.63
Mass (µg/m^3)	100	17.69	7.71	17.76	0.50	41.14

TABLE 5-5: CONCENTRATION OF COARSE PM - ELEMENTS, BC AND MASS (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Element /ng/m^3	# of Days	Mean	StDev	Median	Min	Max
Al	43	12889.96	15874.20	5396.71	937.75	52309.42
Si	47	47291.35	61286.19	19919.45	120.01	233707.50
S	47	1224.69	826.17	991.58	188.41	3425.45
Cl	47	2070.95	1659.78	1438.02	158.36	6981.94
K	47	4839.69	5861.45	2094.16	219.75	24135.81
Ca	47	8039.03	10977.46	3336.12	342.28	49899.12
Ti	47	1391.15	1743.45	507.47	54.37	7413.49
V	27	56.20	60.51	20.65	3.67	233.23
Cr	37	15.98	14.91	9.47	3.18	70.18
Mn	46	271.54	355.30	101.90	11.34	1644.17
Fe	47	12364.79	15424.33	4490.79	498.41	67143.01
Co	10	42.64	38.58	43.41	4.23	120.46
Ni	47	16.64	17.28	8.49	2.65	64.08
Cu	47	20.77	21.27	10.68	3.78	89.71
Zn	47	55.49	58.17	26.51	4.86	210.55
Br	47	22.63	20.71	12.54	3.78	84.58
Rb	47	24.09	30.42	10.04	1.08	137.12
Sr	46	75.10	104.19	29.89	2.70	495.94
Pb	46	20.23	19.73	10.44	1.62	78.94
BC(µg/m^3)	47	5.30	5.58	2.63	0.63	20.03
Mass (µg/m^3)	47	473.37	549.55	192.85	24.35	1794.01

TABLE 5-6: CONCENTRATION OF FINE PM - ELEMENTS, BC AND MASS (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Element/ng/m^3	# of Days	Mean	StDev	Median	Min	Max
Al	36	1366.06	1336.78	869.96	320.84	6601.87
Si	47	4080.85	4478.26	2402.82	483.59	22310.09
S	47	518.24	285.93	458.89	153.83	1158.51
K	47	678.39	413.09	609.34	182.37	2283.64
Ca	47	391.58	509.03	220.02	46.18	2702.69
Ti	47	91.54	92.67	53.61	13.27	465.19
Mn	46	17.39	17.15	9.99	3.20	84.58
Fe	47	772.43	751.27	477.03	133.77	3909.44
Ni	47	5.75	4.28	3.65	2.12	18.80
Cu	47	7.22	6.33	5.13	2.29	37.22
Zn	47	10.02	8.45	6.80	2.98	45.61
Br	47	6.53	3.26	5.71	2.11	15.38
Rb	45	2.25	1.93	1.81	0.52	9.40
Sr	46	4.42	5.10	2.33	0.52	23.49
Pb	45	3.57	2.28	2.70	1.19	10.02
BC (µg/m^3)	47	2.44	1.27	2.11	0.46	5.97
Mass (µg/m^3)	47	85.91	83.09	51.84	22.09	430.23

The PCA analysis value of the Coarse data for 2nd November 2006 – 15th February 2007 is presented as an example in **Table 5-7**. The PCA score less the "tracer" scores for the same set of samples is also presented in **Table 5-8**. The mean values obtained for the mass balance computation were as follows: 400.91, 199.19, 283.31, 81.07 and 0.36 for the factor scores 1 to 5 respectively.

The computed source, **S**, values greater than zero (S>0) are presented in **Table 5-9**. The source profile values are presented in **Table 5-10**.

Fig. 5-1, **5-2**, **5-3** and **5-4** show the correlation between the model values and experimental data for some selected species of the aerosol (mass, BC, Fe and Cl respectively). **Fig. 5-5**, **5-6**, **5-7**, and **5-8** show a time series plot of the model and experimental data for the selected species above.

The same procedures were repeated for the fine and coarse data for the dataset with statistical values given in **Tables 5-1** to **5-6**. The gradients, squared correlation coefficient – R^2, intercept are given in **Tables 5-11** to **5-16**.

TABLE 5-7: PCA FACTOR SCORES FOR COARSE DATA (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Filter #	F Score1	F Score2	F Score3	F Score4	F Score5
C248	-0.399	-0.503	-0.373	-0.796	0.001
C249	-0.390	-0.358	-0.452	-0.813	0.103
C250	-0.362	-0.296	-0.403	-0.856	0.288
C251	-0.322	-0.440	-0.301	-0.845	0.485
C252	-0.400	-0.304	-0.427	-0.427	0.250
C254	-0.321	-0.594	-0.002	-0.235	-0.327
C255	-0.269	-0.153	-0.349	-0.291	0.226
C256	-0.337	-0.177	-0.198	0.231	-0.383
C257	-0.204	-0.657	-0.193	0.393	-0.111
C258	-0.458	-0.555	-0.038	0.308	0.261
C260	-0.280	-0.218	0.113	-0.509	0.470
C261	-0.338	-0.341	0.077	-0.344	0.276
C262	-0.207	-0.127	-0.048	-0.264	1.222
C263	-0.465	-0.208	-0.374	-0.163	-0.736
C264	-0.362	-0.273	-0.634	-0.472	0.974
C266	-0.460	-0.447	-0.316	-0.047	-0.469
C267	-0.458	-0.220	-0.396	-0.266	-0.421
C268	-0.523	0.351	-0.585	0.547	0.120
C269	-0.478	0.444	-0.633	1.247	-0.996
C270	-0.525	-0.052	-0.224	0.665	-1.105
C271	-0.586	-0.268	-0.139	0.522	-1.071
C272	-0.453	-0.075	-0.252	0.012	-0.532
C274	-0.462	-0.086	-0.182	-0.200	-0.135
C275	-0.473	-0.126	-0.302	-0.076	-0.205
C276	-0.568	-0.262	-0.271	0.294	-0.775
C277	-0.551	-0.161	-0.405	0.490	-0.702
C278	-0.551	-0.178	-0.366	0.322	-0.262
C279	-0.580	-0.024	-0.489	0.513	-0.233
C281	1.334	-0.107	-1.410	1.173	-0.998
C282	1.643	4.124	-0.388	-3.573	-0.464
C283	5.300	-1.215	-2.956	1.103	0.720
C284	2.238	-2.761	3.266	-0.814	-0.691
C285	1.497	1.276	2.094	-0.733	-0.492
C286	0.550	1.770	1.291	1.891	-1.038
C287	0.277	0.410	1.863	0.439	-1.798
C288	-0.268	1.791	0.314	3.323	2.262
C289	0.111	-0.958	1.562	1.303	-0.798
C290	0.011	1.420	0.893	0.774	3.650
C291	0.135	1.584	0.383	1.363	-0.359
C292	0.505	-1.081	2.721	-0.490	2.407
C293	0.659	1.567	0.884	-0.080	-1.431
C294	-0.256	-0.099	-0.196	-0.750	1.170
C296	-0.269	0.133	-0.457	-1.158	0.590
C297	-0.336	-0.182	-0.289	-0.595	0.617
C298	-0.401	-0.153	-0.385	-0.410	-0.119
C299	-0.229	-0.541	-0.334	-0.580	1.213
C300	-0.308	-0.138	-0.258	-0.118	-0.358
C000	-0.410	-0.533	-0.436	-1.008	-0.299
StDev	1	1	1	1	1
Mean	-6.6×10^{-17}	-4.7×10^{-16}	-3.7×10^{-16}	-8.6×10^{-16}	-3×10^{-16}

TABLE 5-8: PCA FACTOR SCORES LESS TRACER VALUE (C000) FOR COARSE DATA (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Filter #	FS1-Zero	FS2-Zero	FS3-Zero	FS4-Zero	FS5-Zero
C248	0.011	0.030	0.063	0.213	0.300
C249	0.021	0.175	-0.017	0.196	0.402
C250	0.049	0.237	0.033	0.152	0.587
C251	0.088	0.093	0.134	0.164	0.784
C252	0.010	0.229	0.009	0.581	0.548
C254	0.089	-0.061	0.434	0.773	-0.028
C255	0.142	0.380	0.087	0.717	0.525
C256	0.074	0.356	0.238	1.239	-0.085
C257	0.207	-0.124	0.242	1.401	0.187
C258	-0.048	-0.022	0.398	1.316	0.560
C260	0.130	0.316	0.549	0.500	0.769
C261	0.072	0.193	0.513	0.664	0.574
C262	0.203	0.407	0.387	0.744	1.520
C263	-0.054	0.325	0.061	0.845	-0.437
C264	0.048	0.260	-0.199	0.536	1.273
C266	-0.049	0.086	0.120	0.961	-0.170
C267	-0.048	0.313	0.040	0.742	-0.123
C268	-0.112	0.884	-0.149	1.555	0.419
C269	-0.068	0.977	-0.197	2.256	-0.698
C270	-0.114	0.481	0.211	1.673	-0.806
C271	-0.176	0.265	0.296	1.530	-0.772
C272	-0.043	0.458	0.183	1.021	-0.233
C274	-0.052	0.447	0.253	0.808	0.164
C275	-0.063	0.408	0.133	0.932	0.093
C276	-0.157	0.271	0.165	1.302	-0.477
C277	-0.141	0.372	0.031	1.498	-0.403
C278	-0.141	0.355	0.069	1.330	0.037
C279	-0.170	0.510	-0.054	1.522	0.066
C281	1.745	0.426	-0.974	2.182	-0.699
C282	2.053	4.657	0.047	-2.564	-0.165
C283	5.711	-0.682	-2.521	2.111	1.019
C284	2.649	-2.228	3.702	0.195	-0.393
C285	1.907	1.809	2.529	0.275	-0.193
C286	0.960	2.303	1.727	2.899	-0.739
C287	0.688	0.943	2.299	1.447	-1.500
C288	0.143	2.324	0.749	4.331	2.561
C289	0.522	-0.425	1.998	2.311	-0.499
C290	0.421	1.953	1.329	1.782	3.948
C291	0.545	2.117	0.818	2.371	-0.061
C292	0.915	-0.548	3.157	0.518	2.706
C293	1.069	2.101	1.320	0.929	-1.132
C294	0.155	0.434	0.240	0.258	1.469
C296	0.142	0.666	-0.022	-0.150	0.888
C297	0.075	0.351	0.146	0.413	0.916
C298	0.010	0.381	0.050	0.598	0.179
C299	0.182	-0.008	0.101	0.429	1.512
C300	0.102	0.396	0.178	0.890	-0.059
C000	0.000	0.000	0.000	0.000	0.000

TABLE 5-9: COMPUTED SOURCE CONTRIBUTION TO THE VARIOUS COARSE FILTER MASS (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Filter #	Source 1	Source 2	Source 3	Source 4	Source 5
C248	4.57	5.99	17.71	17.23	0.11
C249	8.27	34.94	0.00	15.87	0.15
C250	19.62	47.19	9.34	12.34	0.21
C251	35.42	18.60	38.03	13.27	0.29
C252	4.17	45.66	2.44	47.11	0.20
C254	35.68	0.00	122.87	62.70	0.00
C255	56.82	75.71	24.63	58.12	0.19
C256	29.55	70.89	67.31	100.44	0.00
C257	82.83	0.00	68.59	113.56	0.07
C258	0.00	0.00	112.72	106.71	0.20
C260	52.26	62.84	155.54	40.51	0.28
C261	28.91	38.35	145.26	53.84	0.21
C262	81.48	80.95	109.74	60.34	0.55
C263	0.00	64.69	17.36	68.50	0.00
C264	19.29	51.83	0.00	43.47	0.46
C266	0.00	17.21	33.98	77.93	0.00
C267	0.00	62.38	11.25	60.16	0.00
C268	0.00	175.98	0.00	126.09	0.15
C269	0.00	194.62	0.00	182.85	0.00
C270	0.00	95.793	59.83	135.63	0.00
C271	0.00	52.76	83.92	124.04	0.00
C272	0.00	91.29	51.91	82.74	0.00
C274	0.00	89.10	71.82	65.53	0.06
C275	0.00	81.15	37.80	75.55	0.03
C276	0.00	53.93	46.74	105.54	0.00
C277	0.00	74.02	8.69	121.45	0.00
C278	0.00	70.65	19.65	107.83	0.01
C279	0.00	101.48	0.00	123.35	0.02
C281	699.56	84.78	0.00	176.86	0.00
C282	823.23	927.26	13.42	0.00	0.00
C283	2289.41	0.00	0.00	171.13	0.37
C284	1061.92	0.00	1048.81	15.79	0.00
C285	764.72	360.29	716.63	22.33	0.00
C286	384.87	458.60	489.24	235.01	0.00
C287	275.66	187.76	651.27	117.34	0.00
C288	57.16	462.72	212.31	351.12	0.93
C289	209.15	0.00	566.03	187.36	0.00
C290	168.85	388.89	376.47	144.50	1.43
C291	218.52	421.63	231.87	192.24	0.00
C292	366.86	0.00	894.42	42.01	0.98
C293	428.63	418.27	374.00	75.29	0.00
C294	61.97	86.35	67.95	20.94	0.53
C296	56.76	132.65	0.00	0.00	0.32
C297	29.94	69.92	41.44	33.47	0.33
C298	3.97	75.77	14.26	48.52	0.07
C299	72.86	0.00	28.71	34.74	0.55
C300	40.89	78.77	50.32	72.18	0.00
C000	0.00	0.00	0.00	0.00	0.00
Mean	180.99	123.16	147.80	86.32	0.18

TABLE 5-10: COMPUTED SOURCE PROFILE VALUES FOR COARSE DATA (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Element (ng/m^3)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Al		59.51	31.30	9.13	2046.65
Si	4.16	177.91	186.71		
S		1.22	1.95	6.90	16.62
Cl	2.23	3.95	2.77	4.13	989.840
K	9.84	9.67	8.01	9.55	
Ca	20.90	10.95	13.53	10.94	722.27
Ti	2.93	2.65	2.18	3.32	
V	0.10	0.08	0.04	0.08	
Cr		0.08		0.02	
Mn	0.67	0.49	0.34	0.47	13.02
Fe	26.63	23.43	18.21	28.95	
Ni	0.02	0.02	0.03	0.04	8.56
Cu	0.03	0.03	0.02	0.07	14.44
Zn	0.07	0.18	0.04	0.17	9.95
Br	0.03	0.04	0.03	0.06	9.95
Rb	0.06	0.05	0.03	0.05	
Sr	0.21	0.09	0.109	0.120	6.35
Pb	0.02	0.05	0.02	0.10	
BC ($\mu g/m^3$)		0.01	0.01	0.02	
Mass($\mu g/m^3$)	0.64	1.21	1.09	0.69	0.66

FIGURE 5-1: COARSE PM MASS – MODEL COMPARED WITH EXPERIMENTAL

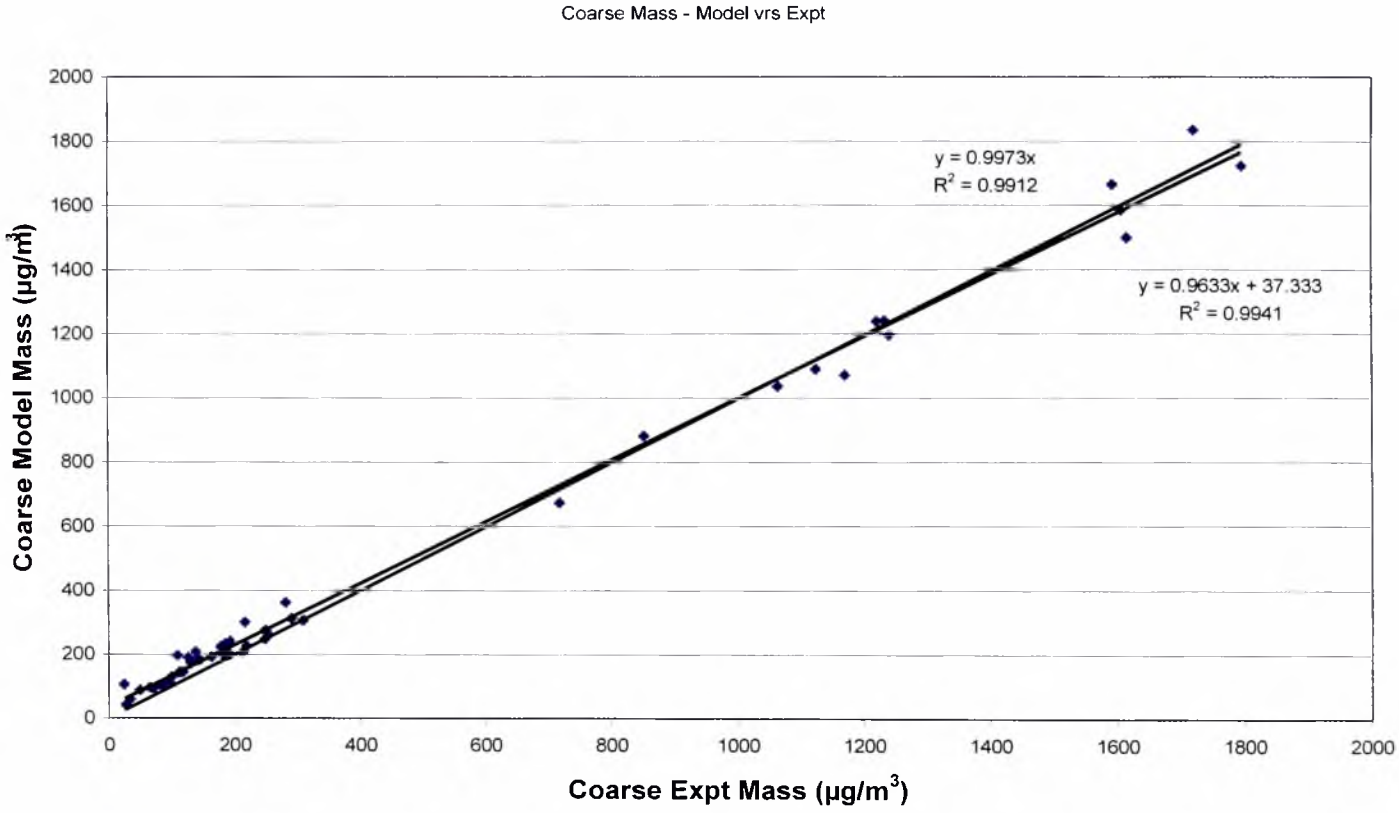


FIGURE 5-2: COARSE BC – MODEL COMPARED WITH EXPERIMENTAL

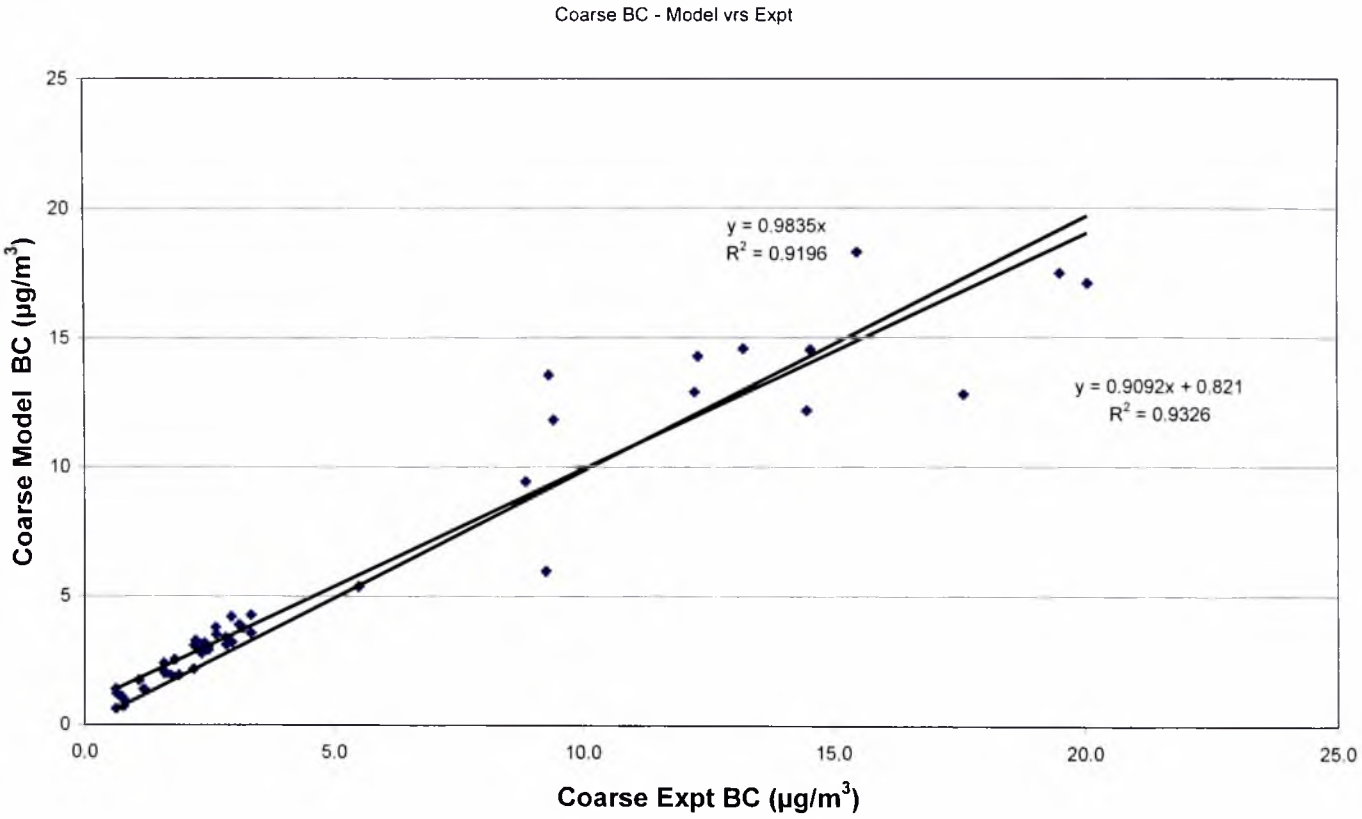


FIGURE 5-3: COARSE Fe – MODEL COMPARED WITH EXPERIMENTAL

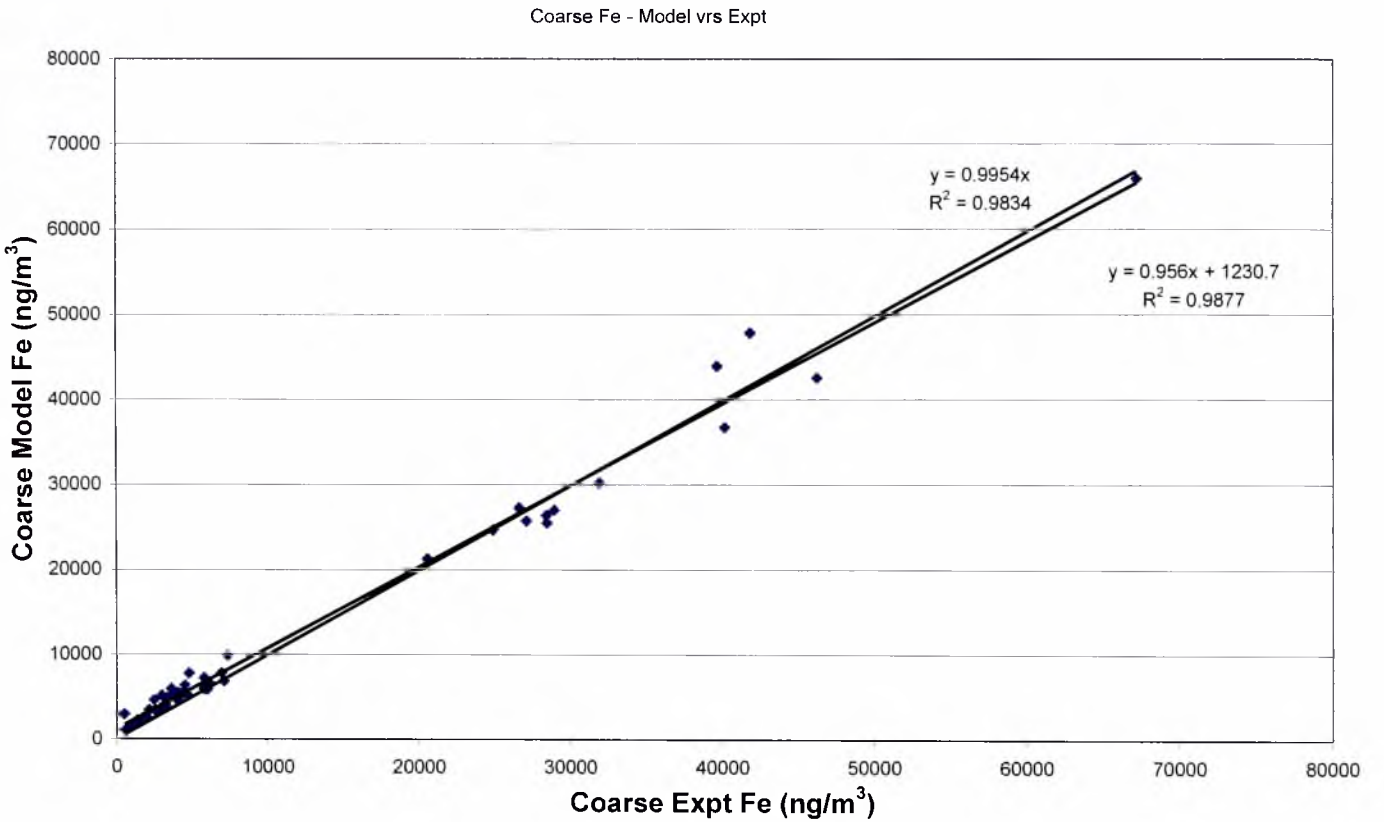


FIGURE 5-4: COARSE Cl – MODEL COMPARED WITH EXPERIMENTAL

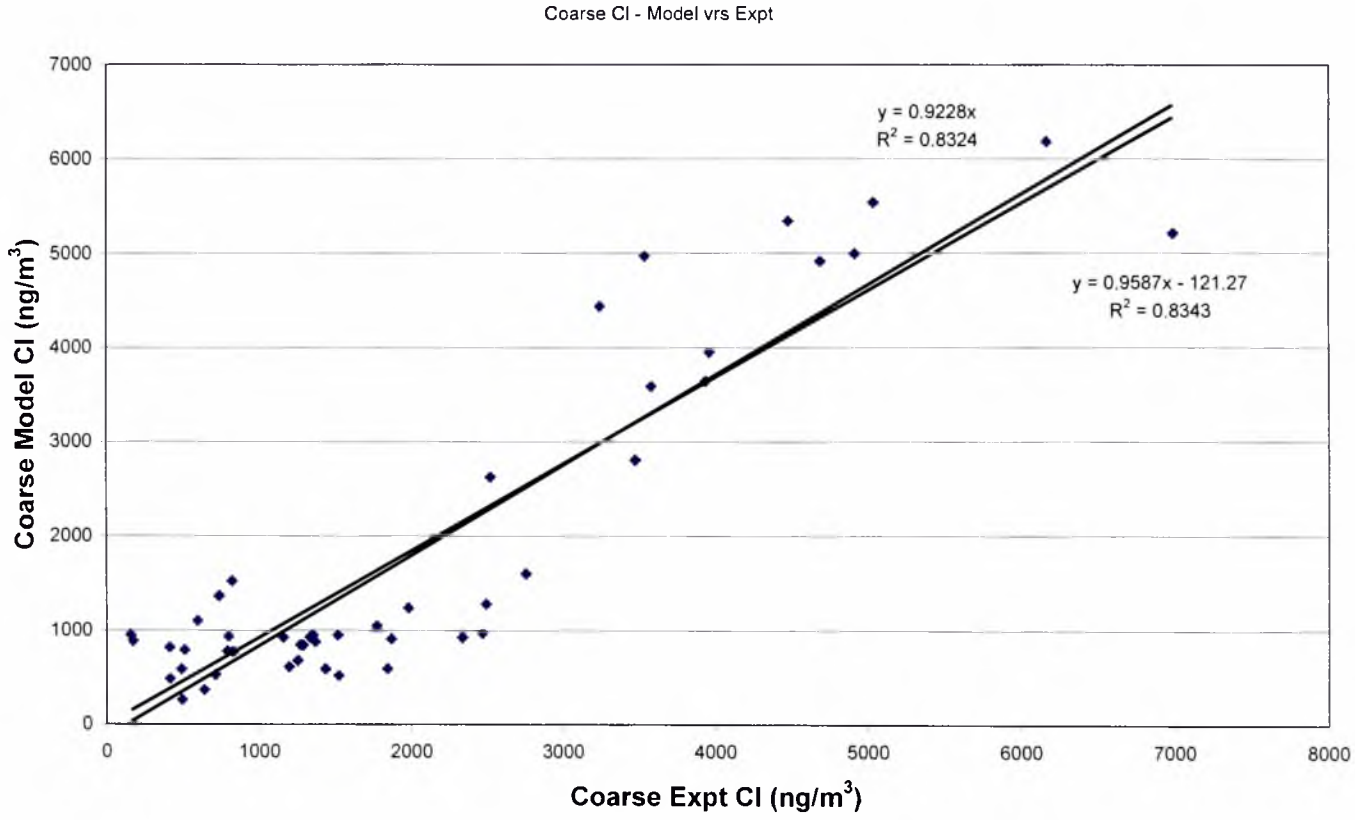


FIGURE 5-5: COARSE PM MASS – COMPARISON OF MODEL AND EXPERIMENTAL

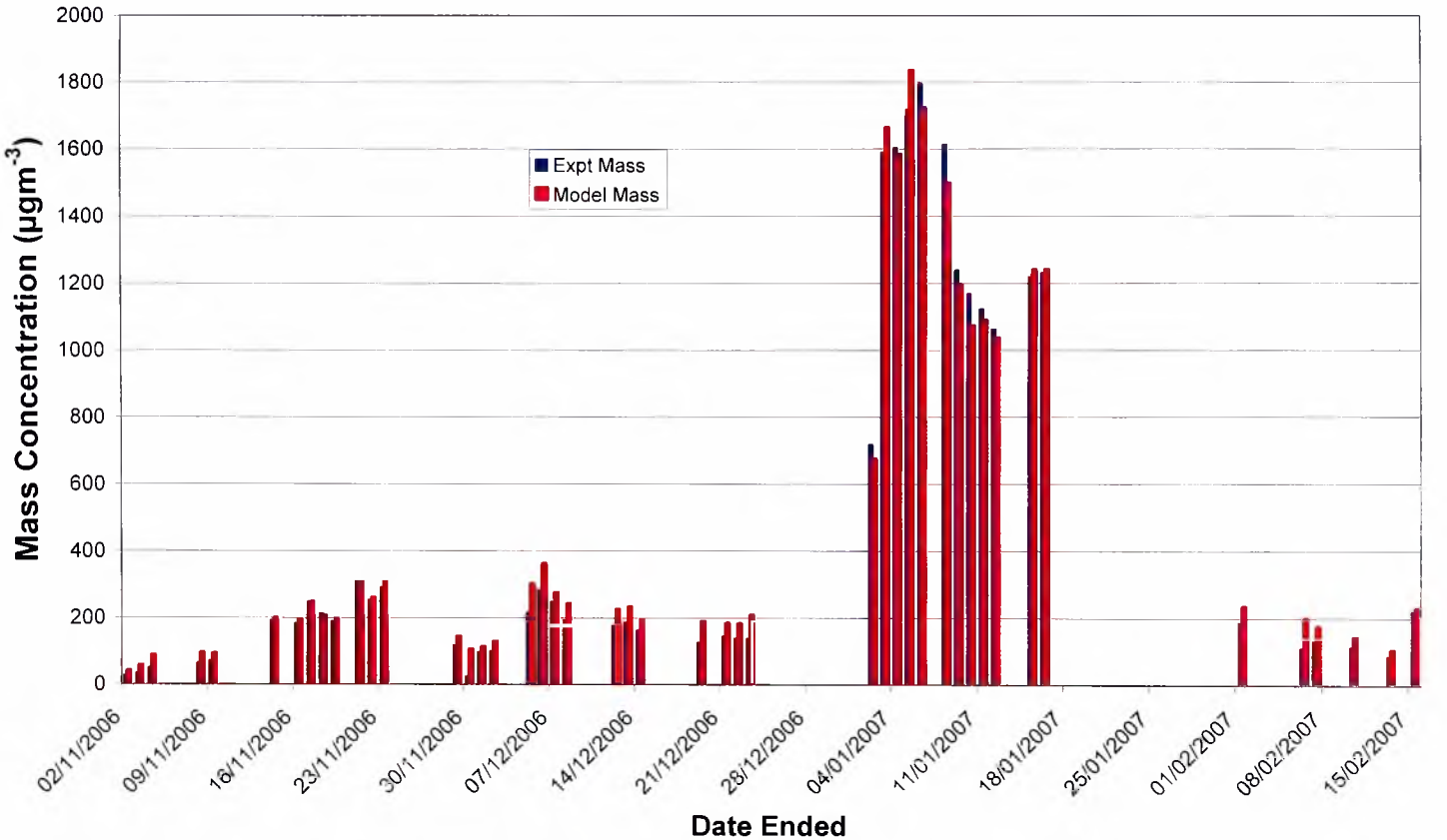


FIGURE 5-6: COARSE BC – COMPARISON OF MODEL AND EXPERIMENTAL

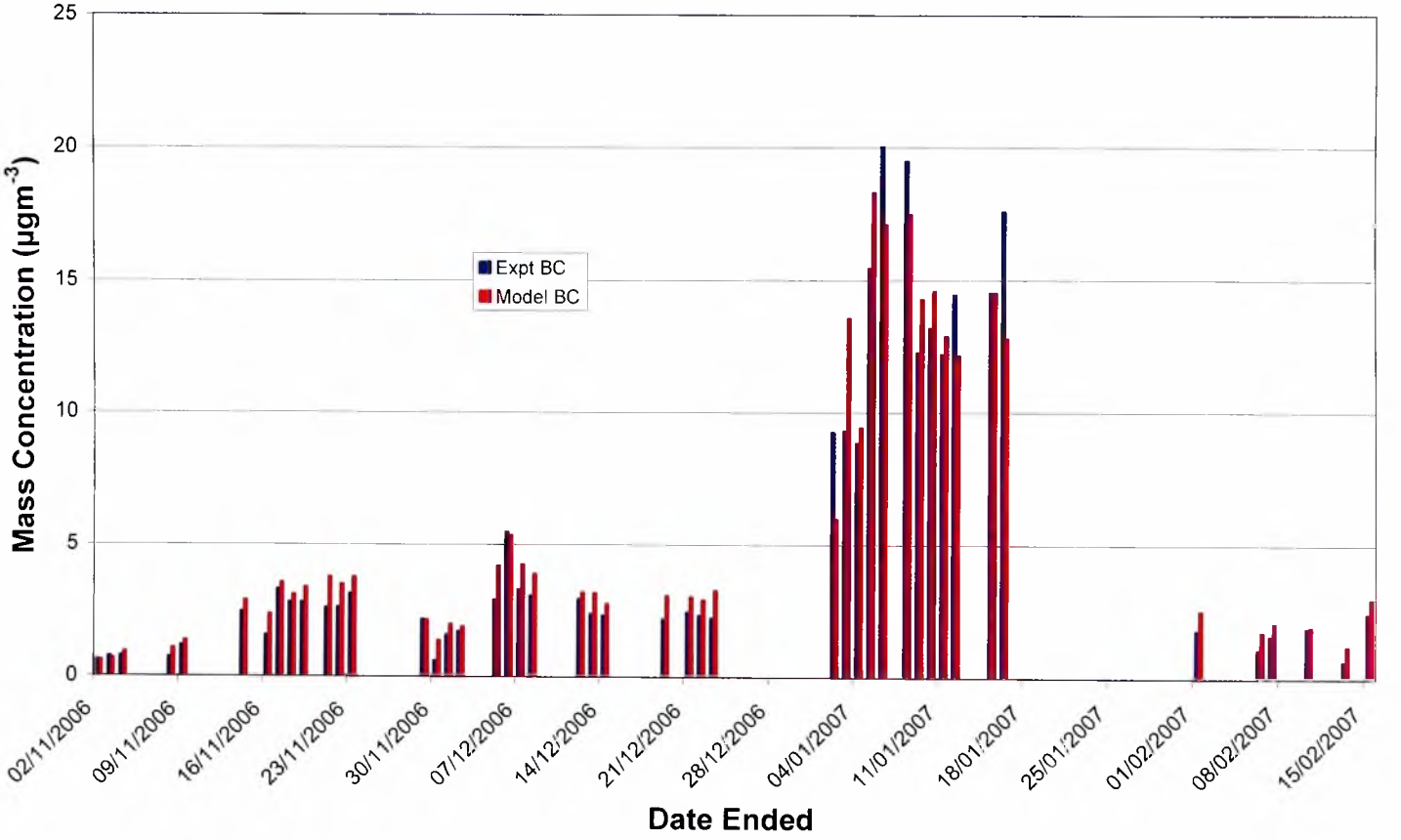


FIGURE 5-7: COARSE Fe – COMPARISON OF MODEL AND EXPERIMENTAL

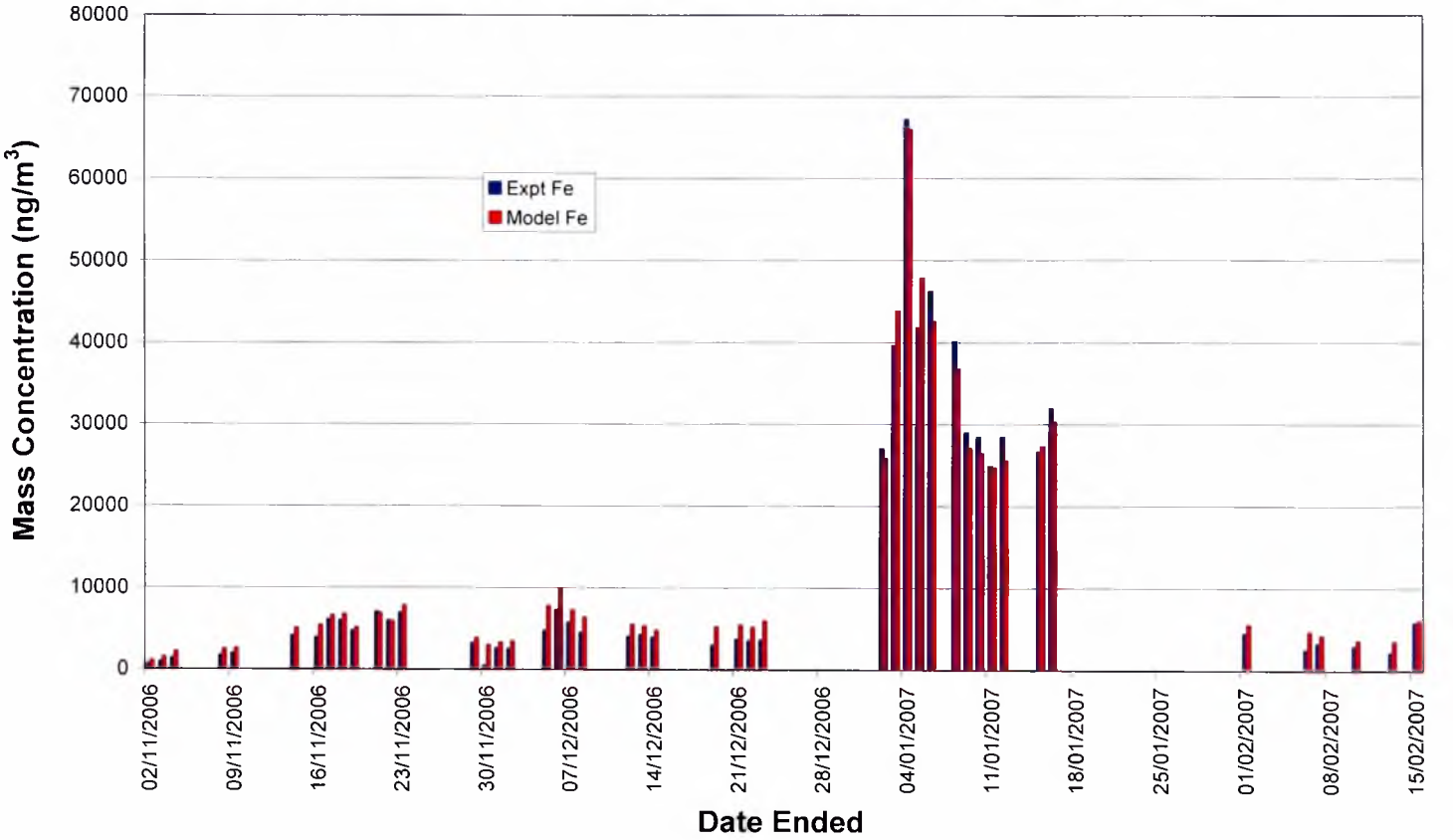


FIGURE 5-8: COARSE Cl – COMPARISON OF MODEL AND EXPERIMENTAL

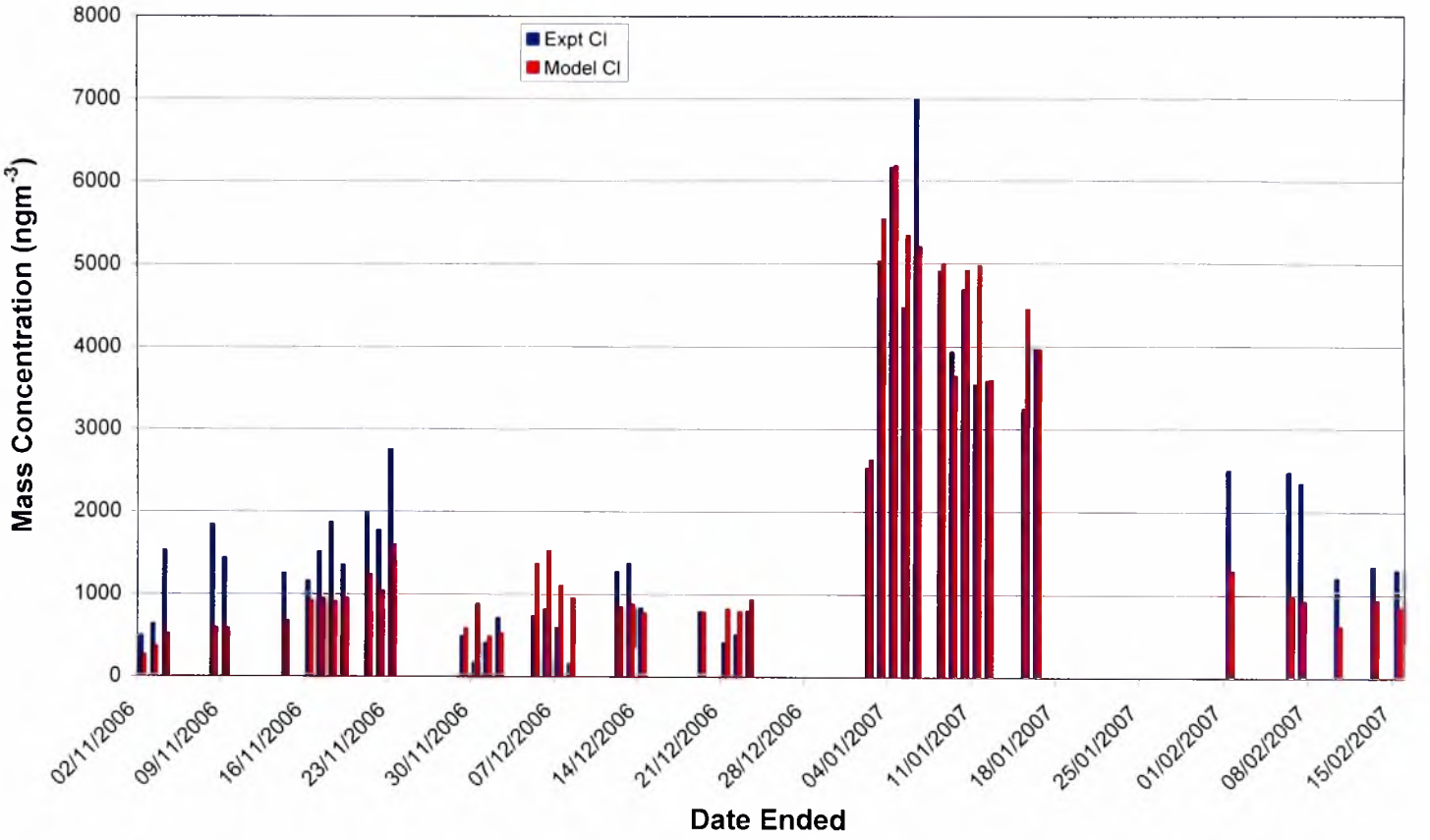


TABLE 5-11: COARSE PM CONCENTRATION MODEL AND EXPERIMENTAL DATA FIT – ELEMENTS, BC AND MASS (28TH DECEMBER 2005 – 31 MARCH 2006)

	Zero Fit		Non Zero Fit		
Element	Gradient	R^2	Gradient	Intercept	R^2
Al	0.99	0.95	0.94	89.96	0.95
Si	0.99	0.96	0.92	380.29	0.96
S	0.99	0.94	0.94	15.84	0.94
Cl	0.98	0.88	0.85	101.01	0.91
K	0.99	0.97	0.97	13.27	0.97
Ca	0.96	0.83	0.79	154.37	0.89
Ti	0.99	0.95	0.97	3.54	0.95
V	0.98	0.86	0.92	0.75	0.86
Cr	0.93	0.84	0.96	-0.18	0.84
Mn	0.99	0.96	0.94	1.64	0.97
Fe	0.99	0.97	0.96	52.37	0.97
Zn	0.98	0.95	0.95	0.43	0.95
Br	1.00	0.89	1.10	-0.36	0.90
Rb	0.99	0.94	0.93	0.15	0.94
Sr	0.97	0.90	0.85	0.97	0.92
Pb	0.96	0.79	0.83	0.45	0.82
BC	0.97	0.88	0.91	0.05	0.88
Mass	0.97	0.96	1.04	-5.53	0.96

TABLE 5-12: FINE PM CONCENTRATION MODEL AND EXPERIMENTAL DATA FIT ELEMENTS, BC AND MASS (28TH DECEMBER 2005 – 31 MARCH 2006)

	Zero Fit		Non Zero Fit		
Element	Gradient	R^2	Gradient	Intercept	R^2
Si	1.00	0.94	0.98	27.83	0.94
S	0.99	0.94	0.98	2.66	0.94
K	0.95	0.95	0.92	5.88	0.95
Ca	0.98	0.93	0.96	2.49	0.93
Ti	0.98	0.89	0.96	0.75	0.89
Mn	0.97	0.84	0.96	0.07	0.84
Fe	0.99	0.90	0.97	5.16	0.90
Zn	1.01	0.88	1.06	-0.15	0.88
Br	0.97	0.77	1.11	-0.33	0.78
BC	0.95	0.89	0.81	0.19	0.95
Mass	0.99	0.98	1.00	-0.11	0.98

TABLE 5-13: COARSE PM CONCENTRATION MODEL AND EXPERIMENTAL DATA FIT – ELEMENTS, BC AND MASS (4TH APRIL – 31 OCTOBER 2006)

	Zero Fit		Non Zero Fit		
Element	Gradient	R^2	Gradient	Intercept	R^2
Al	0.97	0.83	0.92	65.05	0.84
Si	0.99	0.94	0.95	150.47	0.94
S	1.02	0.92	0.92	37.60	0.93
Cl	1.10	0.78	0.86	549.65	0.87
K	1.01	0.85	0.93	35.20	0.86
Ca	0.99	0.90	0.90	45.52	0.91
Ti	0.99	0.94	0.96	3.54	0.94
V	0.94	0.47	0.76	0.96	0.50
Cr	0.95	0.34	0.60	1.85	0.61
Mn	0.98	0.88	0.92	1.20	0.89
Fe	0.98	0.89	0.87	120.73	0.91
Ni	0.99	0.79	0.85	0.46	0.81
Cu	0.99	0.82	0.92	0.36	0.83
Zn	0.97	0.78	0.78	1.87	0.83
Br	0.99	0.83	0.86	0.84	0.85
Rb	0.97	0.74	0.80	0.30	0.79
Sr	0.99	0.90	0.94	0.24	0.90
Pb	1.03	0.80	0.83	0.73	0.87
BC	0.98	0.80	0.86	0.09	0.82
Mass	0.99	0.92	0.94	2.45	0.93

TABLE 5-14: FINE PM CONCENTRATION MODEL AND EXPERIMENTAL DATA FIT – ELEMENTS, BC AND MASS (4TH APRIL – 31 OCTOBER 2006)

	Zero Fit		Non Zero Fit		
Element	Gradient	R^2	Gradient	Intercept	R^2
Al	0.85	0.90	1.05	-82.50	0.95
Si	0.98	0.98	0.99	-11.55	0.98
S	1.00	0.91	0.92	50.12	0.92
K	1.02	0.95	0.94	34.28	0.96
Ca	1.04	0.94	0.95	9.13	0.96
Ti	0.97	0.96	0.99	-0.58	0.96
Mn	0.96	0.91	0.95	0.04	0.91
Fe	0.99	0.98	0.97	3.04	0.98
Ni	1.00	0.97	0.97	0.07	0.97
Cu	1.00	0.99	1.00	-0.01	0.99
Zn	1.01	0.81	0.84	1.32	0.86
Br	0.98	0.88	0.89	0.81	0.89
Rb	1.07	0.74	0.83	0.29	0.82
Sr	0.89	0.96	0.97	-0.10	0.97
Pb	0.97	0.87	0.90	0.19	0.87
BC	0.98	0.88	0.92	0.13	0.89
Mass	0.96	0.76	0.79	3.48	0.81

TABLE 5-15: COARSE PM CONCENTRATION MODEL AND EXPERIMENTAL DATA FIT – ELEMENT, BC AND MASS (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

	Zero Fit		Non Zero Fit		
Element	Gradient	R^2	Gradient	Intercept	R^2
Al	0.95	0.94	0.88	2196.10	0.96
Si	1.02	0.97	0.97	5237.70	0.98
S	0.98	0.95	1.06	-130.75	0.96
Cl	0.92	0.83	0.96	-121.27	0.83
K	1.00	0.99	0.97	328.59	0.99
Ca	0.99	0.99	0.97	458.77	0.99
Ti	0.99	0.98	0.95	161.52	0.99
V	0.99	0.96	0.99	-0.88	0.96
Cr	0.99	0.97	1.04	-1.43	0.98
Mn	0.99	0.99	0.97	18.83	0.99
Fe	1.00	0.98	0.96	1230.70	0.99
Ni	0.99	0.97	0.95	1.22	0.98
Cu	0.97	0.94	0.90	2.88	0.95
Zn	0.98	0.95	0.91	7.65	0.96
Br	0.97	0.94	0.98	-0.30	0.94
Rb	1.00	0.99	0.97	1.75	0.99
Sr	0.99	0.99	0.97	5.03	0.99
Pb	0.97	0.92	0.87	3.97	0.94
BC	0.98	0.92	0.91	0.82	0.93
Mass	1.00	0.99	0.96	37.33	0.99

TABLE 5-16: FINE PM CONCENTRATION MODEL AND EXPERIMENTAL DATA FIT – ELEMENT, BC AND MASS (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

	Zero Fit		Non Zero Fit		
Element	Gradient	R^2	Gradient	Intercept	R^2
Al	1.01	0.97	1.04	-80.77	0.97
Si	0.99	0.99	0.98	113.25	0.99
S	0.98	0.93	0.95	22.85	0.93
K	0.98	0.94	0.95	34.33	0.94
Ca	1.02	0.94	0.97	49.50	0.95
Ti	0.99	0.97	0.97	3.46	0.98
Mn	1.00	0.98	0.99	0.14	0.98
Fe	0.99	0.98	0.97	26.17	0.98
Ni	0.98	0.93	0.91	0.56	0.93
Cu	0.97	0.98	0.98	-0.04	0.98
Zn	1.08	0.94	0.99	1.40	0.95
Br	1.00	0.97	1.01	0.14	0.97
Rb	0.97	0.97	0.96	0.05	0.97
Sr	1.02	0.98	1.01	0.13	0.98
Pb	1.04	0.73	0.86	0.90	0.78
BC	0.99	0.96	0.95	0.12	0.96
Mass	1.00	1.00	1.00	0.31	1.00

CHAPTER 6

QUALITY CONTROL AND DISCUSSION OF RESULTS

6.1 QUALITY ASSURANCE AND QUALITY CONTROL AS APPLIED TO AEROSOL ANALYSIS

Modern societies rely on measurements to function, hence the need for sound, accurate and reliable measurements cannot be overstated.[201] These measurements inform decisions on important matters such as air pollution, forensic and criminal investigations, pharmaceutical and narcotic issues, public surveys, etc. It is very essential that the user of the results is confident and assured that the data are truly representative of the sample and that the results are defendable, traceable and can be trusted by other laboratories or analysts. The social and economic impact of "wrong" result is too enormous to be left to chance. For example, in environmental monitoring, under reporting of values could lead to serious health hazards while over reporting could also lead to identification of unreal hazards.

Analysis of aerosol involves the use of different analytical techniques and different measuring instruments. Much effort has been put into the development of analytical techniques and instruments aimed at improving the sensitivity, selectivity and reliability of operation. Hence these techniques and instruments over the years have demonstrated their ability to yield reproducible results of repeated measurements. The detection limits of most of the analytical techniques have improved. This is mainly due to improved electronics, which are usually the cause of high signal to noise-ratio. But all these are still not free from the bias (systematic errors) of the analyst undertaking the analysis. In addition, sampling, sample preparation (where applicable) and analysis of limited quantity materials usually affect the quality of trace element analysis. It is therefore

necessary that the entire analytical procedure has to be taken into account to be able to estimate the reliability of the method. Hence there is the need to develop guidelines to ensure that the results are within control. These guidelines should ensure that:

- Measurements are accurate, precise and credible
- Data are representative of ambient conditions
- Results are comparable and traceable
- Measurements are consistent over time
- High and evenly distributed data capture are ensured

Quality assurance and control (QA/QC) are very important in any analytical or monitoring program such as aerosol analysis. These activities will ensure that the measurements meet the defined objective of the project. It must however be noted that the function of QA/QC is not to achieve the highest possible data quality.[202,203] This is not attainable because of resource constraints but it is a set of activities that will ensure that the data generated meet the specific objectives of the project.

Quality assurance activities cover all activities undertaken before sampling including the thesis objectives and data quality objectives, site selection, equipment evaluation and operation. Quality assurance also addresses the process-related functions such as project design, project management and process audit.

Quality control activities cover the direct measurement-related activities such as operation, calibration, data management and field audits. This includes ensuring the integrity of output-related measurement activities among others, sample site operations,

maintenance of samplers and other equipments, calibration, sample analysis, data collation and reporting.

Fig. 6-1 shows the stages in the aerosol analysis used in this thesis. These stages can be grouped into three main classes – sampling, analytical process and data evaluation. Each main class had at least a quality control activity to check the value being generated.

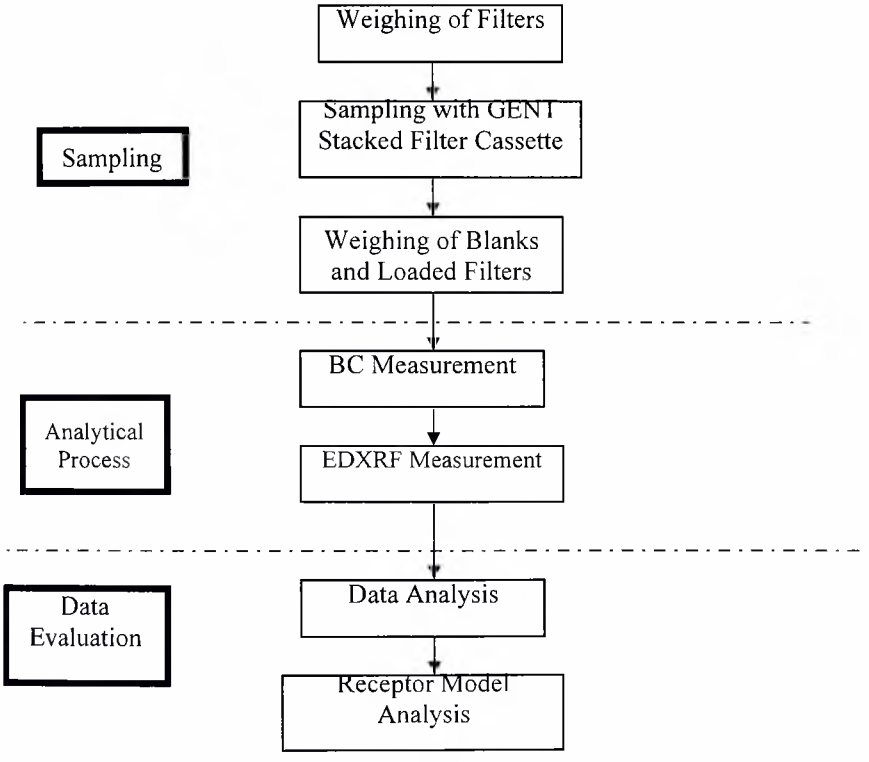


FIGURE 6-1: STAGES IN THE AEROSOL ANALYSIS USED IN THIS THESIS WORK

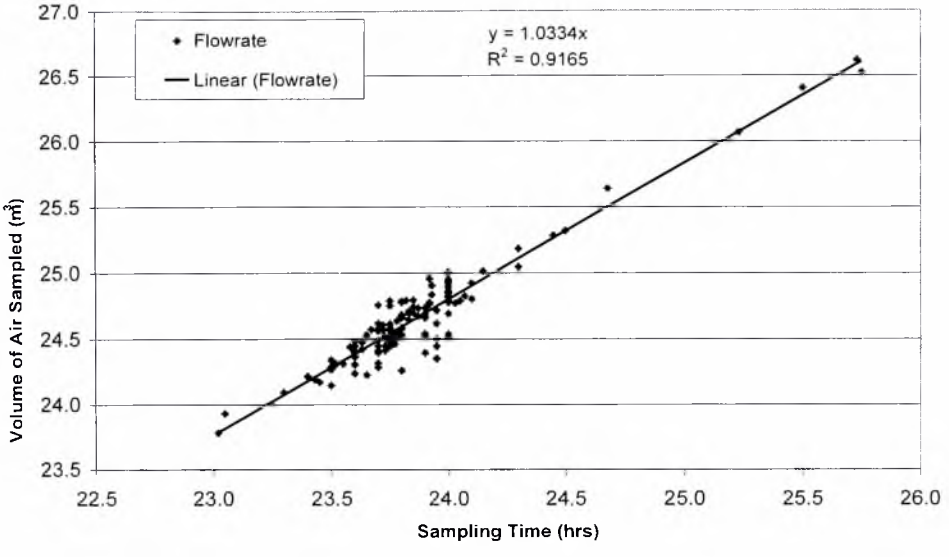
It is the successful implementation of each component of the measurement chain that ensures the success of this work.

Sampling:

- Site selection – In this work the objective was not to study any major source but the general ambient air. Hence the sampling site was selected such that it is not near any major source and the aerodynamic clearance was good and no sheltering of the sampler by any object.
- The consistency of the microbalance and the humidity of the weighing environment were checked by weighing a blank filter after every 10^{th} filter weighing throughout the weighing period.
- The microbalance used undergoes periodic review and calibration by SWEDAC – The Swedish Board of Accreditation and Conformity Assessment.
- More than 2 stacked filter cassettes with covers are used in the sampling, hence filters are loaded and removed in a clean laboratory environment instead of at the sampling site.
- Gent sampler flow rate is checked at least 3 times during the 24 hours sampling period for any pressure drop.
- The Gent flow rate is again checked after sampling by plotting of volume of air sampled against sampling time as shown in **Fig. 6-2**. The correlation coefficient (R^2= 0.91) and the gradient of the slope (1.03) show that correlation between the volume of air sampled and sampling time is very good.
- Blank filter mass, which followed the same analytical procedure as the loaded filters, are also used as a check on the microbalance, the filter media and the sampling process as shown in **Fig. 6-3**. The very good agreement between the

masses implies that the microbalance performance was excellent. In addition, it shows that the sampling process was free from contamination.

FIGURE 6-2: VARIATION OF VOLUME OF AIR SAMPLED WITH SAMPLING TIME OF THE GENT SAMPLER

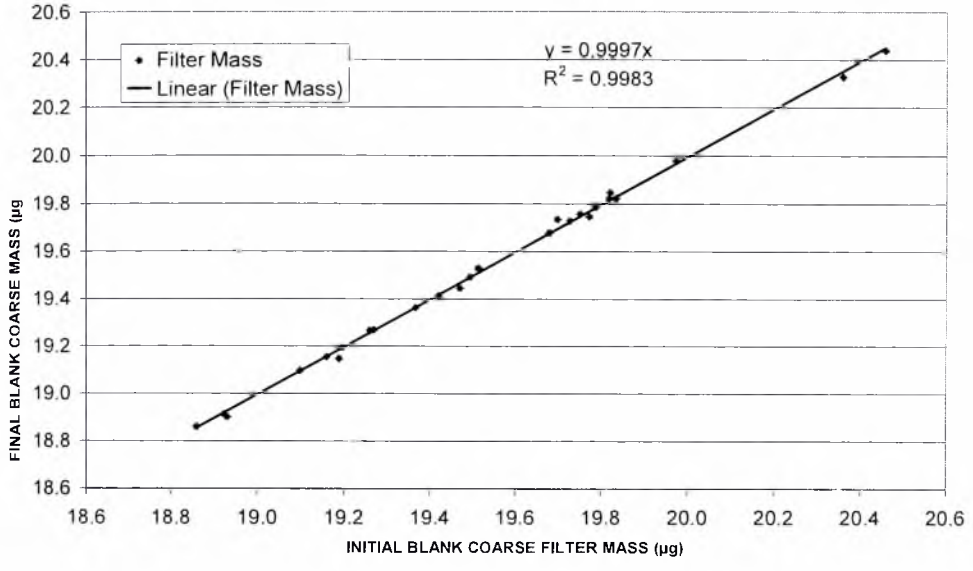


Analytical Process:

- In the BC analysis, measurements are repeated 4 times at different parts of the filter to check for the homogeneity of the filters and the average used in the analysis (**Table 6-1**). The very small differences in the values showed that the aerosol deposited on the filters are homogeneous.
- Since EDXRF is a non-destructive technique, some selected filters have their measurements repeated to verify the repeatability of the elemental analysis and correlation between related measurements are checked.
- EDXRF analysis of blank filters to check for concentrations influenced by either the filter media and/or signals from the EDXRF spectrometry.

- Analysis of Standard Reference Material (SRM), which is closely matched in major and trace elements, to check analytical procedure as shown in **Table 4-1**.

FIGURE 6-3: COMPARISON OF INITIAL BLANK COARSE FILTER MASS WITH FINAL BLANK COARSE MASS



Data Evaluation:

- The data are routinely checked for internal consistency. For example, the BC and mass are independently measured in both fractions. The BC should always be less than the loaded mass before the BC value could be meaningful. The BC values are checked against the respective mass.
- Inter-element relationships of various elements which originate from a common source are checked as shown in **Fig. 4-10** (where there is a very good correlation between elements like Al, Si, Mn, Fe, etc.)

- The physical model constraints are checked with the data generated i.e. the factor loading scores from the PCA should have mean =0 and standard deviation=1 (an example is shown in **Table 5-7**).
- The model determined - mass, elemental concentrations, BC and the experimentally determined - mass, elemental concentrations and BC are compared as shown in **Fig. 5-1 to 5-8** and **Tables 5-11 to 5-15**.

TABLE 6-1: SOME OUTPUT VOLTAGE MEASUREMENT FOR BLACK CARBON DETERMINATION

Filters	Voltages				Aver. Voltage
White	8.0	8.0	8.0	8.0	8.00
Black	0.4	0.4	0.4	0.4	0.40
C101	7.0	6.8	7.0	7.0	6.95
C102	7.0	6.8	6.9	6.9	6.90
C103	6.6	6.4	6.5	6.5	6.50
C104	6.8	6.6	6.7	6.8	6.73
C105	6.9	6.7	6.8	6.8	6.80
C106	7.3	6.9	7.1	7.1	7.10
C107	7.5	7.3	7.4	7.4	7.40
C108	7.5	7.4	7.5	7.5	7.48
C109	7.3	7.0	7.1	7.1	7.13
C110	7.2	7.0	7.0	7.1	7.08
C111	7.3	7.0	7.1	7.1	7.13
C112	6.6	6.4	6.5	6.6	6.53
C113	8.0	7.9	8.0	8.0	7.98
C114	6.4	6.2	6.3	6.4	6.33
C115	6.3	6.1	6.2	6.2	6.20
C116	7.8	7.5	7.7	7.7	7.68
C117	6.2	6.1	6.2	6.2	6.18
C118	6.4	6.3	6.3	6.4	6.35
C119	7.1	6.9	7.0	7.0	7.00
C120	6.0	5.9	6.0	6.0	5.98

6.2 DISCUSSION OF RESULTS

6.2.1 MASS CONCENTRATION

The sampling period (28th December 2005 – 12th February 2007) included two harmattan seasons and a rainy season. The 2006/07 harmattan was very severe and the Meteorological Services Department of Ghana reported it to be the most severe harmattan in about 40 years. This was evident in the mass concentration of the air particulate matter (APM) deposited on the filters. The total mass of particulate matter collected on the filters varied from day to day as shown in **Fig. 4-4, 4-5** and **4-6**. The PM_{10} data is mainly influenced by the coarse mass concentration as this is more than three times the fine mass concentration in all cases.

6.2.1.1 COARSE MASS CONCENTRATION

The data of the coarse mass concentration is given in **Table 6-2**. The mean mass concentrations of APM for the 2005/06 and 2006/07 Harmattan seasons were 88.66 and 473.37 μgm^{-3} respectively. These were higher than the 2006 rainy season of 42.81 μgm^{-3}, which was expected since Harmattan dust is absent during the rainy season and the washout effect of the rains are also pronounced. There were still days which had very low mass concentration in the Harmattan seasons than the rainy season as shown in the Minimum (Min) mass concentration values. Some days in the rainy season also had very high values. This could be due to a long period of stable weather conditions.

The median values for the 2005/06 Harmattan and the 2006 Rainy seasons showed that the data was evenly spread around the mean. This is further confirmed by the relatively small standard deviation of the 2005/06 Harmattan and 2006 Rainy seasons. The data

spread for the 2006/07 Harmattan shows that there were some few days with extreme high mass concentration which influenced the mean as shown by the standard deviation and median.

TABLE 6-2: COARSE MASS CONCENTRATION (μgm^{-3})

Period	No. of Days	Mean	StDev	Median	Min	Max
2005/06 Harmattan	69	88.66	48.25	89.59	8.64	228.17
2006 Rainy	100	42.81	16.56	42.58	0.16	87.84
2006/07 Harmattan	47	473.37	549.55	192.85	24.35	1794.01
All Data	216	151.14	308.04	57.04	0.16	1794.01

6.2.1.2 FINE MASS CONCENTRATION

The fine mass concentration data is given in **Table 6-3**. The mean fine mass concentration for the 2005/06 Harmattan, 2006 Rainy, and 2006/07 Harmattan were 10.59, 17.69 and 85.91 μgm^{-3} respectively. The 2005/06 Harmattan fine mass concentration was less than the 2006 Rainy season which was expected since the harmattan season is usually characterized by high coarse mass concentration. The 2006/07 Harmattan values were very high (about 800% and 500% of the 2005/06 Harmattan and 2006 Rainy seasons respectively). As stated above this was a very abnormal Harmattan season.

TABLE 6-3: FINE MASS CONCENTRATION (μgm^{-3})

Period	No. of Days	Mean	StDev	Median	Min	Max
2005/06 Harmattan	69	10.59	7.72	7.91	2.03	37.84
2006 Rainy	100	17.69	7.71	17.76	0.50	41.14
2006/07 Harmattan	47	85.91	83.09	51.84	22.09	430.23
All Data	216	30.27	48.97	18.03	0.50	430.23

The median and standard deviation values for the 2006 Rainy seasons showed that the data was evenly spread around the mean. The influence of high extreme values for the

Harmattan seasons were more pronounced in the 2006/07 Harmattan than the 2005/06 Harmattan.

6.2.1.3 COMPARISON OF THIS WORK WITH SOME SELECTED WORKS AND INTERNATIONAL STANDARDS

Comparing the results from this work with work done by other researchers is presented in **Table 6-4.** The results show that the coarse fraction is very high but the fine fraction which contains most of the respirable particulate matter is low except for the 2006/07 Harmattan season where there were few days with extreme high values affecting the average for the period. The fine fraction values from most of the developed countries were higher than the coarse fraction showing that their air particulate matter (APM) is mainly from anthropogenic sources.

TABLE 6-4: COMPARISON OF PM WITH RESULTS FROM LITERATURE

Place	Concentration (µg/m^3)		Reference
	Fine	Coarse	
Skukuza (South Africa)	9.4	16.2	Maenhaut[204]
Prestoriaskop (South Africa)	12.3	19.4	"
Palmer (South Africa)	18.0	15.2	"
Watertown, Boston (USA)	17.4	8.6	Chan[205]
Long Beach, Califonia (USA)	48.6	22.5	"
Tapada du Quterio (Portugal)	18.5	13.1	Alves[206]
Calgary (Canada)	11.1	26.3	Cheng[207]
Sofia (Bulgaria)	44.0	38.0	Houthuijs[208]
Ostrava (Czech)	60.0	29.0	"
Dorog (Hungary)	42.0	25.0	"
Swietochlowice (Poland)	58.0	22.0	"
Brastislava (Solvak)	36.0	13.0	"
Serowe (Botswana)	10.1	18.4	Moloi[136]
Goteborg (Sweden)	7.0	7.2	"
Vienna (Austria)	18.6	7.9	Hauck[19]
Streithofen (Austria)	15.0	6.1	"
Linz (Austria)	18.8	11.1	"
Graz (Austria)	21.1	9.9	"
Kwabenya (Ghana) – All Data	30.3	151.1	This work
Kwabenya (Ghana) – 2005/06 Harmattan	10.6	88.7	"
Kwabenya (Ghana) – 2006 Rainy Season	17.7	42.8	"
Kwabenya (Ghana) – 2006/07 Harmattan	85.9	473.4	"

The world-wide guidelines values given by the World Health Organization[209] are:

$PM_{2.5}$ – 10 μgm^{-3} (annual mean) and 25 μgm^{-3} (24-hours mean) and

PM_{10} – 20 μgm^{-3} (annual mean) and 50 μgm^{-3} (24-hour mean) respectively.

The Ghana Environmental Protection Agency (Ghana EPA) has a guideline limit only for PM_{10} – 50 μgm^{-3} (annual mean) and 70 μgm^{-3} (24-hour mean) respectively.

It should be noted that in this work the PM_{10} is not measured directly. The Gent size-fractionate into Coarse fraction ($PM_{10-2.5}$) and Fine fraction ($PM_{2.5}$). Both fractions have to be added to get the PM_{10} values. Averagely, the PM_{10} value have been exceeded and in the extreme over eight times the guideline limits, while the $PM_{2.5}$ values are far below the guideline values except during the 2006/07 Harmattan season where some extremely high values were measured. In the said WHO guideline it has been stated that there is no threshold below which damage to health is not observed so effort needs to be made to limit these PM_{10} emission.

6.2.2 BLACK CARBON (BC) CONCENTRATION

Generally, black carbon (BC) is not measured in the coarse fraction, but it was determined in this work. This was done taking into account the peculiar situation in the country (Ghana) where most people and City Authorities indiscriminately burn waste. The high incidence of bush fires during the Harmattan period which gives rise to the coarse fraction BC was also considered. The Coarse was about 1.09% (1.65 μgm^{-3}) as shown in **Table 6-5**.

For fine particulates the mean contribution of black carbon (BC) for the whole sampling period was about 5.45% (5.45 μgm^{-3}) of the fine mass concentration (**Table 6-6**). The daily BC concentration is shown in **Fig. 4-8** and that in terms of percentage is shown in **Fig. 4-9**. This shows that the finer fraction is dominated by BC, which is mostly generated by anthropogenic activities.

The BC of the coarse fraction is low but that of the fine fraction (about 5.5%) is on the higher side, especially that for the Rainy season which is about 10.85%. This value is comparable to industrialized countries. Some of the effects of BC include lowering of intelligent quotient (IQ)[210] in children and global warming.[211] BC is mainly from anthropogenic sources hence serious effort need to be made to reduce its generation.

6.2.2.1 COARSE BLACK CARBON CONCENTRATION

The data of the coarse BC concentration is given in **Table 6-5.** The coarse black carbon (BC) concentration for the 2005/06 Harmattan, 2006 Rainy and 2006/07 Harmattan were 0.57, 0.67 and 5.30 μgm^{-3} respectively. In terms of percentage of mass of particulates it was 0.64%, 1.57% and 1.12% for the 2005/06 Harmattan, 2006 Rainy and 2006/07 Harmattan respectively. The percentage contribution to particulate mass was expected; during the Harmattan period dust from the Sahel region dominate the particulate matter. Though bush fires are common occurrences, the amount of coarse BC generated is not proportionally high enough to significantly affect the BC-to-mass ratio.

The median and standard deviation value for the BC for the 2005/06 Harmattan and the 2006 Rainy seasons showed that the data was evenly spread around the mean. The BC

data for the 2006/07 Harmattan shows that there were some few days with extreme high concentration which influenced the mean.

TABLE 6-5: COARSE BLACK CARBON CONCENTRATION (μgm^{-3})

Period	Number of Days	Mean	StDev	Median	Min	Max	% of Mass
2005/06 Harmattan	69	0.57	0.33	0.50	0.00	1.69	0.64
2006 Rainy	100	0.67	0.24	0.68	0.04	1.46	1.57
2006/07 Harmattan	47	5.30	5.58	2.63	0.63	20.03	1.12
All Data	216	1.65	3.24	0.71	0.00	20.03	1.09

6.2.2.2 FINE BLACK CARBON CONCENTRATION

The fine fraction BC concentration is shown in **Table 6-6**. The mean concentrations (percentage of mass) of fine black carbon were 0.70 (6.61%), 1.92 (10.85%) and 2.44 μgm^{-3} (2.84%) for the 2005/06 Harmattan, Rainy and 2006/07 Harmattan season respectively. The fine BC was evenly distributed around the mean as shown by the median and standard deviation. Though the Harmattan data were influenced by few extremely high values it did not significantly affect the mean.

TABLE 6-6: FINE BLACK CARBON CONCENTRATION (μgm^{-3})

Period	Number of Days	Mean	StDev	Median	Min	Max	% of Mass
2005/06 Harmattan	69	0.70	0.66	0.52	0.01	2.96	6.61
2006 Rainy	100	1.92	0.86	1.90	0.10	4.63	10.85
2006/07 Harmattan	47	2.44	1.27	2.11	0.46	5.97	2.84
All Data	216	1.65	1.13	1.68	0.10	5.97	5.45

6.2.2.3 COMPARISON OF BC VALUES WITH SOME SELECTED WORKS

Comparing the results from this work with those of other researchers is presented in **Table 6-7.** From the table the BC from Africa (Tanzania, Sudan, Botswana and Ghana) are very high, considering the fact that these countries are not very industralised. In terms

of BC-to-mass ratio the values from Ghana and Botswana is slightly lower than those from the industrialized countries. This would be further discussed under sources of the particulate matter.

TABLE 6-7: COMPARISON OF BC WITH RESULTS FROM LITERATURE

Place	Concentration ($\mu g/m^3$)		Ratio BC-Mass (%)		Reference
	Fine	Coarse	Fine	Coarse	
Vaxjo (Sweden)	0.96	BDL			Selin Lindgren[190]
Gothenbuirg (Sweden)	0.90	0.01	13.0	0.1	Moloi[136]
Serowe (Botswana)	0.96	0.03	9.5	0.2	,,
Gaborone (Botswana)	0.90	0.01			Bennet[212]
Dar es Salam (Tanzania)	4.90	0.54			,,
Khartoum (Sudan)	3.00	0.30			El-Tahir[213]
Riga (Latvia)	2.40	0.11			Viskna[214]
Vienna (Austria)	3.60	0.59	19.0	0.5	Gromiscek[215]
Streithofen (Austria)	2.30	0.10	12.7	1.2	,,
Ghent (Belgium)	3.80	0.59	19.6	0.5	Maenhaut[216]
Waasmunster (Belgium)	3.40	0.49	14.2	0.4	,,
Kwabenya (Ghana) – All Data	1.65	1.65	5.45	1.09	This work
Kwabenya (Ghana) – 2005/06 Harmattan	0.70	0.57	6.61	0.64	,,
Kwabenya (Ghana) – 2006 Rainy Season	1.92	0.67	10.85	1.57	,,
Kwabenya (Ghana) – 2006/07 Harmattan	2.44	5.30	2.84	1.12	,,

BDL = below detection limit

From **Table 6-7**, it is very evident that the fine fraction contains most part of the BC and this needs to be taken into account in mass comparison from different location. Apart from the health and radiation balance consideration, the fine fraction with its high BC concentration presents a large surface to volume ratio than the coarse particles. Other gases could therefore attach themselves to the BC surface and are deposited directly into the lungs.

6.2.3 ELEMENTAL CONCENTRATIONS

The following elements were identified and quantified in both coarse and fine filters collected during the sampling period: Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr and Pb. In addition, the following elements were identified and quantified in only the coarse filters: Cl, V, Cr and Ni. The following elements were also identified but not used in modeling because they are present in very few samples or below detection limit: P, Co and Se in the coarse fraction and Cl, V, Cr and Co for the fine fraction.

The elemental concentrations in the two fractions vary from season to season; this additional information is an advantage that is not possible with only gravimetric analysis. Using simple correlation analysis some elements correlate well and could serve as possible source indicators as specified below. For example Al, Si, Mn and Fe are typical elements from dust or soil. These correlations also vary from season to season. Below are some examples:

Fine 2005/06 Harmattan:

1. Si, Ca, Ti, Mn, Fe, Zn
2. S, K, Zn, Br

Fine 2006 Rainy:

1. Al, Si, Ca, Ti, Mn, Fe, Sr
2. S, K, Br, Rb,
3. K, Zn, Br, Pb,
4. Zn, Pb

Fine 2006/07 Harmattan:

1. Al, Si, Ca, Ti, Mn, Fe, Rb, Sr
2. S, K, Br, Pb
3. Al, Si, Ca, Ti, Mn, Fe, Ni, Cu, Rb, Sr
4. Cu, Zn, Pb
5. S, Cu, Zn, Pb

Coarse 2005/06 Harmattan:

1. Al, Si, S, K, Ca, Mn, Fe, Br, Rb, Sr
2. S, Cl, V, Br, Sr
3. Cu, Zn

Coarse 2006 Rainy:

1. Al, Si, Ca, Ti, Mn, Fe, Rb, Sr
2. S, Cl, Br
3. Zn, Pb

Coarse 2006/07 Harmattan:

All elements seem to have some amount of correlation with each other except Cr which has no correlation with Ca, V and Sr. In addition, V does not correlate with Al.

The high correlation between elements in the 2006/07 Harmattan could be attributed to the high air particulate matter concentration dominated by dust from the Sahel region. This dust particulate acts as nucleation point for all the other elements emitted by the other prevailing sources to be attached to.

In the fine fraction it was observed that S during the Harmattan correlates with K, Br and Zn but during the Rainy season S does not correlate with Zn. It was also observed that some elements correlate but not all these elements collate with other elements. For example during the Rainy season in the fine fraction, S correlated with K and Br likewise Pb correlated with K and Br but not with S. This suggests that there are more than one source emitting K and Br.

6.2.4 SOURCE PROFILES

To identify the major aerosol sources and to apportion the various elements to these sources, the data generated over the measuring period were subjected to principal component analysis[217] (PCA) with varimax rotation. Statistical methods have been commonly used for identification of the relative importance of different sources.[129,133,190,200,218,219] Input data for the source assignments were chemical species namely elemental, black carbon and mass.

In the PCA analysis, several runs were made. The number of factors was varied and varimax as well as promax rotations were performed. The pollution sources were assumed to be independent of each other and because varimax gave the most consistent results it was the rotation that was used in the factor analysis. The same factors appeared in the analysis even if some variables were omitted, although the factor loadings for the different elements varied slightly.

6.2.4.1 COARSE FRACTION PARTICULATE MATTER

Table 6-8 shows the five source profiles generated by the receptor model used in this work (as per **Eqn. 5-6**) for the coarse particulate for the 2005/06 Harmattan which resulted in an average contribution of:

- Profile 1: 4.84 μg /m^3/day (5.5%)
- Profile 2: 68.46 μg /m^3/day (78.2%)
- Profile 3: 1.30 μg /m^3/day (1.5%)
- Profile 4: 8.73 μg /m^3/day (10.0%)
- Profile 5: 4.12 μg /m^3/day (4.8%)

The elements and BC values in the profile are per unit mass of aerosol deposited on the filter. Hence the Mass values should be 1.0 and the values obtained also shows the accuracy of the modeled profile fit to the data. Source profile values shown in bold are the suggested main species contributing to the respective sources. The criteria used includes: the species high values compared with their respective standard deviations and the contribution of the element distributed over the total number of sources.

Using source information from other researchers in both Africa and Europe[136,190,218] the most likely sources which fit the profiles in the coarse fraction of the 2005/06 Harmattan are:

- Profile 1- *Soil/Dust*
- Profile 2 – *Biomass burning intermixed with long distance transport (LDT) and dust*
- Profile 3 – *Metal Industrial – Cu and Zn*

- Profile 4 – *Sea spray intermixed with long distance transport (LDT)*
- Profile 5 – *Industrial emission – Pb*

Profile 1 in the 2005/06 Harmattan contains over 56% Al, 58% Si, 54% Ca, 53% Ti, 47% Mn, 47% Fe, 46% Rb and 56% of Rb which are all strong signatures of soil/dust. This is not surprising since it was during the harmattan season but its contributing to the mass is only about 5% and hence attributed to activities in the vicinity of the sampler.

Profile 2 which contains 82% of the mass looks like a mixture of three sources with 31% of BC, 27% Al, 24% Si, 41% S, 32% K, 21% Ca, 35% Mn, 28% Fe, 35% Zn, 32% Rb and 22% Sr. The very high S is major signature of long distance transport (LDT). Al, Si, Ca, Mn, Fe, Rb, and Sr are all signatures of soil/dust. BC, K and Zn are also signature of biomass. The coarse biomass is due to the localised bush fires and domestic waste burning.

Profile 3 contains 76% Cu and 34 % Zn with less than 5% BC which shows that it is not associated with combustion process. This is appearing in the coarse fraction so can only be attributed to metal polishing/grinding industry.

Profile 4 contains 31% S, 63% Cl, 52% Br and 35% BC. Kwabenya is less than 10 km from the sea hence the presence of Cl and Br, which are strong signature of sea spray, was expected. The high percentage of S and BC in the source shows that it is intermixed with LDT.

TABLE 6-8: COARSE PARTICLE SOURCE PROFILE (28TH DECEMBER 2005 – 31ST MARCH 2006)

Element (ng/µg)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Al	**128.76**	**4.35**	17.89	15.86	3.99
	2.51	*0.27*	*7.45*	*2.36*	*2.34*
Si	**392.16**	**11.42**	53.75	47.17	22.74
	7.36	*0.8*	*21.83*	*6.92*	6.86
S	6.42	**0.97**	3.21	**5.75**	1.66
	0.41	*0.04*	*1.23*	*0.39*	*0.39*
Cl	22.26	0.37	1.8	**27.74**	1.39
	2.02	*0.22*	*6.01*	*1.91*	*1.89*
K	**26.69**	**1.48**	5.78	6.43	3.33
	0.59	*0.06*	*1.75*	*0.55*	*0.55*
Ca	**50.89**	**1.44**	2.75	10.4	3.31
	2.58	*0.28*	*7.66*	*2.43*	*2.41*
Ti	**10.80**	**0.40**	2.06	1.26	1.12
	0.23	*0.02*	*0.67*	*0.21*	0.21
V	0.16	**0.06**	0.05		0.03
	0.01	*0.002*	*0.04*		0.01
Cr	0.07	**0.06**	0.13	0.06	
	0.01	*0.001*	*0.04*	*0.01*	
Mn	**1.72**	**0.09**	0.18	0.24	0.18
	0.03	*0.003*	*0.09*	*0.03*	*0.03*
Fe	**88.39**	**3.74**	19.11	16.58	10.33
	1.31	*0.14*	*3.9*	*1.24*	*1.22*
Ni	**0.2**		0.11	**0.10**	
	0.01		*0.03*	*0.01*	
Cu	0.11		**1.75**	0.02	
	0.01		*0.04*	*0.01*	
Zn	0.14	**0.03**	**1.35**	**0.07**	0.07
	0.02	*0.002*	*0.05*	*0.01*	*0.01*
Br	**0.20**		0.13	0.14	
	0.01		*0.02*	*0.01*	
Rb	**0.13**	**0.01**	0.02	0.03	0.01
	0.003	*0.0003*	*0.01*	*0.003*	*0.003*
Sr	**0.45**	**0.01**		0.09	0.01
	0.01	*0.001*		*0.01*	*0.01*
Pb	**0.11**		0.03	0.03	**0.10**
	0.005		*0.02*	*0.005*	*0.005*
BC (µg/µg)	0.02	**0.01**	0.01	**0.01**	
	0.002	*0.002*	*0.005*	*0.002*	
Mass (µg/µg)	0.84	**1.02**	1.36	0.61	1.28
	0.19	*0.02*	*0.58*	*0.18*	*0.18*

NB: 1. Values in *italics* are the standard deviation of the various species.
2. Bold values are suggested main species contributing to Source.

Profile 5 contains over 27% Pb and account for about 5% of the loaded mass, which is significant. This could be attributed to an industrial source emitting Pb.

The coarse fraction source profiles for the 2006 Rainy Season is given in **Table 6-9** with an average contribution of:

- Profile 1: 14.94 μg /m^3/day (34.5%)
- Profile 2: 13.46 μg /m^3/day (31.1%)
- Profile 3: 3.98 μg /m^3/day (9.2%)
- Profile 4: 8.46 μg /m^3/day (19.6%)
- Profile 5: 2.82 μg /m^3/day (5.6%)

The most likely sources that fit the profiles are:

- Profile 1 – Soil/Dust
- Profile 2 – Sea spray/LDT
- Profile 3 – Biomass
- Profile 4 – Industrial – Cr, Ni, Cu
- Profile 5 – Industrial – V, Cr

The 2006/07 Harmattan coarse fraction source profiles are given in **Table 6-10** with an average contribution of:

- Profile 1: 180.99 μg /m^3/day (33.6%)
- Profile 2: 123.16 μg /m^3/day (22.9%)
- Profile 3: 147.80 μg /m^3/day (27.4%)
- Profile 4: 86.32 μg /m^3/day (16.0%)
- Profile 5: 0.18 μg /m^3/day (0.03%)

TABLE 6-9: COARSE PARTICULATE SOURCE PROFILE (4TH APRIL 2006 – 31ST OCTOBER 2006)

Element (ng/µg)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Al	**36.38**	11.62	28.46	18.57	18.51
	1.55	*2.56*	*7.35*	*5.65*	*9.02*
Si	**114.12**	32.98	107.45	68.57	59.31
	2.79	*4.61*	*13.21*	10.16	16.22
S	2.23	**18.88**	**11.39**		8.9
	0.28	*0.46*	*1.33*		*1.63*
Cl	13.92	**125.42**			50.14
	2.5	*4.14*			*14.58*
K	**7.43**	**14.89**	**20.58**	1.33	
	0.69	*1.14*	*3.28*	*2.52*	
Ca	**13.25**	7.95	12.15	10.64	9.47
	0.44	*0.72*	*2.07*	*1.59*	*2.54*
Ti	**3.29**	0.35	3.29	2.41	1.33
	0.08	*0.14*	*0.39*	*0.3*	*0.48*
V	0.03	0.02	0.17		**0.57**
	0.006	*0.01*	*0.03*		*0.04*
Cr	0.01	0.04		**0.21**	**0.63**
	0.01	*0.02*		*0.06*	*0.66*
Mn	**0.49**	0.17	0.75	0.39	0.28
	0.02	*0.03*	*0.08*	*0.06*	*0.1*
Fe	**29.81**	11.29	**57.58**	17.33	18.5
	1.04	*1.72*	*4.94*	*3.8*	6.07
Ni	0.03		0.04	**0.29**	0.02
	0.003		*0.01*	*0.01*	*0.02*
Cu	0.02	0.02	0.23	**0.32**	0.03
	0.003	*0.005*	*0.01*	*0.01*	*0.02*
Zn	0.07	0.06	**1.26**	0.09	0.10
	0.01	*0.02*	*0.06*	*0.05*	*0.07*
Br	0.03	**0.18**	**0.31**	**0.22**	0.08
	0.005	*0.01*	*0.02*	*0.02*	*0.03*
Rb	**0.04**	0.02	0.07	0.02	0.01
	0.002	*0.003*	*0.01*	*0.01*	*0.01*
Sr	**0.10**	**0.88**	0.07	0.09	0.08
	0.003	*0.006*	*0.02*	*0.01*	*0.02*
Pb	0.06		**0.43**		0.08
	0.004		*0.02*		*0.02*
BC (µg/µg)	0.01	**0.01**	**0.07**	0.01	0.01
	0.001	*0.001*	*0.003*	*0.002*	*0.004*
Mass (µg/µg)	**1.08**	**1.06**	0.89	0.71	0.96
	0.03	*0.05*	*0.16*	*0.12*	*0.20*

TABLE 6-10: COARSE PARTICULATE SOURCE PROFILE (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Element (ng/µg)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Al		**59.51**	**31.3**	9.13	2046.65
		5.2	*3.75*	*10.5*	*2884.16*
Si	4.16	**177.91**	**186.71**		
	3.62	*7.92*	*5.71*		
S	0.57	**1.22**	**1.95**	**6.89**	16.61
	0.08	*0.18*	*0.13*	*0.37*	*100.91*
Cl	**2.23**	**3.95**	**2.77**	4.13	989.84
	0.31	*0.67*	*0.48*	*1.35*	*371.13*
K	**9.84**	9.67	**8.01**	9.55	
	0.28	*0.61*	*0.43*	*1.22*	
Ca	**20.9**	10.95	**13.53**	10.94	722.27
	0.45	*0.98*	*0.71*	*1.98*	*336.13*
Ti	**2.93**	2.65	2.18	3.31	
	0.01	*0.21*	*0.15*	*0.42*	
V	**0.10**	0.08	0.04	0.08	
	0.005	*0.01*	*0.01*	*0.02*	
Cr		0.08		0.02	
		0.002		*0.004*	
Mn	**0.67**	0.49	0.35	0.47	13.01
	0.01	*0.03*	*0.02*	*0.06*	*16.91*
Fe	**26.63**	**23.43**	18.21	28.95	
	0.78	*1.72*	*1.24*	*3.46*	
Ni	**0.02**	0.02	**0.03**	0.04	**8.56**
	0.001	*0.003*	*0.002*	*0.005*	*1.39*
Cu	**0.03**	0.03	0.02	**0.07**	**14.44**
	0.002	*0.004*	*0.003*	*0.01*	*2.46*
Zn	0.07	**0.18**	0.04	**0.17**	9.95
	0.005	*0.01*	*0.01*	*0.02*	*6.27*
Br	**0.03**	**0.04**	**0.03**	**0.06**	9.95
	0.002	*0.005*	*0.003*	*0.01*	*2.59*
Rb	**0.06**	**0.05**	**0.03**	0.05	
	0.001	*0.003*	*0.002*	*0.005*	
Sr	**0.20**	0.09	0.11	0.12	6.35
	0.004	*0.01*	*0.1*	*0.02*	*5.06*
Pb	0.02	**0.05**	0.02	**0.10**	
	0.002	*0.005*	*0.003*	*0.01*	
BC (µg/µg)		0.01	0.01	**0.02**	
		0.001	*0.001*	*0.002*	
Mass (µg/µg)	**0.64**	**1.21**	1.09	0.69	0.66
	0.02	*0.04*	*0.03*	*0.09*	*0.29*

The most likely sources that fit the profiles are:

- Profile 1 – Sea spray + Industrial Zn
- Profile 2 – Soil/Dust + Zn
- Profile 3 – Soil/Dust + Ni
- Profile 4 – Biomass intermixed with LDT
- Profile 5 – Industrial – Ni, Cu

6.2.4.2 FINE FRACTION PARTICULATE MATTER

Three source profiles were generated by the receptor model for the fine particulates in 2005/06 Harmattan as shown in **Table 6-11** with an average contribution of:

- Profile 1: 0.69 μg /m^3/day (6.3%)
- Profile 2: 3.89 μg /m^3/day (35.2%)
- Profile 3: 6.46 μg /m^3/day (58.5%)

The fine fraction of the 2005/06 Harmattan Profile 1 contains over 35% Si, 40% Ca, 34% Ti, 27% Mn and 32% Fe. These are all strong signatures of soil/dust, though the Rb and Sr levels in the samples for the period were too few to be used for the model, this is still a soil/dust source. This profile contributes only about 6.3% to the loaded mass on the filter.

Profile 2 contains over 78% S, 66% K, 46% Mn, 42% Fe, 78% Zn, 75% Br and 85% BC. The high S levels indicate long distant transport (LDT) and the high K, Br and BC indicate biomass burning. Hence this profile is a mixture of LDT and Biomass burning.

Profile 3 is similar to Profile 1 but without Ti, it contains over 36% Si, 27% Ca, 26% Mn, 24% Fe. This profile account for 62.7% of the loaded mass, and contains all the signature of dust/soil. It appears that there were two sources of fine particulate soil/dust during the 2005/06 harmattan season.

TABLE 6-11: FINE PARTICLE SOURCE PROFILE (28TH DECEMBER 2005 – 31ST MARCH 2006)

Element (ng/µg)	Profile1	Profile2	Profile3
Si	**165.22**	22.37	**18.17**
	3.93	*2.69*	*1.54*
S	7.66	**19.37**	2.38
	0.73	*0.5*	*0.29*
K	13.61	**15.65**	3.33
	0.65	*0.45*	*0.26*
Ca	**19.70**	**2.77**	**1.46**
	0.44	*0.3*	*0.17*
Ti	**4.65**	1.02	0.34
	0.14	*0.1*	*0.05*
Mn	**0.78**	**0.23**	**0.08**
	0.03	*0.02*	*0.01*
Fe	**38.93**	**9.05**	**3.08**
	0.99	*0.68*	*0.39*
Zn	0.24	**0.29**	0.02
	0.01	*0.01*	*0.01*
Br	0.11	**0.24**	0.03
	0.02	*0.01*	*0.005*
BC (µg/µg)	0.04	**0.11**	
	0.01	*0.003*	
Mass (µg/µg)	1.01	0.81	**1.01**
	0.05	*0.03*	*0.02*

The most likely sources that fit the profiles are:

- Profile 1 – Soil/Dust with Ti
- Profile 2 – LDT/Biomass
- Profile 3 – Soil/Dust without Ti

TABLE 6-12: FINE PARTICULATE SOURCE PROFILE (4TH APRIL 2006 – 31ST OCTOBER 2006)

Element (ng/µg)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Al	**52.69**	2.03		**11.62**	21.17
	2.31	*0.75*		*2.31*	*9.58*
Si	**175.36**		5.54	1.37	40.69
	3.1		*6.63*	*3.1*	*12.84*
S		**44.38**	38.09	10.52	1.82
		1.14	*7.45*	*3.48*	*14.43*
K	6.37	**28.97**	19.98		
	1.81	*0.59*	*3.87*		
Ca	**22.39**	0.47	5.04		5.24
	0.48	*0.16*	*1.04*		*2.01*
Ti	**4.60**		0.61	**0.33**	1.1
	0.11		*0.24*	*0.11*	*0.47*
Mn	**0.75**	0.06	**1.03**	0.02	0.46
	0.03	*0.01*	*0.07*	*0.03*	*0.13*
Fe	**49.82**	1.41	13.02	0.17	11.21
	0.81	*0.26*	*1.73*	*0.81*	*3.35*
Ni	0.02	0.01	0.02	**0.39**	0.23
	0.01	*0.002*	*0.01*	*0.005*	*0.02*
Cu	0.1	0.01	0.23	0.12	**1.89**
	0.004	*0.001*	*0.01*	*0.004*	*0.02*
Zn	0.16	**0.22**	**2.62**		**1.19**
	0.06	*0.02*	*0.12*		*0.23*
Br		**0.54**	0.57	0.14	0.17
		0.02	*0.12*	*0.05*	*0.22*
Rb	0.03	**0.08**	0.05		0.05
	0.01	*0.003*	*0.02*		*0.04*
Sr	**0.15**	0.01	0.01		**0.10**
	0.01	*0.01*	*0.01*		*0.02*
Pb	0.14	0.05	**1.06**	0.01	0.33
	0.02	*0.01*	*0.04*	*0.02*	*0.08*
BC (µg/µg)	0.02	**0.12**	**0.46**	0.05	0.07
	0.01	*0.004*	*0.03*	*0.01*	*0.06*
Mass (µg/µg)	0.99	**1.01**	0.94	**0.99**	1.01
	0.15	*0.05*	*0.31*	*0.15*	*0.61*

The fine fraction source profiles for the 2006 Rainy Season is given in **Table 6-12** with an average contribution of:

- Profile 1: 1.06 µg /m^3/day (6.1%)
- Profile 2: 9.49 µg /m^3/day (54.8%)
- Profile 3: 0.94 µg /m^3/day (5.4%)

- Profile 4: 4.79 μg /m^3/day (27.7%)
- Profile 5: 1.04 μg /m^3/day (6.0%)

The most likely sources that fit the profiles are:

- Profile 1 – Soil/Dust
- Profile 2 – LDT/Biomass
- Profile 3 – Industrial – Mn, Zn and Pb
- Profile 4 – Industrial – Al, Ti and Ni
- Profile 5 – Industrial – Cu and Zn

The 2006/07 Harmattan fine fraction source profiles are given in **Table 6-13** with an average contribution of:

- Profile 1: 50.60 μg /m^3/day (58.0%)
- Profile 2: 23.93 μg /m^3/day (27.4%)
- Profile 3: 7.97 μg /m^3/day (9.1%)
- Profile 4: 4.70 μg /m^3/day (5.4%)
- Profile 5: 0.11 μg /m^3/day (0.1%)

The most likely sources that fit the profiles are:

- Profile 1 – Soil/Dust
- Profile 2 – LDT/Biomass
- Profile 3 – Industrial – Cu, Zn and Pb
- Profile 4 – Industrial – Ca, Ni and Br
- Profile 5 – Industrial – Ni and Cu

TABLE 6-13: FINE PARTICULATE SOURCE PROFILE (2ND NOVEMBER 2006 – 15TH FEBRUARY 2007)

Element (ng/µg)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Al	**16.22**	12.51	0.76		
	0.6	*2.25*	*3.41*		
Si	**55.47**	37.32	11.38	49.34	
	1.04	*3.90*	*5.91*	*15.37*	
S	0.2	**19.48**	3.06	0.5	11.98
	0.14	*0.56*	*0.84*	*2.18*	*52.01*
K	**3.94**	**16.39**	0.43	11.2	136.18
	0.19	*0.72*	*1.09*	*3.17*	*67.83*
Ca	**6.08**			**23.70**	
	0.22			*3.17*	
Ti	**1.12**	1.00	0.30	1.13	17.55
	0.03	*0.11*	*0.16*	*0.42*	*10.09*
Mn	**0.21**	0.17	0.06	0.37	
	0.01	*0.02*	*0.03*	*1.97*	
Fe	**9.08**	**8.36**	3.25	16.04	
	0.21	*0.77*	*1.18*	*3.06*	
Ni	**0.04**	**0.07**	0.03	**0.29**	**5.27**
	0.002	*0.01*	*0.01*	*0.03*	*0.77*
Cu	**0.02**	0.03	**0.39**	0.31	**4.54**
	0.004	*0.01*	*0.01*	*0.04*	*0.83*
Zn	**0.02**	**0.23**	**0.54**		
	0.004	*0.02*	*0.02*		
Br	0.02	**0.13**	0.04	**0.40**	
	0.001	*0.004*	*0.01*	*0.02*	
Rb	**0.02**	**0.04**		0.01	1.12
	0.001	*0.006*		*0.01*	*0.33*
Sr	**0.06**	0.02	0.01	0.16	
	0.001	*0.004*	*0.01*	*0.02*	
Pb		**0.12**	**0.10**		
		0.01	*0.01*		
BC (µg/µg)		**0.08**	0.01	0.03	0.28
		0.002	*0.003*	*0.01*	*0.18*
Mass (µg/µg)	**1.03**	**1.04**	1.26	1.06	0.67
	0.01	*0.04*	*0.66*	*0.16*	*0.28*

6.2.5 COMPARISON BETWEEN MODEL AND EXPERIMENTAL DATA

Generally, the model was able to reproduce the experimental data as shown in **Tables 5-11** to **5-16** with the very high R^2 values. The gradient of the fits was also very close to 1. The fit for Cl in the coarse fraction consistently gave R^2 value (0.88, 0.78 and 0.83 for the zero fit and 0.91, 0.87 and 0.83, 2005/06 Harmattan, 2006 Rainy Season and 2006/07 Harmattan respectively) which were among the lowest.

The fine particulate BC and the Coarse BC for the 2005/06 Harmattan and 2006 Rainy seasons model fit the data very well. The 2006/07 Harmattan Coarse BC (as shown in **Fig. 5-2**), the model fits the experimental data better for BC concentrations less than 10 μgm^{-3}. In the theory for the calculation of the BC (**Eqn 3-13**) it was assumed that a thin layer of aerosol would be deposited on the filter giving rise to a single dust layer thickness. For the extreme Harmattan of 2006/07, it appears that the particulate matter deposited on some of the filters was more than a single layer thick.

CHAPTER 7

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

7.1 SUMMARY

Airborne particulate matter (APM) in the semi-rural town of Kwabenya, near Accra-Ghana, was collected using Gent sampler onto nuclepore filters. The Gent sampler size-segregated the APM into coarse (2.5<aerodynamic diameter<10 μm) and fine (aerodynamic diameter < 2.5 μm). A total of 216 samples were collected from 28th December 2005 to 12th February 2007. The sampling period spanned two Harmattan seasons and one rainy season. The parameters determined were mass, elemental and black carbon concentrations. This was achieved using gravimetric analysis, EDXRF and reflectometric techniques respectively.

The filters used for air pollution studies are very important, in terms of the material they are made of, since all the parameters measured come from the loaded filter. It was therefore very important that the filter type used had very low blank values since this will give very low detection limit. The nuclepore filters used in this work satisfy this condition. The mass of the loaded filter is also very critical in atmospheric aerosol analysis, because all the other measurement will be fractions of this. To minimize any discrepancy in the weighing procedure before and after sampling, measurements were done with microgramme-sensitive (μg) balance in a temperature- and relative humidity-controlled environment.

The mass concentration of the particulate matter (PM_{10}) at Kwabenya was dominated by the coarse particles ($PM_{10-2.5}$). The average mass concentration for the whole measuring

period was 151.14 μgm^{-3} for the coarse fraction and 30.26 μgm^{-3} for the fine fraction. The coarse mass concentration for the Harmattan seasons generally was higher than the Rainy season. The coarse-to-fine ratios were also higher for the Harmattan seasons than the Rainy season. A total of 185 days out of the 216 days of sampling had PM_{10} values above the WHO limit of 50 μgm^{-3} for 24-hour mean. Using the Ghana EPA guideline limit of 70 μgm^{-3} for 24 hours, 130 days had values above the guideline limit. A total of 60 days had $PM_{2.5}$ values that exceeded the WHO limit of 25 μgm^{-3} for 24-hour mean. Though mass concentration alone does not provide sufficient information when the limit values are exceeded, it serves as basis for the recommendation of abatement strategies and high PM_{10} concentrations are not favourable for people with respiratory health problems (asthma, cough and catarrh), allergic eye diseases, and sickle cell anaemia.

Black carbon (BC), also known as elemental carbon (EC) is essentially a primary pollutant emitted during incomplete combustion of fossil and biomass carbonaceous fuels. The "Black smoke" or Gagel[150] method was used to measure the BC concentration on the loaded filters. On the average the BC concentration in the fine fraction was higher than the coarse fraction except for the 2006/07 Harmattan period. In terms of percentages of loaded mass on filter, the fine fraction BC was much higher than the coarse fraction BC.

Elemental concentration was determined on the loaded filters using energy dispersive x-ray fluorescence analysis. The spectrometer used was optimised for air filter analysis through the design of the sample holder. This facilitated the reduction of scattering of x-rays into the detector, enhancement of signal-to-background ratio, and consequently

lower detection limits. The x-ray spectra were fitted using the AXIL[188,189] software and the fundamental parameters' quantitative method. The analytical procedure was validated using a NIST air filter standard reference material SRM2783. The elements identified in the coarse fraction and quantified were Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr and Pb. In addition, the following elements were identified; P, Co and Se but not quantified in the coarse fraction because they were mostly below detection limit or were present in very few samples. In the fine fraction the following elements were identified Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr and Pb and quantified. Cl, V, Cr and Co were identified but were not quantified in the fine fraction. The elemental concentrations varied from season to season. As expected those of the crustal origin – Al, Si, Ti, Mn, Fe, Rb and Sr had higher values during the Harmattan seasons. The correlation between the various elements served as pointers to the sources emitting the particulate matter.

A receptor model using principal component and regression analysis was used for the pollution source apportionment of the loaded aerosol. The species used for the receptor model were – mass, BC and elemental concentrations. The coarse aerosol was influenced by some specific sources over the study period, including Soil/Dust, Biomass/LDT and Sea aerosol/spray in addition to other sources depending on the season. The fine fraction is dominated by Soil/Dust, Biomass/LDT and some metal industrial sources. The model data generated fitted the experimental data very well.

7.2 CONCLUSIONS

This work is the first known sustained air particulate matter measurement in Ghana spanning fourteen months. Other works sited in Chapter 1 of this thesis (Section 1.2.3.) were for brief periods sometimes lasting less than three weeks. The sampling period covered two Harmattan seasons and a Rainy season. The Harmattan season with its characteristic dry desert wind from the Sahara is very peculiar to the West African region and the study of the Harmattan dust is currently among one of the focused area of air pollution experts[53,68,220-224] because of the aerosol load that it generates and its effect on health and climate. Hence studies that can multi-characterise the Harmattan aerosol (mass, BC and elemental concentrations) are very important, as in this work.

The project design and the type of filters used in this work allowed for the measurement and analyses of different parameters such as mass, BC and elemental concentration. The mass was further segregated into fine ($PM_{2.5}$), coarse ($PM_{10-2.5}$) fractions. Consistently, the mass concentration of the particulates showed low values during the rainy season and very high levels during the harmattan period, especially during the 2006/07 Harmattan. The coarse PM ranged from 0.16 $\mu g/m^3$ to 1794.01 $\mu g/m^3$; $PM_{2.5}$ (fine) fraction from 0.5 $\mu g/m^3$ to 430.23 $\mu g/m^3$; PM_{10} from 0.87 $\mu g/m^3$ to 2064.89 $\mu g/m^3$.

Though fine particles can originate from natural sources in addition to anthropogenic sources, it is a well known fact that the coarse-to-fine (C/F) ratio can be used as possible indicator for natural and anthropogenic emissions. Usually elements of natural origin have high C/F ratios (>1.5) and elements of anthropogenic origin have low C/F ratio.[136,225] In this work, for all the data the coarse-to-fine ratio average is 5.0 (8.4 for the 2005/06

Harmattan; 2.4 for the Rainy Season and 5.5 for the 2006/07 Harmattan). From this result it can be said that most of the APM source at Kwabenya are from natural origin.

The fine fraction ($PM_{2.5}$) aerosols are more mobile in the environment than the coarse fraction. The fine fraction impact on the environment is therefore greater since it can incorporate in raindrops or be easily transported in the biosphere, etc. It also has implication for human health as they are easily absorbed in the human body. All these facts are important in epidemiological and hazard evaluation when aerosol particles are being investigated.

Determination of BC by reflectometer on the nuclepore filters shows that the coarse fraction contains very little BC contribution. The fine fraction mass however is dominated by BC accounting for over 10% during the 2006 Rainy Season. This shows that the BC is coming from anthropogenic sources.

Conventional EDXRF is severely limited in air filter analysis because of the low mass loading; this limitation arises because the results generated are very close to the detection limit. One of the factors contributing to this high detection limit is scattering of excitation radiation into the detector thereby producing a high background. The EDXRF spectrometer used at the Royal Veterinary and Agricultural University of Denmark, Copenhagen - Denmark was optimised for air filter analyses.[187] This was achieved by the modification of the source-sample-detector arrangement (**Fig. 4-10**) such that the scattered radiation are mainly transmitted through the filter giving rise to a high signal-to-background ratio and lower detection limits. A total of 21 elements ranging from Al – Pb

were identified but 18 quantified in the coarse fraction (with concentrations ranging from 0.5 ngm^{-3} to 47295 ngm^{-3}). In the fine fraction 18 elements were identified and 14 quantified (with concentration ranging from 0.67 ngm^{-3} to 4080 ngm^{-3}). The elemental analysis of the loaded aerosol show high levels of air pollution originating from natural and anthropogenic sources. Ghana is a developing country and the level of industrialisation is quite low but the levels of BC and elements-such as S, Ni and Pb, are comparable to that of Sweden[212] which is a developed country. However S is a strong indicator of long distance transport (LDT), this could be resolved in future work when air mass trajectories are added to determine if the S from local sources is more dominating than that from LDT.

This work did not set out to do direct source measurements, measurements sited at the pollutant emission points (as shown in **Fig. 2-4**), because it is difficult and very expensive. In addition, the modification and transformation of the species in the atmosphere is not fully understood because the atmosphere is a very complex system. It is for this reason that the receptor model approach was used. It is satisfying that some characteristic elements appeared which were used to explain the source profiles from the receptor model used in this work. The metal industries' signature in the fine are very striking since during the study no known metal processing industries/smelters were in operation in the Accra Metropolitan Area.

Biomass burning was identified as a major source contributing to the APM at Kwabenya, especially in the fine fraction with the high BC, K and Br. In the coarse fraction sea spray

(aerosol) is a major source of Cl. The high source of Cl in the air could account for the high corrosion of appliances at Kwabenya and along the coast of Ghana.

The lack of vital meteorological data from the Ghana Atomic Energy Commission mini-weather station, such as wind speed and direction, has hampered the ability of this work to identify the source directions. The nearest station that could be used is from the Kotoka International Airport which is about fifteen kilometers away but given the topology and rainfall patterns at the two stations, the airport results could not be applied to this work. This situation is currently being addressed with the installation of a new weather station.

Developed countries have a well coordinated air quality management system, including routine air particulate matter monitoring. Most of these developed countries are in the temperate regions. To fully understand the behaviour of aerosol particles under different climatic conditions there is the need to characterise aerosol particles from different places including developing countries like Ghana. This work is therefore contributing to the bridging of this information gap on the nature and characteristics of aerosol in Ghana in terms of mass, BC, elemental concentrations and sources emitting them.

The high aerosols load during the Harmattan dominated by sources of crustal origin is in agreement with the findings of other researchers.[53,68,221]

The ability of this work to use source signatures from outside the region to identify sources contributing to the APM at Kwabenya is very interesting. This will curtail the need for direct source measurement and characterisation of all identifiable sources since this is very expensive and tedious.

For any nation to develop appropriate air policy there is the need for sound scientific evidence backed by reliable monitoring for public acceptance. This would assist to make regulatory and mitigation actions more acceptable to those who have to pay in the short-term to achieve the long-term benefits. Other pollutants such as gaseous (SOx, CO, O_3 and NOx) and chemical carcinogens (PAHs, Benzene and formaldehydes) are all very important to assess air quality but the equipment for their measurements and monitoring are not available in the country. Without reliable and well-trusted monitoring, carried out with techniques tailor-made to the specific situation and equipment available, policy development may be severely hampered. This is very crucial in a developing country like Ghana, where resources are scarce given a host of competing priorities. Hence studies that can generate multiple parameters such as mass, elemental concentrations, and BC concentrations are preferred, as in this work. In addition, air pollution monitoring is very expensive (in terms of equipment, logistics and consumables) hence monitoring in combination with modeling is the best and preferred option. These were the criteria that influenced this thesis.

7.3. RECOMMENDATIONS

From the results, discussions and conclusions of this work it is recommended that:

- The measurement currently continuing at Kwabenya should be supported to generate a larger data set for the improvement of the model and developed into a monitoring site with data spanning decades (like the super sites in the USA) for long term trend studies.

- Source profiles of some of the local sources identified are to be determined (at source) and compared with those generated in this work (at the receptor).
- There is also the need to study the amount of loaded aerosol that will make the BC concentration exceed the single layer of particulate matter on the filter.
- According to Reichhardt[32] there exists credible evidence that PM_{10} (24 hour mean) in the range 30 – 200 μgm^{-3} has effects on human health. There is also the need to combine the mass concentration measurements with epidemiological studies to establish the possible effects in Ghana. This study is very important for developing countries because most of the studies have come from countries where there is a high fine-to-coarse ratio. This could be helpful in showing whether fine concentrations are more important with regard to health effects than Coarse in the PM_{10}.
- The high anthropogenic (especially fine) S, Ni, Pb and BC is worrying and there is the need to take some mitigation measures to reduce the level.
- For a more complete air quality situation in the country there is the need to set monitoring stations in the Northern sector (for example in Navorongo or Tamale), the Central sector (preferably Kumasi) and the one at Kwabenya in the South.
- Finally, with the discovery of oil on the Western coast of the country, it would be very appropriate to setup a monitoring station in the area to determine the baseline data upon which the production of oil would impact.

References

1. Hinds, W. C., *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, John Wiley, New York, 1999, pp1-6.
2. Colbeck I., Particle Emission from Outdoor and Indoor Sources. , in *The Handbook of Environmental Chemistry: Airborne Particulate Matter*, Kouimtzis T. and Samara C. (eds.), Springer, Berlin, 1995, pp 2 – 34.
3. Harrison R.M., Air Pollution: Sources, Concentration and Measurement, in *Pollution: Causes, Effects and Control*, Harrison R.M. (ed), The Royal Society of Chemistry, Cambridge, 1996, pp 144-168.
4. Jaenicke R., Atmospheric Aerosol Size Distribution, in *Atmospheric Particles*, Harrison and van Grieken R. E. (ed), John Wiley, Chichester 1998, pp 1-25.
5. Colls J., *Air Pollution – An Introduction*, E & FN Spon, London, 1997, pp1.
6. Buseck P. R. and Posfai M., Aerosol minerals and related aerosol particles: Effects on climate and the environment. *Proceedings of the National Academy of Sciences of the United States of America*, **96**, pp3372-3379, (1999)
7. Graedel T. E. and Crutzen P. J., *Atmospheric Change*: An Earth System Perspective, W. H. Freeman and company, New York, pp77, (1993).
8. Raes F., Dingenen R. V., Vignati E., Wilson J., Putaud J., Sienfeld J. H. and Adams P., Formation and cycling of aerosols in the global troposphere, *Atmospheric Environment*, **34**(25), pp4215-4240, (2000).
9. World Health Organisation (WHO), WHO *guidelines for air quality. Fact sheet no. 187*, 2000, [http://www.who.int/inf-fs/fact187.html]

10. Salby M. L., *Fundamentals of Atmospheric Physics*, Academic Press, San Diego, 1996, pp258-262.

11. Brimblecombe P., Air Pollution and Health History, in *Air Pollution and Health*. Holgate S. T., Samet J. M., Koren H. S. and Maynard R. L. (eds.), Academic Press, London, 1999, pp5-18.

12. Ramazzini B., *De morbis artificium* (1713), Reprinted by Arbetsmiljöfölaget, 1989.

13. Linné C. von, Dalaresan (Iter Dalekarlicum), 1734, Reprinted in Bertil Gullander (ed.), 1980, *Linné i Dalarna. Forum*, Stockholm.

14. Loomis D., Sizing up air pollution research, *Epidemiology* **11**, pp2-4, (2000).

15. Mark D., Atmospheric Aerosol Sampling, In *Atmospheric Particles*. Harrison RM, van Grieken R (ed). Wiley: Chichester; 1998, pp29-94.

16. Schwartz J and Neas LM., Fine particles are more strongly associated than course particles with acute respiratory health effects in school children, *Epidemiology* 11: pp6-10, (2000).

17. Donaldson K, Li XY, MacNee W., Ultrafine (nanometre) particles mediated lung injury, *Aerosol Science*; **29**: pp553-560, (1998).

18. Harrison, RM., *Pollution Causes, Effects and Control*, Royal Society of Chemistry, Cambridge, 2001.

19. Hauck H., Berner A., Frischer T., Gomiscek B., Kundi M., Neuberger M., Puxbaum H., Preining O. and AUPHEP- Team , AUPHEP – Austrian Project on Health Effects of Particulates – general overview, *Atmospheric Environment*, 38, pp3905-3915, (2004).

20. Anderson K. R., Avol E. L., Edwards S. A., Shamoo D. A., Peng R. C., Linn W. S., and Hackney J. D., Controlled exposures of volunteers to respirable carbon and sulphuric acid aerosol, *Journal of Air and Waste Management Association*, **42**, pp770-776, (1992).

21. CSIRO Atmospheric Research, Air Pollution: eight thousand deaths per day, [http://www.dar.csiro.au/news/1999/mr997.html]

22. Statement on behalf of the American Academy of Pediatrics before the *Clean Air Scientific Advisory Committee on the USEPA* regarding National Ambient Air Quality Standards for Particulate Matter on April 7, 2005.

23. American Academy of Pediatrics, Committee on Environmental Health, Ambient Air Pollution: Health Hazards to Children, *Pediatrics*, **114**, pp1699-1707, (2004)

24. Gauderman W. J., Avol E., Gilliland F., Vora H., Thomas D., Berhane K., Mc-Connell R., Kuenzli N., Lurmann F., Rappaport E., Margolis H., Bates D., and Peters J., The effect of Air pollution on Lung development from 10 to 18 years of age, *New Engl. J. Med.*, **351**(11), pp1057-1067, (2000).

25. Yang C., Chang C., Chuang H., Ho C. and Tsai S., Evidence for Increased Risks of Preterm Delivery in a Population Residing near a Freeway in Taiwan, *Archives of Environmental Health*, **58** (10), pp649-654, (2003).

26. Walters S. and Ayres J., Health Effects of Particulates, in *Pollution: Causes, Effects and Control*, Harrison R.M. (ed), The Royal Society of Chemistry, Cambridge, 1996, pp 248-250.

27. Dockery D. and Pope A., Epidemiology of Acute Health Effects: Summary of Time-Series Studies, in *Particles in Our Air: Concentration and Effects*, Wilson R and Spengler J. D. (eds), Harvard University, Cambridge, 1996, pp123-148.

28. Vedal S., Ambient Particles and Health: Lines that Divide, *J. Air & Waste Management Assoc.*, **47**, pp551-581 (1997)

29. Hornberg C., Maciuleviciute L., Seemayer N. H., and Kainka E., Induction of sister chromatid exchanges (SCE) in human tracheal epithelial cells by the fractions PM-10 and PM-2.5 of airborne particulates, *Toxicol. Lett.* **96**, **97**, pp215-220, (1998)

30. Nriagu J., Jinabhai C. C., Naidoo R. and Coutsoudis A., Lead Poisoning of Children in Africa, II. Kwazulu/Natal, South Africa, *Sci. Total Environ.*, **197**, pp1-11, (1997).

31. Cohen B.S., Xiong J. Q., Fang C. and Li W., Deposition of Charged particles on Lung Airways, *Health Phys.*, **74**, pp554-560, (1998).

32. Reichhardt T., Weighing the Health Risks of Airborne Particulates, *Environ. Sci. Technol.* **29 No.8**, pp360-364, (1995).

33. Pope A. and Dockery D., Epidemiology of Chronic Health Effects: Cross-Sectional Studies, in *Particles in Our Air: Concentrations and Effects*, Wilson R and Spengler J. D. (eds), Harvard University, Cambridge, 1996, pp149-167.

34. Zhang J., Song H., Tong S., Li L., Liu B., and Wang L., Ambient Sulfate Concentration and Chronic Disease Mortality in Beijing, *Sci. Total Environ.*, **262**, pp63-71, (2000).

35. Kiehl J. T. and Briegleb B. P., The Relative Roles of Sulfate Aerosols and greenhouse Gases in Climate Forcing, *Science*, **260**, pp311-314, (1993).

36. Coakley Jr. J. A., Cess R. D. and Yurevich F. B., The effect of tropospheric aerosols on the earth's radiation budget: a parameterization for climate models, *J. Atmospheric Sciences*, **40**, pp116-138, (1983)

37. Hansen J. E., Sato M., Lacis A., Ruedy R., Tegen I. and Matthews E., Climate forcing in the industrial era, *Proceedings of the National Academy of Science of the United State of America,* **95**, pp12753-12758, (1998).

38. Charlson R. J. and Heintzenberg J., *Aerosol Forcing of Climate*, John Wiley, Chichester, 1995, pp403.

39. Houghton J. T., Meira Filho L. G., Bruce J., Lee h., Callander B. A., Haites E., Harris N., Maskell K. (eds), *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, Cambridge University, 1995, pp15.

40. Charlson R. J., Schwartz S. E., Hales J. M., Cess R. D., Coakley J. A., Hansen J. E., and Hofmann D. J., Climate forcing by Anthropogenic Aerosol, *Science*, **255**, pp423-430, (1992).

41. Andreae M. O., Raising dust in the greenhouse, *Nature*, **380**, pp 389-390, (1996).

42. Sokolik I. N. and Toon O. B., Direct Radiative Forcing by Anthropogenic Airborne Mineral Aerosols, *Nature*, **381**, pp681-683, (1996).

43. Langmann B., Herzog M. and Graf H., Radiative Forcing of Climate by Sulfate Aerosols as Determined by a Regional circulation Chemistry Transport Model, *Atmospheric Environment*, **32 No.16**, pp2757-2768, (1998).

44. Jacobson M. Z., Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, Nature **409**: pp695-697, (2001).

45. National Aeronautics and Space Administration (NASA), NASA ties El Nino induced drought to air pollution from fires, [http://www.nasa.gov/home/hqnews/2003/apr/HP_news_03128.html]

46. Nash T. H., The Effect of Air Pollution on Other Plants, Particularly Vascular Plants, in *Air Pollution and Lichens*, Ferry B. W., Baddeley M. S. and Hawksworth D. L. (eds), The Athlone Press of the University of London, London, 1973, pp208-209.

47. Gytarsky M. L., Karaban R. T., Nazarov I. M., Sysygina T. I. and Chemeris M. V., Monitoring of Forest Ecosystems in the Russian Subarctic: Effects of Industrial Pollution, *Sci. Total Environ.*, **164**, pp57-64, (1995).

48. Mankovska B. and Steinnes E., Effects of Pollutants from an Aluminium Reduction Plant on Forest Ecosystems, *Sci. Total Environ.*, **163**, pp11-23, (1995).

49. Vike E., Air-Pollutant Dispersal Patterns and Vegetation Damage in the Vicinity of Three Aluminium Smelters in Norway, *Sci. Total Environ.*, **236**, pp75-90, (1999).

50. Clarke A.G., Azadi-Boogar G.A and Andrews G.E., Particle Size and Chemical Composition of Urban Aerosols, *Sci. Total Environ.*, **235**, pp15-24, (1999).

51. Landsberger S. and Biegalski S., Analysis of Inorganic Particulate Pollutants by Nuclear Methods, in *The Handbook of Environmental Chemistry: Airborne Particulate Matter*, Kouimtzis T. and Samara C. (eds.), Springer, Berlin, 1995, pp175–198.

52. Kent G. S., Trepte C. R., Skeens K. M., Winker D. M., LITE and SAGE II Measurement of Aerosol in the Southern Hemisphere Upper Troposhere, *J. Geophys. Res.*, **103**, D15, 19 111-19 127, (1998)

53. Baumbach G., Vogt U., Hein K. R. G., Oluwole A. F., Ogunsola O. J., Olaniyi H. B. and Akeredolu F. A., Air pollution in a large tropical city with high traffic density – results of measurements in Lagos, Nigeria, *Sci. Total Environ.*, **169**, pp25-31, (1995).

54. World Bank, Rural Energy and Development: Improving energy supplies for two billion people, **The World Bank**, 1996, pp26.

55. Jayarantne E. R. and Verma T. S., The impact of biomass burning on the environmental aerosol concentration on Gaborone-Botswana, *Atmospheric Environment*, **35**, pp1821-1828, (2001).

56. Mbuligwe S. E. and Kassenga G. R., Automobile air pollution in Dare es Salaam City -Tanzania, *Sci. Total Environ.*, **199**, pp227-235, (1997).

57. Cooper W. C., The health implications of increased manganese in the environment resulting from the combustion of fuel additives: a review of the literature, *J. Toxicol. Environ. Health*, **14**, pp23-46, (1984).

58. Loranger S. and Zayed J., Environmental and occupational exposure to manganese: a multimedia assessment, *Int. Arch. Occup. Environ. Health*, 67, pp101-110, (1995).

59. Sierra P., Loranger S., Kennedy G. and Zayed J., Occupational and environmental exposure of automobile mechanics and nonautomotive workers to airborne man-

ganese arising from combustion of methylcyclopentadienyl manganese tricarbonyl (MMT), *Am. In. Hyg. Assoc. J.*, **56**, pp713-716, (1995).

60. Ferraz H. B., Bertolucci P. H. F., Pereira J. S., Lima J. G. C., Andrade L. A. F., Chronic Exposure to the fungicide maneb may produce symptoms and signs of CNS manganese intoxication, *Neurology*, **38**, pp550-553, (1988).
61. Roels H., Lauwerys R., Buchet J. P., Genet P., Sarhan M. J., Hanotiau I., deFays M., Bernard A., Stanescu D., Epidemiological survey among workers exposed to manganese: effects on lung, central nervous system, and some biological indices, *Am. J. Ind. Med.*, **11**, pp307-327, (1987).
62. Wang D. X., Zhou W. M., Wang S. Z., Zheng W., Occupational exposure to manganese in welders and associated neurodegenerative diseases in China, *Toxicol. Sci.*, **42**, pp24, (1998).
63. Zheng W., Ren S. and Graziano J. H., Manganese inhibits mitochondrial aconitase: a mechanism of manganese neuroxicity, *Brain Research*, **799**, pp334-342, (1998).
64. http://:www.epa.gov/ttnatw01/hlthef/manganese.htlm
65. Barbeau A., Inoue N. and Cloutier T., Role of Manganese in dystonia, *Adv. Neurol.*, **14**, pp339-352, (1976).
66. Mena I., Court J., Fuenzalida S., Papavasiliou P. S., and Cotzias G. C., modification of chronic manganese poisoning treatment with L-dopa or 5-OH tryptophane, *New Engl. J. Med.*, **282**, pp5-10, (1970).
67. Tepper L. B., Hazards to Health: Manganese, *New Engl. J. Med.*, **264**, pp347-348, (1961).

68. Schwanghart W. and Schütt B., meteorological causes of Harmattan dust in West Africa, *Geomorphology*, 95, pp412-428, (2008)

69. Levin Z, Ganor E. and Gladstein V., The effects of desert particles coated with sulfate on rain formation, *J. of Appl. Meteorol.*, **35**, pp1511-1523, (1996)

70. Yin Y., Levin Z., Reisin T. G. and Tzivion S., The effects of giant cloud condensation nuclei on the development of a precipitation in convective clouds – a numerical study, *Atmos. Res.*, **53**, pp91-116, (2000)

71. Rosenfeld D., Rudich Y. and Lahav R., Desert Dust suppressing precipitation: A possible desertification feedback loop, *Proceedings of the National Academy of Science of the United State of America*, **98** (11), pp5975-5980, (2001)

72. Etyemezian V., Kuhns H., Gillies J., Green M., Pitchford M. and Watson J., Vehicle-based road dust emission measurement 1: Methods and Calibration, *Atmospheric Environment.*, 37, pp4559-4571, (2003).

73. Martens C. S., Wesolowski J. J., Harriss R. C. and Kaifer R, Chlorine loss from Puerto Rican and San Francisco Bay area marine aerosol, *J. Geophys. Res.*, **78**, pp8778-8792, (1973)

74. Mouri H., Nagao I., Okada K., Koga S. and Tanaka H., Elemental compositions of individual aerosol particles collected over the Southern Ocean: A case study, *Atmos. Res.*, **43**, pp183-195, (1997).

75. United Nations, World urbanization prospects: the 2003 revision, United Nations, New York, 2004.

76. Mukoko S., On sustainable urban development in sub-Saharan Africa, *Cities*, **13**, pp265-271, (1996).

77. Stren R and Halfani M., The cities of sub-Saharan Africa: from dependency to marginality, in *Handbook of Urban Studies*, Paddison R. (ed.), Sage Publications, 2001, pp466-485.

78. Cohen B., Urban growth in developing countries: a review of current trends and a caution regarding existing forecasts, *World Development*, **32**, pp23-51, (2004).

79. Miller R. B. and Small C., Cities from space: potential applications of remote sensing in urban environmental research policy, *Environmental Science and Policy*, **6**, pp129-137, (2003).

80. Tirabassi T., Listening out for urban air pollution, *Atmospheric Environment*, **33**, pp4219- 4220, (1999).

81. Fenger J., Urban air quality, *Atmospheric Environment*, **33**, pp4877- 4900, (1999).

82. Mage D., Ozolins G., Peterson P., Webster A., Orthofer R., Vandeweerd V. and Gwynne M., Urban air pollution in megacities of the world, *Atmospheric Environment*, **30**, pp681- 686, (1996).

83. Cuhadaroglu B. and Demirci E., Influence of some meteorological factors on air pollution in Trabzon city, *Energy and Buildings*, 25, pp179-184, (1997).

84. Romero H., Ihl M., Rivera A., Zalazar P. and Azocar P., Rapid urban growth – land use changes and air pollution in Santiago-Chile, *Atmospheric Environment*, **33**, pp4039-4047, (1999).

85. Cariñanos P., Galan C., Alcazar P. and Dominguez E., Meteorological phenomena affecting the presence of solid particles suspended in the air during winter, *Int. J. of Biometeorology*, **44**, pp6-10, (2000).

86. Panter B. C., Hooper M. A. and Tapper N. J., A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments, *Atmospheric Environment*, **33**, pp4087-4099, (1999).

87. Public Agenda Newspaper of 20th June 2005, under the heading Bloody Gold, as corporate interest clashes with people's right.

88. Nyarko B.J.B.,Serfor-Armah Y., Akaho E. H. K. and Kyere A. W. K., Biomonitoring of trace-element air pollution in a gold mining area in Ghana using the generalized k0-standardization NAA method, *International Conference on Isotopic and Nuclear Analytical Techniques for Health and Environment*, **IAEA-CSP22/CD**,2004.

89. Nyarko B.J.B., Serfor-Armah Y., Akaho E.H.K., Adomako D. and Osae S., Determination of heavy metal pollution levels in lichens at Obuasi gold mining area in Ghana, *J. of Applied Scie. Tech. (JAST)*, **9** No. 1&2, pp215-228, (2004).

90. Pilinis C. and Pandis S. N., Physical, Chemical and Optical Properties of Aerosols, in *The Handbook of Environmental Chemistry: Airborne Particulate Matter*, Kouimtzis T. and Samara C. (eds.), Springer, Berlin, 1995, pp 102.

91. Chow J. C., Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles, *J. Air and waste Management Assoc.*, **45**, pp320-382, 1995.

92. Finlayson-Pitts B. J. and Pitts Jr. J. N., *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press, San Diego, 2000, pp. 297, 349, 354, 383.

93. O'Dowd C. D., Lowe J. A. and Smith M. H., Observations and modeling of aerosol growth in marine stratocumulus – case study, *Atmospheric Environment*, **33**, pp3053-3062, 1999.

94. Colls J., *Air Pollution – An Introduction*, E & FN Spon, London, 1997, pp148.

95. Zhuang H., Chan C. K., Fang M. and Wexler A. S., Size distributions of particulates sulfate, nitrate, and ammonium at a costal site in Hong Kong, *Atmospheric Environment*, **33**, pp843-853, 1999.

96. Haaf W. and Jaenicke R., Results of improved size distribution measurements in the Aitken range of atmospheric aerosols, J. Aerosol Sci., **11**, pp321-330, (1980).

97. Foltescu V. L., *Fine Atmospheric Particles: Formation, Transport and Deposition, PhD thesis*, Chalmers University of Technology – Sweden, 1995.

98. Kerminen V-M. and Wexler A. S., Post-fog nucleation of H_2SO_4-H_2O particles in smog, *Atmospheric Environment*, **28 (15),** pp2399-2406, (1994).

99. Blando J. D. and Turpin B. J., Secondary organic aerosol formation in cloud and fog droplets – A literature review of plausibility, *Atmospheric Environment*, **34**, pp1623-1632, (2000).

100. Lavanchy V. H. M., Gäggeler H. W., Nyeki S. and Baltensperger U., Elemental Carbon (EC) and Black Carbon (BC) measurements with thermal methods and an aethalometer at the high-alpine research station Jungfraujoch, *Atmospheric Environment*, **33**, pp2759-2769, (1999).

101. Mark D., Atmospheric Aerosol Sampling, In *Atmospheric Particles*. Harrison RM, van Grieken R (ed). Wiley: Chichester; 1998, pp31-42.

102. Zufall M. J. and Davidson C. I., Dry Deposition of Sulphur at High-Altitude Background Station in South Africa, In *Atmospheric Particles*. Harrison RM, van Grieken R (ed). Wiley: Chichester; 1998, pp426-463.

103. Seinffeld J. H. and Pandis S. N., Particulates Matter (Aerosols), in Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley, New York, 1998, pp97-108.

104. McMurry P. H., A review of atmospheric aerosol measurements, *Atmospheric Environment*, **34**, 1959-1999, 2000.

105. International Atomic Energy Agency, Sampling and Analytical Methodologies for Instrumental Neutron Activation Analysis of Airborne Particulate Matter, *Training Course Series No. 4*, Vienna, 1992

106. Wedding J. B., Weigand M., John W. and Wall S., Sampling effectiveness of the inlet to the dichotomous sampler, *Environ. Sci. Technol.*, **14**, pp1367 – 1370, (1980).

107. Liu B. Y. H. and Pui D. Y. H., Aerosol sampling inlets and inhalable particles, *Atmospheric Environment*, **15**, pp589-600, (1981).

108. Esmen N. A. and Lee T. C., Distortion of cascade impactor measured size distribution due to bounce and blow-off, *Am. In. Hyg. Assoc. J.*, **41**, pp410-419, (1980).

109. Lawson D. R., Impaction surface coatings intercomparison and measurements with cascade impactors, *Atmospheric Environment*, **14**, pp195-199, (1980).

110. Wang L., Yan Q. and Liu L., Effect of a stick on the flow field in a cyclone and the pressure drop reduction mechanism, *Aerosol Sci. Technol.*, **35**, pp909-913, (2001).

111. Enliang L. and Yingmin W., A new collection theory of cyclone separators, *AIChE Journal*, **35 (4)**, pp666 – 669, (1989).

112. Wang L. and Ye L., Reducing pressure drop in cyclones by a stick, *Aerosol Sci. Technol.*, **31**, pp187 – 193, (1999).

113. Mothes H. and Löffler F., Prediction of particle removal in cyclones separators, *International Chemical Engineering*, **28(2)**, 1988

114. Coker A. K., Understanding Cyclone design, *Chemical Engineering Progress*, **December**, pp51 -55, (1993).

115. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York, NY, 1992

116. U. S. EPA Office of Air Quality Planning and Standards, Stationary Source Control Techniques Document for Fine Particulate Matter, *EPA-452/R-97-001*, Research Triangle, NC, October, 1998

117. Perry's Chemical Engineer's handbook, Robert Perry and Don Green (eds.), 6th Edition, McGraw-Hill, New York, NY, 1984.

118. U. S. EPA, Air Pollution Control Technology Fact Sheet *EPA-452/F-03-005*, 2003.

119. British Columbia Ministry of Water, Land and Air Protection, Particulate Matter in British Colombia - A report on PM10 and PM2.5 mass concentration up to 2000, May 2003, pp21.

120. Spurny K. R., Lodge Jr. J. P., Frank E. R. and Sheesley D. C., Aerosol filtration by means of nuclepore filters structural and filtration properties, *Environ. Sci. Technol.*, **3**, pp453-468, (1969).

121. Liu B.Y. H. and Lee K. W., Efficiency of membrane and Nuclepore filters for submicron aerosols, *Environ. Sci. Technol.*, **10**, pp345-350, (1976).

122. John W. and Reischl G., Measurement of the filtration efficiencies of selected filter types, *Atmospheric Environment*, **12**, pp2015-2019, (1978).

123. Dzubay T. G. and Barbour R. K., A method to improve adhesion of aerosol particles on Teflon filters, *J. Air Pollution Contr. Assoc.*, **33**, pp692-695, (1983).

124. Watson J. G. and Chow J. C., Clear Sky Visibility as a Challenge for Society, *Annual Rev. Energy Environ.*, **19**, pp241-266, (1994).

125. Brimblecombe P., The Big Smoke: A History of Air Pollution in London since Medieval Times, *Methuen*, London (1987).

126. Engelbrecht D. R., Cahill T. A. and Feeney P. J., Electrostatic effects on Gravimetric Analysis of Membrane Filters, *Journal of Air Pollution Control Association*, **30**, pp391-392, (1980).

127. Witz S., Eden R. W., Wadley M. W., Dunwoody C., Papa R. P. and Torres K. J., Rapid Loss of Particulate Nitrate, Chloride and Ammonium on Quartz Fiber Filters during storage, *J. Air Waste Manage. Assoc.*, **40**, pp53-61, (1990).

128. Witz S., Eden R. W., Liu C. S. and Wadley M. W., Water Content of Collected Aerosols in the South Coast and Southeast Desert Air Basins, *Journal of Air Pollution Control Association*, **38**, pp418-419, (1988).

129. Begum B. A., Kim E., Jeong C-H., Lee D-W. and Hopke P. K., Evaluation of the potential source contribution function using the 2002 Quebec forest fire episode, *Atmospheric Environment*, **39**, pp3719-3724, 2005

130. Wierzbicka A., Lillieblad L., Pagels J., Strand M., Gudmundsson A., Swietlicki E., Sanati M. and Boghard M., Aerosol optical, chemical and physical properties at Gosan, Korea during the Asian dust and pollution episode in 2001, *Atmospheric Environment*, **39**, pp39-50, 2005

131. Duan F., Liu X., Yu T. and Cachier H, Identification and estimate of biomass burning contribution to the urban aerosol organic concentrations in Beijing, *Atmospheric Environment*, **38**, pp1275-1282, 2004

132. Wang Y., Zhung G., Tang A., Yuan H., Sun Y, Chen S. and Zheng A., The ion chemistry and the source of $PM_{2.5}$ aerosol in Beijing, *Atmospheric Environment*, **39**, pp3771-3784, 2005

133. Yli-Toumi T., Hopke P., Paatero P., Basumia M. S., Landsberger S., Viisanen Y., Paatero J., Atmospheric aerosol over Finnish Arctic: Source analysis by the multilinear engine and the potential source contribution function, *Atmospheric Environment*, **37**, pp4381-4392, 2003

134. Graham B., Falkovich A. H., Rudich Y., Maenhaut W., Guyon P. and Andreae M. O., Local and regional contribution to the atmospheric aerosol over Tel Aviv, Israel: a case study using elemental, ionic and organic tracers, *Atmospheric Environment*, **38**, pp1593-1604, 2004

135. Venkataraman C., Reddy C. K., Josson S. and Reddy M. S., Aerosol size and chemical characteristics at Mumbai, India during the INDOEX-IFP (1999), *Atmospheric Environment*, **36**, pp1979-1991 , 2002

136. Moloi K., Chimidza S., Selin Lindgren E., Viksna A. and Standzenieks P., Black carbon, mass and elemental measurements of airborne particles in the village of Serowe, Botswana, *Atmospheric Environment*, **36**, pp2447-2457, 2002

137. Jenkins Ron, Gould R.W. and Gedcke Dale, *Quantitative X-ray Spectrometry*, Mercel Dekker Inc, New York and Basel, 1981, pp1.

138. Jaklevic J. M. and Giauque R. D., Energy-Dispersive X-ray Fluorescence Analysis using X-ray tubes Excitation, in Handbook of X-ray Spectrometry: Methods and Techniques, van Grieken R. E. and Markowicz A. A. (eds), Marcel Dekker, New York, 1993, pp151-180

139. Jenkins Ron, Gould R.W. and Gedcke Dale, *Quantitative X-ray Spectrometry*, Mercel Dekker Inc, New York and Basel, 1981, pp35.

140. Aboh I. J. K., Developing a Model for Multi-element Analysis of Prestea Gold Ore using Energy Dispersive X-Ray Fluorescence Technique- M. Phil Thesis submitted to the University of Ghana, Legon, 1990

141. Dzubay T. G. and Nelson R. O., Self absorption corrections for x-ray analysis of aerosol, *Advances in X-ray Analysis*, **18**, pp619-631, (1975)

142. Pierson W. R., Brachaczek W. W., Gorse R. A. Jr., Japar S. M., Norbeck J. M. and Keeler J. G., Atmospheric acidity measurements on Allegheny Mountain and the origin of ambient acidity in northeastern United States, *Atmospheric Environment*, **23**, pp431-459, (1989).

143. Shah J. J., Johnson R. L., Heyerdahl E. K., and Huntzicker J. J., Aerosol chemical composition and light scattering in Portland, Oregon: the role of carbon, *Atmospheric Environment*, **18**, pp235-240, (1984).

144. Japar S. M. and Szkarlat A. C., Measurement of diesel vehicle exhaust particulates using photoacoustic spectroscopy, *Combustion Science and Technology*, **24**, pp215-219, (1981).

145. Japar S. M., Szkarlat A. C. and Gorse R. A. Jr., Optical properties of particulate emissions from on-road vehicles, *Atmospheric Environment*, *15*, pp2063-2070, (1981)

146. Huntzicker J. J., Heyerdahl E. K., McDow S. R., Rau J. A., Griest W. H. and MacDougall C. S., Combustion as principal source of carbonaceous aerosol in the Ohio River Valley, *Journal of Air Pollution Control Association*, **36**, pp705-709, (1986).

147. Gray H. A., Cass G. R., Huntzicker J. J., Heyerdahl E. K. and Rau J. A., Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles, *Environmental Science and Technology*, **20**, pp580-589, (1986).

148. Chow J. C., Waston J. G., Prichett L. C., Pierson W. R., Frazier C. A., and Purcell R. G., The Dri Thermal/Optical reflectance carbon analysis system: description, evaluation and applications in U. S. air quality studies, *Atmospheric Environment*, **27A(8)**, pp1185-1201, (1993).

149. Waston J. G., Chow J. C., Lowenthal D. H., Pritchett L. C., Frazier C. A., Neuroth G. R. and Robbins R., Differences in carbon compositionof source pro-

files for diesel- and gasoline-powered vehicles, *Atmospheric Environment*, **28**, pp2493-2505, (1994).

150. Gagel A., Simultaneous black smoke and airborne particulate emission measurement by means of an automated combined instrument, VDI-Report, **1257**, pp631-645, 1996

151. Bem H, Gallorini M, Rizzio E. and Krzeminska M., Comparative studies of the concentrations of some elements in the urban air particulate matter in Lodz City of Poland and in Milan, Italy, *Environment International*, **29**, pp423-428, (2003).

152. Landsberger S., Improved Methodology for the Determination of the Seven Elemental Tracer Long-Distance Pollution signatures Using Thermal and epithermal Neutron Activation Analysis, *Analytical Chemistry*, **60**, pp1842-1845, (1988).

153. Var F., Narita Y. and Tanaka S., The concentration, trend and seasonal variation of metals in the atmosphere in 16 Japanese cities shown by the results of National Air Surveillance Network (NASN) from 1974 to 1996, *Atmospheric Environment*, **34**, pp2755-2770, (2000).

154. Heller-Zeiller S. F., Borgoul P. V., Moore R. R., Smoliar M., Suarez A. E. And Ondov J. M., Comparison of INAA and RNAA methods with thermal-ionization mass spectrometry for iridium determinations in atmospheric tracer studies, Journal *of Radioanalytical and Nuclear Chemistry*, **244(1)**, pp93-96, (2000).

155. Hashimoto Y., Sekine Y., Kim H. K., Chen Z. L. and Yang Z. M., Monitoring of atmospheric aerosol components by multielement neutron activation ana-

lysis in Seoul, Korea, April 1987 – March 1989, *Journal of Japan Society of Air Pollution*, 25, pp330-323, (1990).

156. Guinn V. P., Nuclear Analytical Methods in the Life Sciences, Zeisler, R., and Guinn, V. P. (eds), Humana Press, Clifton, NJ, 1990, pp1-7, 1990.

157. Ehmann W. D. and Vance D. E., Radiochemistry and Nuclear Methods of Analysis, Wiley, Toronto, 1991, pp271-272.

158. DeSoete, D., Gijbels, Hoste, J., Neutron Activation Analysis, Wiley-Interscience, Toronto, 1972, pp445-447.

159. El Nimr T., De Corte F., Moens L., Simonts A. and Hoste J., Epicadmium neutron activation analysis (ENAA) based on the k0 comparator method, Journal *of Radioanalytical Chemistry*, **67**, pp421-435, (1981).

160. Allen C. C., Desert varnish of Sonoran Desert – optical and electron microprobe analysis, *Journal of Geology*, **86**, pp743-752, (1978)

161. Casuccio G. S., Janocko P. B., Lee R. J., Kelly J. F., Dattner S. I. and Mgebroff J. S., The use of computer controlled scanning electron microscopy in environmental studies, *Journal of Air Pollution Control Association*, **33**, pp973-943, (1983).

162. Wernisch J., Quantitative electron microprobe analysis without standards, *X-ray Spectrometry*, **14**, pp109-119, 1985

163. Davis B. L., Additional suggestions for x-ray quantitative analysis of high-volume filters, *Atmospheric Environment*, **12**, pp2403-2406, (1978)

164. Davis B. L., Standardless x-ray diffraction quantitative analysis, *Atmospheric Environment,* **14**, pp217-220, (1980)

165. Davis B. L., A study of the errors in x-ray quantitative analysis procedures for aerosol collected on filter media, *Atmospheric Environment*, **15**, pp291-296, (1981)

166. Davis B. L., Johnson L. R., Stevens R. K., Courtney W. J. and Safriet D. W., The quartz content and elemental composition of aerosols from selected sites of the EPA inhalable particulate network, *Atmospheric Environment*, **18**(4), pp771-782, (1984)

167. Elsma R., Vermeulen A. T. and Kieskamp W. M., Determination of European emission using concentration and isotopic measurements, *Environmental Mon. Assess.*, **31**(1-2), pp197-202, (1995)

168. Goldstein S. L., O'Nions R. K. and Hamilton P. J., A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems, *Earth Planet Sci. Lett.*, **70**, pp221-236, (1984)

169. Johnson B. J and Dawson G. A., A preliminary study of carbon isotopic content of ambient formic acid and two selected sources: automobile exhaust and formicine ants, *J. Atmos. Chem.*, **17**(2), pp123-140, (1993)

170. Kelly W. R., Chen L-T., Gramlich J. W. and Hehn K. E., Determination of sulphur in low sulphur steels isotope dilution thermal ionization mass spectrometry, *Analyst*, **115**, pp1019-1024, (1990)

171. Kelly W. R., Paulsen P. J., Murphy K. E., Paulsen P. J., Vocke R. D. Jr. and Chen L-T., Determination of sulphur in fossil fuels by isotope dilution-thermal ionization mass spectrometry, *Anal Chem*, **66**, pp2505-2513, (1994)

172. Lin Z-C., Ondov J. M., Kelly W. R., Paulsen P. J. and Stevens R. K., Tagging diesel and residential oil furnance emissions in Roanoke, VA, with enriched isotopes of Samarium, *J. Air Waste Mange. Assoc.*, **42**, pp1057-1062, (1992)

173. Lin Z-C., Ondov J. M.and Kelly W. R., Tracing emissions from coal-fired power plants with enriched rare-earth isotopes, *FUEL*, **72**, pp697 (1993)

174. Ondov J. M., Kelly W. R., Holland J. Z., Lin Z-C., and Wight S. A., Tracing fly ash emitted from a coal-fired power plant with enriched rare-earth isotopes, An urban scale test, *Atmospheric Environment*, **26B**, pp453-462, (1992).

175. Sohns E. Gerling P. and Faber E., Improved stable nitrogen isotope ratio measurements of natural gases., *Analytical Chemistry*, **66**(17), pp2614-2620, (1994)

176. Currie L. A., Klouda G. A. and Voorhees K. J., Atmospheric carbon: the importance of accelerator mass spectrometry, *Nucl. Instr. Methods*, **233**, pp371-379, (1984)

177. Klouda G. A., Currie L. A., Donahue D. J., Jull A. J. T. and Naylor M. H., Urban atmosphere ^{14}CO and 14CH4 measurements by accelerator mass spectrometry, *Radiocarbon*, **28**(2A), pp625-633, (1986)

178. Linick T. W., Jull A. J. T., Toolin I. J. and Donahue D. J., Operation of the NSF-Arizona accelerator facility for radioisotope analysis and results from selected collaborative research projects, *Radiocarbon*, **28**, pp522, (1986)

179. Verkouteren R. M., Klouda G. A., Currie L. A., Donahue D. J., Jull A. J. T. and Linick T. W., Preparation of microgram samples on iron wool for radiocar-

bon analysis via accelerator mass spectrometry: a closed-system approach, *Nucl. Instr. Methods*, **B294**, pp1-4 (1987)

180. Venegas L. E. and Mazzeo N. A., Design methodology for background air pollution monitoring site selection in an urban area, *International Journal Environment and Pollution*, **20**(1-6), pp185-195 (2003).

181. Wu. H. W. Y. and Chan L. Y., Comparative study of air quality surveillance networks in Hong Kong, *Atmospheric Environment*, **31**, pp935-945, (1997)

182. Seinfeld J. H., Optimal location of pollutant monitoring stations in an airshed, *Atmospheric Environment*, **6**, pp847-858, (1972)

183. Noll K. E., Miller T. L., Norco J. E. and Raufer R. K., An objective air monitoring site selection methodology for large point sources, *Atmospheric Environment*, **11**, pp1051-1059, (1977)

184. Noll K. E. and Mitsutomi S., Design methodology for optimum dosage air monitoring site selection, *Atmospheric Environment*, **17**, pp2583-2590 (1983)

185. Mazzeo N. A. and Venegas L. E., Practical use of the ISCST3 model to select monitoring site locations for air pollution control, *International Journal Environment and Pollution*, **14**(1-6), pp246-259, (2000)

186. Haas T. C., Redesigning continental-scale monitoring networks, Atmospheric Environment, 26, pp3323-3333, (1992)

187. Laursen J, Stikans M, Karlsen K, Pind N. A versatile and easy to handle EDXRF instrumentation. In. *Proceedings of European Conference on Energy Dispersive X-ray Spectrometry 1998.* Fernández JE, Tartari. A. (ed). Editrice Compositori, Bologna, Italy, 1999, pp139-144.

188. Van Espen P., Janssens K. and Nobels J., AXIL-PC, Software for the analysis of complex x-ray spectra, *Chemometrics and Intelligent Laboratory System*, **1**, pp109-114, (1986)

189. Vekemans B., Janssens K., Vincze L., Adams F., Van Espen P., Analysis of X-ray Spectra by Iterative Least Squares (AXIL): New Developments, *X-Ray Spectrom.*, **23**, 278-285,(1994)

190. Selin Lindgren E, Henriksson D, Lundin M. Therning P, Laursen J. and Pind N.,. Possible indicators for biomass burning in a small Swedish City as studied by energy dispersive x-ray (EDXRF) spectrometry, *X-Ray Spectrom*, **35**, pp19-26, (2006)

191. IAEA, QXAS 3.6 – Quantitative X-ray Analysis System – Developed Under the Auspices of the International Atomic Energy Agency, Vienna, **2005** [Cited March 27, 2009].
http://www.iaea.org/OurWork/ST/NA/NAAL/pci/ins/xrf/pciXRFdown.php>

192. Zannetti P., Numerical simulation modeling air pollution: an overview, in Air Pollution, Zannetti et al (eds), Computational Mechanics Publications, Southampton, 1993, pp3-14

193. Kukkonen J., Air quality modeling – Dispersion models, in *Monitoring Ambient Air Quality for Health Impact Assessment*, WHO Regional Publications, European Series No. 85, 1999, pp155-160

194. Noorduk H., The national smog warning system in the Netherland: a combination of measuring and modeling, in Air Pollution 2, Pollution control and

monitoring, Baldasano J. M. et al (ed), Southampton, Computational Mechanics Publications, 1994, pp35 – 42

195. Hopke P. K., Receptor Modeling for Air Quality Management, in Air Quality Management, Hester R. E. and Harrison R. M. (eds.), Royal Society of Chemistry, Cambridge, 1997, pp95 – 117

196. Henry R. C., Hopke P. K. and Williamson H. J., Review of Receptor Model fundamentals, Atmospheric Environment, 18, pp1507 – 1515, 1984

197. Henry R. C., Current Factor Analysis Receptor models are ill-posed, *Atmospheric Environment*, **21**, pp1815 – 1820, 1987

198. Antilla P., Paatero P., Tapper U. and Järvinen O., Source Identification of bulk wet deposition in Finland by Positive Matrix Factoration, *Atmospheric Environment*, **29**, pp1705 – 1718, 1995

199. Huang S., Rahn K. A. and Arimoto R., Testing and optimizing two factor-analysis techniques on aerosol at Narragansett, Rhode Island, *Atmospheric Environment*, **33**, pp2169 – 2185, 1999

200. Thurston G. D. , Spengler J. S., A quantitative assessment of source contribution to inhalable particulate matter pollution in Metropolitan Boston, *Atmospheric Environment*, **19,** pp9-25, (1985)

201. Prichard E. and Barwick V., Quality Assurance in Analytical Chemistry, Analytical Techniques in the Sciences, Wiley, 2007, pp1

202. Bower J. and Mucke H-G., Design, operation and quality assurance and control in a monitoring system, in Monitoring Ambient Air Quality for Health Im-

pact Assessment, World Health Organisation Regional Publications, European Series No. 85, 1999, pp41

203. Bower J., Ambient Air Quality Monitoring, in Issues in Environmental Science and technology 8 - Air Quality Management, Hester R. E. and Harrison R. M. (eds.), Great Britain Royal Society of Chemistry, 1997, pp43-44

204. Maenhaut W. Salma I., and Cafmeyer J., Regional atmospheric aerosol composition and sources in the Eastern Transval, South Africa, and impact of biomass burning, *J. Geophys. Res.*, **101 D19**, pp23631-23650, 1996.

205. Chan Y. C., Vowles P. D., McTainsh G. H., Simpson R. W., Cohen D.D., Bailey G. M., and McOrist G. D., Characterisation and source identification of PM10 aerosol collected with a high volume cascade impactor in Brisbane (Australia), *Scie. Tot Environ.*, **262**, pp5–19, 2000.

206. Alves L. C., Reis M. A. and Freitas M. C., Air particulates matter characterization of rural area in Portugal, *Nucl. Instrum. Methods Phys. Res.*, **B136-138**, pp941-947, 1998

207. Cheng L., Sandhu H. S., Angle R. P., McDonald K. M., and Myrick R. H., Rural particulate matter in Alberta, Canada, *Atmospheric Environment*, **34**(20), pp3365-3372, 2000

208. Houthuijs D., Breugelmans O., Hoek G., Vaskovic E., Mihalikova E., Pastuszka J. S., Jirik V., Sachelarescu S., Lolova D., Meliefste K., Uzunova E., Marinescu C., Volf J., de Leeuw F., van de Wiel H., Fletcher T., Lebret E. and Brunekreef B., PM10 and PM2.5 concentrations in Central and Eastern Europe: results from the Cesar study, *Atmospheric Environment*, **35**, 2757-2771, 2001

209. World Health Organisation, www.who.int/mediacentre/factsheet/fs313/en, 2006

210. Suglia S. F., Gryparis A., Wright R. O., Schwartz J. and Wright R. J., Association of black carbon with cognition among children in a prospective birth cohort study, *American Journal Epidemilogy*, **167(3),** 280-286, 2008

211. Ramanathan V., Transported black carbon a significant player in pacific ocean climate, ScienceDaily, March 27, 2008

212. Bennet C., Jonasson P., and Selin Lindgren E., Concentrations and sources of trace elements in particulate air pollution, Dar es Salam, Tanzania, studied by EDXRF, *X-ray Spectrometry*, **34**, 1-6, 2005

213. El-Tahir H. M., Selin Lindgren E., and Habbani F. I., Elemental characterization of airborne particles in Khartoum, Sudan, *X-ray Spectrometry*, **34**, 144-152, 2005

214. Viksna A., Selin Lindgren E., Standzenieks P. and Jacobsson J., EDXRF and TXRF analysis of elemental size distributions and environmental mobility of airborne particles in the city of Riga, Latvia, *X-ray Spectrometry*, **33**, 414-420, 2004

215. Gomiscek B., Frank A., Puxbaum H., Stopper S., Preining O. and Hauck H., Case study analysis of PM burden at an urban and rural site during the AUPHEP, *Atmospheric Environment*, **38**, 3935-3948, 2004

216. Maenhaut W. and Cafmeyer J., Long-term atmospheric aerosol study at urban and rural sites in Belgium using multi-elemental analysis by particle-in-

duced x-ray emission spectrometry and short-irradiation instrumental neutron activation analysis, *X-ray Spectrometry*, **27**, 236-246, 1998

217. SPSS, Factor analysis, in SPSS for Windows version 16, 2007

218. Aboh I. J. K., Henriksson D., Laursen J., Lundin M., Pind N., Selin Lindgren E., Wahnström T., EDXRF characterisation of elemental contents in PM2.5 in a medium-sized Swedish city dominated by a modern waste incineration plant, *X-Ray Spectrometry*, **36**, 104-110, (2007)

219. Morishita M, Keeler G.J, Wagner, J. G, Harkema, J. R., Source identification of ambient PM2.5 during summer inhalation exposure studies in Detroit, MI, *Atmospheric Environment*; **40**: 3823-3834, (2006)

220. Wong S., Colareo P. R. and Dessler A. E., Principal component analysis of the evolution of the Saharan air layer and dust transport: Comparisons between a model stimulation and MODIS and AIRS retrievals, *J. Geophys. Res.*, **111**, D20109 (1-12), (2006).

221. Bou Karam D., Flamant C., Knippertz P., Reitebuch O., Pelon J., Chong M. and Dabas A., Dust emissions over the Sahel associated with the West African monsoon intertropical discontinuity region: A representative case, Q. J. R. Meteorol. Soc., 134, pp621 – 634, (2008)

222. Antoine D. and Nobileau D., Recent increase of Sahara dust transport over the Mediterranean Sea, as revealed from ocean color satellite (SeaWIFS) observations, *J. Geophys. Res.*, **111**, D12214 (1-19), (2006).

223. Caminade C., Terray L. and Maisonnave E., West African monsoon response to greenhouse gas and sulphate aerosol forcing under two emission scenarios, *Climate Dynamics*, **26**, pp531 – 547, (2006).

224. Ogunjobi K. O., He Z. and Simmer C., Spectral aerosol properties from AERONET Sun-photometric measurement over West Africa, *Atmospheric Research*, **88**, pp89 – 107, (2008).

225. Oblad M. and Selin E., Measurement of elemental composition in background aerosol on the West Coast of Sweden, *Atmospheric Environment*, **20**, pp1419-1432, (1986).