UNIVERSITY OF GHANA, LEGON

CHARACTERIZATION AND SOURCE APPORTIONMENT OF AIRBORNE PARTICULATE MATTER IN SOME URBAN NEIGHBOURHOODS OF ACCRA, GHANA

By

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DECLARATION

I, Allison Felix Hughes, 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.

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DEDICATION

This thesis is dedicated to the Almighty God, my wife – Mrs. Nejay Fraddee Bull Hughes and my children – Margaretta, Sarah, Allison Neal, Alice Nealla and Samuel Nealix.

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THESIS RELATED PUBLICATIONS

Part of the work presented in this thesis appears in the following publications:

1. Zheng Zhou , Kathie L Dionisio, Thiago G Verissimo, Americo S Kerr, Berent Coull, Raphael E Arku, Petros Koutrakis, John D Spengler, **Allison F Hughes**, Jose Vallarino, Samuel Agyei-Mensah and Majid Ezzati. (2013). Chemical composition and Sources of Particle Pollution in Affluent and Poor Neighbourhoods of Accra, Ghana. *Environmental Research Letters*, (8) doi:10.1088/1748-9326/8/4/044025
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ABSTRACT

A year-long campaign which accounted for seasonal differences have been conducted to examine the levels, chemical composition and sources of ambient particulate matter in multiple neighbourhoods of varying socio-economic status in Accra, Ghana. Between September 2007 and August 2008, simultaneous measurements of $PM_{2.5}$ and PM_{10} aerosols at five monitoring sites in four neighbourhoods (Asylum Down, East Legon, Nima and James Town/Ussher Town) were done for one 48-hour period every six days. Harvard Impactor with polytetrafluorethylene (PTFE) Teflon filter of 37 mm supported by a Whatman drain disc were used to sample air particles in the Accra neighbourhoods. Gravimetric analysis and energy dispersive X-ray fluorescence (EDXRF) were used to determine the chemical composition and concentration of the aerosol particles. The mean mass concentration values for $PM_{2.5}$ obtained at the five sites during the study period varied from 45.9 $\mu g\ m^{-3}$ to 74.8 $\mu g\ m^{-3}$. The mean mass concentration for PM_{10} also varied from 93.9 $\mu g\ m^{-3}$ to 134.8 $\mu g\ m^{-3}$. These levels were all substantially higher than the EPA (Ghana) guidelines values and other international air quality standards from WHO, USEPA and EU. Weak relationships were obtained between PM and weather parameters. Crustal elements were most abundant during the seasonal Harmattan period between late December and early February when Saharan dust is transported across West Africa. Enrichment factor analysis was used to provide an initial indication of the species of anthropogenic origin in the measured elemental composition. Source contributions were analysed using positive matrix factorization (PMF) model separately for Harmattan and non-Harmattan periods because large

changes to source profiles is expected during the Harmattan period. Anthropogenic sources resolved by PMF model (biomass burning, solid waste burning, resuspended dust and traffic/industry emissions) during both Harmattan and non-Harmattan periods had significant influence on the four neighbourhoods in Accra.

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ABBREVIATIONS

AD	Asylum Down
ADT	Average daily traffic
AGL	Above ground level
AMA	Accra Metropolitan Area
AQG	Air Quality Guidelines
BC	Black carbon
CA	Cluster Analysis
CBD	Central Business District
CMB	Chemical mass balance
DMS	Dimethylsulphide
DVLA	Driver and Vehicle Licensing Authority
EC	Elemental carbon
ECG	Electricity Company of Ghana
EDAS	Global Data Assimilation System
ED-XRF	Energy dispersive X-ray fluorescence
EF	Enrichment factor
EL	East Legon
EPA-Ghana	Environmental Protection Authority of Ghana
EU	European Union
FRM	Federal Reference and Equivalent Method
HI	Harvard Impactor
HSPH	Harvard School of Public Health
HYSPLIT	Hybrid Single-Particle Integrated Trajectory

IMPROVE	Interagency Monitoring of Protected Visual Environments
INAA	Instrumental neutron activation analysis
ITCZ	Inter-Tropical Convergence Zone
JT	James Town/Ussher Town
NM	Nima
NOAA	National Oceanic and Atmospheric Administration
NO_X	Nitrogen oxides
O_3	Ozone
OC	Organic carbon
OECD	Organization for Economic Co-operation and Development
PCA	Principal component analysis
PIXE	Particle-induced X-ray emission
PM	Particulate matter
PM_{10}	Particulate matter with aerodynamic diameter smaller than 10 µm
$PM_{2.5}$	Particulate matter with aerodynamic diameter smaller than 2.5 µm
PMF	Positive matrix factorization
PTFE	Polytetrafluoroethylene
PUF	Polyurethane foam
PVC	Polyvinyl chloride
SD	Standard deviation
SES	Socioeconomic status
SO_2	Sulphur dioxide
SSA	Sub-Saharan Africa
SSI	Size selective inlet

UNEP	United Nations Environment Programme
USAID	United States Agency for International Development
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
VRA	Volta River Authority
WHO	World Health Organization
XRF	X-ray fluorescence

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CHAPTER 1: INTRODUCTION

1.1 URBAN AMBIENT AIR POLLUTION

Air pollution has become one of the most serious environmental concerns in urban cities throughout the world – especially in developing countries (Mayer, 1999; Faiz and Sturm, 2000). The United Nations (UN) estimate that more than half of the world's 7 billion human population lives in urban areas and occupies just about 3% of the earth's land mass (UNEP, 2012). By the year 2030, the world's urban population is expected to increase to almost 65% and a large amount of the new urban dwellers will be in slums and squatter settlements with poor air quality in low-income countries. Sub-Saharan Africa (SSA) is one of the poorest regions in the world. With an urban population growth rate of more than 2% annually, SSA has the fastest urbanization rate in the world (UNEP, 2012). According to an extensive report by UN Habitat (2010), the urban population of African cities is projected to triple by 2050 to about 1.23 billion people. Many of the large SSA cities have experienced rapid urbanization, industrialization and motorization over the last decade. The shape of cities in these developing countries, and how it will affect the well-being of future urban residents and the global environment, will depend greatly on decisions made now in preparation for this growth (UNFPA, 2007). The low income levels and lack of economic resources to deal with these problems have led to these SSA cities being included among the most polluted cities in the world.

Air pollution can be defined as the introduction of particulate matter, chemicals, or biological materials into the atmosphere in such concentration and duration which may adversely affect human health, the environment, materials, and have economic impact. Urban ambient air pollution is a more specific term which refers to the outdoor air pollution experienced by populations living in urban areas, typically in or around cities.

Air pollution at the local urban level has negative health effects on the exposed population. The World Health Organization (WHO) reports that urban air pollution is responsible for 2.0% of premature deaths (about 1.2 million people) every year from lung cancer, cardiovascular and respiratory diseases caused by outdoor air pollution (WHO, 2009). The Organization for Economic Co-operation and Development (OECD) in a recent study on the global environmental outlook warned that air pollution from particulate matter could become the biggest environmental cause of premature deaths by 2050 if no action is taken to improve air quality. In the OECD report, the number of premature deaths linked to particulate matter is projected to reach 3.6 million people per year globally, with most of the deaths occurring in developing countries (OECD, 2012). In Africa, urban ambient air pollution is currently responsible for an estimated 49,000 premature deaths annually with indoor use of solid fuels being responsible for eight times this value, the main burden being borne by sub-Saharan African countries (World Bank, 2012). Direct causes associated with air pollution-related deaths include aggravated asthma, bronchitis, emphysema, lung and heart diseases, and respiratory allergies (Breslow and Goldsmith, 1958; Krzyzanowski *et al*, 2005; HEI, 2010).

Sources of air pollution are numerous and highly variable. The sources of air pollution in African urban cities differ from those in many other regions of the world (Cohen *et al.*, 2002; Wang *et al.*, 2003; Arku *et al.*, 2008). However, large gaps exist in understanding particulate matter (PM) sources and their relative contributions in SSA cities. Routine monitoring of PM_{10} or $PM_{2.5}$ anywhere in SSA other than South Africa is scarce. Aerosol monitoring has become a special concern, especially in SSA urban cities. The lack of ambient monitoring data for particulate matter in SSA cities has seriously hampered the ability to characterize and understand the patterns of PM concentrations, and to promote policy initiatives to address air quality.

Some SSA countries have begun measurements on size specific fractions of particulate matter (i.e., PM_{10} and $PM_{2.5}$) and their chemical characteristics (Nerquaye-Tetteh, 2006; van Vliet and Kinney, 2007; Mkoma *et al.*, 2009). Understanding the composition of atmospheric aerosol particles is necessary for identifying their sources and predicting their effect on various atmospheric processes and health effects. For this reason, the process of identification and apportionment of particulate matter to their sources using the powerful multivariate receptor model – positive matrix factorization (PMF) is a crucial step in air quality management.

In some African cities where monitoring has been carried out, levels of air pollution have been found to exceed the WHO recommended air quality guidelines standards (WHO, 2012). Urban air pollution in SSA results mainly from biomass combustion for cooking and heating (Akbar and Kojima, 2002; Smith *et al.*, 2004; Bailis *et al.*, 2005;

Barnes *et al.*, 2005) and the use of fossil fuels in transport, power generation, industry and domestic sectors. Other sources include open burning of refuse, re-suspended dust from unpaved roads, construction particles and natural windblown particles (Akbar and Kojima, 2002).

1.2 AIRBORNE PARTICULATE MATTER

Aerosol or particulate matter (PM) is defined as suspension of liquid and solid particles in a gaseous phase – in this case, the atmosphere. Technically, the term aerosol refers to both the particles and the gas in which it is suspended. However, it is common practice in literature to use aerosol to refer only to the particles or particulate component inside the atmosphere (Vallero, 2008; Place, 2009, Kulkarni *et al.*, 2011; Friend, 2012). It is the particulate component which is of the greatest interest in this study due to its impact on human health and the environment. The behaviour of particulate matter in the urban environment and its potential to affect human health and atmospheric visibility depends on the following characteristics:

- physical (size and shape),
- chemical (composition and concentration),
- geographic location, season, day and time of day of emissions.

Moreover, these physical and chemical characteristics also depend on the source type and on the formation processes that particles undergo within the atmosphere or at the emission source (CEPA, 1998). Particulate matter is not a single pollutant but is a complex mixture of different chemical species including elemental and organic carbon compounds; oxides of silicon, aluminium and iron; trace metals; sulphates; nitrates and ammonium.

Particulate matter may be produced naturally or as a direct or indirect result of human activities (Godish, 1997) and they include a wide range of particles of different sources, sizes and compositions. They can be classified as primary or secondary depending on their formation mechanism. Particles that are directly emitted into the atmosphere from sources are referred to as primary particles while particles that are formed from atmospheric processes (i.e., photochemistry) or those which undergo changes in chemical composition following emission are called secondary particles (Wilson and Spengler, 1996). Primary particles can also be grouped as anthropogenic or natural depending on their origin. The origin of secondary particles is more difficult to link to their original sources because particulate matter is not a single pollutant but is a complex mixture of different chemical species including elemental and organic carbon compounds; oxides of silicon, aluminium and iron; trace metals; sulphates; nitrates and ammonium.

However, secondary particles for example can result from the chemical transformations of primary emissions such as nitrogen oxides (NO_X), sulphur dioxide (SO_2), ozone (O_3), and organic gases from natural and anthropogenic sources. Furthermore, both natural and anthropogenic particles can occur from either primary or secondary processes (Mathys *et. al*., 2002). The concentration of primary particles is a function of their emission rate, transport and dispersion and removal rate from the atmosphere.

Primary particles are mostly present in the coarse size fraction while secondary particles are mostly in the fine fraction (Raes *et al.*, 2000). The coarse fraction includes particles greater than 2.5 μm which are usually released directly into the atmosphere by mechanical processes or from natural sources. The fine fraction contains particles with a diameter less than 2.5 μm, which mainly arises from gas-to-particle conversion – a process whereby gases such as sulphur dioxide (SO_2), nitric oxide and nitrogen dioxide (NO_X), and volatile organic compounds (VOCs) are oxidized and condensed.

1.3 SOURCES OF PARTICULATE MATTER IN URBAN AIR

Urban ambient particulate matter originates from a large variety of sources. These sources can be classified as either natural (produced in the absence of human activity) or anthropogenic (caused by human activity) (Miranda and Tomaz, 2008). Natural aerosols sources are uncontrollable but anthropogenic aerosols sources are controllable although they poses a challenge. Human activities and industrial development influence both anthropogenic and natural emissions. Hence when the effects of air pollutants on health is under consideration, especially in urban areas with high population densities, anthropogenic sources are very important and are those to which attention is usually directed with a view to control. Major sources of air pollution are summarized in Table 1.1.

Table 1.1 Major sources of air pollutants

Source type	Source	Causal action
Natural	Volcano eruption	Release of solid particles, gases and heat waves.
	Sand storm	Dust particles spread through wind circulation around the earth.
	Vegetation fire	Smoke from wildfire or forest management.
	Plant Pollen	Spread of plant pollen through wind motion.
	Sea spray	Liquid droplets spread through wind near coastlines.
Anthropogenic (Man-made)	Transport	Combustion of petrol/diesel and generation of particles and gases.
	Power generation	Release of particles and gases.
	Industry	Manufacturing and processing of steel, non-iron metals, textiles, refining of petroleum, handling of materials.
	Construction	Particle pollution due to material handling and other associated activities.
	Agriculture	Emissions from ploughing and use of fertilizers, pesticides and insecticides.
	Domestic	Burning of solid organic materials indoors such as charcoal, firewood, dung, agricultural residues.

Source: Adapted from (Schwela, 2010)

1.3.1 NATURAL SOURCES

Natural sources of particulate matter include windblown dust, harmattan dust, natural vegetation (plant fragments, microorganism, pollen, etc.), wildfires, and sea spray. Crustal material, biogenic matter and sea-salt comprise the majority of natural aerosols. The major source of crustal elements (e.g. Si, Ca, Fe, Al, Mg, K, Na, Ti and O) is the wind-blown dust suspended from construction sites, roads and natural surfaces. Primary biogenic aerosol particles consist of several different types of particles, including pollen, spores, and micro-organisms such as virus, bacteria, fungus, protozoa, algae and fragments of insects. Virus and bacteria present sizes greater than 2 µm whereas the remains of plants and fungal spores exhibit sizes in the coarse mode of particulate matter both in urban and suburban environments (Posfai and Molnar, 2000; Bauer *et al.*, 2008).

1.3.2 ANTHROPOGENIC SOURCES

Anthropogenic particulate sources are primarily found in urban and industrial locations. In these locations, anthropogenic emissions can become so large that the concentrations of various undesirable chemical species (pollutants) cause significant deterioration in air quality and visibility (Watson, 2002; Cohen *et al.*, 2004), and can pose threats to human health (Dockery and Pope, 1996; Pope *et al.*, 2002; Villeneuve *et al.*, 2003). Anthropogenic aerosols are composed of primary emitted soot (elemental carbon), heavy metals, secondary formed carbonaceous material (organic carbon) and inorganic matter (nitrates, sulphates, ammonium and water). Vehicular emission, industrial emission as well as combustion of fuel for domestic heating and cooking purposes are considered as primary anthropogenic sources for urban air pollution (Kothai *et al.*, 2008). Anthropogenic sources of particulate matter and its precursor gases include vehicular emissions, industrial emissions, cooking, heating, agriculture, wood burning, power plants, heavy duty diesel engine, construction and demolition, and dust from disturbed land. They arise mostly from the combustion of fossil fuels, tire and brake wear, and re-suspended dust (Ricci *et al.*, 1996; US EPA, 1996; Buzorious *et al.*, 1999).

Heavy metals (e.g. V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Ba and Pb) originate from a variety of industrial processes such as incineration, manufacturing, and smelting.

1.4 SIZE DISTRIBUTIONS, FORMATION MECHANISMS, AND CHEMICAL COMPOSITION OF PARTICULATE MATTER

1.4.1 SIZE DISTRIBUTIONS OF PARTICULATE MATTER

The size distribution of particulate matter is crucial in understanding the transport and removal of particles in the atmosphere as well as their deposition in the human respiratory system. Once the particles are emitted into the atmosphere, they are subjected to changes in their size and chemical composition by processes of condensation of vapour species, evaporation, deposition (both wet and dry) and coagulation (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998). The chemical compositions of these particles are determinants for the types of effects caused by particulate matter on humans, vegetation, and materials.

Particle size is one of the most important parameter in characterizing the physical behaviour of particulate matter. The size of a particle affects many of its properties such as volume, mass and settling velocity (CCPA, 2001). Size also influences a particle's transport, deposition and migration through the environment (Aboh, 2009). According to Mkoma (2008) ambient aerosol particles sizes can vary from 1 nm to 100 µm in diameter. Particulate matter in the size range from 0.1 to 10 µm is noted to have serious health, climatic and environmental effects (Finlayson-Pitts and Pitts, 2000).

Particle size is normally defined in terms of its diameter. Due to variations in its shape and density, the particle size is expressed in terms of an "equivalent" diameter, which depends on a physical rather than a geometric property. The aerodynamic diameter is the most commonly used equivalent diameter of a particle (Godish, 2004). It is defined as the diameter of a sphere of unit density (1 g cm^{-3}) that has the same settling velocity in air as the particle of interest (Hinds, 1982). The particle aerodynamic diameter, D_p, is given by Equation 1.1 as

$$D_{\mathrm{p}} = D_g k \sqrt{\frac{\rho_{\mathrm{p}}}{\rho_0}} \qquad (1.1)$$

where D_g is the particle geometric diameter, ρ_p is the density of the particle, ρ_0 is the reference density (1 g cm^{-3}), and k is a shape factor, which is 1.0 in the case of a sphere (Finlayson-Pitts and Pitts, 2000). In this work, particle diameter unless otherwise indicated, refers to the aerodynamic diameter.

For regulatory control and human health effects, atmospheric particulate matter is commonly classified as ultrafine ($PM_{0.1}$: $D_p < 0.1\mu m$), fine or respirable ($PM_{2.5}$: $D_p < 2.5\mu m$) and coarse or inhalable (PM_{10}: $D_p < 10\mu m$) particle size fractions. Respirable particles are mostly deposited in the upper part of the respiratory tract or nasal system. Inhalable particles (also referred to as thoracic particles) are mostly deposited in the pulmonary or lung system and persist in the body. The distinction between the coarse and fine particles is vital because they have different sources, formation mechanisms, composition, atmospheric lifetime, spatial distribution, temporal variability, and health impacts (Johnson *et al.*, 2011). The objective for regulatory control of particulate matter is to reduce the fine and coarse particles mass concentrations rather than number concentrations.

1.4.2 DIFFERENT MODES OF FORMATION

In the atmosphere, the particles size distributions are not uniform but particles typically show a trimodal size log-normal distribution when plotted as mass or volume versus aerodynamic diameter (Figure 1.1). These modes reflect the different source types and the different transformation processes at work in the atmosphere (Seinfeld and Pandis, 1998). The three distinct modes or fractions are generally categorized as follows:

a) Nucleation mode: $D_p < 0.1$ µm,
b) Accumulation mode: 0.1 µm $< D_p <$ 2 µm, and
c) Coarse or sedimentation mode: $D_p >$ 2 µm.

1.4.2.1 NUCLEATION MODE

Nucleation mode (also known as “nuclei mode” or “Aitken mode”) particles are formed from condensation of hot vapours during combustion processes and from gas-to-particle conversion in the atmosphere. Nuclei mode particles consist of freshly formed particles with diameters below about 10 nm resulting from active nucleation events. The Aitken mode particles are the larger aged particles with diameters between about 10 and 100 nm which may result from growth of smaller particles undergoing coagulation or nucleation from higher concentrations of precursors (USEPA, 2004).

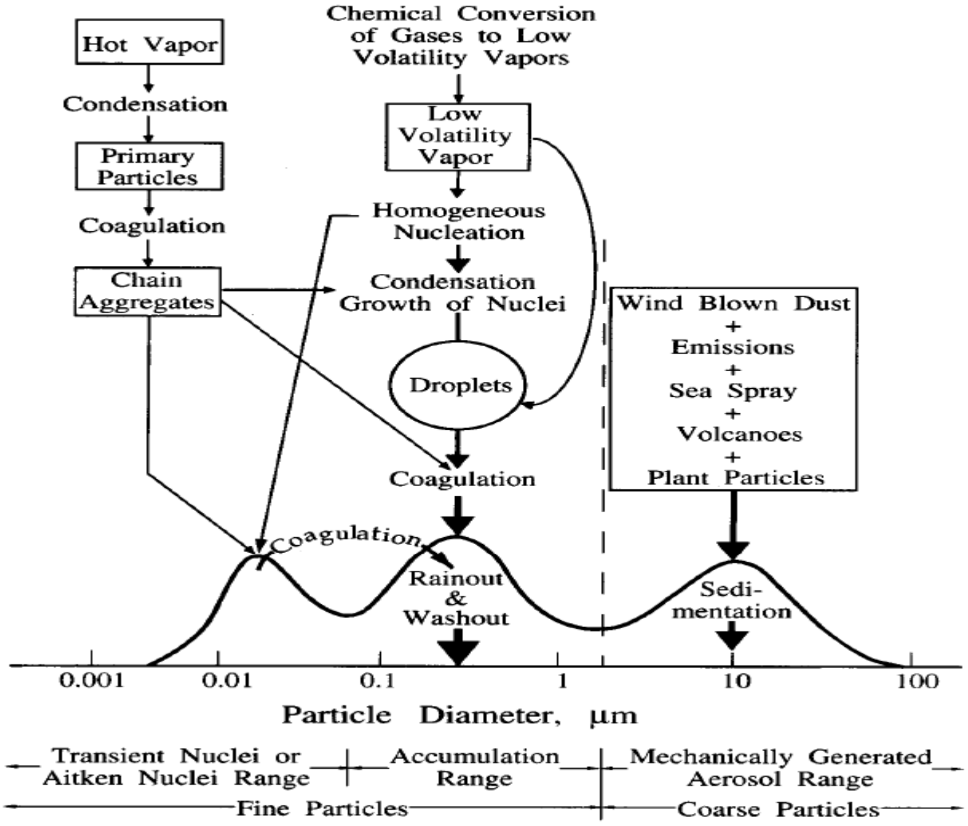


Figure 1.1 Idealized schematic of size distribution, deposition and coagulation of particles in ambient air. (Adapted from Whitby and Sverdrup, 1980)

The nucleation or Aitken mode contains the largest number of particles but due to their small sizes, they account for not much of the total mass. Nucleation mode particles in the atmosphere have very short life of the order of a few minutes to several hours; this is due to their rapid coagulation with larger particles or growth into larger sizes by condensation. They are removed through diffusion of falling rain drops. Ultrafine particles include the nucleation mode and much of the Aitken mode.

1.4.2.2 ACCUMULATION MODE

Accumulation mode particles are generally formed by coagulation of nuclei mode particles and condensation of gas-phase vapours onto existing particles, causing them to grow into this size range (Seinfeld and Pandis, 1998). Particles in accumulation size range can also be emitted directly into the atmosphere as a result of incomplete combustion of wood, oil, coal, gasoline and other fuels. These particles typically contain significant amounts of organic material as well as soluble inorganic such as ammonium, nitrate and sulphate (Alfarra, 2004). They have the largest surface area and therefore account for a significant fraction of the total particle mass. As the mode name suggests, the particle removal mechanisms are least efficient in this size range. Hence, they can be transported over thousands of kilometre and remain airborne for days to weeks. They also account for most of the visibility impairment in the dry atmosphere. Accumulation mode particles can be removed from the atmosphere by rainout or washout (Sillanpää, 2006). Collectively, the accumulation and nucleation mode particles are often referred to as fine particles.

1.4.2.3 COARSE MODE

Coarse or sedimentation mode particles originate mainly from mechanical processes such as grinding, wind or erosion. Particles in the coarse range are relatively large and usually consist of mostly anthropogenic and natural dust particles that normally settle out of the atmosphere relatively quickly by sedimentation and impaction on surfaces (Seinfeld and Pandis, 1998). They can also be removed by falling rain drops.

Moreover, the chemical composition of coarse particles is usually dominated by inorganic material such as sand or large salt particles from sea spray. Because coagulation is very weak for particles in the accumulation mode, little of the mass in the mode is transferred into coarse mode. Together with the accumulation mode, they make up most of the total mass of suspended particles. Their residence time in the atmosphere is only a few hours or days depending on their size, prevailing meteorological conditions, and altitude (Aboh, 2009).

1.4.3 CHEMICAL COMPOSITION

The chemical composition of fine and coarse particulate matter differ substantially from each other, indicating that these particles originate from different sources (Harrison and Yin, 2000). The location of the polluting source, chemical reactions in the atmosphere, time of the day, and meteorological conditions results in significant variations in the chemical composition of these particles (Finlayson-Pitts and Pitts, 1986). The composition of particulate matter is also influenced by other anthropogenic factors such as the degree of urbanization, industrial and agricultural activities, and the type and volume of vehicular traffic. Chemical composition of particles is generally composed of a mixture of species from a number of sources. These particles may be made up of variable amounts of sulphate, ammonium, nitrate, sea salt (sodium, chloride), trace metals, crustal elements and carbonaceous materials (Chow, 1995; Vallius, 2005). Information on the chemical composition aerosol of particles is essential for their health and environmental assessment. Characterization of the chemical compositions of PM is vital for understanding aerosol physical and chemical processes as well as identifying possible sources of ambient particles and their contributions.

Much of the sulphate component in the atmosphere is derived mainly from the oxidation of anthropogenic and natural sulphur-containing compounds such as sulphur dioxide (SO_2) and dimethylsulphide (DMS), respectively (Alfarra, 2004). Most of the sulphate is found in the fine fraction of PM as ammonium sulphate although some are present as sodium sulphate of marine origin. SO_2 emissions originate from anthropogenic as well as natural sources. Anthropogenic SO_2 emissions emanate from the combustion of fossil fuels, biomass combustion, agricultural waste burning, metal smelting, and other industrial processes (Benkowitz *et al.*, 1996; Smith *et al.*, 2011). Natural sources of SO_2 emissions include oxidation of dimethylsulphide (DMS) mainly from the sea in the form of sea salt and from wild fires (Bates *et al.*, 1992). In 2005 it was estimated that typical annual average concentrations of sulphur dioxide in urban areas in developing countries were 40-80 $\mu g\ m^{-3}$, those in North America and Europe were 10-30 $\mu g\ m^{-3}$, and in cities in the European Union (EU) 6-35 $\mu g\ m^{-3}$ (WHO, 2005).

Nitrate (NO_3) is a major constituent in atmospheric aerosols formed primarily by oxidation of atmospheric nitrogen oxides (NO_X). Nitrate can be found in both the fine and coarse particulate matter. Nitrate in fine particles comes mainly from the reaction of gas-phase nitric acid with gas-phase ammonia to for ammonium nitrate. Nitrate in coarse particles comes primarily from the reaction of gas-phase nitric acid with pre-existing coarse particles. The relative humidity and temperature of the atmosphere also have strong influence on the amount of nitrate (Stelson and Seinfeld, 1982). Chloride is mainly emitted as sodium chloride (NaCl) in sea salt particles. Chlorides also enter aerosol particles due to neutralization of hydrochloric acid (HCl) vapour by ammonia.

Carbonaceous compounds in PM consist of two components which are elemental carbon and organic carbon. Elemental carbon (EC) is frequently referred to as black carbon (BC) or soot. It is chemically similar to impure graphite and mainly emitted into the atmosphere from combustion processes such as fossil fuel and biomass burning. EC is commonly used as a tracer for the exhaust of diesel-powered vehicles. Organic carbon (OC) is the dominant fraction of the carbonaceous aerosol. It originates from the combustion of fossil fuels, residential wood burning, meat cooking and biogenic sources (Pandis *et al.*, 1992; Jeong *et al.*, 2004).

Crustal material such as aluminium (Al), silicon (Si), calcium (Ca), titanium (Ti), magnesium (Mg) and iron (Fe) are found predominately in coarse particles and their composition vary according to local geology in addition to surface conditions. Potassium (K) may be found in both fine and coarse particles. Potassium in coarse PM comes from soil and those in fine PM comes from biomass burning. Trace elements such as sodium (Na), potassium (K), iron (Fe), chromium (Cr), cobalt (Co), nickel (Ni), manganese (Mn), cooper (Cu), selenium (Se), barium (Ba), chlorine (Cl), gallium (Ga), caesium (Cs), europium (Eu), tungsten (W), and gold (Au) are found in both fine and coarse particles. Biomass burning which includes residential wood combustion and forest fires, releases trace elements into the atmosphere. Trace metals in fine PM are primarily anthropogenic originating from combustion of fossil fuels, waste incineration and metal smelting activities. Many of these components can be used as tracers for specific sources. For example, sodium (Na) is a tracer that is almost exclusively associated with sea salt. Likewise, silicon and aluminium are tracers for mineral dust, whereas elemental carbon particles are mainly derived from combustion. Finally, the secondary components (sulphate, nitrate and ammonium) can be attributed to their gaseous precursors.

1.4.4 PARTICULATE MATTER IN VEHICULAR TRAFFIC

Transportation is the single largest source of air pollution in urban areas (Agyemang-Bonsu *et al.*, 2007). The United Nations Environment Programme (UNEP) estimates that about 90% of urban air pollution in rapidly growing cities in developing countries is as a result of vehicle emissions (UNEP, 2010). The rapidly growing numbers of motor vehicles in urban cities of developing countries are posing serious risk to the health of the population. Traffic-related particles from vehicles fall mainly into the submicron or fine mode range. They are able to penetrate deep into the respiratory tract, especially into the alveolar regions of the lung. In most sub-Saharan African urban cities, the vehicle emissions problem tend to be dominated by emissions from the high number of old and poorly maintained motor vehicles without catalytic converters, and the use of poor quality fuel (Kojima and Lovei, 2001). Moreover, the increasing numbers of second-hand cars and poor road networks have led to traffic congestion in most African cities. Almost 80% of the vehicles imported into Ghana are second-hand vehicles (Chalfin, 2008). Traffic congestion can cause vehicular emissions to increase appreciably, which can lead to high human exposures to traffic-related pollutants (Vardoulakis *et al.*, 2003; Nesamani *et al.*, 2007). Traffic congestion in urban areas hampers economic productivity, damages people's health, and degrades the quality of their lives.

Exhaust emissions from both diesel and gasoline fuelled vehicles have been identified as a major source of primary and secondary anthropogenic aerosols in urban cities. Road-traffic emissions in urban areas come from a number of sources, which include vehicle exhaust or tailpipe emissions (both fuel and lubricating oil combustion) and contributions from non-exhaust vehicle-related particles emissions (Rogge *et al.*, 1993; Kupiainen, 2007). A study by Kam *et al.* (2012) in developed countries shows that exhaust emissions contribute predominantly to fine PM and non-exhaust emissions contribute mainly to the coarse PM. Vehicle exhaust emissions consist of particles formed in the internal combustion engines as product of incomplete combustion. The particles derived from vehicle exhaust emission are primarily composed of elemental carbon (EC) and organic carbon (OC). Exhaust or tailpipe emissions depend on the type and age of the engine, the type of fuel and lubricant used, and the configuration of the exhaust system (Ondráček *et al.*, 2011). Heavy metals that have often been associated with vehicular emissions include Cu, Zn, Pb, Br, Fe, Ca, Cr, and Ba (Wahlin *et al.*, 2006; Thorpe and Harrison, 2008).

Non-exhaust emissions from on-road vehicles consist of non-combustion particles from tires and brake wear, road surface abrasion and re-suspension of road dust induced by the vehicle-generated turbulence (Thorpe and Harrison, 2008). Abrasion of brake linings and tires and re-suspended road dust, for example, release to the atmosphere particles with traces of elements such as strontium (Sr), copper (Cu), molybdenum (Mo), barium (Ba), cadmium (Cd), chromium (Cr), manganese (Mn) and iron (Fe) (EC, 2004). Re-suspension of road dust depends on a number of factors – road surface, humidity, intensity of traffic and wind speed (Kupiainen, 2007). Significant contributions of Al, Si, K, Ca, Ti, Mn, Fe, Zn and Sr, mostly in the coarse particle fraction, are apportioned to the road/tyres source. Non-exhaust particles can contribute significantly, to overall particulate emissions from the transport sector. However, the scarcity of data in developing countries on non-exhaust emissions makes it difficult to quantify its impact on the overall ambient concentrations.

1.5 LITERATURE REVIEW OF AIRBORNE PARTICULATE MATTER STUDIES IN AFRICA

Africa is the second fastest growing economy next to Asia. This rapid economic development has led to urban air pollution in many urban cities in Africa reaching levels that rival the levels that existed in the old days in cities of developed countries. However, the causes of air pollution are multiple. Air pollution can be transported over long distances and have impacts far from their point of emission. Most of sub-Saharan Africa (SSA) urban cities are now experiencing similar air pollution problems, especially anthropogenic particulate matter arising from the rapid growth of vehicle traffic, open waste burning, and the presence of major industries close to residential areas.

Air pollution research in African countries is still in its infancy. In contrast to the other parts of the world, very few data are available on air pollution derived from particulate matter in most SSA countries and Ghana in particular – despite their adverse implications on human health, visibility and climate. With the exception of South Africa, data on airborne particulate matter in SSA countries are extremely scarce since they are not routinely collected. Only a few source apportionment studies of particulate matter have been carried out in SSA countries. Chemical characteristics and source apportionment of particulate matter using receptor modelling have been studied in South Africa (Engelbrecht *et al.*, 2001; Kgabi, 2010), Ghana and Gambia (Zhou *et al.*, 2013, Zhou *et al.*, 2014), Nigeria (Oluyemi & Asubiojo, 2001), Tanzania (Bennet *et al.*, 2005; Mkoma *et al.*, 2010), Ethiopia (Etyemezian *et al.*, 2005) and Benin (Fourn and Fayomi, 2006).

Some studies to investigate particulate matter characterization and sources in Greater Accra in the past few years have identified three to eight potential sources (Aboh *et al.*, 2009; Ofosu *et al.*, 2012). Much is now known about the levels and sources of air pollution in urban environments, but most information is from more-developed countries. Hence there is an urgent need for measurements of air pollution in African cities. There is also an urgent need to understand the sources and contributions of particulate matter in Accra, Ghana which would enable the development of better emissions control policies and standards.

1.6 OVERVIEW OF ATMOSPHERIC POLLUTION IN GHANA

Ghana is one of the most densely populated countries in the sub-region with a population of about 24,658,823 (2010 estimate), growth rate of 2.5%, birth rate of 31.7 birth/1000 population, and death rate of 7.53 death/1000 population per year. More than 40% of the population lives in the urban areas of the country. In 2009, Ghana attained lower middle-income status and in 2010, became an oil producing country (World Bank, 2012).

In Ghana, and most of the other sub-Saharan Africa (SSA) countries, there is absence of regular and systematic air quality-monitoring for air quality assessment. As a result, there is a lack of data on the concentrations as well as the characteristics of atmospheric particulate matter. There have been routine monitoring programs in Accra by the Environmental Protection Authority of Ghana (EPA-Ghana) to measure only PM_{10}. There is no systematic record of $PM_{2.5}$ concentrations in Accra, partly because air quality standard for $PM_{2.5}$ has not been established in Ghana. The Environmental Protection Agency of Ghana between March 2005 and December 2008 collaborated with the United States Agency for International Development (USAID), the United States Environmental Protection Agency (USEPA) and the United Nations Environment Programme (UNEP) to set up an urban air quality monitoring network in Accra. The objective of the project was to accurately characterize the seriousness and nature of air pollution problems in Accra and to make recommendations for the development of air quality management strategy for Ghana. Results from the study revealed that vehicular exhaust emissions, open burning of waste and other materials, emissions from industrial sources, residential cooking, commercial activities and wind-blown dust are the major contributors to the air quality measured at the monitoring sites (Figure 1.2).

Figure 1.2 (a) Cooking along the side of street for small-scale commercial activity (b) vehicular traffic congestion (c) vehicular exhaust emissions (d) wind-blown/harmattan dust in Accra.

The results from the selected monitoring sites showed that PM_{10} concentrations at the roadside locations (178 µg m^{-3}) were higher than those at commercial (81 µg m^{-3}), industrial (72 µg m^{-3}) and residential (61 µg m^{-3}) during the wet season. The roadside (445 µg m^{-3}) site was also found to be higher than those at the commercial (198 µg m^{-3}), industrial (198 µg m^{-3}) and residential (150 µg m^{-3}) during the dry season (Nerquaye-Tetteh, 2009). High particulate matter concentrations at the roadside locations and commercial areas have the tendency to adversely affect the health of the populace.

Road traffic congestion is becoming the fastest source of pollution in many major urban centres in sub-Saharan Africa. Motorization in the Accra Metropolitan Area (AMA) is high by African standards, at 90 vehicles per 1,000 population, as compared to 20-30 for Nairobi, Dar es Salaam, and Addis Ababa (GEF, 2007). This is partly because of the high number of taxis, trotros and okada (motorcycles used for commercial services).This trend is increasing with 90% of the vehicles imported into the country remaining in the cities.

Table 1.2 shows a summary of the number of vehicles registered by the Driver and Vehicle Licensing Authority (DVLA) for Accra alone from 2000 to 2009. Traffic in Accra is characterized by heavy congestion (particularly during the peak periods), low vehicle utilization, heavy dependence on informal private bus services, weak implementation of traffic management measures, inadequate facilities for pedestrians and bicyclists, poor road safety arrangements and high accident rates. Vehicular exhaust emissions have been a significant cause of poor urban air quality over the years in Ghana (EPA, 2002). This together with heavy traffic in certain urban locations contributes to poor urban air quality.

Table 1.2 Summary of vehicles registered by DVLA for Accra.

Year	Registered Vehicles (cumulative)	Year	Registered Vehicles (cumulative)
2000	511,083	2005	767,067
2001	567,780	2006	841,314
2002	613,153	2007	932,540
2003	643,824	2008	1,033,140
2004	703,372	2009	1,128,138

Source: (DVLA, 2010)

Another major source of airborne particulate matter pollution in Ghana is biomass burning. Wood and charcoal are the most common solid fuels used in Ghana (Benneh *et al.*, 1993). Songsore and McGranahan (1998), based on data from 2000 Population and Housing Census and the 2003 Demographic and Health Survey, report that more than 60% of Accra's population use biomass fuels (charcoal or firewood) as their primary fuel for cooking. Boadi and Kuitunen (2005) in a study undertaken in the Accra Metropolitan Area revealed that biomass use was higher in households with lower income and socioeconomic status. The EPA-Ghana in the Ghana State of Environment Report 2004, listed the following as the main issues related to air quality in the country:

- Inefficient utilization of fuels;
- Poorly planned modes of transport;
- Poorly serviced motor vehicles;
- Inefficient cook-stoves and fireplaces;

- Rudimentary kilns and stoves in industries;
- Charcoal production;
- Widespread bush burning.

1.7 SOURCE APPORTIONMENT OF PARTICULATE MATTER

In order to design effective programmes and strategies for reduction of particulate matter concentration in ambient air, it is important and necessary to identify the original sources of the particulate matter, and to quantitatively apportion the observed aerosol particle concentrations among the various source types. Source apportionment methods provide the tools to formulate efficient and effective particulate matter control strategies and to develop policy to prevent human exposure.

Source apportionment of particulate matter refers to the methods used to quantify the contributions of different source categories to the particulate matter concentrations measured in the atmosphere (Pant and Harrison, 2012). Particulate matter pollution is comprised of myriad of chemical species emitted from multiple sources. Source apportionment models utilize the mass and chemical compositions of the particulate matter measured at a sampling site (receptor site) to resolve the main source types and estimate their contributions to the measured ambient particulate matter at that site (Belis *et al*., 2013). Particulate matter emissions from specific sources often have unique elemental profile by which the contribution of these sources to the total aerosol particles at the receptor can be recognized (Watson, 1984).

Air pollution models can be divided into two primary categories: receptor models and dispersion models. Receptor models are formulated to begin with pollutant information monitored at a receptor and to look backward, using data on several species and information about relative concentrations of those species from possible sources, to apportion the pollutant to the sources (Miller *et al.*, 2002). In contrast, chemical transport, or dispersion models start with the source characteristics and use physics, mathematical, and chemistry calculations to predict pollutant concentration at some distance from the source. Important input for those dispersion models includes information about the emissions from the source, the local atmospheric conditions, and some geographical characterization. Both types of models have been highly developed and forms of them are widely used for prediction and diagnosis of events (USEPA, 2004).

1.7.1 RECEPTOR MODELLING METHODS

Receptor models are mathematical or statistical techniques used to identify and quantify the sources of airborne pollutants at a receptor or sampling site. The fundamental principle of receptor modelling is that mass conservation is assumed and on this basis a mass balance analysis can be used to determine and apportion ambient particulate matter concentrations to individual emitting sources (Hopke *et al.*, 2006). Most receptor models used for source apportionment are in principle based on the assumption that the concentration of the pollutants measured at the receptor site is equal to the sum of the concentrations induced by the surrounding emission sources emitting the pollutants

(Fabretti *et al.*, 2009; Belis *et al.*, 2013). The main objective of receptor models is, therefore, to identify the possible sources of particulate contaminant and to obtain data on their contributions to the bulk particle mass.

Receptor models are commonly divided into two primary categories: chemical mass balance and multivariate methods (Henry *et al.*, 1984; Pollice, 2009). The selection of the appropriate method depends on prior knowledge on the sources and source profiles. If the sources are known and detailed information on source profiles is available, Chemical Mass Balance (CMB) models can be applied. Alternatively, in cases where the sources are unknown and only the concentration of ambient pollution is known, multivariate methods such as Positive Matrix Factorization (PMF) methods are preferred. Examples of the commonly used receptor model software in physical and chemical sciences applications include the USEPA's Positive Matrix Factorisation ((PMF 3.0) USEPA, 2008), Unmix 6.0 (USEPA, 2007) and Chemical Mass Balance ((CMB 8.2) USEPA, 2004).

Enrichment factor analysis and multivariate techniques such as correlations and Positive Matrix Factorization (PMF) were used to define a relationship between the sources and the receptor. These analytical methods were combined to assist in the identification of sources and the apportionment of the observed pollutant concentrations to those sources in the urban area of Accra, Ghana. Receptor models of positive matrix factorization (PMF) and enrichment factor (EF) were used in this study.

1.7.2 POSITIVE MATRIX FACTORIZATION

Positive matrix factorization (PMF) is a powerful and widely used multivariate method used extensively for source apportionment of ambient particulate matter (Paatero and Tapper, 1994; Paatero, 1997). PMF model resolves the dominant positive factors that contribute to PM samples without prior knowledge of the sources. This is achieved by using measured concentrations of particulate matter to estimate the number of sources, the source composition, and the source contribution to each sample.

The goal of PMF modelling is to

- determine the number of factors (sources or chemical/physical processes) that adequately explain the input data set variability and
- find correlation among the measured variables.

The advantages of the PMF relative to the traditional factor analysis methods such as Cluster Analysis (CA) and Principal Component Analysis (PCA) are:

- Unreliable data, such as observations below detection limit or missing values, can be included in the PMF analysis by giving them low weights to decrease their influence in the modelling (Paatero and Tapper, 1994).
- Data characterized by heavy positive skewed distribution can also be handled by down-weighting those extreme points to reduce undue influence in the model (Huang and Conte, 2009).

- PMF model assumes the non-negativity of factors and does not rely on information from the correlation matrix but utilizes a point-by-point least-squares minimization scheme by taking into account the uncertainty of each data point (Pongkiatkul and Oanh, 2012).

In PMF, a matrix X ($n \times m$), where n is the number of samples and m is the number of chemical species is factored into two matrices, G ($n \times p$) and F ($p \times m$), where p is the number of independent source types or factors extracted, and a residual matrix E is used to account for the unexplained part of X. The factor analysis model can be written in matrix form as shown in equation 1.2:

$$X = G \cdot F + E \tag{1.2}$$

or in component form as

$$x_{ij} = \sum_{k=1}^{p} \mathrm{g}_{ik} f_{kj} + e_{ij} \tag{1.3}$$

where x_{ij} is the measured concentration at a receptor for the j^{th}species in the i^{th} air sample, g_{ik} is the particulate mass concentration from the k^{th} source type contributing to the i^{th} air sample, f_{ik} is the j^{th}species mass fraction from the k^{th} source, and e_{ij} is the residual between measured and modelled concentrations for the j^{th}species in the i^{th} sample.

The objective of the multivariate receptor modelling is to determine the number of sources (p), the source contributions (g_{ik}), and the chemical profiles (f_{ik}) of the identified sources that best reproduce x_{ij}. To obtain the best fit of the model, PMF minimizes the object function, Q, or chi-squared based upon the uncertainties σ_{ij} of each observation.

The object function is given by the equation:

$$Q = \sum_{i=1}^{m}\sum_{j=1}^{n}\left(\frac{e_{ij}}{s_{ij}}\right)^2 \tag{1.4}$$

$$= \sum_{i=1}^{m}\sum_{j=1}^{n}\frac{\left(x_{ij} - \sum_{k=1}^{p} g_{ik}f_{kj}\right)^2}{{s_{ij}}^2} \tag{1.5}$$

where s_{ij} is the uncertainty in the j^{th}species in the i^{th}sample; $g_{ik} \geq 0$; and $f_{ik} \geq 0; k = 1, \dots, p$. PMF simultaneously adjust the elements of *G* and *F* in each iterative step until a minimum value of Q is obtained (Paatero, 1997; Polissar *et al.*, 1998). The Q value can be used to determine the optimum number of the factors. The theoretical Q value should be approximately equal to a value of $n \times m$, the number of entries of data array or the number of degree of freedom of the datum in the data set.

1.7.3 ENRICHMENT FACTOR

Enrichment factor model helps to differentiate between elements originating from anthropogenic activities and those from natural sources. It is used mainly to provide an initial assessment on the degree of contributions from man-made activities to that of the measured atmospheric elemental concentrations. Consequently, it is used to estimate the degree of anthropogenic contamination. Enrichment factor (EF) analyses have been extensively used in particle source apportionment studies to identify the major sources of air pollution and to quantify contributions of all sources of all measured pollutants (Winchester, 1981; Davidson *et al*., 1986; Chao and Wong, 2002; Cao et al., 2003; Zhang *et al*., 2008).

1.8 MOTIVATION AND OBJECTIVES OF STUDY

Urban air pollution from particulate matter is on the rise in sub-Saharan Africa. Rapid growths in population, urbanization, industrialization, and motorization have led to serious deterioration of the air quality in urban cities in developing countries like Ghana. Increasing epidemiological evidence has established the adverse health effects associated with ambient particulate matter pollution (Pope *et al*., 1992, Dockery *et al*., 1993, Dockery *et al*., 1994). Little or no data exists on particulate matter levels and composition in Ghana to gauge the severity or nature of the air pollution problem and its impact on the population. This presents a challenge for those actively producing the emissions and agencies involved with monitoring and regulating emissions. Thus, there is an urgent need to better monitor and manage urban air quality and identify the most effective measures to reduce pollution.

In order to assess and to lessen the impacts of particulate matter pollution, any program aimed at regulating the levels of particles in the urban atmosphere requires knowledge on the size distribution, chemical composition and sources of aerosol particles. Monitoring of particulate matter pollution was performed so that the data can be analysed to obtain more information about the trends, nature and concentrations of the particles.

For these reasons, $PM_{2.5}$ and PM_{10} particles were measured at four neighbourhoods in Accra:

(i) the indigenous older inner core low-income areas of James Town/Usher Town;

(ii) the informal migrant, low-income settlements of Nima/Maamobi outside the Ring Road;

(iii) Asylum Down, a middle-income neighbourhood located between the above two low-income areas; and

(iv) the high-income area of East Legon.

The above data collected were analysed for particle mass and composition. Data on particle composition allowed for the determination of within-neighbourhood and between-neighbourhood variations of particle levels and sources. The chemical characteristics (composition) of particulate matter, source apportionment, the influence of meteorological processes and their relationships at the four neighbourhoods are addressed in this study. The advanced data analysis modelling techniques called receptor models provided the tool to determine the information describing the origin of pollution emissions. Positive Matrix Factorisation (PMF) was the receptor model used in this thesis to identify and apportion the sources of pollution emissions.

1.8.1 OBJECTIVES OF STUDY

The overall objective of this study is to contribute to current knowledge on the characteristics and sources of urban ambient particulate matter in Accra, Ghana. It also seeks to resolve the number of relevant sources, their chemical composition, the amount that each source contributes to particulates matter and the influence of meteorological processes on particles in Accra, Ghana. This will improve understanding of the sources that should be included within an air quality control program within a sub-Saharan developing country.

1.8.2 SPECIFIC OBJECTIVES OF THE STUDY

The specific objectives are:

- To determine the mass concentrations of the $PM_{2.5}$ and PM_{10} in Accra, Ghana.
- To characterize chemical composition and concentrations of particulate matter using EDXRF.
- To determine and compare major sources of ambient fine particulate matter in specific neighbourhoods of Accra.
- To investigate the natural and anthropogenic contributions to particulate matter pollution in Accra, Ghana.
- To investigate the influence of meteorological conditions in Accra on particulate matter emissions.
- To investigate the influence of seasonal variations in particle mass and concentrations.

CHAPTER 2: CLIMATE AND METEOROLOGY OF GHANA

2.1 OVERVIEW OF THE CLIMATE OF GHANA

Ghana (Figure 2.1) lies on the west coast of Africa along the Gulf of Guinea between latitude 4.5°N and 11.5°N and longitude 3.5° W and 1.3°E with a total land area of 239,460 km^2 and 8,520 km^2 of water (EPA, 2002). It is bordered on the East by the Republic of Togo, the West by Cote d'Ivoire, the North by Burkina Faso and the South by the Gulf of Guinea or Atlantic Ocean. The country is divided into 10 administrative regions.

The climate of Ghana is tropical and humid. Ghana's climate is controlled by three air masses namely, the Tropical Maritime Air Mass (mT) or South-West Monsoon, the Tropical Continental Air Mass (cT) or North-East Trade Wind and the Equatorial Eastern (E). The cool and moisture saturated South-West Monsoon which originate from the Atlantic Ocean and the warm, dry and dusty Tropical Continental Air Mass (Harmattan) from the Saharan desert approach the tropics from opposite sides of the equator and flow towards each other into a low pressure belt known as the Inter-Tropical Convergence Zone (ITCZ) (Ojo, 1977).

Most of the country experiences two rainy seasons which occur from March to July and from September to November. The only exception is in the northern savannah where only one rainy season occurs from May to September, with the most rain falling in August and September, and one dry season.

Figure 2.1 Map of Ghana showing administrative regions and borders (Ghana Homepage, 2014).

Generally, the forested zones experience heavier rainfall and higher temperatures than the coastal zones while the northern savannah area experiences hotter and drier conditions with daytime temperatures mainly about 90 °C and above for much of the year. The quantity of rainfall in Ghana is variable. This seasonal variation in the rainfall patterns in the country is due to the annual north-south movement of the low pressure belt known as the Inter-Tropical Convergence Zone (ITCZ).

The ITCZ is where the hot, dry and dust Harmattan air mass from the Sahara in the North meets the cool, moist monsoon air mass from the South Atlantic (Afeti and Resch, 2000; Andah *et al*, 2003; Breuning-Madsen and Awadzi, 2005). Figure 2.2 depicts the movement of both the northern and southern ITCZ. From October to April, the cold and dusty northeasterly Harmattan winds blow south-west from the Sahara Desert, reducing visibility to as little as 1 km and slightly decreasing night temperatures. According to Salm and Falola (2002), the harmattan condition is widespread in the north between November and March, but reaches south to the coastal regions, usually for a few weeks to a month during December and January.

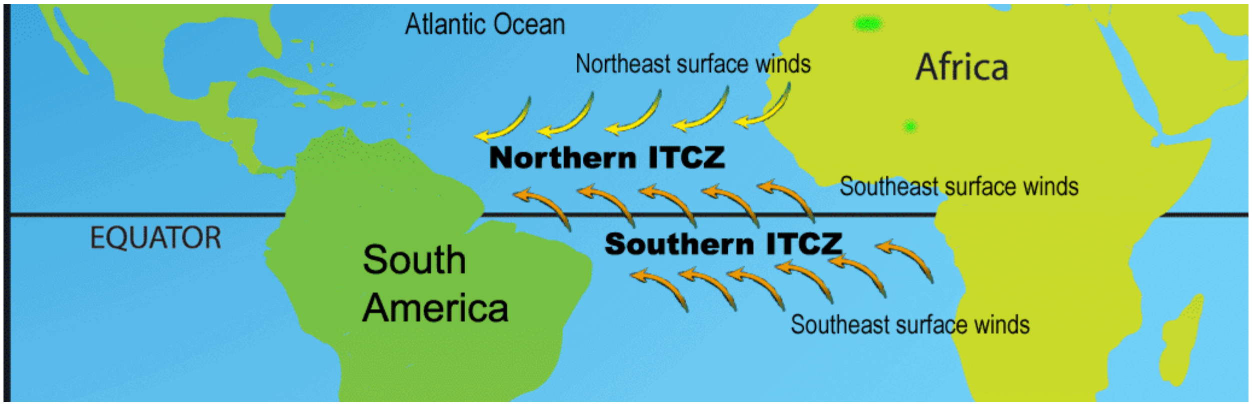


Figure 2.2 Movements of the Inter-Tropical Convergence Zones
(Source: http://winds.jpl.nasa.gov_images_equatormap1.gif.htm)

Annual rainfall ranges from about 1,100 mm in the north to about 2,100 mm in the south-western part of the country. The average relative humidity in the northern and southern parts of the country is approximately 44% and 80%, respectively (Dickson and Benneh, 1988). Moreover, temperatures within the country vary with seasons and elevation. Hence, most parts of the country record the highest and lowest temperatures in March and August, respectively. The average temperature is usually between 25 °C and 30 °C (Breuning-Madsen and Awadzi, 2005).

2.2 LOCAL METEOROLOGY

Ghana is geographically divided into six agro-ecological zones on the basis of their prevalent climatic conditions and vegetation (Figure 2.3). The agro-ecological zones are rainforest, coastal savannah, semi-deciduous forest, transitional zone, Guinea savannah and Sudan savannah zones.

The city of Accra lies within the coastal-savannah zone with a relatively humid climate and low annual rainfall varying between 600 and 900 mm, with an annual average of about 800 mm distributed over less than 80 days (Obuobie *et al*., 2006; Oppong and Badu, 2013). Relative humidity is generally high, ranging from 65% in the mid-afternoon to 95% at night.

Accra's rainfall pattern is bimodal with the major rainy season occurring from March to July, and the minor rainy season from September to October (Table 2.1). The major dry season occurs between November to the middle of March or early April (Gordon *et al*., 2003). This dry period coincides with the Harmattan season which occurs from November to March. The Harmattan is dry and dusty winds from the Sahara Desert which blows from the northeast. It is characterized by dry, hot days and relatively cool nights. The mean monthly temperature in the city varies from 24 ºC in August to 28 ºC in March, with an annual average of 27 ºC. The city lies close to the equator and therefore the daylight hours are quite uniform throughout the year. The predominant wind direction in Accra is from the WSW to NNE sectors with wind speeds normally varying from 8 km h^{-1} to 16 km h^{-1}. The maximum wind speed recorded in Accra is 107.4 km h^{-1}.

In this study, seasonal variations are divided into Harmattan and non-Harmattan seasons. The Harmattan period was from 27th December 2007 to 7th February 2008. The period from 1st September 2007 to 26th December 2007 and 8th February to 17th August 2008 will be described as non-Harmattan. Hence, the entire study spanned the period 27th December 2007 to 17th August 2008.

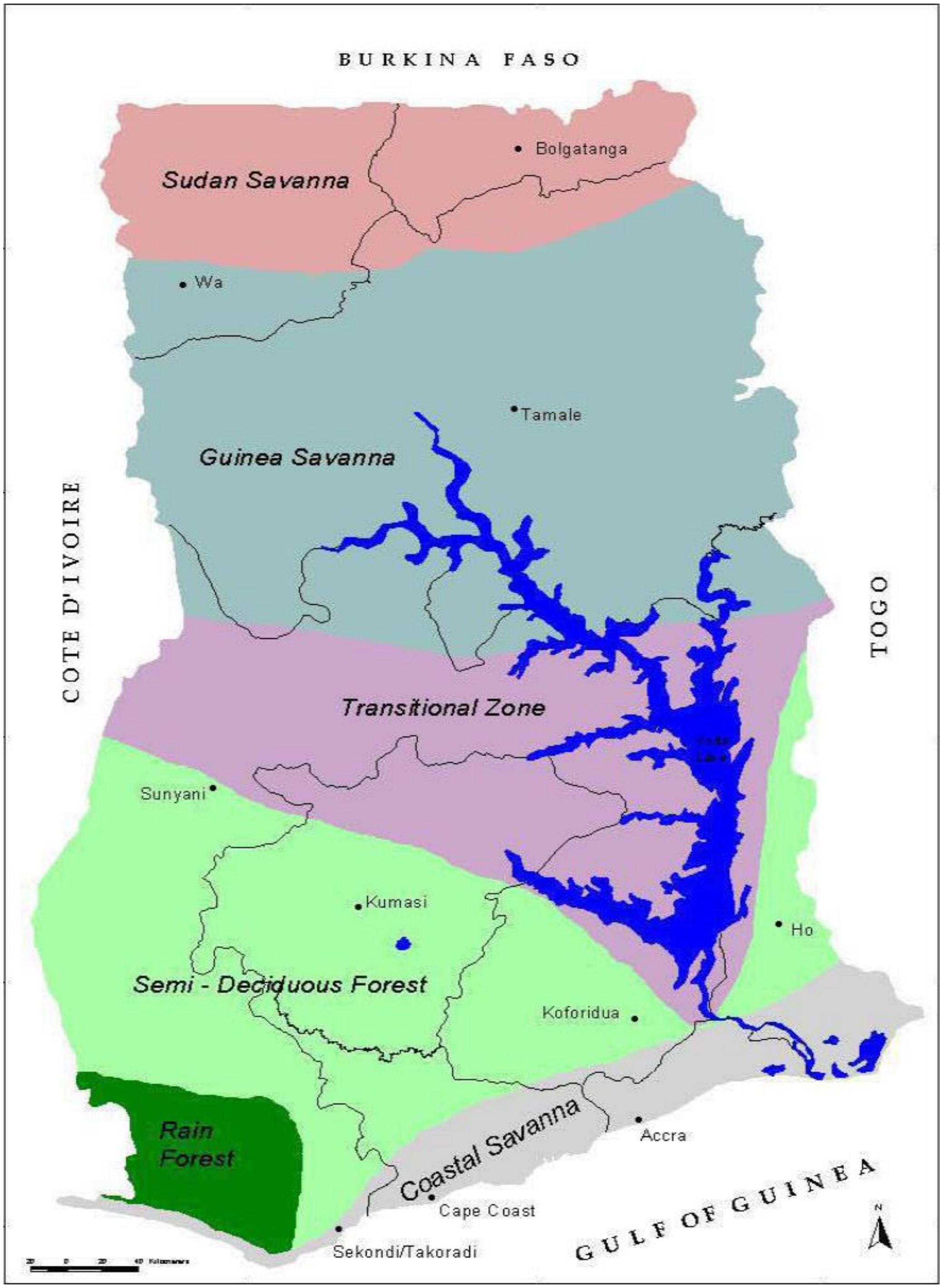


Figure 2.3 Map of Ghana showing the various agro-ecological zones (Benneh andAgyapong, 1990).

Table 2.1 Typical rainfall characteristics of agro-ecological zones in Ghana

Agro-ecological zone	**Area (km^2)**	**Mean annual rainfall (mm)**	**Range (mm)**	**Major rainy season**	**Minor rainy season**
Sudan savannah	2200	1000	No data	May–Sept	No data
Guinea savannah	147900	1000	800–1200	May–Sept	No data
Transitional zone	8400	1300	1100–1400	Mar–July	Sept–Oct
Deciduous forest	66000	1500	1200–1600	Mar–July	Sept–Nov
Rain forest zone	9500	2200	800–2800	Mar–July	Sept–Nov
Costal savannah	4500	800	600–1200	Mar–July	Sept–Oct

Source: Data adapted from the Ghana Meteorological Authority, Accra, Ghana.

2.3 PARTICULATE MATTER AND METEOROLOGICAL PARAMETERS

The inclusion of meteorological parameters in ambient particulate matter studies has become important since they can determine the transport and dilution of pollutants in the atmosphere, influence chemical transformations of species in the air, and affect the mechanisms and rates of removal of pollutants from the atmosphere. Many studies have shown that PM_{10} and $PM_{2.5}$ concentrations in the ambient air are influenced by various meteorological parameters such as temperature, relative humidity (RH), wind speed, wind direction, and precipitation (Rajkumar and Chang, 2000; DeGaetano and Doherty, 2004; Tsai and Cheng, 2004; Karar *et al*., 2006; Tecer *et al*., 2008; Mkoma and Mjemah, 2011).

The meteorology of an area can change many times in one day and affect the PM levels, hence the need to investigate the relationship between meteorological variables and PM levels. In the absence of site-specific meteorological data for the four neighborhoods, temperature, rainfall, relative humidity, wind speed and wind direction, were obtained from the Ghana Meteorology Authority, Accra. The meteorological parameters obtained were thought as being representative of the monitoring sites.

In view of the fact that meteorological conditions influence the concentration of particulate matter, the Harmattan season (December – February) and the non-Harmattan season (September – December and February – August) were examined separately. During this study, the Harmattan season was rather dry with no rainfall in Accra. Moreover, there was little or no variation in the average local ambient temperature for both seasons. The relative humidity fluctuated between 18 – 92% and 57 – 91% for Harmattan and non-Harmattan seasons respectively (Table 2.2).

The mean monthly values for temperature, relative humidity and rainfall are presented for the days with particulate sampling (Figure 2.4). The rainfall and relative humidity exhibited an inverse relationship with temperature. The mean wind speed varied over the entire sampling period with the highest (10.5 m s^{-1}) in August 2008 and the lowest (6.3 m s^{-1}) in January 2008.

Table 2.2 Average (or total amount) of meteorological parameters and ranges during the sampling periods in Accra, Ghana.

Parameters			
	Min	Max	Total/Mean
Harmattan season			
Precipitation (mm)	0	0	0
Relative humidity (%)	18	92	57 ± 23
Temperature (°C)	28	30	29 ± 0.7
Wind speed (m s^{-1})	4	10	6.5 ± 2.1
Non-Harmattan season			
Precipitation (mm)	0	62.8	179
Relative humidity (%)	57	91	74 ± 11
Temperature (°C)	23	30	28 ± 2
Wind speed (m s^{-1})	3	12	8 ± 2

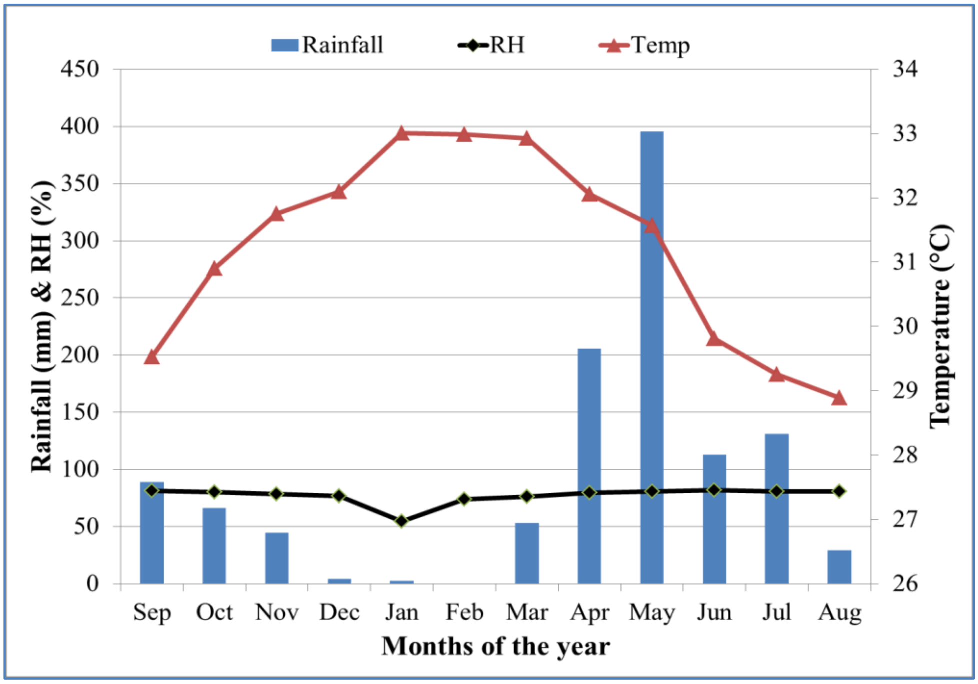


Figure 2.4 Monthly average of atmospheric temperature (°C), relative humidity (RH, in %) and rainfall (mm) for the period September 2007 – August 2008 in Accra. (Source: Drawn using data from Ghana Meteorological Authority, Accra, Ghana.)

2.4 AIR MASS CLIMATOLOGY AND BACKWARD TRAJECTORY ANALYSIS

Backward trajectory analysis is very useful in air pollution studies and can provide important information on air mass origins. Backward trajectory analysis can be used to track the history of air masses in which atmospheric aerosols are transported to the measurement site. In this study, air mass backward trajectory analysis was performed using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT version 4) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler and Rolph, 2003). The model runs on the principle, which is based on the integration of the position of air mass with regard to time. Backward air trajectories are presented in graphical forms indicating the pollutant sources and vertical heights above ground level (AGL).

Air mass backward trajectory analyses were calculated between September 2007 and August 2008 at 00:00 UTC or 24 h local time for the non-Harmattan and Harmattan seasons. Each four-day isentropic air mass backward trajectory was routed through three different heights (500, 1500 and 3000 m) AGL. This was to identify pollutants which are transported by air parcels near ground level (≤ 500 m) and those associated with long-range transport (between 500 m and 3000 m) which are likely to be free of the influence of local wind patterns caused by buildings, trees and other objects.. The model was run for days during which high PM source contributions were observed at the four sites.

The three-dimensional motion was obtained using 3-hourly output from the Global Data Assimilation System (GDAS) for both horizontal and vertical air mass streams. Results of backward trajectory analysis can be combined with observations to better explain the chemical characteristics of $PM_{2.5}$ at a receptor site (Aneja *et al*., 2006).

CHAPTER 3: METHODOLOGY

3.1 DESCRIPTION OF SAMPLING SITES

Accra (5^o 33' N, 0^o 13' W), the capital city of Ghana is one of the fastest-growing cities in sub-Sahara Africa (Møller-Jensen *et al*., 2005; CIA, 2011). With an estimated population growth rate of about 4% per annum, Accra has an estimated population of about 1.7 million (GSS, 2010). The Accra Metropolitan Area (AMA) with a population density for 112 per kilometre squared, has almost 42% of the total population of the Greater Accra Region (www.ghanadistricts.com).

Ambient aerosol samples were collected in four neighbourhoods of varying socioeconomic status (SES) located in Accra between September 2007 and August 2008. The four study neighbourhoods of James Town/Ussher Town (JT), Asylum Down (AD), Nima (NM), and East Legon (EL) lie on a line from the coast of the Atlantic Ocean to the northern boundaries of the Accra Metropolitan Area (AMA) (Figure 3.1).

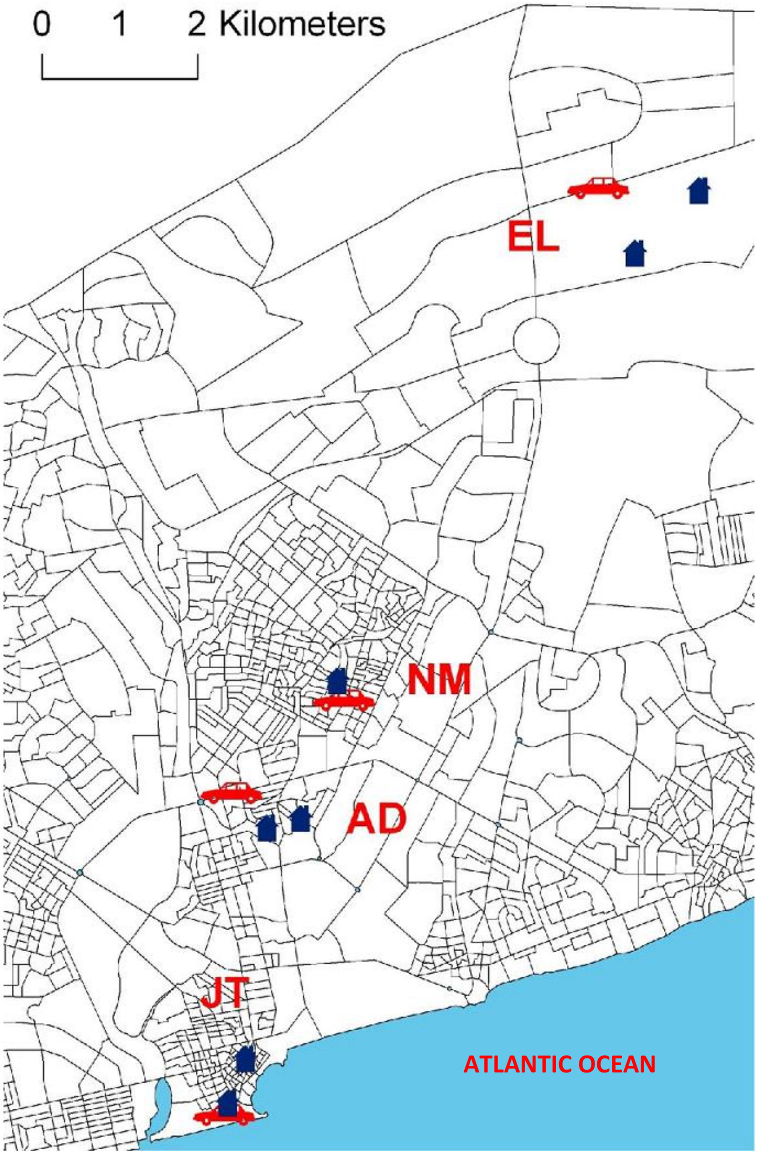


Figure 3.1 Four study neighbourhoods lying on a line from the coast to the northern boundaries of the Accra Metropolitan Area (AMA). AD, EL, JT and NM represent Asylum Down, East Legon, James Town/Ussher Town and Nima neighbours respectively.

3.1.1 JAMES TOWN/USSHER TOWN (JT) NEIGHBOURHOOD

James Town/Ussher Town (JT), a low lying area (less than 5 m above sea level), is a low-income indigenous area of Accra. It is one of the oldest neighbourhoods in Accra and remains an active fishing centre lying between the coast and the Central Business District (CBD). JT with a population density of 329 people per 10,000 m^2 is one of the densely populated areas within the Accra Metropolitan Area. The major road through this neighbourhood is paved but large blocks of residential areas have only pedestrian alleys paved with either cement or pavement blocks. The main local sources in JT are biomass burning mainly for domestic and commercial cooking, open burning of refuse and used tires, road and re-suspended soil dust, sea spray, emissions from vehicles and industrial processes.

3.1.2 NIMA (NM) NEIGHBOURHOOD

Nima (NM) is a low-income non-indigenous area of Accra. The population of Nima has increased substantially from 29,797 in 1960 to 52,906 in 1984, to 69,044 in 2000. Like JT, NM is an overcrowded, unsanitary, and unplanned neighbourhood with few public amenities. Nima is located to the northeast of Accra city centre and about five miles away from it. It extends over an area of about 351.6 acres of sloping ground; bounded in the west by Maamobi, east by Kanda, north by Kokomlemle and south by Accra New Town. The major road in Nima is the Nima Highway which links this neighbourhood to all the surrounding neighbourhoods. For most of the daytime period, this road is extremely busy and congested with vehicular traffic. In this neighbourhood, traffic, road and re-suspended soil dust, open burning of refuse, biomass burning by domestic houses and commercial street food vendors, are the main local sources.

3.1.3 ASYLUM DOWN (AD) NEIGHBOURHOOD

Asylum Down (AD) is a middle-income, mostly residential neighbourhood bordered by the Ring Road Central, one of the largest, busiest and congested roads in Accra. AD has a combination of residential and commercial buildings. It is located 3 km inland from the coast lying north of Castle Road and east of Barnes Road. Traffic through this neighbourhood is generally light, although the Ring Road Central is congested in the afternoon and evening most days of the week. The main local sources in AD are road and re-suspended soil dust, small businesses such as dry cleaners and auto body shops, outdoor burning and traffic.

3.1.4 EAST LEGON (EL) NEIGHBOURHOOD

The high-income East Legon (EL) neighbourhood is a sharp contrast to the low-income areas of JT and NM. It is an upper-class, sparsely populated, planned residential neighbourhood with well-developed infrastructure. It has a population density of 5 people per 10,000 m^2. EL is located about 10 km inland away from the coast and lies north of Accra International Airport, 13 km northeast of Central Business District. There is heavy vehicular traffic (from cars, trotros, buses and taxis) on the main road which connects EL to the city centre, primarily during the morning and evening commute periods. The main local sources in EL are road and soil dust, traffic and biomass burning.

3.1.5 STUDY DESIGN

In this study, measurements of particulate matter in samples collected from four selected neighbourhoods in Accra were carried out between September 2007 and August 2008. Monitoring sites within the neighbourhoods were selected as follows:

1. One site in the Nima neighbourhood was located on a road with medium to heavy traffic for the whole day or parts of the day. This site was designated as the neighbourhood traffic site (NM-T).
2. One site in each of the four neighbourhoods was located in areas selected to be typical residential parts of the neighbourhoods. The residential sites in Asylum Down, East Legon, James Town/Ussher Town, and Nima were designated as AD-R, EL-R, JT-R and NM-R respectively. They were situated on secondary roads or alleys with no or significantly less traffic than the Nima neighbourhood traffic site (NM-T), although within these sites there could be other polluting sources such as biomass burning or small-scale industries.
3. Other criteria for site locations were security of the equipment, access to electricity, free from public interference, and uninterrupted access to the equipment for operation and maintenance. The sites were also chosen to allow for free flow of air around the samplers' inlet, thus preventing the sampling of stagnant air or highly sheltered microenvironment. The characteristics of measurement sites are provided in Table 3.1.

This study was designed to characterize the particulate matter pollution over the city of Accra by examining its seasonal and daily patterns as well as its variation between neighborhoods. Moreover, the design will be used to identify and quantify the primary contributions of air pollution sources responsible for the airborne particulate matter pollution in the city using receptor-based modeling.

Table 3.1 Characteristics of measurement sites

	Residential (R)	**Traffic (T)**
JT		
Height (m)	6.24	
Distance to nearest primary road (m)	192	
Road surface	Paved	
Traffic pattern [a]	Connecting secondary road with light traffic	
AD		
Height (m)	2.85	
Distance to nearest primary road (m)	166	
Road surface	Paved	
Traffic pattern [a]	Connecting secondary road with medium-heavy traffic during morning and evening rush hours and light traffic at other times	
NM		
Height (m)	6.61	3.33
Distance to nearest primary road (m)	188	25
Road surface	Paved	Paved
Traffic pattern [a]	Local secondary road with light traffic	Primary road with heavy moving traffic all day and light traffic over night [b]
EL		
Height (m)	2.88	
Distance to nearest primary road (m)	330	
Road surface	Paved	
Traffic pattern [a]	Local secondary road with light traffic	

[a] Traffic patterns are based on qualitative assessment by study investigators. Road type was categorized as alley, local secondary road, connecting secondary road and primary road.

[b] NM-T was located next to a busy central bus station which frequently had idling vehicles.

3.2 DESCRIPTION OF SAMPLER AND FILTER MEDIA USED

3.2.1 AEROSOL SAMPLER

Several particulate matter (PM) sampling methods which allow for collection of particles on a filter that is weighed and subsequently subjected to analytical analysis have been deployed for PM studies (Wilson *et al*., 2002). These methods employ samplers such as dichotomous samplers, United States Environmental Protection Agency (USEPA) Federal Reference and Equivalent Method (FRM) samplers, Interagency Monitoring of Protected Visual Environments (IMPROVE) samplers and Harvard Impactor (HI) samplers which are some of the most commonly used particle samplers for the collection of $PM_{2.5}$ and PM_{10} integrated samples.

Manual sampling devices are needed to collect atmospheric particles for subsequent gravimetric mass measurement and elemental analysis by energy dispersive X-ray fluorescence (ED-XRF). The collection is usually done on a filter placed inside a sampler to obtain an integrated sample and a time averaged concentration measurement. A relatively low sampling flow rate of a few liters per minute is adequate if a highly sensitive technique, such as proton-induced X-ray emission (PIXE) fluorescence or energy dispersive X-ray fluorescence (ED-XRF), is used to analyze the collected particle sample (Pui and Liu, 1988).

Harvard Impactors (Marple and Willeke, 1976; Marple *et al.*, 1987) were used for integrated particles mass measurement in this study. HI is a relatively low flow particle sampler that uses an oiled impactor plate to minimize particle bounce and provide a sharp cut point, giving measurements similar to U.S. EPA reference methods (Chow, 1995). The Harvard Impactor samplers consist of a particle size selective inlet (SSI), an acceleration nozzle, either oiled impaction plates or polyurethane foam (PUF) pad, and Teflon membrane filter mounted in a plastic holder. The filter holder consists of a filter cassette top and a filter cassette bottom that press a plastic filter slide between two gaskets (Marple *et al.*, 1987). Figure 3.2 adapted from a similar figure by Sarnat *et al.* (2003) shows a schematic diagram of the Harvard Impactor.

In this study, PM_{10} concentration was measured using a HI with a D_{50} (50% collection efficiency) of 10 μm (aerodynamic diameter) at a flow rate of 4 l min^{-1} (± 10%), with two consecutive pre-oiled impactor plates serving as the impaction surface to reduce the effects of particle bounce. $PM_{2.5}$ concentration was measured using a modified HI combined with a polyurethane foam (PUF) $PM_{2.5}$ size-selective inlet, with a D_{50} of 2.5 μm at a flow rate of 5 l min^{-1} (±10%), with a PUF pad serving as the impaction surface. At each monitoring site, Harvard Impactor samplers were installed on rooftops of either homes or businesses, at heights ranging from 4 to 7 meters above ground level so that the air was relatively well mixed and less likely to be strongly affected by a source in the immediate vicinity (Dionisio *et al.*, 2010). The inlet nozzles of the samplers were approximately 1.2 meters above rooftop level with about a meter spacing between the inlets to ensure that the sampler inlet was able to sample wind coming from all directions. A typical set-up of the ambient monitoring system is shown in Figure 3.3.

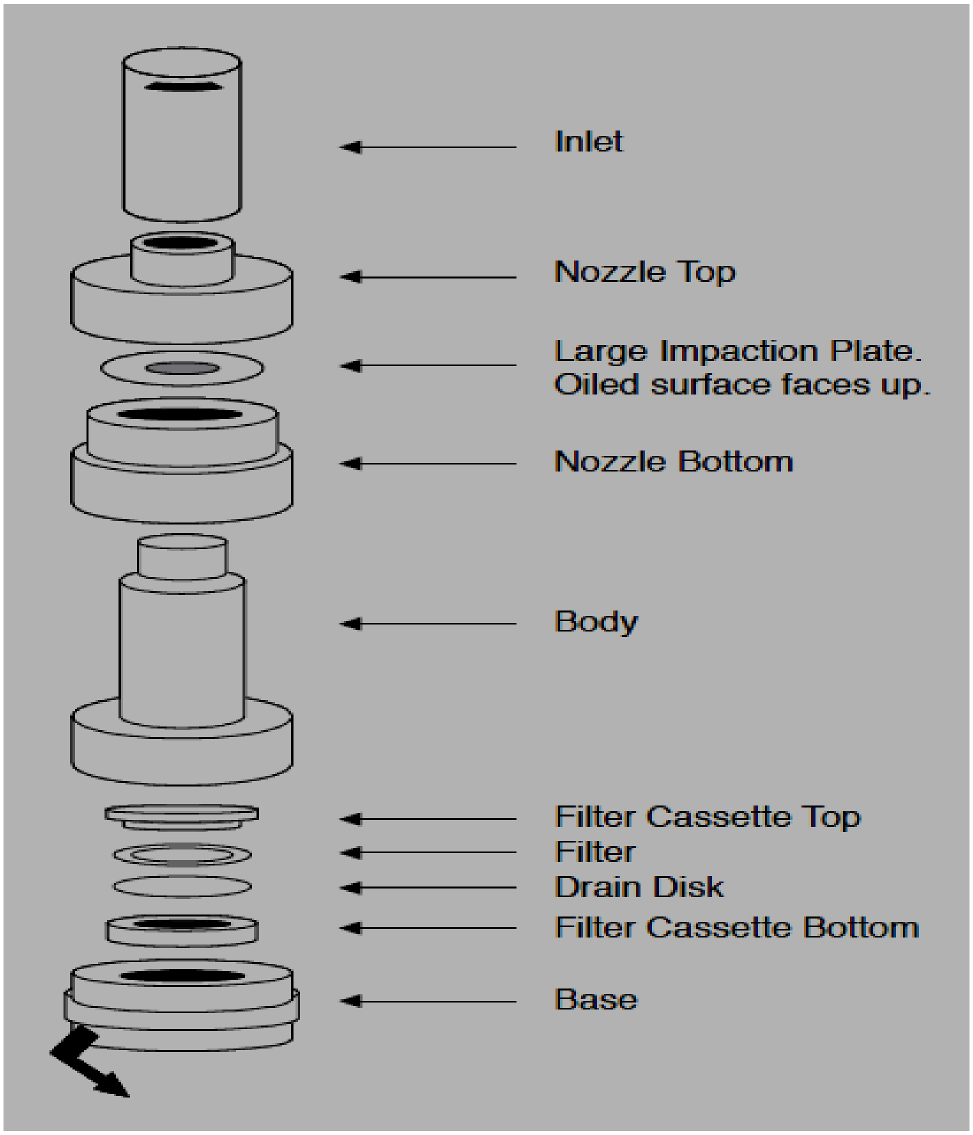


Figure 3.2 Schematic diagram of Harvard Impactor particle sampler (Sarnat *et al*., 2003).

Figure 3.3 A typical set-up of the ambient monitoring system. Residential site (left) and traffic site (right) with integrated ambient 48-hour Harvard Impactor (below) mounted on roofs of buildings to measure PM_{10} and $PM_{2.5}$ concentrations.

3.2.2 FILTERS

The most effective and prevalent method of capturing aerosol particles is by filtration. Filters are porous media for collecting particulate matter. Filters used for aerosol sampling are made of a tightly woven fiber mat or plastic membrane penetrated by microscopic pores. The two general types of filters are fibrous filters and membrane filters. Fibrous filters are characterized by low pressure drop and high collection efficiencies for all particle sizes. Examples of the most common types of fibers in this filter are cellulose wood fibers, glass fibers, quartz fibers and plastic fibers. Glass and quartz fiber filters exhibit a high retention of particles with sizes above 0.3 µm (IAEA, 1992). Membrane filters retain particles on the surface of the filter, enabling non-depth analyses such as X-ray fluorescence (XRF). They generally have higher flow resistance and lower loading capacities than fiber filters, and are also more expensive. Membrane filters are more suitable for trace elemental analysis studies using analytical methods such as instrumental neutron activation analysis (INAA), PIXE, ED-XRF or microscopic analysis. They are available in a wide range of materials including Teflon, polyvinyl chloride (PVC), cellulose ester and polycarbonate. Filter media used in monitoring activities must display the physical and chemical properties appropriate for the sampling methodology and the laboratory analysis methods used. A summary for some useful properties of filters are shown in Table 3.2.

Table 3.2 Example of summary of useful filter properties (USEPA, 1999).

Filter and Filter Composition	Density mg/cm^2	pH	Filter Efficiency %
Teflon® (Membrane) $(CF_2)n$ (2µm Pore Size)	0.5	Neutral	99.85
Cellulose (Whatman 41) $(C_6H_{10}O_5)n$	8.7	Neutral (Reacts with HNO_3)	58% at 0.3 µm
Glass Fiber (Whatman GF/C)	5.16	Basic pH - 9	99.0
"Quartz" Gelman Microquartz	6.51	pH - 7	98.5
Polycarbonate (Nuclepore) $C_{15}H_{14}+CO_3$ (0.3µm Pore Size)	0.8	Neutral	93.9
Cellulose Acetate/Nitrate Millipore $(C_9H_{13}O_7)n$ (1.21 µm Pore Size)	5.0	Neutral (Reacts with HNO_3)	99.6

All $PM_{2.5}$ and PM_{10} samples in this work were collected on polytetrafluoroethylene (PTFE) Teflon filters with ring (Pall Life Science, Teflon, 0.2 µm pore size, 37 mm diameter), back-supported by a Whatman drain disc. These PTFE Teflon filters have been used in low volume sampling applications due to their advantage of minimizing particle bounce and preserving unstable compounds, low background levels of many analytes and cleanest IR absorbance spectrum (Harrison and Yin, 2004). Therefore, Teflon was chosen as a medium for particle collection. The collected aerosol particles on the Teflon filter were used to obtain the mass concentration by gravimetric analysis and the elemental characterization by nondestructive energy dispersive X-ray Fluorescence (ED-XRF) spectrometry. The net mass of particles is determined by the difference in the filter pre-weighed mass and after-sampling mass. Volumetric airflow rates through each filter were measured at the start and end of each 48-hour measurement using a pre-calibrated rotameter.

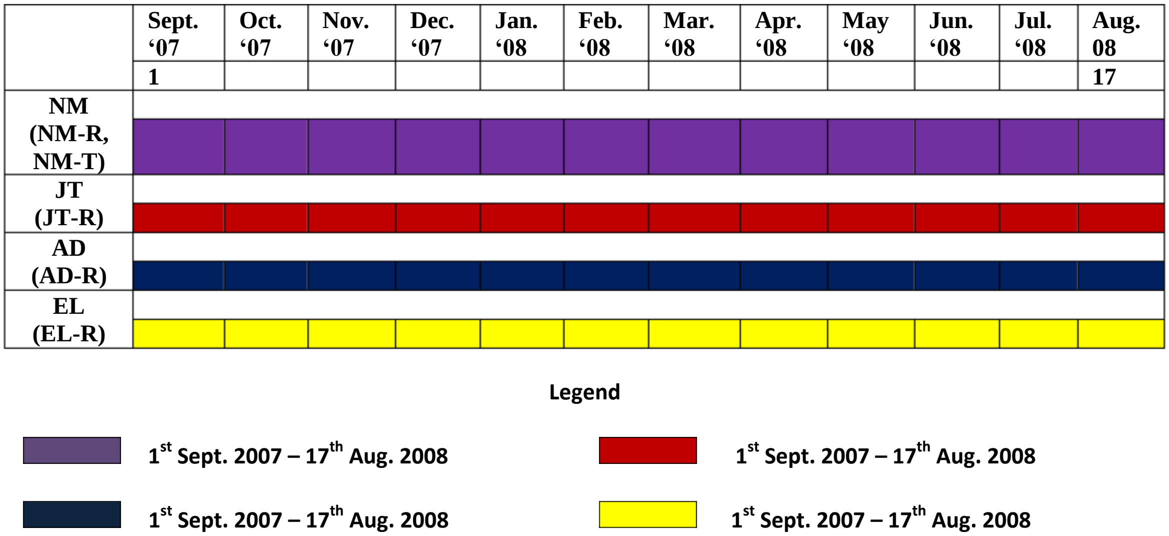
The equipment and air flow rates of the pumps were checked at 24-hours intervals and adjusted as needed. The average flow rate for each sample was calculated from the mean of the initial and final sampler flows. Field blanks and duplicate filters were collected at multiple sites routinely on a rotating basis. The Teflon filters were changed manually every 48 hours during the sampling period. Durations of each sampling event were recorded by a timer on the pumps. All the filters used for this study were prepared at Harvard School of Public Health (HSPH) and shipped to Accra for deployment at the sampling sites. The exposed filters and field blanks were placed into polycarbonate Petri dishes and returned to the HSPH laboratory for gravimetric analysis.

3.3 SAMPLING PERIODS

Ambient sampling of particulate matter was collected for one year in James Town/Ussher Town (JT), Asylum Down (AD), Nima (NM), and East Legon (EL) – four neighbourhoods located the Accra Metropolitan Area (AMA). The sites were designated as follows:

- James Town/Ussher Town (JT-R),
- Asylum Down (AD-R),
- Nima (NM-R and NM-T), and
- East Legon (EL-R).

Data was collected from 1st September 2007 to 17th August 2008 (Figure 3.4). The samples were collected over 48-hour sampling periods once every six days simultaneously at five rooftop monitoring sites. The 48-hour measurements started at 6:00 am during each sampling period throughout the entire study period.



	Sept. '07	Oct. '07	Nov. '07	Dec. '07	Jan. '08	Feb. '08	Mar. '08	Apr. '08	May '08	Jun. '08	Jul. '08	Aug. 08
	1											17
NM (NM-R, NM-T)												
	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
JT (JT-R)												
	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
AD (AD-R)												
	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
EL (EL-R)												
	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨

Legend

🟪 1st Sept. 2007 – 17th Aug. 2008

🟥 1st Sept. 2007 – 17th Aug. 2008

🟦 1st Sept. 2007 – 17th Aug. 2008

🟨 1st Sept. 2007 – 17th Aug. 2008

Figure 3.4 Diagram of 48 h averaging sampling schedule at four Accra neighbourhoods during study period.

As a result of unannounced or planned load shedding exercise embarked upon by the Volta River Authority (VRA) and the Electricity Company of Ghana (ECG) during study period, frequent and extended electric power outages necessitated using a power backup system at each monitoring site to prevent or limit the effects of data lost. The system consisted of 12-V 100-Ah batteries connected to chargers and inverters.

3.4 ANALYTICAL METHODS

Determination of the composition of ambient particulate matter involves the analysis of deposits collected on filter media. The chemical composition of particulate matter in ambient air provides essential information for assessment of contribution from different sources. For this reason, analytical techniques such as gravimetric analysis and energy dispersive X-ray fluorescence (EDXRF) are widely used to analyze the filter samples of air particulate matters.

There are several other analytical methods available for the determination of multi-element on filter media and the choice of the most appropriate method depends on the analytes of interest, the specificity needed (i.e., screening vs. fully quantitative) and the sensitivity needed, commonly referred to as the detection limit. The sensitivity, which indicates the ability of an analytical method to detect specific elements at the lower end of the range of concentrations of concern, may change from instrument to instrument because of X-ray generator frequency, multichannel analyzer sensitivity, and sample interferences (US EPA, 1999a; US EPA, 1999b). Specificity is the ability of an analytical technique to differentiate between a certain substance and other similar chemicals.

Other analytical techniques used for elemental analysis of particulate matter on filter materials are instrumental neutron activation analysis (INAA), inductively-coupled plasma with mass spectroscopy (ICP-MS), inductively-coupled plasma with atomic emission spectroscopy (ICP-AES), particle-induced X-ray emission (PIXE), proton (or particle) elastic scattering analysis (PESA), total reflection X-ray fluorescence (TRXRF), synchrotron induced X-ray fluorescence (S-XRF) and scanning electron microscopy with X-ray fluorescence (SEM/XRF). Brief descriptions of analytical techniques used in the studies on which this thesis is based will follow in subsequent subsections.

3.4.1 GRAVIMETRIC ANALYSIS

The integrated mass concentration of particulate matter in air can be measured in several ways. The most common and traditional way is through filter-based gravimetric methods. Gravimetric measurement is the net mass on a filter found by weighing the filter before and after sampling with a microbalance in a temperature and relative humidity controlled environment (Feeney *et al.*, 1984). The principle of the gravimetric method is that air is drawn into the size selective inlet (SSI) of a sampler and through a pre-weighed Teflon filter by means of a low-flow volume electrically powered pump, so that particulate matter is collected quantitatively on the filter surface (US-EPA, 1999). The Harvard Impactor (HI) operates on a measurement principle based on gravimetric analysis which is similar to the US EPA’s Federal Reference Method (FRM) used for regulatory compliance. The HI collected particles on 37 mm Teflon filter over a 48-hour period. At the end of this period, the sampled filters were removed from the HI manually and placed into Petri dishes. Fresh filters were loaded into the impactor to start the next sampling period. Gravimetric analysis of the filters was performed with a microbalance.

All filters used in this study were weighed before and after sampling on a Mettler Toledo MT-5 microbalance with a sensitivity of 1 µg located in a clean weighing room at the Harvard School of Public Health Laboratory, Boston, Massachusetts. The samples were allowed to stabilize and conditioned in the weighing room under controlled temperature (20.5 ± 0.2) ºC and relative humidity (39 ± 2) % for at least 24 hours prior to weighing. Residual charge on a Teflon filter could produce an electrostatic discharge between the filter on the pan and the metal casing of the microbalance (Engelbrecht *et al.*, 1980; Allen *et al.*, 1999; Koistinen *et al.*, 1999; Hänninen *et al.*, 2002). Gravimetric analysis is strongly affected by such charges. The electrostatic charges of the sample were eliminated via a polonium radioactive source by moving the filters near the source (Allen *et al.* 1999; Lawless and Rodes, 1999).

In both pre- and post-weighing, filters were weighed twice; if these two masses were not within a precision 5 µg of one another, they were weighed a third time. This method was employed to improve the precision of the gravimetric analysis and to eliminate outliers due to large analytical errors. The mean of the two masses within 5 µg of one another was used for calculating concentrations. After every batch of 10 filters, the zero, span, and linearity of the balance were checked via a set of class "S" weights. Final filter weights were adjusted using an air buoyancy correction (Koistinen *et al.*, 1999). In cases where duplicate measurements were taken, the two measurements were averaged so as to use all available data. All sample weights were corrected by subtracting the mean field blank weights.

The total mass of the particulate matter collected on a Teflon filter in µg is given by equation 3.1.

$$M = \left[\left(M_f - M_i\right)\mathrm{mg} \times 10^3\right]\mu\mathrm{g} \tag{3.1}$$

where,

M = total mass of particulate matter collected during sampling period (µg)

M_f = final mass of conditioned filter after sample collection (mg)

M_i = initial mass of the conditioned filter before sample collection (mg)

Equation 3.2 gives the total volume of ambient air passing through the sampler (V) in cubic meters.

$$V = \left[\left(Q_{\mathrm{avg}}\right)\mathrm{l\ min^{-1}} \times t\ \mathrm{min} \times 10^{-3}\right]\mathrm{m^3} \tag{3.2}$$

where

V = total sample volume ($\mathrm{m^3}$)

Q_{avg} = average flow rate over the entire duration of the sampling period (l/min)

t = duration of sampling period (min)

Consequently, the PM concentration in $\mu\mathrm{g\ m^{-3}}$ can be calculated using equation 3.3.

$$PM = \frac{M}{V} \tag{3.3}$$

where

PM = mass concentration of PM ($\mu\mathrm{g\ m^{-3}}$)

M = total mass of PM collected during sampling period (µg)

V = total volume of air sampled ($\mathrm{m^3}$)

3.4.2 ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS

Energy dispersive X-ray fluorescence (EDXRF) spectrometry is one of the most commonly used analytical technique to determine the elemental composition of airborne particulate matter collected onto filter (Bandhu *et al*., 2000). It is capable of providing the composition of a variety of materials in a non-destructive manner. This technique is able to provide qualitative and quantitative information on multi-elemental concentration data of particulate matter. This data is essential for source identification work and for application of receptor models for source apportionment. A large number of studies on the elemental concentration of particulate matter using EDXRF spectrometry technique have been reported (Watson *et al*., 1999; Markowicz *et al*., 2002; Aboh *et al*., 2009).

In EDXRF method, the sample on the filter is irradiated with a high intensity beam of X-rays. This causes electrons to be ejected from the inner shell orbital of atoms in the sample and the vacancies created are filled by electrons in the outer atomic shells. The excess energy is released in the form of (fluorescence) X-rays which is seen as a line in a spectrum whose energy is characteristic of the elements present. The intensity of the characteristic (fluorescent) X-rays is proportional to the concentration of the element in the sample. The X-ray fluorescence emitted from the irradiated sample is captured by the semiconductor detector and processed by the signal processing unit.

Some advantages of EDXRF over other analytical techniques are:

- It is non-destructive; therefore samples are left intact after analysis so they can be submitted for additional analyses by other methods as needed.
- It requires little or no sample preparation or operator time after the samples are loaded into the analyser.
- It is fast and can be used to simultaneously quantify the concentrations of elements with atomic numbers ranging from 11 (Na) to 92 (U).

A basic X-ray spectrometer system consists of a source that generates X-rays, a solid state detector that measures the different energies of the characteristic radiation from the sample, a sample holder and a signal processing unit that records the emission or fluorescence energy signals and calculates the elemental concentrations in the sample.

3.4.2.1 ANALYSIS OF ELEMENTAL COMPOSITION

The elemental concentrations of PM_{10} and $PM_{2.5}$ samples from all monitoring sites in Accra were quantified by energy dispersive X-ray fluorescence spectrometry analysis (EDXRF) using a Shimadzu EDX-700HS spectrometer (Shimadzu Corp., Japan) at the Institute of Astronomy, Geophysics and Atmospheric Science, University of Sao Paulo, Brazil. The spectrometer used a low power Rh-target tube and operated with a voltage varying from 5 to 50 kV and a current from 1 to 1000 μA (Andrade *et al.*, 2010). The characteristic X-ray radiation was detected by a Si (Li) detector.

3.4.2.2 METHOD DETECTION LIMIT (DL) OF EDXRF

The detection limit (DL) is usually defined as the amount of analytes that gives a net intensity peak equal to three times the standard deviation of the background intensity. In this work the MDL was calculated as three times the standard deviation of the field blanks. It depends upon the specific element and the sample matrix.

An element was said to be detected if the following condition in equation 3.4 was satisfied:

$$\frac{N_p}{\sqrt{N_b}} \geq 3 \qquad (3.4)$$

where

N_p = the number of counts measured on the peak

N_b = the number of counts measured on the background.

3.5 TRAFFIC COUNT METHODOLOGY AND MEASUREMENTS

Local variations in vehicular traffic volume were measured at the same intersection where air monitoring occurred using manual traffic count method at all sites (both residential and traffic) in the four Accra neighbourhoods. Manual traffic counts were conducted on 15-minute intervals with a 10-minute break after each interval for a 12-hour period (6:00 am to 6:00 pm) for two weeks (Monday to Sunday) on all roads at each monitoring site. Vehicular traffic counts were measured for each direction separately and the data were aggregated on a direction by direction basis. The vehicles were classified into 4 categories, namely: cars, buses/4WD, trucks, and motorbikes/scooters (Figure 3.5). Manual counts were used to provide detailed information about the vehicle categories and diurnal variation. Diurnal patterns of ambient PM concentrations were examined using the traffic and air quality data measured. Manual counts usually require trained observers to collect specific information that cannot be efficiently obtained through automated means. These may include vehicle occupancy, pedestrians, turning movements and vehicle classification. To conduct manual traffic count, tally sheets, mechanical count boards and electronic count boards are the most commonly used method. For this study, a manual traffic count using the tally sheet method was adopted because of the lack of access to a mechanical or electronic counting board and also because it is the least expensive tool for manual data collection.

Manual traffic counting for this study was performed by two teams consisting of two observers in each team. Prior to commencement of the data collection, the observers were trained on how to conduct a manual traffic count using a specially prepared tally sheet, proper identification of traffic lanes and directions to be counted, and the identification of the four categories of vehicles to be counted.

Cars - passenger cars, taxis, mini-vans

Buses/4WD - trotros, school buses, large buses, 4WD vehicles (Jeeps, SUVs, and small pick-up trucks)

Trucks - large trucks, multi-axle pick-up trucks

Motorbikes/Scooters - scooters, motorbikes, zoomlions

Figure 3.5 Classification of vehicles counted

Pilot /trial runs were conducted after the training by the observers for a period of one week on selected roads within the various neighbours to test the counting methodology. Observers were positioned at a vantage point at each location away from the edge of the roadway so that their views were not blocked by trucks, buses, parked cars or signs and also for safety considerations. Counting of traffic was done simultaneously in the same direction by a team of two observers. The first team of two observers counted traffic from 6:00 am to 12:00 pm while the second team counted from 12:00 pm to 6:00 pm daily. Vehicle counts per unit time were determined visually at each road for each day of sampling. Traffic data from the tally sheets were entered onto a spreadsheet. These daily counts were then averaged across days at each site and expressed in counts per hour for each vehicle category.

The use of a tally sheet involves the observer to make a tick mark for every vehicle in a given classification or movement. The tally sheet was prepared prior to going into the field allowing space for all information to be marked easily once the count began. The tally sheet was used in conjunction with a stopwatch to time the desire interval. Once these counts are collected, they are tallied and summarized. The average daily traffic (ADT) which is the sum of all vehicles that pass through a street during a day (unit = vehicles/day) averaged over the observed period was calculated. For this study, daily traffic flow data are based on daily average observations including all weekdays and weekends.

3.6 ENRICHMENT FACTOR

Enrichment factor (EF) analyses can be used to distinguish between elemental composition of aerosol particles originating from either anthropogenic activities or natural sources and to also evaluate the extent of anthropogenic influence (Duce *et al*., 1975; Zhang *et al*., 2008; Yongjie *et al*., 2009). EF compares the ratios for various elements in measured PM concentrations to the corresponding ratios in geological material as a means of confirming the man-made and natural contributions.

Although there is no fixed rule for choosing the reference element, elements such as Aluminium (Al), Silicon (Si), Titanium (Ti), Iron (Fe) are most commonly used as reference element because they all have an abundant natural content in the soil, good chemical stability and less affected by anthropogenic pollution (Basha *et al*., 2010).

In this study, Fe was used as reference, and the upper continental compositions of the earth's crust were taken from Taylor and McLennan (1985). The enrichment factor (EF) for the each element in $PM_{2.5}$ and PM_{10} at the four sampling sites was calculated using the following formula in equation 4.1:

$$EF = \frac{\left(\frac{X}{E}\right)_{\text{aerosol}}}{\left(\frac{X}{E}\right)_{\text{crust}}} \qquad (3.5)$$

where X and E refer to the concentration (in µg m^{-3}) of the element of interest X and the reference element respectively.

The EF of an element is usually taken as being from a crustal or natural source if EF < 10. However, if EF > 10 then it is considered to indicate that a significant fraction of the element is contributed from non-crustal or anthropogenic source (Braga *et al.*, 2005; Chimidza *et al.*, 2001; Kothai *et al.*, 2011). EF values >100 and 1000 are taken as highly and heavily enriched respectively. Table 3.5 shows the average of the crustal elements that were used in the study.

Table 3.3 Averages of crustal elements used to calculate enrichment factors of PM at all sampling sites in Accra

Atomic Number	**Element**	**Crustal Average (ppm)**	**Crustal average (µg/m^3)**
11	Na	23600	22.19
12	Mg	23300	23.16
13	Al	82300	90.82
14	Si	281500	323.36
15	P	1050	1.33
16	S	260	0.34
17	Cl	130	0.19
19	K	20900	33.42
20	Ca	41500	68.03
22	Ti	5700	11.16
23	V	135	0.28
24	Cr	100	0.21
25	Mn	950	2.1
26	Fe	56300	128.59
29	Cu	55	0.14
30	Zn	70	0.19
35	Br	2.5	0.0082
38	Sr	375	1.34
40	Zr	165	0.62
82	Pb	12.5	0.11
Source: (Taylor and McLennan, 1985)			

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 $PM_{2.5}$ AND PM_{10} MASS CONCENTRATIONS

Statistics for mass concentrations of $PM_{2.5}$ and PM_{10} samples at five monitoring sites in Accra for the period September 1, 2007 – August 17, 2008 are shown in Table 4.1. The statistics include the average, standard deviation, minimum and maximum. The standard deviation of the concentration values represents the dispersion of the data around the average value (i.e. data variability during the investigated period). Overall, average $PM_{2.5}$ and PM_{10} at the residential site, JT-R, had higher concentrations than other sites, 74.8 and 134.8 μg m^{-3}, respectively. The next highest mass $PM_{2.5}$ and PM_{10} concentrations were recorded at the only traffic site NM-T. JT-R site is located on a secondary road in James Town/Ussher Town with less traffic than NM-T. The higher mass concentration observed at the JT-R site may likely be associated with the widespread use of biomass fuels, especially firewood, for home and small-commercial cooking purposes in a very densely populated area (Dionisio *et al*., 2010). JT-R site is about 0.5 km from the James Town beach located along the coast of the Atlantic Ocean where fish smoking and goat roasting are carried out by burning wood and used rubber tires (Obiri-Danso *et al*., 2008). The lowest $PM_{2.5}$ concentrations were obtained at the EL-R site. $PM_{2.5}$ concentrations at this site were, on the average, 39% less than at JT-R. However, there were no significant differences observed on average PM_{10} levels among residential sites EL-R, AD-R and NM-R. This indicates that PM_{10} levels at these sites are influenced by similar sources in urban area.

JT-R had slightly higher overall $PM_{2.5}/PM_{10}$ ratio (0.55) than the other sites (0.47-0.51). $PM_{2.5}/PM_{10}$ ratios > 0.5 have been observed in many urban areas in developed countries (US-EPA, 2002; Tecer *et al.*, 2008). Qian *et al.* (2001) found $PM_{2.5}/PM_{10}$ ratios of 0.51-0.72 during a study of four urban areas in China. The lower ratio in Accra could be attributable to coarse fraction contributions from re-suspended dust and geologic and marine sources which has higher coarse fraction (Arku *et al.*, 2008).

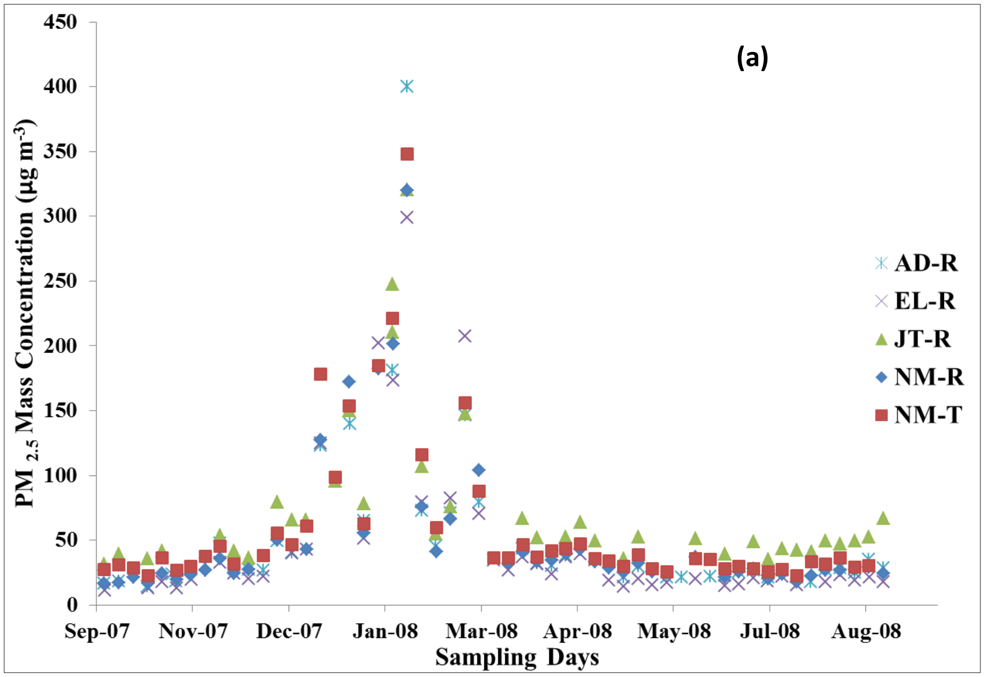
Table 4.1 Statistical summary of average PM_{10} and $PM_{2.5}$ in Accra during entire sampling period.

Average PM_{10} and $PM_{2.5}$ concentrations in ($\mu g\ m^{-3}$)							$PM_{2.5}$/
Sites	Type	*n*	Average	SD	Min	Max	PM_{10} ratio
AD-R	PM_{10}	44	108.2	121.2	29.4	655.4	0.47
	$PM_{2.5}$	46	50.4	64.1	14.2	399.9	
EL-R	PM_{10}	46	96.9	118.1	22	581.3	0.47
	$PM_{2.5}$	46	45.9	60.2	10.7	298.73	
JT-R	PM_{10}	38	134.8	121.6	52.9	652.6	0.55
	$PM_{2.5}$	39	74.8	61.6	31.3	320.4	
NM-R	PM_{10}	51	93.9	108.98	27.3	569.6	0.51
	$PM_{2.5}$	51	48.3	56.8	16.3	319.8	
NM-T	PM_{10}	57	111.9	108.9	41	593.44	0.51
	$PM_{2.5}$	55	57.5	60	22.4	348.4	

n = Number of samples, SD =Standard deviation

Figures 4.1(a) and (b) illustrates the temporary variations of daily mass concentration of $PM_{2.5}$ and PM_{10} at the five sites during the investigation period. Peaks in the data suggest the influence of meteorology during the study period. It was observed that PM concentration peaked sharply in all neighbourhoods between December and February.

This period corresponds to the seasonal Harmattan season when the northeast trade winds blow large amount of dust from the Sahara desert laden with emissions from dry-season bushfires towards the Gulf of Guinea in a south-westerly direction at an altitude of about 1500 m above sea level (Afeti and Resch, 2000). It is clear that the large PM concentrations measured during the few days of Harmattan period may distort information on the actual levels of aerosol concentrations. Aboh *et al*. (2009) separated total particulate matter concentrations and compositions data into seasonal Harmattan and non-Harmattan conditions to examine the extent to which the extreme conditions influence the identification of aerosol particle sources at a semi-rural site in Accra. Olic *et al*. (1999) identified fingerprints of individual sources by investigating aerosols particles using seasonal haze and non-haze conditions in Singapore.



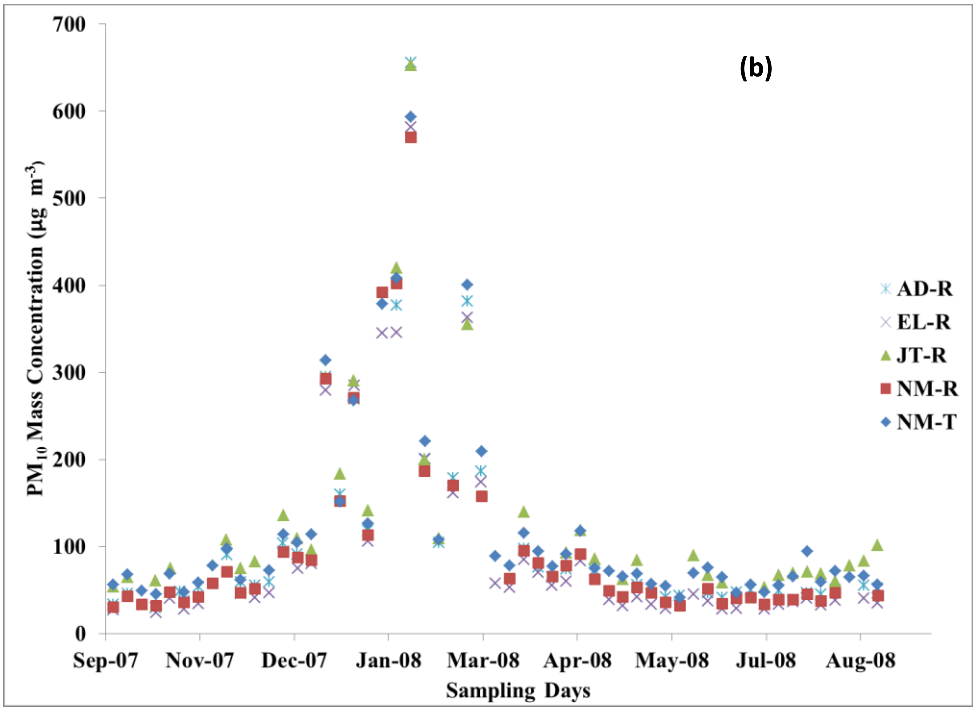


Figure 4.1 Time series plots of (a) $PM_{2.5}$ and (b) PM_{10} mass concentrations during study period.

4.1.1 NON-HARMATTAN CONDITIONS, $PM_{2.5}$ AND PM_{10} FRACTIONS

The arithmetic annual mean and standard deviation of $PM_{2.5}$ and PM_{10} mass concentrations and elemental compositions at the five neighbourhood sites are presented in Table 4.2 and Table 4.3 for non-Harmattan period. The highest mean for both $PM_{2.5}$ and PM_{10} mass concentrations during this period were obtained at JT-R site (49 and 82 µg m^{-3}, respectively) which was closely followed by NM-T site (34 and 70 µg m^{-3}, respectively). The results shows that during non-Harmattan conditions, $PM_{2.5}$ and PM_{10} at neighbourhood sites ranged from 22 to 49 µg m^{-3} and 45 to 70 µg m^{-3} respectively. Currently Ghana has no standard limits for $PM_{2.5}$ levels but the PM_{10} levels were just within the EPA-Ghana standard (70 µg m^{-3}). However these levels are considerably higher than the World Health Organization (WHO) Air Quality Guidelines (AQG) of 10 µg $m^{-3}$for $PM_{2.5}$ and 20 µg m^{-3} for PM_{10}. Moreover, in some cases these levels observed are even higher than the WHO Interim Target 1 (IT-1) of 35 µg m^{-3} ($PM_{2.5}$) and 75 µg m^{-3}(PM_{10}). The high average aerosol particles values denoted a severe urban air pollutant problem in these neighbourhoods. However, the measured concentrations in this study are consistent with other studies in sub-Saharan African, such as PM_{10} concentrations of 40-100 µg m^{-3} at urban site of Addis Ababa, and $PM_{2.5}$ and PM_{10} concentrations of 86 µg m^{-3} and 97 µg m^{-3}, respectively, in South Africa (Engelbrecht *et al.*, 2001; Etyemezian *et al.*, 2005). These annual mean levels are also comparable to or slightly less than concentrations in large cities in South and East Asia and in the Eastern

Mediterranean, but much higher than those in Latin America and high-income countries (Cohen *et al*., 2004; Dionisio *et al*., 2010).

Table 4.2 Average concentration of total $PM_{2.5}$ mass (μg m^{-3}) and its elemental components (ng m^{-3}) at five monitoring sites during the non-Harmattan months.

Species	**AD-R (*n* =36)**		**EL-R (*n* = 37)**		**JT-R (*n* = 29)**		**NM-R (*n*= 41)**		**NM-T (*n* = 44)**	
	Mass	SD	Mass	SD	Mass	SD	Mass	SD	Mass	SD
Total mass	28	8	22	9	49	12	27	8	34	8
Na	244	216	221	175	456	349	271	246	181	134
Mg	103	87	144	100	166	86	132	87	90	96
Al	532	528	643	656	689	748	569	591	795	604
Si	1190	1356	1430	1597	1554	1882	1258	1457	1702	1447
P	15	7	14	9	18	6	13	7	18	8
S	662	256	639	229	833	270	662	230	662	225
Cl	247	274	145	115	1443	886	359	265	379	220
K	586	229	619	231	1841	410	843	250	930	218
Ca	242	181	247	210	380	276	282	186	451	218
Ti	33	31	49	34	42	46	36	35	54	37
V	1	1	1	1	1	1	1	1	1	1
Cr	2	1	1	1	1	1	1	1	1	1
Mn	7	4	9	4	8	6	6	5	8	5
Fe	365	280	412	334	400	381	361	291	537	304
Cu	5	4	2	2	5	3	5	4	5	5
Zn	37	15	18	18	44	16	28	12	32	10
Br	14	8	22	20	20	12	20	17	17	14
Sr	4	5	3	5	5	3	5	4	3	4
Zr	3	3	2	5	3	2	2	2	2	3
Pb	14	8	11	7	12	7	13	7	15	14

Table 4.3 Average concentration of total PM_{10} mass (µg m^{-3}) and its elemental components (ng m^{-3}) at five monitoring sites during the non-Harmattan months.

Species	**AD-R (*n* = 33)**		**EL-R (*n* = 36)**		**JT-R (*n* = 28)**		**NM-R (*n* = 41)**		**NM-T (*n* = 45)**	
	Mass	SD	Mass	SD	Mass	SD	Mass	SD	Mass	SD
Total mass	56	19	45	19	82	23	51	20	70	21
Na	985	613	570	459	1966	831	687	500	762	526
Mg	287	182	248	201	455	220	248	200	308	196
Al	1654	1248	1834	1330	1720	1478	1679	1340	2591	1496
Si	4137	3260	4283	3290	4310	3793	4002	3316	5736	3454
P	26	10	22	10	30	16	24	11	41	15
S	862	280	695	232	1115	299	750	246	885	252
Cl	2031	930	1161	570	4930	1407	1696	651	2152	753
K	886	334	851	331	2215	515	1111	357	1318	335
Ca	1118	611	911	555	1642	779	1183	685	1920	825
Ti	126	87	129	91	130	101	124	92	203	112
V	2	1	3	1	2	1	2	2	3	2
Cr	3	1	3	1	4	2	3	2	5	2
Mn	20	12	17	13	21	15	17	13	26	14
Fe	1491	773	1463	790	1291	869	1346	848	2034	892
Cu	8	5	2	2	7	4	6	3	9	5
Zn	53	17	25	13	67	24	39	18	54	16
Br	20	18	28	24	23	17	25	28	30	33
Sr	4	4	7	6	6	4	7	5	6	5
Zr	2	2	5	4	5	3	5	4	4	4
Pb	19	18	20	14	16	11	17	12	15	7

The three most abundant PM_{10} crustal species are Si (5736 to 4002 ng m^{-3}), Al (1654 to 2591 ng m^{-3}), and Fe (1291 to 2034 ng m^{-3}). PM_{10} calcium concentrations are low, in the range of 911 to 1920 ng m^{-3} at the four sites. $PM_{2.5}$ crustal species are less than a quarter of the corresponding PM_{10} concentrations. This is consistent with the notion that a majority of crustal material is in the coarse particle size fraction.

The $PM_{2.5}$ and PM_{10} contributions from P, S, Cu, Zn and Pb did not exhibit significant variations between the sites. However, these elements in $PM_{2.5}$ are emitted mainly by anthropogenic sources. JT-R had relatively higher sodium (Na) and chlorine (Cl) concentration. In comparison with the other sites, JT-R is the closest to the ocean; hence it received more particles from sea spray. JT-R is about 0.5 km from the ocean compared to approximately 3 km for AD-R, 4.5 km for NM and 9 km for EL-R.

4.1.2 HARMATTAN CONDITIONS, $PM_{2.5}$ AND PM_{10} FRACTIONS

The data of average concentrations of $PM_{2.5}$ and PM_{10} mass ($\mu g\ m^{-3}$) and their elemental components ($ng\ m^{-3}$) at five monitoring sites during the Harmattan conditions are given in Tables 4.4 and Table 4.5, respectively. During the Harmattan period, which in Accra, Ghana started on 27th December 2007 and lasted till 7th February 2008, the average wind speed was 6.5 $m\ s^{-1}$ (Dionisio *et al.*, 2010). It is interesting to note that both $PM_{2.5}$ and PM_{10} mass concentrations during the Harmattan period were found to be approximately 5 times higher than non-Harmattan period. Aboh *et al*. (2009) found large differences in mass and elemental levels between both the coarse and fine particles fraction during Harmattan as compared to non-Harmattan conditions. They observed similarly as found in this study that mass concentrations increased by more than five times during the Harmattan season.

Table 4.4 Average concentration of total $PM_{2.5}$ mass (μg m^{-3}) and its elemental components (ng m^{-3}) at five monitoring sites during the Harmattan months.

Species	**AD-R (*n* = 10)**		**EL-R (*n* = 9)**		**JT-R (*n* = 10)**		**NM-R (*n* = 10)**		**NM-T (*n* = 11)**	
	Mass	SD	Mass	SD	Mass	SD	Mass	SD	Mass	SD
Total mass	132	104	143	83	149	86	134	86	152	84
Na	97	82	117	50	106	95	84	44	108	62
Mg	1004	685	1345	751	837	620	982	611	1162	653
Al	6338	4303	7902	4071	5649	3796	6217	3706	7257	3718
Si	16447	2793	21367	12231	14802	11058	15711	10450	18480	10979
P	25	11	24	13	32	19	27	4	33	15
S	1142	174	988	192	1251	165	1103	180	1160	197
Cl	528	499	660	603	1393	593	724	489	772	416
K	2698	1501	2799	1216	3891	1225	3125	1532	3271	1369
Ca	2387	2337	3239	2230	2384	1898	2487	1934	3023	1991
Ti	417	359	526	311	365	269	406	285	486	293
V	6	4	8	5	6	4	6	3	7	4
Cr	5	5	7	5	5	4	6	4	7	5
Mn	69	68	85	56	61	50	65	52	77	54
Fe	3727	3266	4736	2873	3301	2466	3686	2577	4320	2624
Cu	10	8	9	4	13	12	11	9	12	6
Zn	70	52	53	48	104	84	61	44	74	47
Br	34	39	64	107	58	33	48	32	37	35
Sr	33	29	22	23	25	14	60	41	34	30
Zr	21	16	15	12	17	9	37	25	23	21
Pb	24	12	24	19	32	19	36	24	26	22

Table 4.5 Average concentration of total PM_{10} mass (µg m^{-3}) and its elemental components (ng m^{-3}) at five monitoring sites during the Harmattan months.

Species	**AD-R (*n* = 11)**		**EL-R (*n* = 10)**		**JT-R (*n* = 10)**		**NM-R (*n* = 10)**		**NM-T (*n* = 11)**	
	Mass	SD	Mass	SD	Mass	SD	Mass	SD	Mass	SD
Total mass	266	160	284	137	281	164	270	146	289	148
Na	273	229	173	136	546	426	126	113	171	134
Mg	1951	931	2271	957	1898	958	1891	847	2008	955
Al	12297	6050	14234	5918	11599	981	12708	5653	13404	5791
Si	33311	18762	37526	17629	31647	18606	33130	16550	34710	17791
P	38	10	35	16	64	26	56	32	65	27
S	1408	156	1198	118	1734	192	1333	166	1433	119
Cl	2093	777	1530	574	4625	1197	2199	597	2275	562
K	3898	1821	4150	1768	5198	1612	4568	2041	4528	1782
Ca	6485	4085	7154	4021	6949	4467	7172	4154	7825	4217
Ti	947	574	1099	577	909	591	991	546	1076	549
V	14	8	18	11	13	8	15	9	15	8
Cr	13	9	16	10	14	10	15	9	17	9
Mn	156	110	170	101	149	108	155	98	168	102
Fe	8733	5406	10121	5552	8119	5389	9333	5403	9769	5172
Cu	21	13	16	10	24	16	24	14	24	11
Zn	100	64	76	64	140	108	107	70	114	64
Br	44	35	51	43	35	27	100	135	48	36
Sr	42	22	25	26	28	24	54	44	28	21
Zr	28	13	15	12	20	19	33	28	18	11
Pb	39	19	32	19	29	17	46	27	34	26

4.2 $PM_{2.5}$ TO PM_{10} RATIOS

Table 4.6 and Table 4.7 presents annual average $PM_{2.5}$ and PM_{10} mass concentrations with standard deviations and their ratios for the five sites during non-Harmattan and Harmattan conditions respectively. The annual average mass concentrations for $PM_{2.5}$ and PM_{10} during non-Harmattan showed a 5-fold increment during Harmattan conditions. However, the ratios of $PM_{2.5}$ to PM_{10} during non-Harmattan and Harmattan conditions showed only marginal variations. The average $PM_{2.5}/PM_{10}$ ratio observed in this study is much lower than those found by other studies. He *et al*. (2001) and Ye *et al*. (2003) reported an average $PM_{2.5}/PM_{10}$ ratio 0.64 and 0.55 for their entire period.

Table 4.6 $PM_{2.5}$ and PM_{10} annual average mass concentration [± SD (standard deviation)] for the five monitoring sites during non-Harmattan conditions.

Urban sites	Mean Annual Concentrations				Ratio
	$PM_{2.5}$ ($\mu g\ m^{-3}$)		PM_{10} ($\mu g\ m^{-3}$)		$PM_{2.5}/PM_{10}$
	Mean	SD	Mean	SD	
AD-R	28	8	56	19	0.50
EL-R	22	9	45	19	0.50
JT-R	49	12	82	23	0.55
NM-R	27	8	51	20	0.54
NM-T	34	8	70	21	0.49

Table 4.7 $PM_{2.5}$ and PM_{10} annual mean mass concentration [± SD (standard deviation)] for the five monitoring sites during Harmattan conditions.

Urban sites	Mean Annual Concentrations				Ratio
	$PM_{2.5}$ (µg m^{-3})		PM_{10} (µg m^{-3})		$PM_{2.5}/PM_{10}$
	Mean	SD	Mean	SD	
AD-R	132	104	266	160	0.50
EL-R	143	83	284	137	0.50
JT-R	149	86	281	162	0.53
NM-R	134	86	270	146	0.50
NM-T	152	84	289	148	0.50

It was noted that during the non-Harmattan season between 49% and 55% of PM_{10} mass was in the fine of $PM_{2.5}$ fraction at different sites. However, 50% to 53% of PM_{10} mass was in fine fraction during the Harmattan season. The average $PM_{2.5}/PM_{10}$ ratio of elemental components at five monitoring sites during the non-Harmattan period is given in Table 4.8. The quantity of mass in $PM_{2.5}$ fraction was less than 40% for crustal elements such as Al, Si, Ca, Ti and Mn. A similar trend was noted for Na and Cl which are principal constituents of sea salt. This trend indicates that these elements were mainly in the form of coarse particles. Other elements such as K, Cu, Zn, Br and Pb had 60% or more of their mass in the fine fraction. These elements are associated with anthropogenic sources such as biomass burning, solid waste burning, motor vehicles emissions and industrial emissions.

Table 4.8 Average $PM_{2.5}/PM_{10}$ ratio of PM elemental components at five monitoring sites during the non-Harmattan period.

Species	AD-R	EL-R	JT-R	NM-R	NM-T
Na	0.25	0.39	0.23	0.39	0.24
Mg	0.36	0.58	0.36	0.53	0.29
Al	0.32	0.35	0.39	0.34	0.31
Si	0.29	0.33	0.36	0.31	0.30
P	0.59	0.66	0.59	0.56	0.43
S	0.77	0.92	0.75	0.83	0.75
Cl	0.12	0.13	0.29	0.21	0.18
K	0.66	0.73	0.83	0.76	0.71
Ca	0.22	0.27	0.23	0.24	0.23
Ti	0.26	0.38	0.33	0.29	0.27
V	0.59	0.35	0.54	0.38	0.33
Cr	0.51	0.39	0.39	0.35	0.29
Mn	0.35	0.56	0.38	0.32	0.32
Fe	0.24	0.28	0.31	0.27	0.26
Cu	0.55	0.79	0.64	0.84	0.55
Zn	0.70	0.70	0.66	0.70	0.59
Br	0.71	0.77	0.88	0.82	0.56
Sr	1.22	0.47	0.84	0.67	0.49
Zr	1.57	0.53	0.67	0.42	0.45
Pb	0.75	0.56	0.74	0.77	0.97

4.3 METEOROLOGICAL INFLUENCES ON THE CONCENTRATION OF PARTICULATE MATTER MASS

4.3.1 INFLUENCE OF METEOROLOGY ON PM MASS

Meteorology plays a very important role in the distribution of aerosol particles. Several studies have shown that particulate matter mass concentrations are influenced by various meteorological parameters such as precipitation, temperature, wind speed and relative humidity (Karar *et al*., 2005; Bhaskar *et al*., 2010). These meteorological variables also affect the emissions of aerosol from ground surface, their residence time in the ambient air and the formation of secondary pollutants. Hence there is a need to understand the physical processes leading to an observed concentration of PM at a given location. Precipitation is one of the reasons for low aerosol particles in the non-Harmattan season as the particles are washed out by rain. Wet deposition by precipitation or wet removal is one of the major mechanisms for removal of aerosols from the atmosphere (Bhaskar *et al.*, 2010). Daily average of temperature, wind speed, cumulative precipitation and relative humidity were obtained from the Ghana Meteorological Authority and are summarized in Table 2.1 of Chapter 2.

The daily average wind speed ranged from 3 to 12 m s^{-1} while daily average temperature ranged from 23 °C to 30 °C during the study period. The daily mean relative humidity also ranged from 18% to 92 %, with the lower value usually recorded in the Harmattan season. The cumulative precipitation during the study period varied from zero during the Harmattan season to 62.8 mm during the non-Harmattan season.

The correlations of the different meteorological parameters with $PM_{2.5}$ mass concentrations measured during the period of investigation were examined.

4.3.1.1 RELATIONSHIP WITH PRECIPITATION

The $PM_{2.5}$ mass concentration was consistently low during precipitation occurrences (Figure 4.2). The best line obtained to explain the relationship between $PM_{2.5}$ mass concentrations and rainfall was linear. $PM_{2.5}$ mass concentrations and rainfall were negatively correlated but it is not significant. It was found that rainfall explained less than10% of the variance in $PM_{2.5}$ concentration for the overall period of monitoring time.

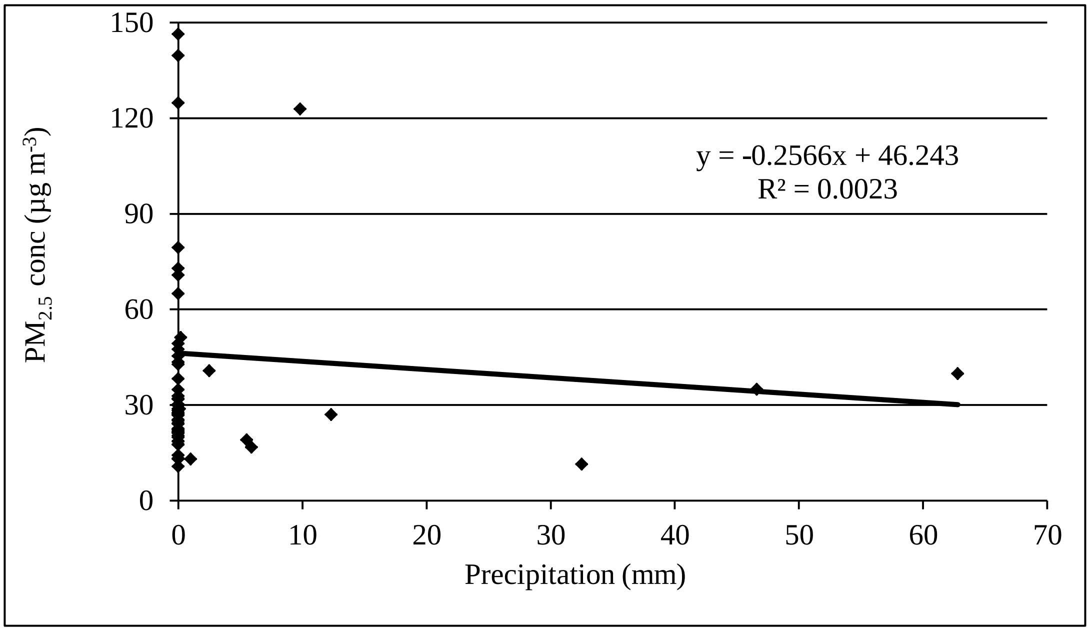


Figure 4.2 Relationship between $PM_{2.5}$ and total daily cumulative precipitation.

4.3.1.2 RELATIONSHIP WITH TEMPERATURE

The variation of $PM_{2.5}$ mass concentration with temperature is shown in Figure 4.3. It was observed that concentration was high at higher temperature. $PM_{2.5}$ mass concentration was positively correlated with temperature but this correlation is weak. It means that $PM_{2.5}$ increases or reduces as temp increases or reduces. The influence of temperature over PM is attributed to the fact that more favourable atmospheric dispersion conditions occur under a warm air than cold air mass (Owoade *et al*., 2012).

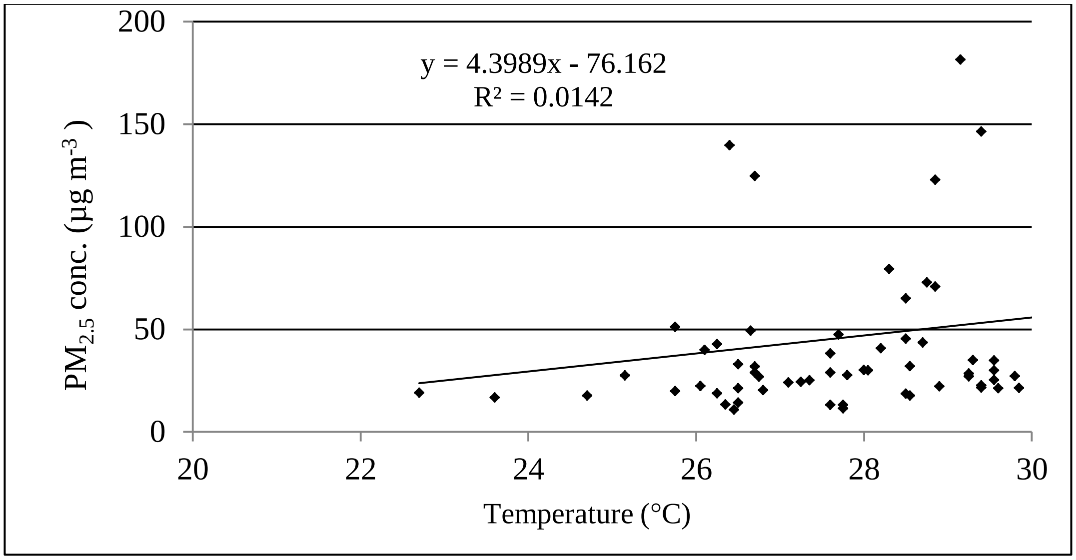


Figure 4.3 Relationship between $PM_{2.5}$ and total daily average temperature.

4.3.1.3 RELATIONSHIP WITH WIND SPEED

Wind speed had a negative relationship with $PM_{2.5}$ (Figure 4.4). Karar and Gupta (2006) suggest that such an inverse relationship between $PM_{2.5}$ and wind speed indicates a dominance of local sources. Wind speed plays a leading role in cleansing the atmosphere of PM. Strong winds disperse particulate matter out of the atmosphere, whereas low winds allow particles levels to increase.

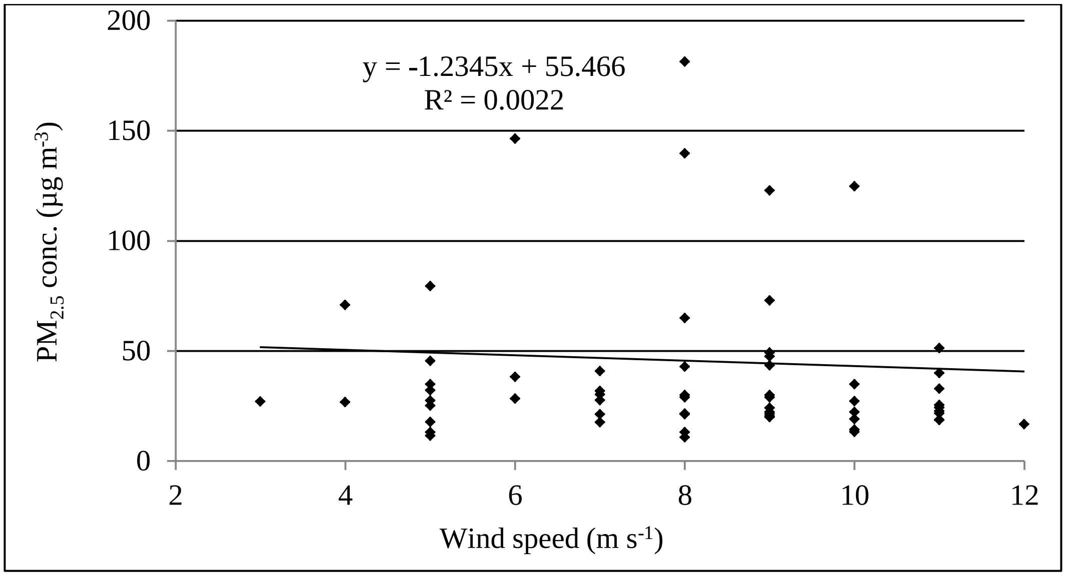


Figure 4.4 Relationship between $PM_{2.5}$ mass concentrations and daily wind speed.

4.3.1.4 RELATIONSHIP WITH RELATIVE HUMIDITY

Relative humidity showed an inverse relationship with $PM_{2.5}$ mass concentration. Relative humidity factor influences particles to gather mass and settle down on the ground rather than getting airborne. Hence, relative humidity largely removes pollutants from the atmosphere.

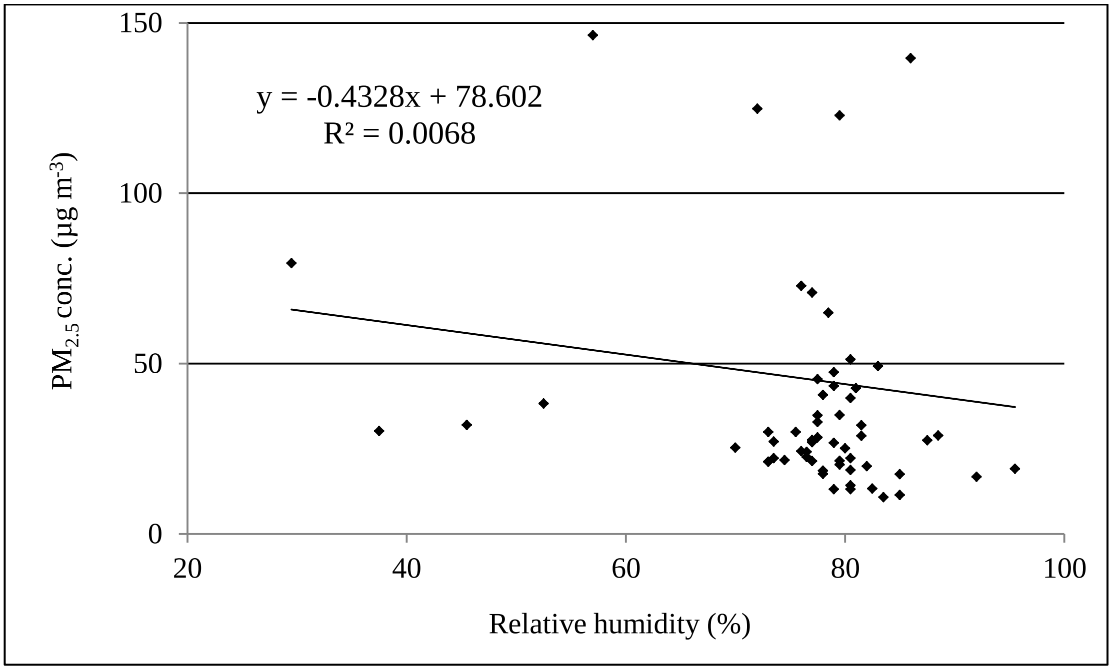


Figure 4.5 Relationship between $PM_{2.5}$ mass concentrations and relative humidity.

4.4 ENRICHMENT FACTOR ANALYSIS

Enrichment factor (EF) calculations were employed as a tool for interpretation of tracer selection in each source category especially for trace element contributions. Enrichment factor analysis was used to provide an initial indication on the extent of the anthropogenic contributions to the measured elemental composition of $PM_{2.5}$ and PM_{10} at the five urban sites in Accra. Average concentrations of all elements detected in PM samples were used for the calculations of EFs. By convention, elements with EF < 10 is usually taken as being from a crustal or natural source, while EF > 10 is usually considered to indicate that a significant fraction of the element is contributed from non-crustal or anthropogenic source (Braga *et al*., 2005; Chimidza *et al*., 2001; Kothai *et al*., 2011). EF values >100 and 1000 could be seen as highly and heavily enriched respectively.

Enrichment factors were calculated according to equation 3.5 and aluminium was used as the reference element (see section 3.6 of Chapter 3.0). Results of enrichment factor analysis for each of the five sampling sites (AD-R, EL-R, JT-R, NM-R and NM-T) $PM_{2.5}$ elemental concentrations are presented in Table 4.9.

Table 4.9: Calculated enrichment factor (EFs) (using Al as reference) for all analysed elements in $PM_{2.5}$. EFs were calculated using the average concentration of all samples from each site (see equation 3.5). Crustal concentrations were taken from Taylor and McLennan (1985).

	AD-R	**EL-R**	**JT-R**	**NM-R**	**NM-T**
Na	1.9	1.4	2.7	1.9	0.9
Mg	0.8	0.9	0.9	0.9	0.4
Al	1	1	1	1	1
Si	0.6	0.6	0.6	0.6	0.6
P	2.0	1.5	1.8	1.6	1.5
S	331.5	264.6	322.2	291.1	221.6
Cl	223.2	108.8	1009.2	303.8	229.6
K	3.0	2.6	7.3	4.0	3.2
Ca	0.6	0.5	0.7	0.7	0.8
Ti	0.5	0.6	0.5	0.5	0.6
V	0.8	0.5	0.5	0.5	0.4
Cr	1.3	0.8	0.9	0.8	0.8
Mn	0.5	0.6	0.5	0.4	0.4
Fe	0.5	0.5	0.4	0.4	0.5
Cu	5.6	1.9	4.2	5.9	4.0
Zn	33.8	13.3	31.1	23.6	19.6
Br	302.8	373.9	321.5	400.2	236.8
Sr	0.6	0.4	0.5	0.6	0.2
Zr	1.0	0.6	0.7	0.5	0.4
Pb	23.0	15.0	14.8	20.3	15.8

Figure 4.6 shows the averages of the EFs of elements in $PM_{2.5}$ for all sampling sites in Accra. In the category of EF<10 for $PM_{2.5}$ are Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Sr and Zr at all sampling sites. The EF results displayed almost similar values at each sampling site. These elements are typical of crustal origin and they were attributable predominantly to crustal or soil dust. Although these elements were mainly

from natural sources, the influences of anthropogenic sources cannot be ignored. K is emitted from wood and biomass burning; Ca, a component of some detergents used in engines lubricating oils, is emitted from motor vehicles; Sr is emitted from vehicle brake wear; Fe is emitted as from wear and tear of brake pads and other automobile parts (Schauer, 2006). In the $PM_{2.5}$ fraction Mn and Cu are also attributed to brake wear and vehicle tailpipe emission (Cadle *et al*., 1999; Garg *et al*., 2000).

Among the various sites NM-R represented higher EFs value for Cu, i.e., 5.9, while the lowest was shown by EL-R with value of 1.9. In the group of EF>10 but less than 100 were the elements Zn and Pb at all sampling sites. It indicated that Pb and Zn were moderately enriched. Pb and Zn are traditional tracers of vehicle emissions and their EF value suggested a large contribution from vehicle emission.

Besides fuel and motor oil combustion, brake wear, industry emission, long-range transported dust and the re-suspended soil containing the deposition of those from previously emitted leaded gasoline could be the important sources of Pb (Miguel *et al*., 1997; Yele *et al*., 2006). It has been reported (Miguel *et al*., 1997) that Zn compounds have been used extensively as antioxidants (e.g., zinc carboxylate complexes and zinc sulphonates) and as detergent or dispersant improvers for lubricating oils.

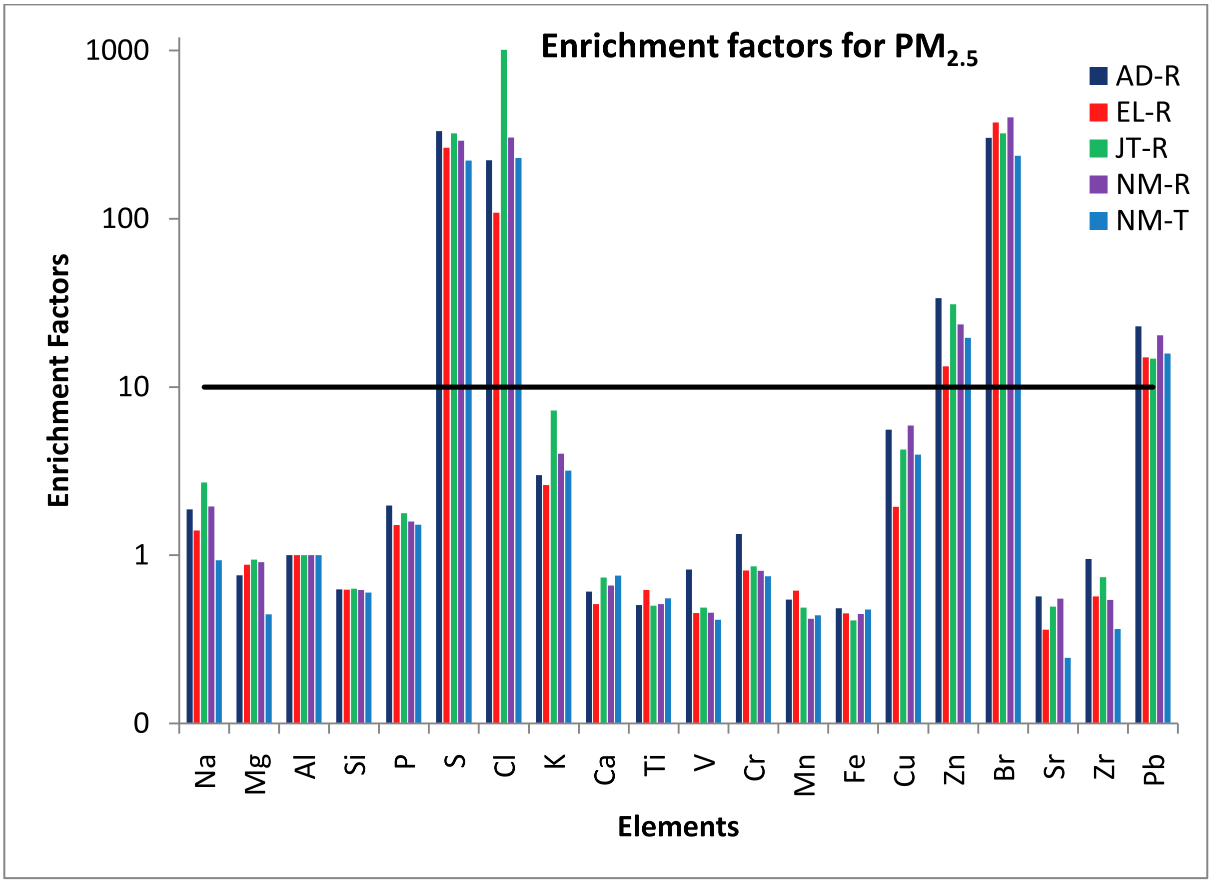


Figure 4.6 Enrichment factors for $PM_{2.5}$ chemical components for all sites in Accra.

Mechanical abrasion of vehicles, metal processing industrial activities, and the wear and tear of vulcanized vehicle tires can contribute significantly to Zn of urban dust (Ellis and Revitt, 1982; Jiries *et al*., 2001; Li et al, 2001). Elements with EF>100 were S, Cl and Br. These elements are highly enriched with emission sources likely from traffic and refuse burning, respectively. The S concentration is important because it includes the sulphates and most toxic trace metals exist in the atmosphere in the form of sulphates and/or nitrates. In the group with EF>1000 was only the element Cl at the

JT-R site. The heavily enriched Cl at the JT-R is not surprising since the JT-R site was the closest to the Atlantic Ocean. Cl is mainly derived from sea salt.

The average EFs for PM_{10} of the various elements at all sampling locations are shown in Table 4.10. In the PM_{10} fraction, Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Sr, Zr, Pb (all sites) and Zn (EL-R and NM-T) all had their enrichment factors below 10 (Figure 4.7). For these elements, their predominant source could be classified as soil dust (or other crustal matter, such as road dust).

Table 4.10: Calculated enrichment factor (EFs) (using Al as reference) for all analysed elements in PM_{10}. EFs were calculated using the average concentration of all samples from each site (see equation 3.5). Crustal concentrations were taken from Taylor and McLennan (1985).

	AD-R	**EL-R**	**JT-R**	**NM-R**	**NM-T**
Na	2.4	1.3	4.7	1.7	1.2
Mg	0.7	0.5	1.0	0.6	0.5
Al	1	1	1	1	1
Si	0.7	0.7	0.7	0.7	0.6
P	1.1	0.8	1.2	1.0	1.1
S	138.8	100.9	172.6	119.0	91.0
Cl	591.4	304.9	1380.8	486.6	400.3
K	1.5	1.3	3.5	1.8	1.4
Ca	0.9	0.7	1.3	0.9	1.0
Ti	0.6	0.6	0.6	0.6	0.6
V	0.4	0.5	0.4	0.4	0.4
Cr	0.8	0.7	0.9	0.8	0.8
Mn	0.5	0.4	0.5	0.4	0.4
Fe	0.6	0.6	0.5	0.6	0.6
Cu	3.3	0.9	2.7	2.4	2.2
Zn	15.5	6.6	18.9	11.4	10.1
Br	137.6	171.4	146.8	165.6	128.8
Sr	0.2	0.3	0.2	0.3	0.2
Zr	0.2	0.4	0.4	0.4	0.2
Pb	9.8	9.4	8.0	8.9	5.0

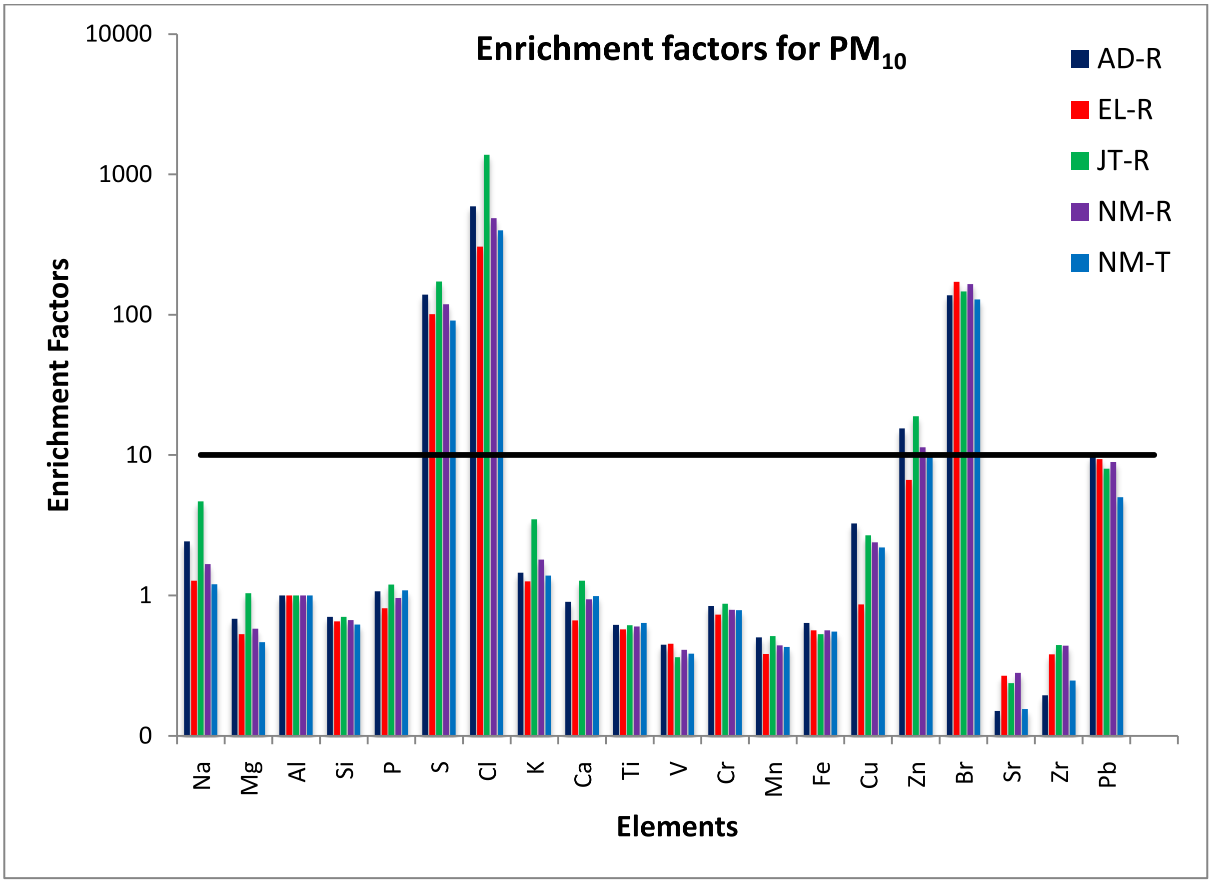


Figure 4.7 Enrichment factors for PM$_{10}$ chemical components for all sites in Accra.

In the group of moderately enriched elements with EF>10 but less than 100 were Zn (AD-R, JT-R and NM-R) and S (EL-R). This gives an indication that these elements have contributions from anthropogenic sources. Zn is emitted from vehicle tire wear, non-ferrous industry emissions as well refuse burning (Schauer *et al*., 1996; Bullock *et al*., 2008). Elements in the highly enriched group with EF>100 are S (AD-R, JT-R and NM-R), and Cl (AD-R, EL-R, NM-R and NM-T) and Br (AD-R, EL-R, JT-R, NM-R and NMN-T). In the category of heavily enriched element with EF>1000 is Cl in JT-R, which is similar to the PM$_{2.5}$ results.

4.5 SOURCE IDENTIFICATION AND APPORTIONMENT USING POSITIVE MATRIX FACTORIZATION

Source identification and apportionment of PM mass by PMF was performed using the EPAPMF version 3.0 modelling software in accordance with the User's Guide (USEPA, 2008). Signal-to-noise ratio (S/N) of an individual species can have a significant influence on a receptor model. S/N ratio shows whether the variability in measured concentrations is real or within the noise of the data. Hence, Paatero and Hopke (2003) strongly recommend that species with S/N ratio <0.2 be categorized as a "Bad" species that should be excluded from the analysis, $0.2 < S/N < 2.0$ as "Weak" that can be down-weighted (i.e., its uncertainty increased), and $S/N > 2.0$ as "Strong" species that should be included in the analysis. The S/N ratios for the measured species at each of the 5 sites are presented in Table 4.11 for $PM_{2.5}$ and Table 4.12 for PM_{10} respectively.

Concentrations of species below MDL were replaced by half of the MDL, and the corresponding uncertainty was set as 5/6 of MDL. Missing concentration was replaced by the geometric mean of the measured concentration, and its uncertainty was set to 4 times this geometric mean value.

The measured PM mass concentrations were included as an independent variable in the PMF model analysis so as to obtain the mass apportionment directly without the usual multilinear regression. The PM mass values were downweighted in the model analysis by setting the uncertainties to 4 times the mass concentrations.

Table 4.11 S/N values for the $PM_{2.5}$ data at AD-R, EL-R, JT-R, NM-R and NM-T

Species	AD-R	EL-R	JT-R	NM-R	NM-T
Na	2.67	2.30	4.20	3.00	1.77
Mg	2.56	3.16	3.20	2.82	2.58
Al	16.68	16.95	17.05	16.81	17.03
Si	18.96	18.97	18.98	18.97	18.98
P	4.61	4.58	5.15	4.05	5.35
S	18.97	18.97	18.98	18.97	18.97
Cl	17.48	17.36	17.52	17.49	17.49
K	18.99	18.99	19.00	19.00	19.00
Ca	18.98	18.98	18.99	18.98	18.99
Ti	18.12	18.47	18.51	18.25	18.56
V	2.36	1.06	1.15	0.91	1.06
Cr	2.03	1.39	1.75	1.36	1.70
Mn	9.14	10.80	10.68	8.59	10.37
Fe	18.99	18.99	18.99	18.99	18.99
Cu	6.70	3.28	5.80	7.07	7.38
Zn	17.66	16.03	18.00	16.83	17.19
Br	13.08	16.33	15.20	15.95	14.91
Sr	5.62	5.61	5.10	5.04	4.36
Zr	3.91	5.57	3.53	2.85	3.32
Pb	6.89	5.50	5.74	6.43	8.44

The initial results were then normalized by the apportionment of PM mass concentrations so that the quantitative source contributions for each source were obtained. The number of species (including particulate mass concentrations) and the number of valid samples used in the PMF analysis at the five sites are shown in Table 4.13. The choice of valid sample depends on the quality of available species measured.

Table 4.12 S/N values for the PM_{10} data at AD-R, EL-R, JT-R, NM-R and NM-T

Species	AD-R	EL-R	JT-R	NM-R	NM-T
Na	6.03	4.92	6.87	5.32	5.55
Mg	5.03	4.87	6.00	4.87	5.23
Al	17.40	17.42	17.42	17.41	17.46
Si	19.00	19.00	19.00	19.00	19.00
P	7.60	6.56	9.11	7.16	10.98
S	18.98	18.97	18.99	18.98	18.98
Cl	17.52	17.52	17.52	17.52	17.52
K	19.00	19.00	19.00	19.00	19.00
Ca	19.00	19.00	19.00	19.00	19.00
Ti	18.92	18.92	18.93	18.92	18.96
V	2.96	3.25	2.56	3.10	3.95
Cr	4.00	3.87	4.40	4.08	5.94
Mn	16.11	15.59	16.54	15.78	17.10
Fe	19.00	19.00	19.00	19.00	19.00
Cu	9.70	3.21	8.68	7.43	10.27
Zn	18.27	16.54	18.55	17.84	18.29
Br	16.06	17.25	16.24	17.27	17.70
Sr	5.03	7.83	5.87	7.19	6.45
Zr	2.83	5.13	4.89	5.52	5.00
Pb	10.24	9.62	7.97	8.56	6.89

Table 4.13 Dataset of number of valid samples and species used in the PMF model.

Sites	AD-R		EL-R		JT-R		NM-R		NM-T	
PM size fraction	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Number of valid samples	36	33	37	36	29	28	41	41	44	45
Number of species	21	21	21	21	21	21	21	21	21	21

4.5.1 NON-HARMATTAN SEASON

PMF model applied to the non-Harmattan months' data for both $PM_{2.5}$ and PM_{10} identified six potential factors (sources) for AD-R and five potential factors (sources) for EL-R, JT-R, NM-R and NM-T. Although many factors were similar, their importance varied based on the differing composition among sites. The potential sources were found based on several methods including the closeness of Q values to the theoretical Q value, FPEAK value of 0.1, comparison of the measured total mass of the sample to the total mass predicted by the model, the observation that the scaled residuals for each element were fairly normally distributed between ± 3 standard deviations (Amato, 2009), and by checking the results to see whether they are realistic for the area around the sites.

4.5.1.1 FINE PARTICULATE MATTER

The reconstructed $PM_{2.5}$ mass concentrations were estimated from the sum of the contributions of the PMF resolved sources. The scatter plots to compare the reconstructed $PM_{2.5}$ mass concentrations using predicted results from the model and the measured $PM_{2.5}$ mass concentrations are shown in Figure 4.8 to Figure 4.12. The high values of r^2 (all greater than 0.73) indicate that resolved sources effectively accounted for most of the variation in $PM_{2.5}$ mass concentrations at the five sites. The performance of PMF model was also evaluated using Table A-1 to Table A-5 in Appendix A by comparing the calculated values with measured concentrations for each species used in the model. The largest uncertainties such as (22.7% for Mg, 18.9% for V, 23% for Cr, 19.7% for Sr, 18% for Zr in AD-R), (20.02% for Cr, 28.82% for Cu, 30.34% for Zn, 27.29 for Sr, 44.52% for Zr in EL-R), (19.77% for Na, 20.76% for Mg, 20.57% for Cr, 22.65% for Sr, 29.77% for Zr in NM-R), and (26.19% for Sr, 19.57% for Zr in NM-T) together with low correlation coefficients, can be attributed to data quality, since species with missing values were replaced by their median values and associated uncertainties assigned to be four times the mean values. However, in general, good correlation coefficient was obtained between measured and calculated concentrations with significant correlation coefficients. Overall, the performance of PMF on the source apportionment of $PM_{2.5}$ at the five study sites was found to be satisfactory. The average source contributions are summarized in Table 4.14.

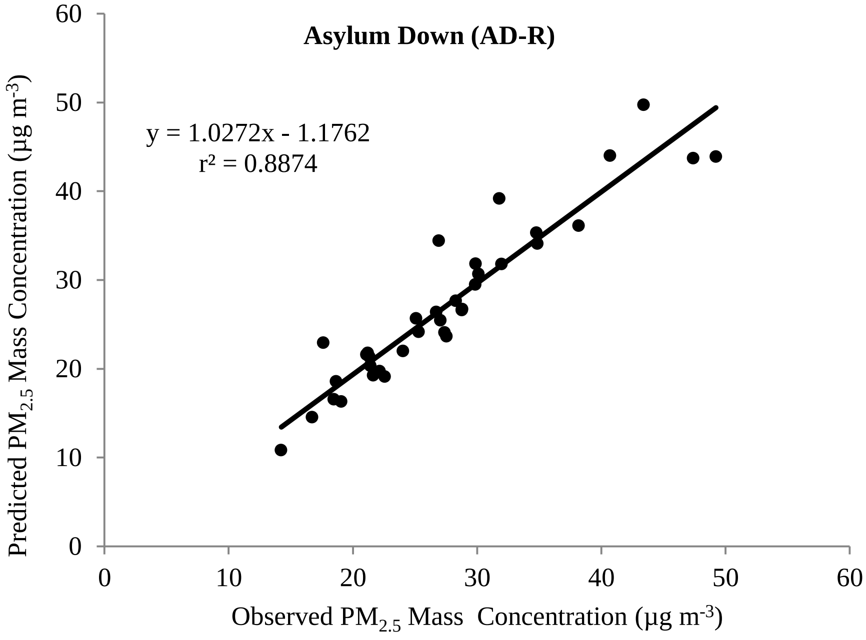


Figure 4.8 Scatter plots of predicted $PM_{2.5}$ mass concentrations and measured $PM_{2.5}$ mass concentrations at AD-R.

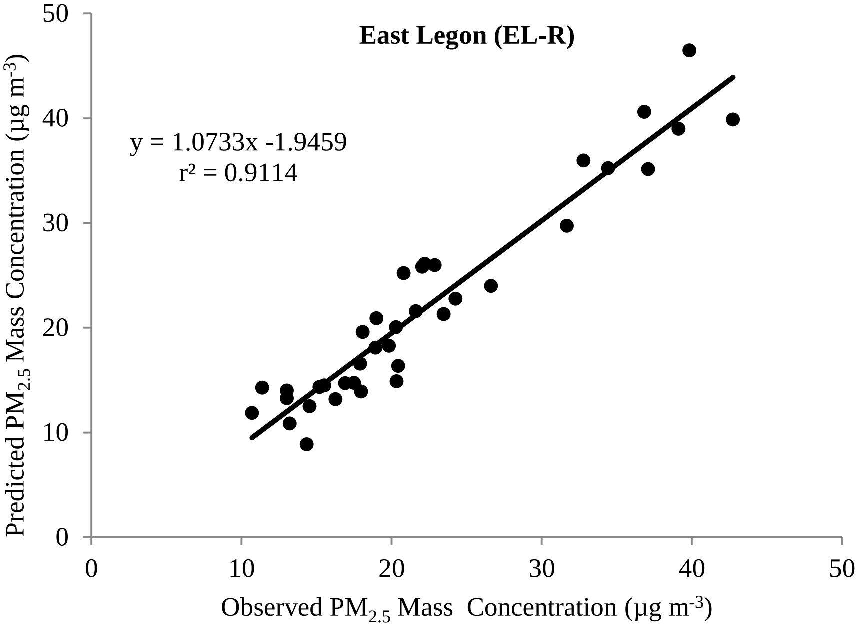


Figure 4.9 Scatter plots of predicted $PM_{2.5}$ mass concentrations and measured $PM_{2.5}$ mass concentrations at EL-R.

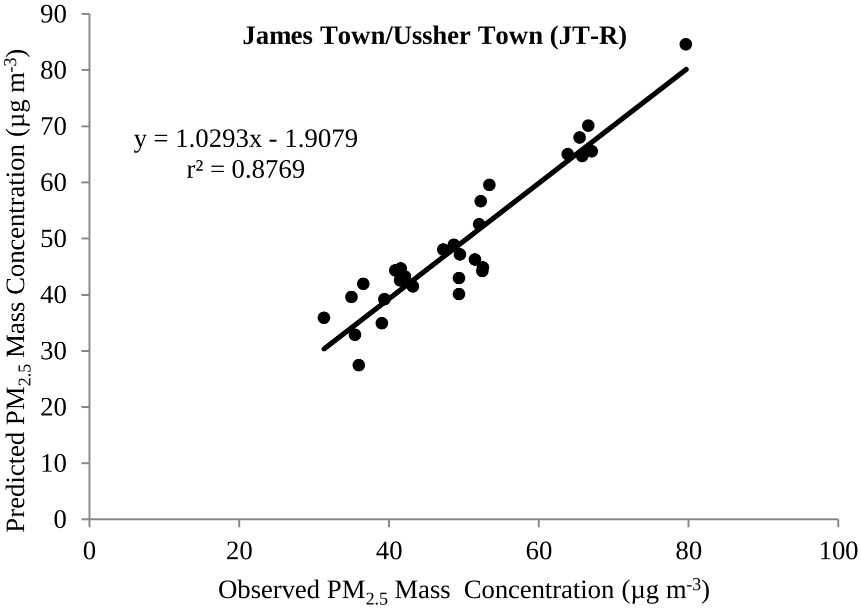


Figure 4.10 Scatter plots of predicted $PM_{2.5}$ mass concentrations and measured $PM_{2.5}$ mass concentrations at JT-R.

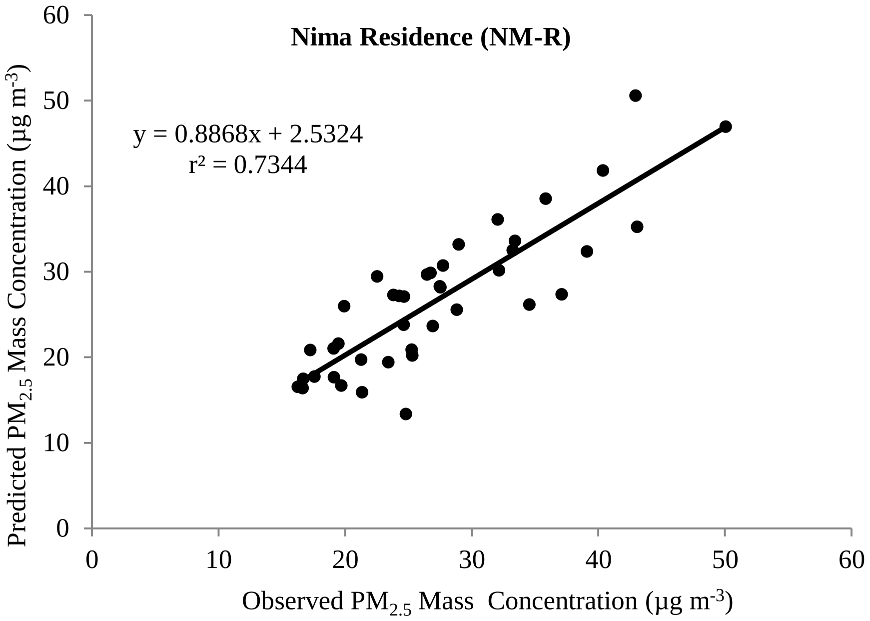


Figure 4.11 Scatter plots of predicted $PM_{2.5}$ mass concentrations and measured $PM_{2.5}$ mass concentrations at NM-R.

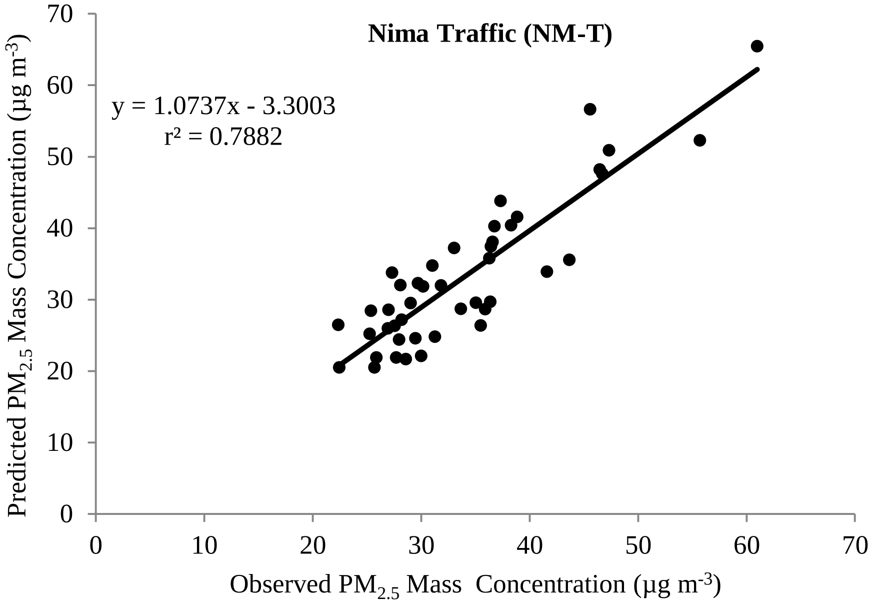


Figure 4.12 Scatter plots of predicted $PM_{2.5}$ mass concentrations and measured $PM_{2.5}$ mass concentrations at NM-T.

Table 4.14 Average contributions of identified sources to PM$_{2.5}$ concentrations.

	AD-R	EL-R	JT-R	NM-R	NM-T
Sea Salt	3.87% (1.05 µg m^{-3})	11.45% (2.51 µg m^{-3})	18.86% (9.21 µg m^{-3})	3.13% (0.84 µg m^{-3})	11.62% (3.86 µg m^{-3})
Biomass burning	18.85% (5.14 µg m^{-3})	38.76% (8.50 µg m^{-3})	29.41% (14.36 µg m^{-3})	41.89% (11.22 µg m^{-3})	37.68% (12.52 µg m^{-3})
Solid waste burning	11.98% (3.27 µg m^{-3})	5.38% (1.18 µg m^{-3})	21.49% (10.50 µg m^{-3})	13.23% (3.54 µg m^{-3})	0.75% (0.25 µg m^{-3})
Soil Dust	23.18% (6.33 µg m^{-3})	44.12% (9.67 µg m^{-3})	15.25% (7.45 µg m^{-3})	28.94% (7.75 µg m^{-3})	34.73% (11.54 µg m^{-3})
Re-suspended dust	31.26% (8.53 µg m^{-3})	0.29% (0.06 µg m^{-3})	15.01% (7.33 µg m^{-3})		
Traffic/Industry	10.86% (2.96 µg m^{-3})			12.81% (3.43 µg m^{-3})	15.22% (5.06 µg m^{-3})

Source 1: A source with high loading mass fractions for sodium (Na), chlorine (Cl) and Sulphur (S) was identified by PMF model at all five sites with the highest contribution at JT-R. The source profiles are shown in Figure 4.13 and the source contributions shown in Figure 4.14. Source profile with dominant Na and Cl as identified in various source apportionment studies conducted in coastal areas was classified as sea salt (Wu *et al*., 2007; Guo *et al*., 2009). Sea salt aerosols are also sources of sulphur (Watson *et al*., 2004). The geographical location of the Accra along the coast of the Atlantic Ocean makes the area susceptible to large-scale influence of sea salt aerosols. The distances of the monitoring sites to the ocean coast were: JT-R 0.5 km, AD-R 3 km, NM 4.5 km, and EL-R 9 km. Thus, source 1 was classified as "sea salt".

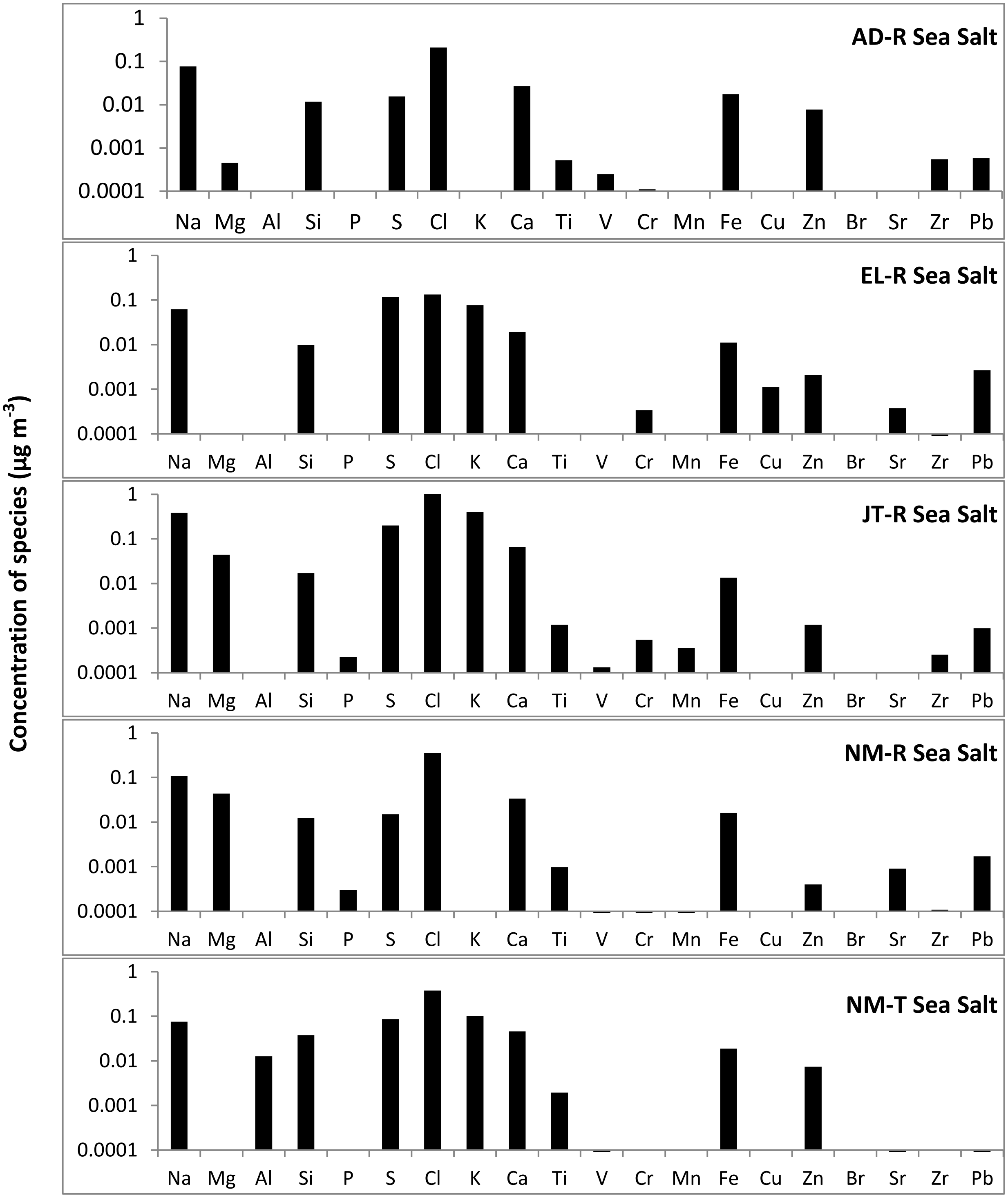


Figure 4.13 $PM_{2.5}$ source profiles for sea salt factors.

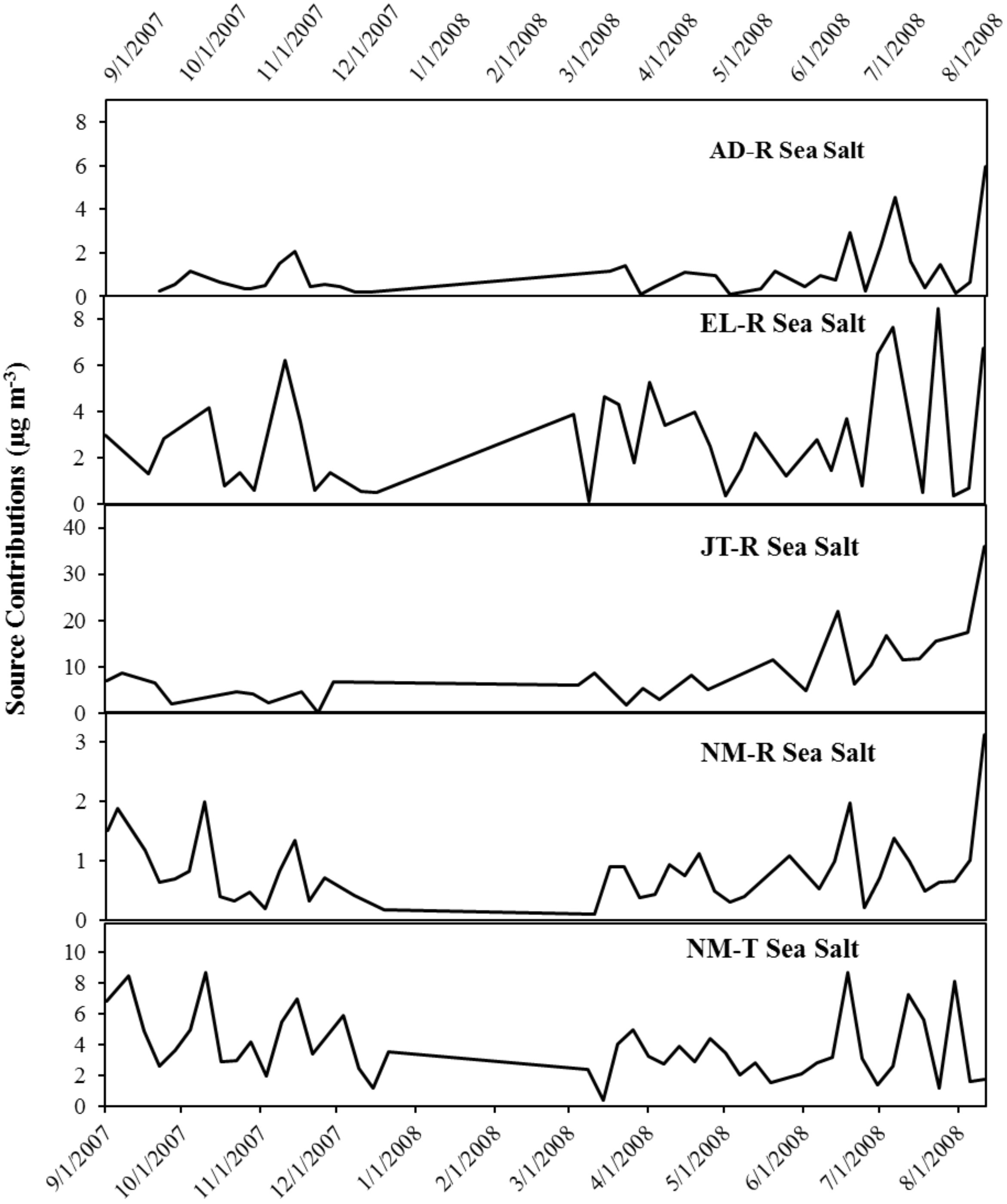


Figure 4.14 Time series of $PM_{2.5}$ source contributions for sea salt factors.

The sea salt contributions to $PM_{2.5}$ were 3.9, 11.5, 18.9, 3.1 and 11.6% at AD-R, EL-R, JT-R, NM-R, and NM-T, respectively. Present in this source are 87, 93, 97, 50 and 50% of total Cl and 36, 34, 91, 100, 100% of total Na at AD-R, EL-R, JT-R, NM-R, and NM-T, respectively. Time series plot shows higher concentrations in November and August. The highest contribution of the source occurred in August. In order to understand the origins of the air masses arriving in Accra on 17 August 2008 (the day with the highest contribution of sea salt), five-day backward air masses trajectories were calculated using the NOAA HYSPLIT model. These trajectories were computed at several altitudes (500, 1500 and 3000 m a.g.l.). Figure 4.15 reveals that air masses reached Accra from the Atlantic Ocean. This shows that probably the sea salt influence detected in Accra is due to the transport of marine aerosols from the ocean during the dry season.

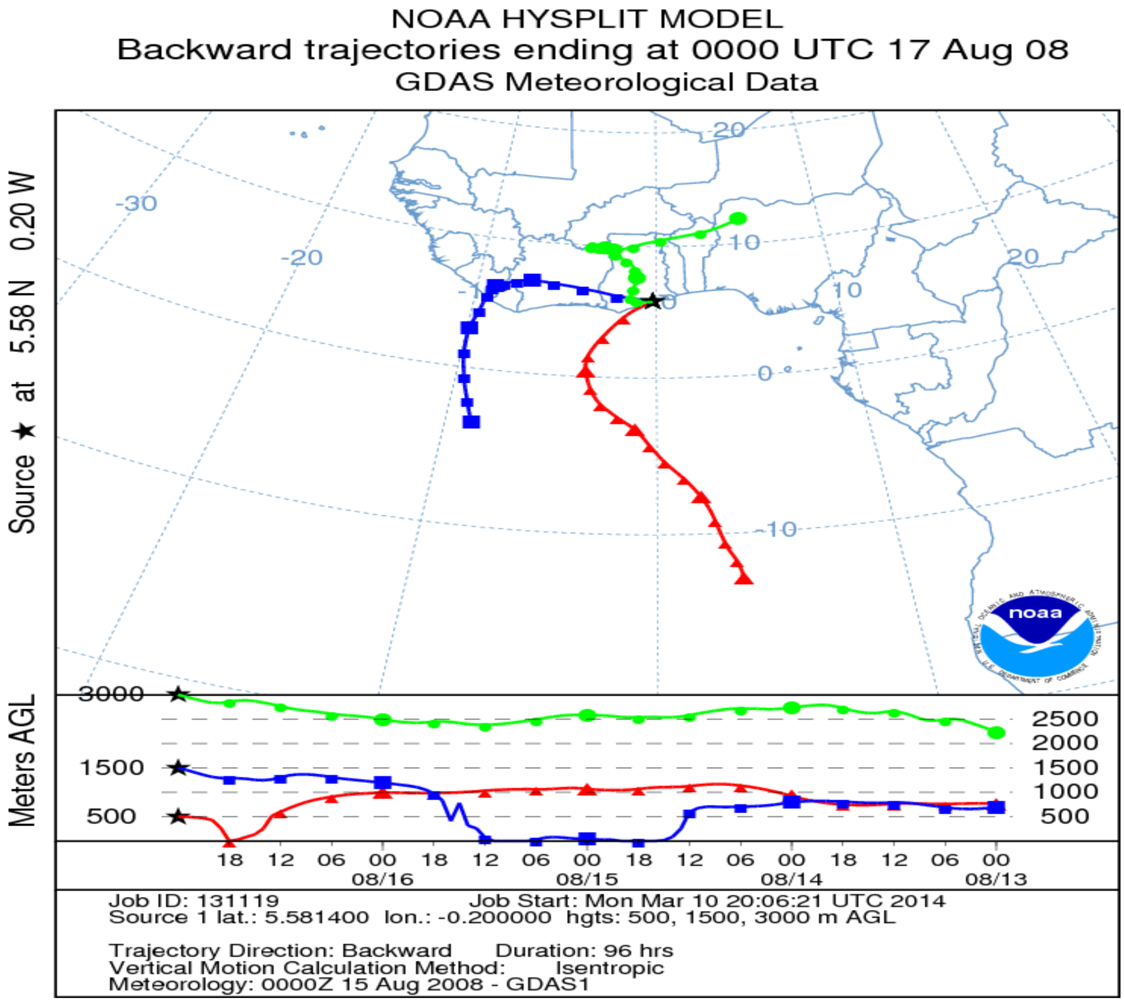


Figure 4.15 Five-day HYSPLIT backward trajectories of air masses reaching Accra on 17 August 2008.

Source 2: The second source with high loading for potassium (K), sulphur (S) and phosphorus (P) was identified at all sites. The source profiles are shown in Figure 4.16 and the time series of contributions are presented in Figure 4.17. It is well known that K is a unique tracer of a biomass burning source (Song *et al.*, 2006). The source contributions to $PM_{2.5}$ mass were about 19, 39, 29, 42 and 38% at AD-R, EL-R, JT-R, NM-R, and NM-T, respectively. However in absolute terms, biomass combustion contributed more particle pollution in James Town/Ussher Town and Nima, where the density of households who use biomass fuels is significantly higher, than in Asylum Down and East Legon (Zhou *et al*., 2013). Therefore, biomass burning accounted for 14.4 µg m^{-3} of $PM_{2.5}$ mass at JT-R, 11.2 µg m^{-3} at NM-R and 12.5 µg m^{-3} at NM-T as compared to 5.14 µg m^{-3} at AD-R and 8.5 µg m^{-3} at EL-R (Table 4.14).

James Town/Ussher Town and Nima are urban slums where many residents use charcoal and especially wood for cooking and heating in their homes. Others use these biomass fuels for small-commercial cooking within the neighbourhoods. For example in James Town/Ussher Town, fish smoking and goat roasting are done by burning wood or old rubber tires (Obiri-Danso *et al*., 2008, Dionisio *et al*., 2010, Adam *et al*., 2013). Trash/wood/grass burning is common in many places. Biomass burning is a major component of $PM_{2.5}$ in Accra. The relatively high source contributions (Figure 4.17) in August and December may be due to the usual bushfires that occur during the dry season.

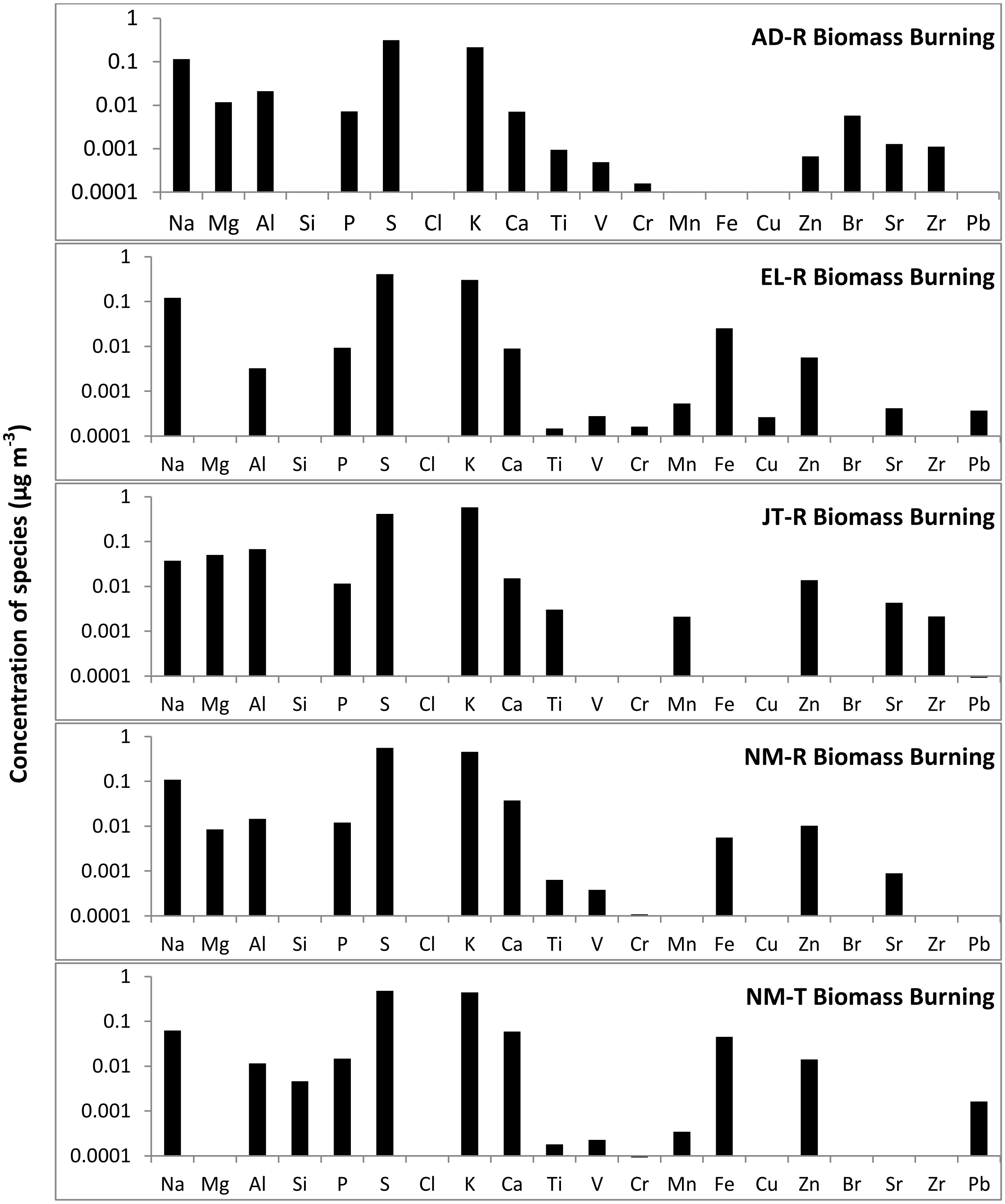


Figure 4.16 PM$_{2.5}$ source profiles for biomass factors.

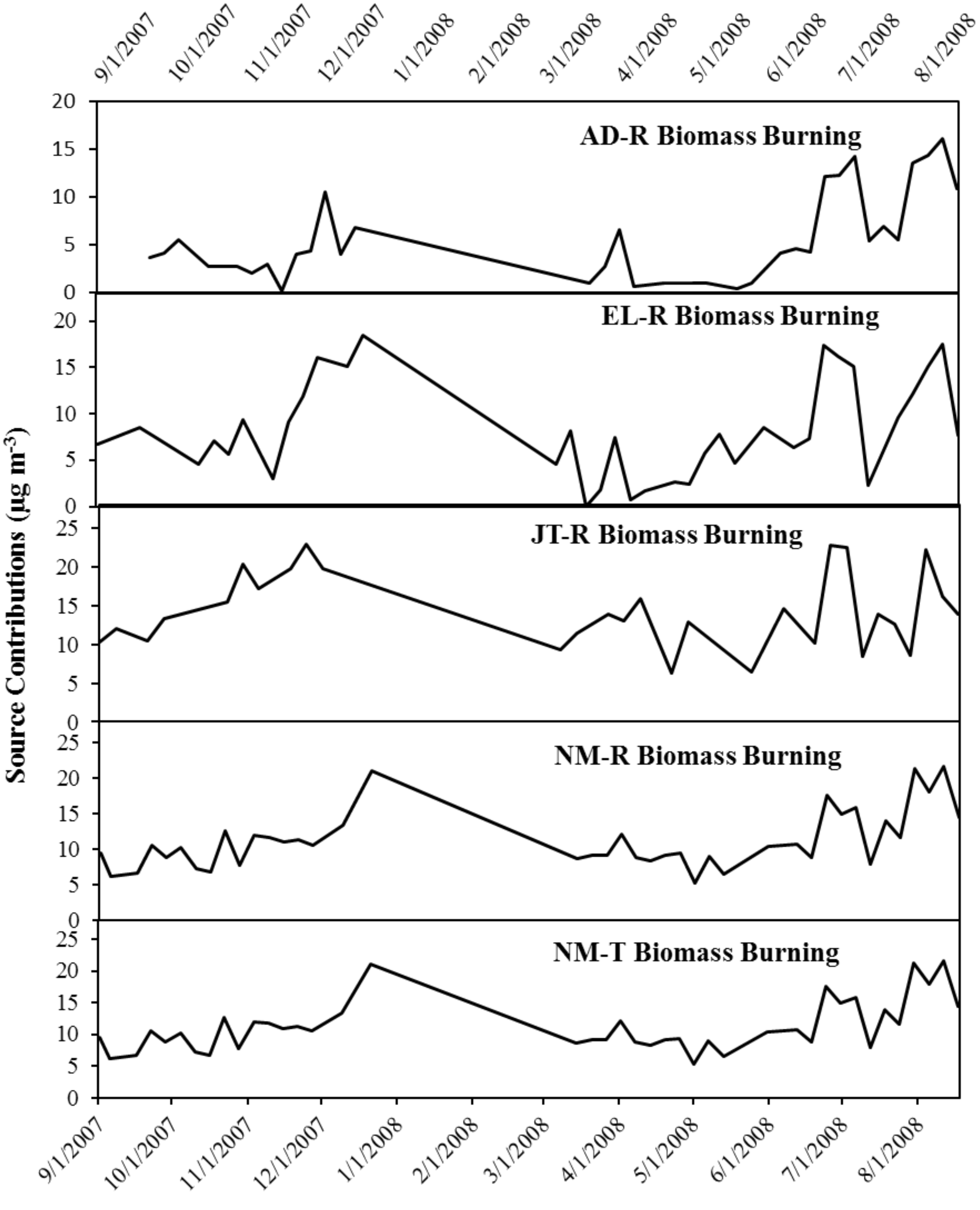


Figure 4.17 Time series of $PM_{2.5}$ source contributions for biomass burning factors.

Source 3: A source with large contributions from bromine (Br) and lead (Pb) was identified by PMF model at all five sites. Minor amounts of other crustal elements were also observed. The third source was attributed to solid waste burning based on the high loadings of Br with Pb. The source profiles and source contributions are shown in Figure 4.18 and Figure 4.19, respectively. The source contributions do not show seasonal variations.

Pb and Br have been linked to incineration and/or traffic in several studies. Solid waste burning is characterized by Br (Vehlow *et al*., 2003). Br is used as the building block for some of the most effective flame retarding agents available to the plastics industry today. Moreover, burning of waste electrical and electronic equipment (WEEE) plastic have been found result in the formation of toxic brominated by-product in most combustion systems (Nnorom and Osibanjo, 2008). The use of leaded petrol in Ghana has been phased out since 2004. The remaining Pb in airborne particulate matter may therefore be a result of resuspended dust, residual lead in petrol, and oil and solid waste burning (Hosiokangas *et al.*, 1995; Arku *et al*., 2008). On average, the solid waste burning source accounted for 12%, 5%, 22%, 42% and 4% of the total $PM_{2.5}$ mass measured at AD-R, EL-R, JT-R, NM-R and NM-T, respectively. This higher mass concentration of this source in James Town/Ussher Town and Nima may be due to small-scale manufacturers of aluminium cooking pots in during the course of smelting add Pb from dry cell batteries to lower the melting point of the aluminium in order to cast the pots. It was observed that the JT-R site had about 3 times more solid waste burning contributions than the NM-R site (Table 4.14).

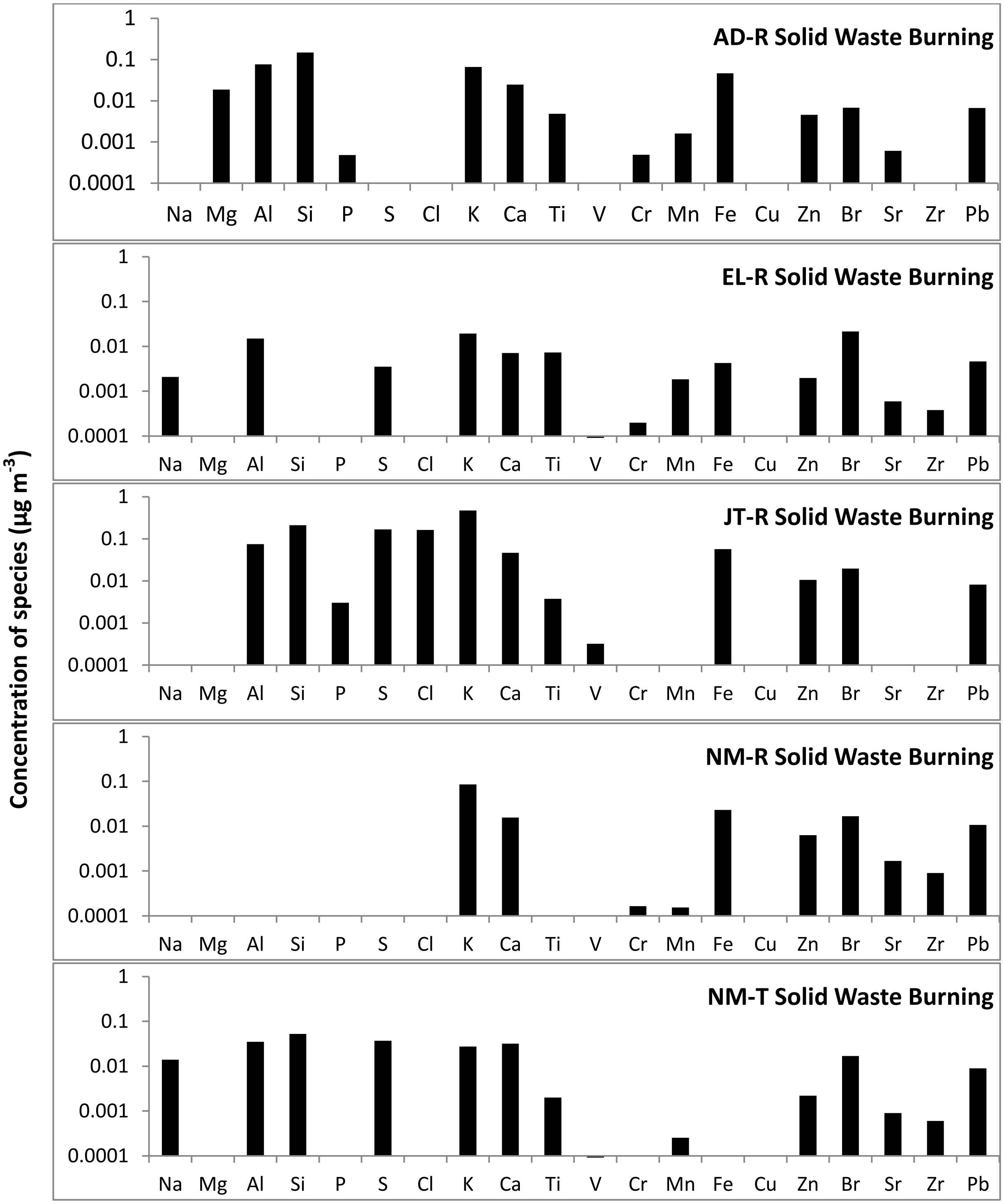


Figure 4.18 PM$_{2.5}$ source profiles for solid waste burning factors.

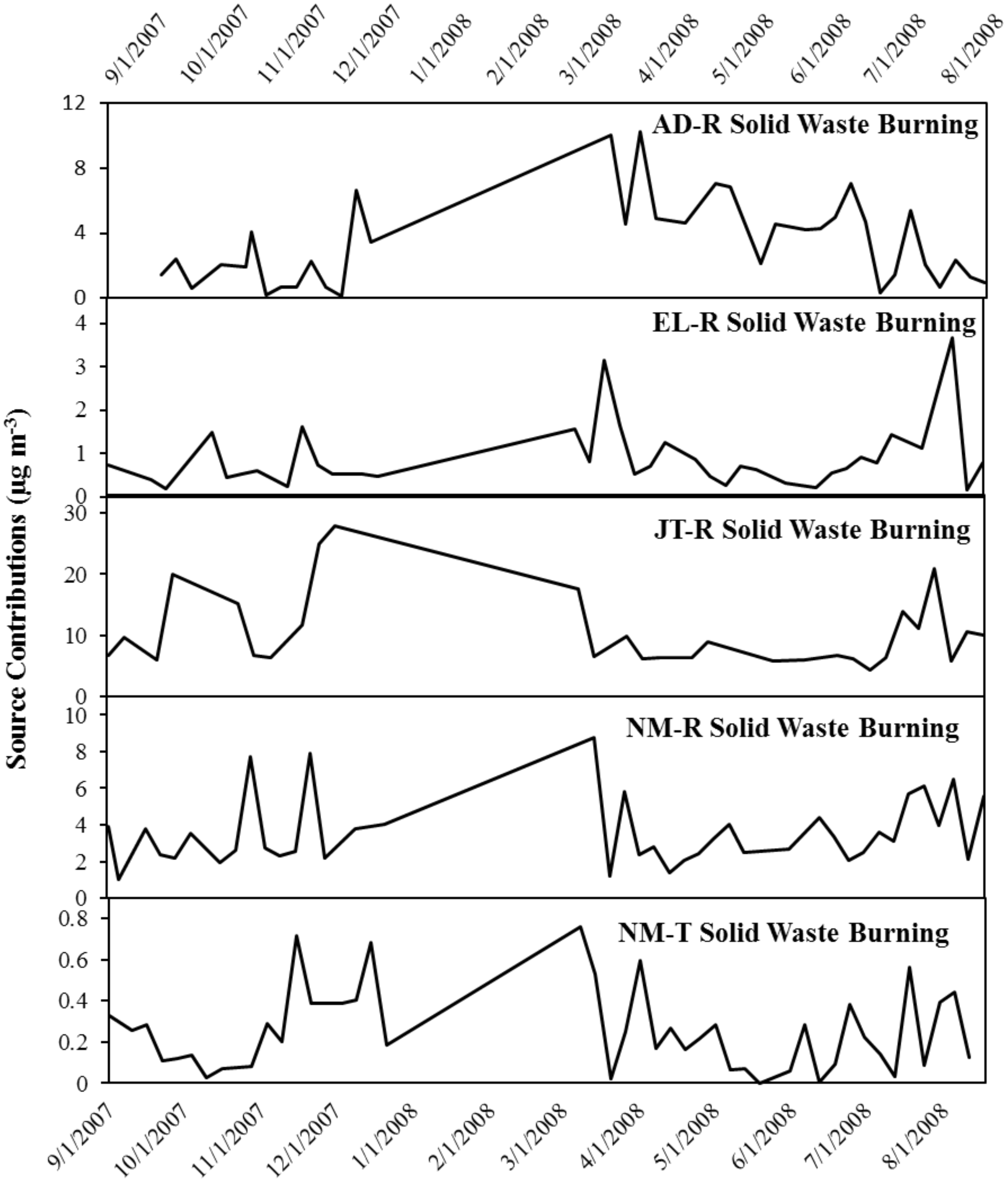


Figure 4.19 Time series of $PM_{2.5}$ source contributions for solid waste burning factors.

Source 4: Figure 4.20 shows source profiles of the fourth source which was characterized with large amounts of Al, Si, Ca, Ti, and Fe, suggesting crustal or soil dust aerosols. Sources with similar chemical composition resolved by other source apportionment studies were classified as resuspended soil dust (Gatari *et al*., 2005), crustal (Aboh *et al*., 2009) or soil dust (Ofosu *et al*., 2012). The soil-derived elements Al, Si, Ca, Ti, and Fe also exhibited variable concentrations at the various sites, signifying localized sources.

Soil dust contributed 23, 44, 15, 29 and 35% to the $PM_{2.5}$ concentrations at the AD-R, EL-R, JT-R, NM-R and NM-T monitoring sites, respectively. Soil dust sources had a larger proportion of total particle mass at EL-R, the northernmost neighbourhood site. Despite having a larger share from the soil dust source, lower total particle mass at the EL-R site meant that the absolute contribution of soil dust particles was only slightly higher than other neighbourhoods, e.g., 9.7 µg m^{-3} in $PM_{2.5}$ compared to 7.8 µg m^{-3} at NM-R. The higher contribution may have been because more spread-out low-rise homes do not block the windblown local dust. Soil dust was a major source of airborne particulate matter identified at all the sites. The only roadside site monitoring site in this study, NM-T, had the highest mass concentration (11.5 µg m^{-3}). However, small fractions of other elements, such as P, K, V, Cr, Mn, Zn, and Pb, were also associated with this source at NM-T, probably because of the resuspension of urban soil containing these elements. The source contributions (Figure 4.21) show high peaks in the dry season when rainfall is at minimum.

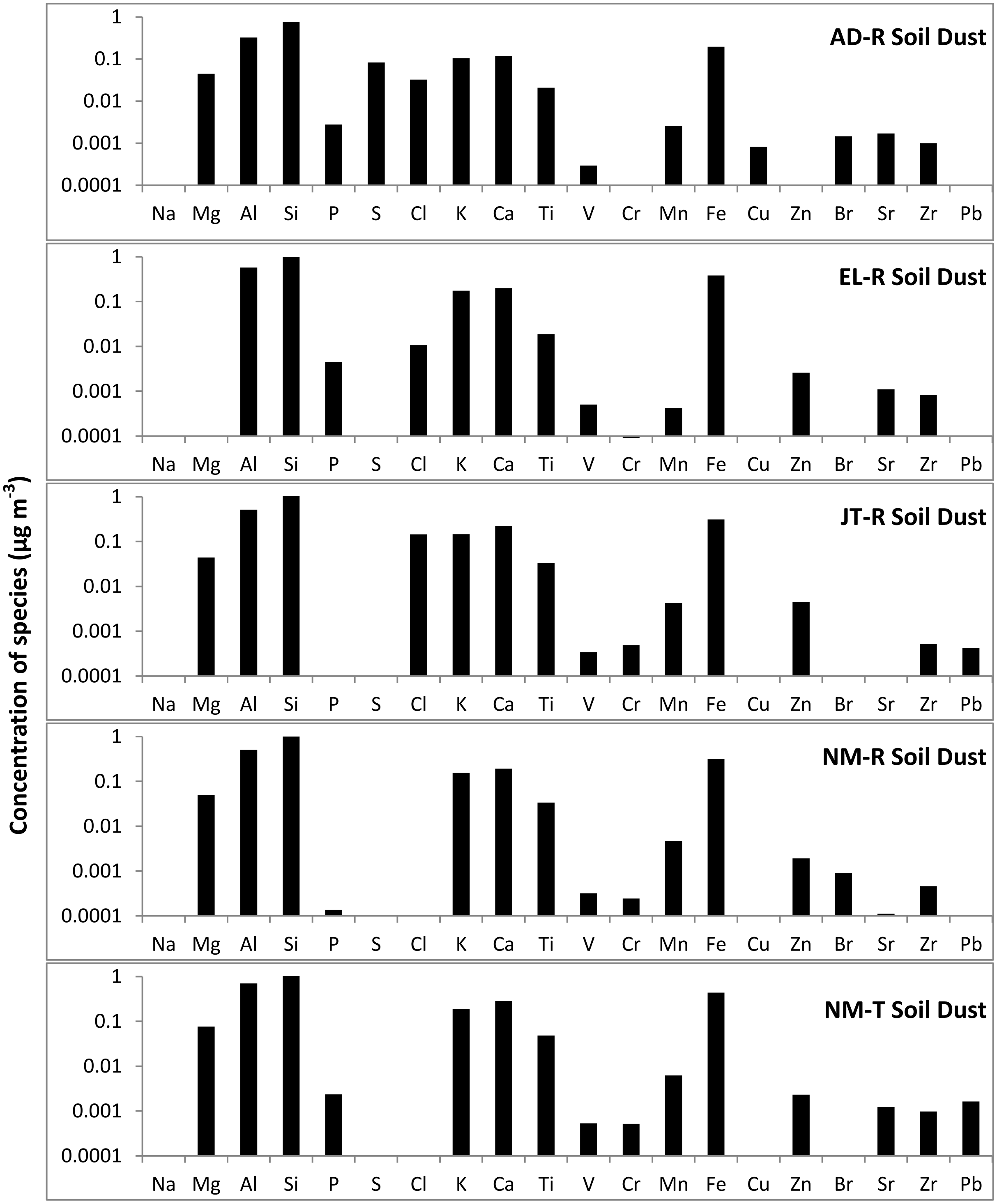


Figure 4.20 $PM_{2.5}$ source profiles for soil dust factors.

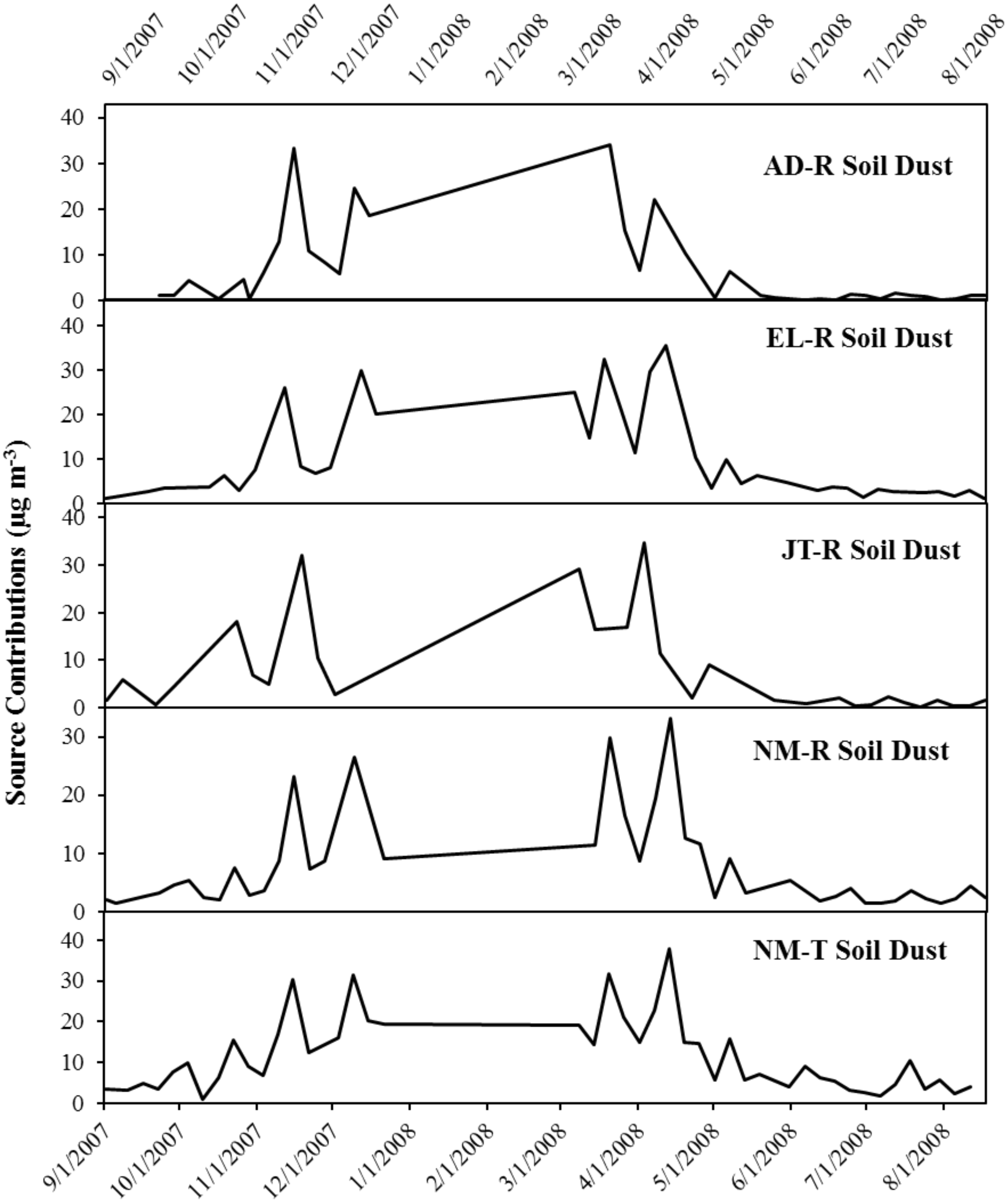


Figure 4.21 Time series of $PM_{2.5}$ source contributions for soil dust factors.

Source 5: A source with significant concentrations of Mg, Al, S, K, Ca, Ti, Mn, Fe, Zn, and Pb was identified at AD-R, EL-R and JT-R (Figure 4.22), but not at NM-R and NM-T. This source was identified as resuspended dust. The resuspended dust source contributions to $PM_{2.5}$ mass were 31, 0.29 and 15% at AD-R, EL-R and JT-R respectively. Resuspended road dust often consists of deposition of vehicle exhausts and industrial exhausts, tire and brake wears, dust from paved roads or potholes, and dust from construction sites.

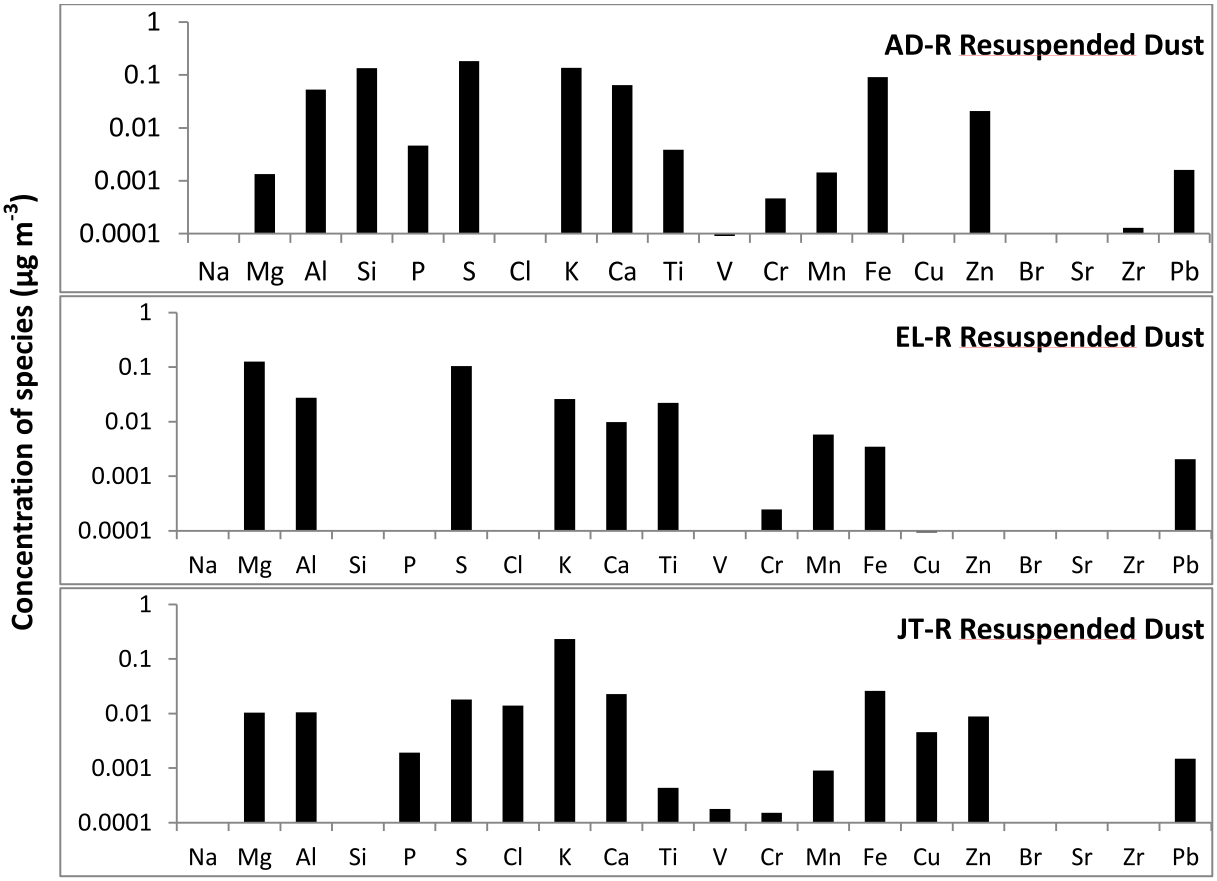


Figure 4.22 $PM_{2.5}$ source profiles for resuspended dust factors.

Iron (Fe) is emitted as a result of wear and tear of brake pads and other vehicular parts. Zinc (Zn) may have its origin from automobile sources such as wear and tear of vulcanized rubber tires, lubricating oil and corrosion of galvanized vehicular parts. Manganese (Mn) has been used as an additive in vehicle fuel (Karar *et al.*, 2006). Al, Mn and K have also been used as tracers for paved road dust (Gupta *et al.*, 2012). Time series plots (Figure 4.23) show higher concentrations in November, December and April, the dry season period.

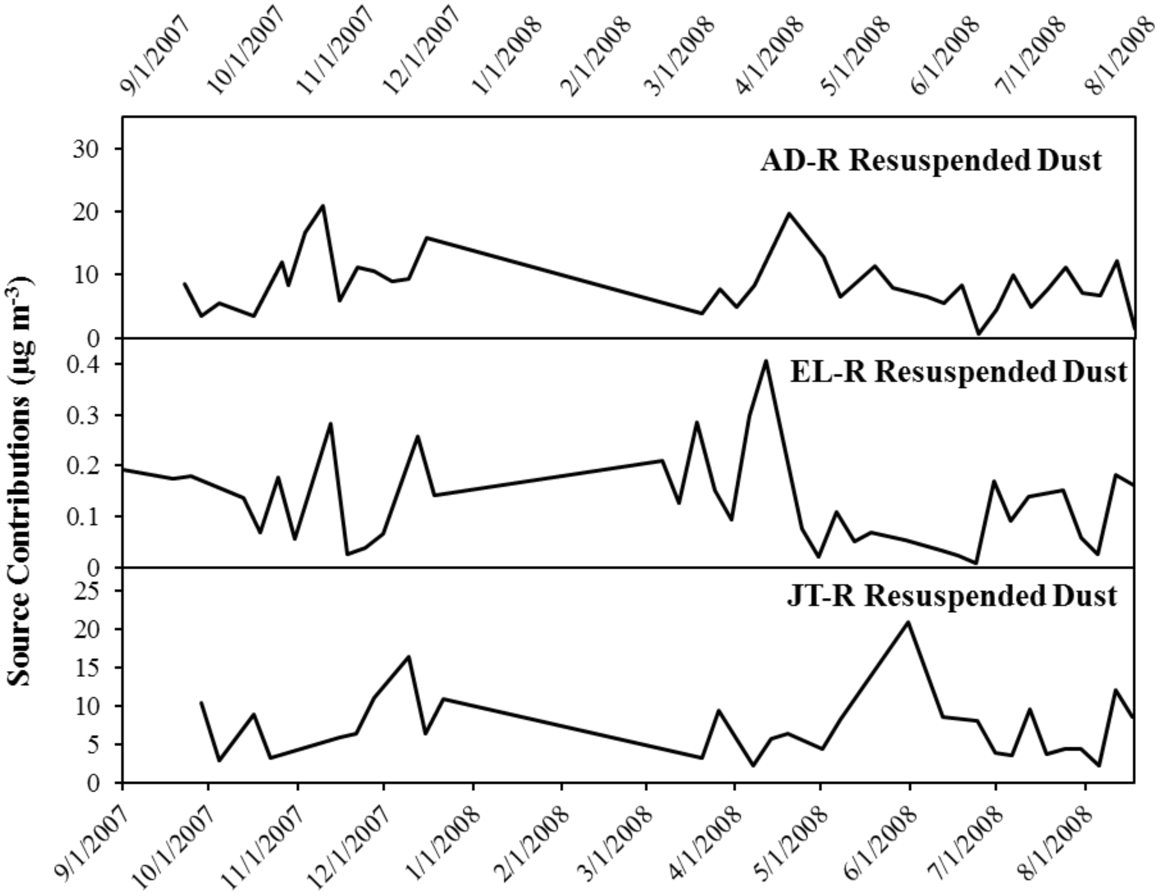


Figure 4.23 Time series of $PM_{2.5}$ source contributions for resuspended dust factors.

Source 6: Source profiles (Figure 4.24) with high loadings for Manganese (Mn), Copper (Cu) and Zinc (Zn) were identified at AD-R, NM-R and NM-T, but not at EL-R and JT-T. Cu and Zn are usually related to vehicular traffic such as motor vehicle exhaust and industrial sources from nonferrous smelting processes (Gao *et al.*, 2002). Traffic produces road dust and air turbulence that can stir up road dust. The presence of Mn in this source profile may be due to the addition of methylcyclopentadienyl manganese tricarbonyl (MMT), a manganese-based gasoline antiknock fuel additive which has been in use in Ghana since January 2004 after the ban on the use of unleaded gasoline in the country.

The source contributions (Figure 4.25) at AD-R show seasonal variations with higher concentrations during rainy season and lower concentrations during the dry season. In contrast, the source contributions at the Nima sites (NM-R and NM-T) show no seasonal variations. The higher source contributions observed at the AD-R site could be attributed to vehicle traffic diversion through the Asylum Down neighbourhood from Ring Road Central which is one of the largest, busiest and congested roads in Accra. Ring Road Central experienced major flooding during the rainy season.

Distance to the nearest primary road at AD-R, NM-R and NM-T sites were 166 m, 188 m, and 25 m respectively (see Table 3.1). Traffic count conducted on the road in front of the AD-R site recorded an average daily traffic (ADT) of 3,114 vehicles/day. Roads in front of the two Nima sites (NM-R and NM-T) were 471 and 7,193 vehicles/day respectively.

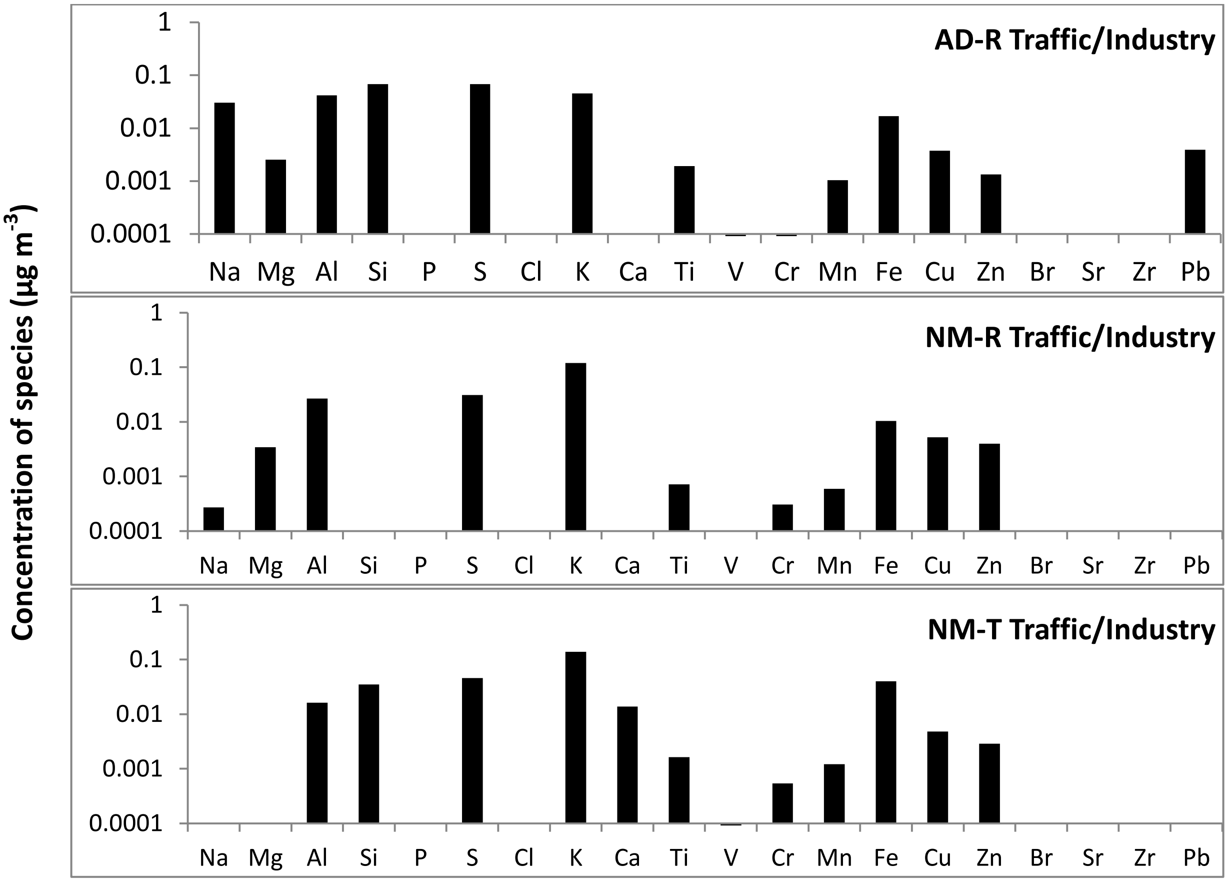


Figure 4.24 PM$_{2.5}$ source profiles for traffic/industry factors.

Higher source concentration at NM-R may be due to diversion of vehicular traffic (especially trotros and taxis) through the Nima residential area mostly on Wednesdays and Fridays which are Nima market days. This results in traffic congestion with idling engines. Road traffic congestion increases PM concentration as compared to free flowing traffic. Amato *et al*. (2010) found a factor with high mass concentrations of Zn, Pb and Mn and attributed it to industrial emissions. The location of Cu or Zn smelter within these neighbours needs further investigation. However, due to improper zoning in Accra, it is common to find some small and medium-scale industries in residential neighbours of Accra.

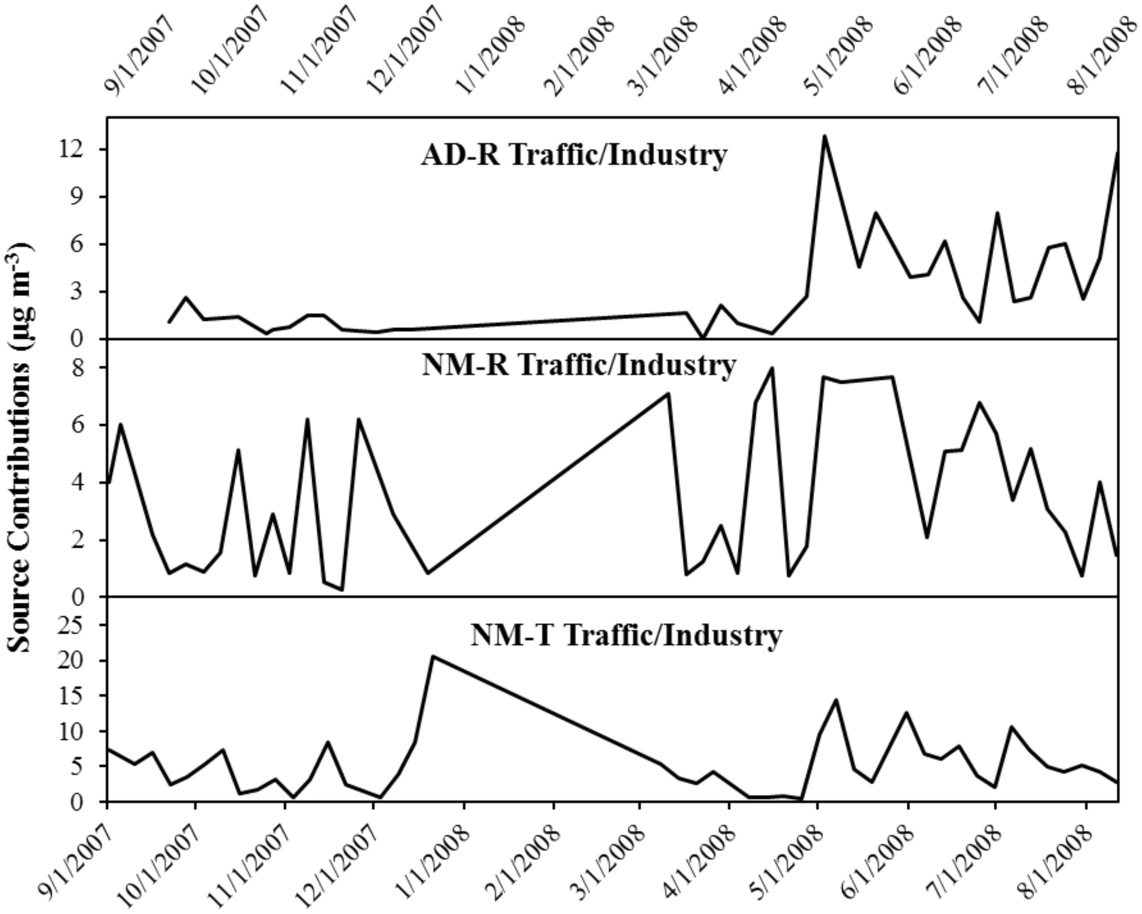


Figure 4.25 Time series of $PM_{2.5}$ source contributions for traffic/industry dust factors.

4.5.1.2 COARSE PARTICULATE MATTER

The reconstructed PM_{10} mass concentrations were estimated from the sum of the contributions of the PMF resolved sources as in the case of the $PM_{2.5}$ mass concentrations. In Figure 4.26 to Figure 4.30, a comparison of the reconstructed PM_{10} contributions from all sources with measured PM_{10} concentrations shows that the PMF resolved sources effectively reproduce the measured total mass. In addition, the PMF derived for most of the variation in the PM_{10} concentrations had high linear correlation coefficient r^2 (all greater than 0.93) at the five sites.

The performance of PMF model was also evaluated by comparing the calculated values with measured concentrations for each species used in the model. These are shown in Table A-6 to Table A-10 in Appendix A. The average source contributions for all sites are summarized in Table 4.15.

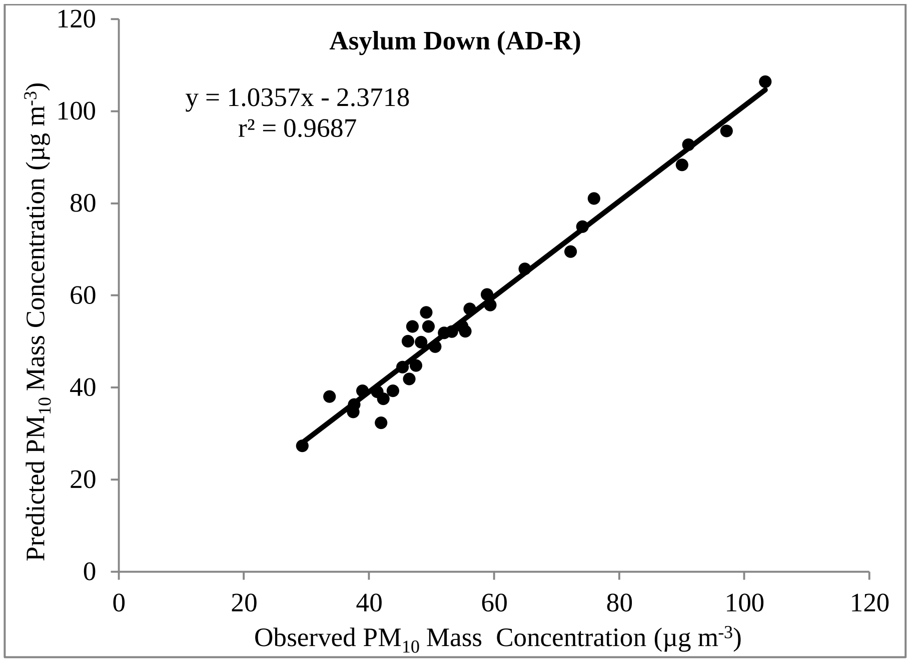


Figure 4.26 Scatter plots of predicted PM_{10} mass concentrations and measured PM_{10} mass concentrations at AD-R.

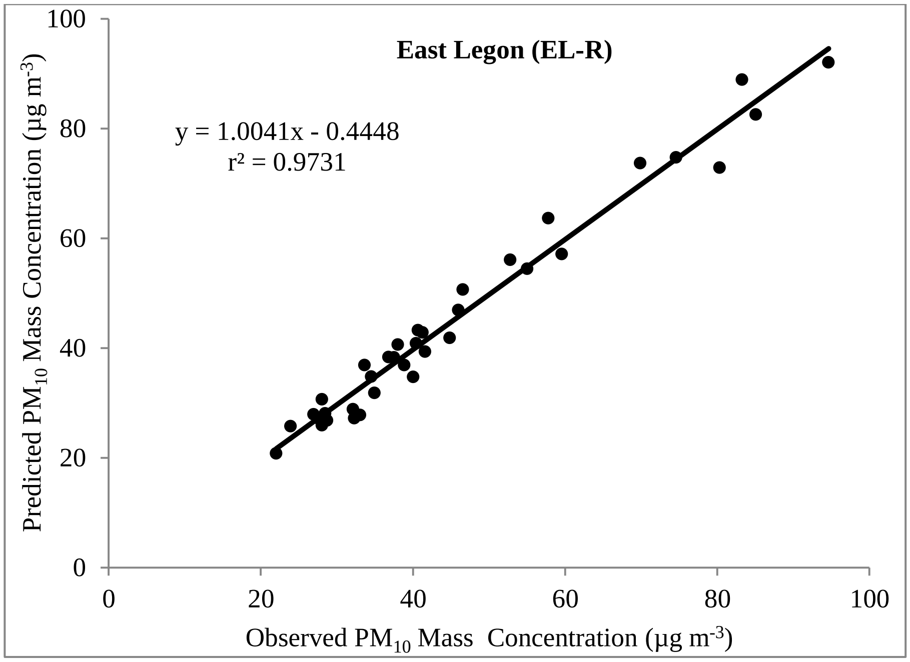


Figure 4.27 Scatter plots of predicted PM_{10} mass concentrations and measured PM_{10} mass concentrations at EL-R

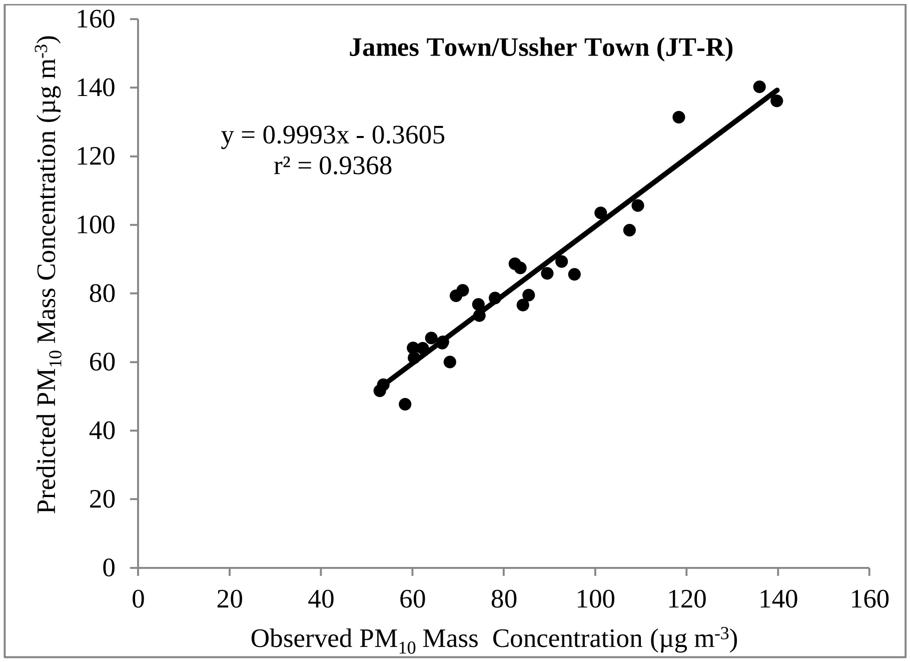


Figure 4.28 Scatter plots of predicted PM_{10} mass concentrations and measured PM_{10} mass concentrations at JT-R.

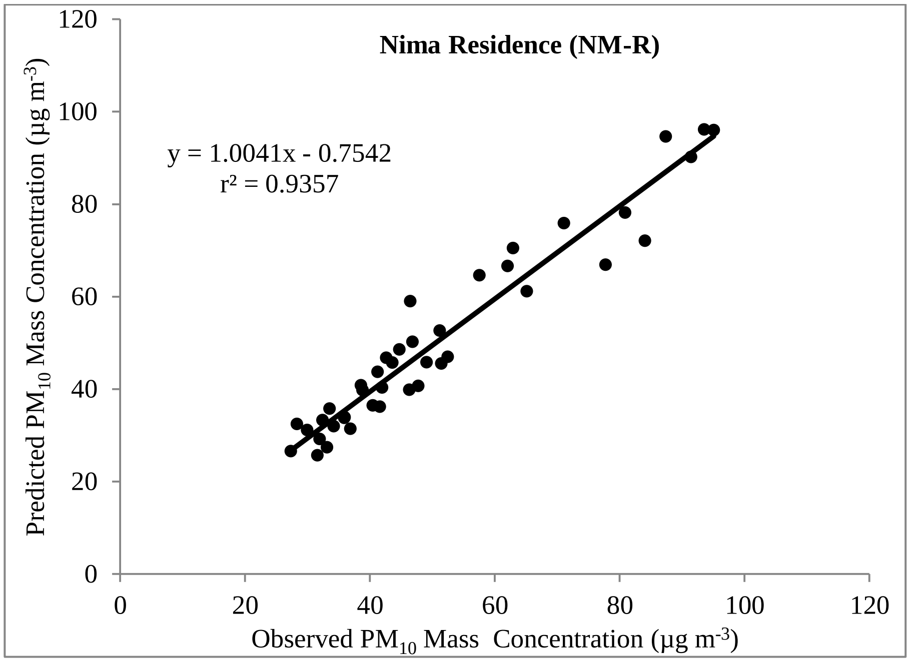


Figure 4.29 Scatter plots of predicted PM_{10} mass concentrations and measured PM_{10} mass concentrations at NM-R.

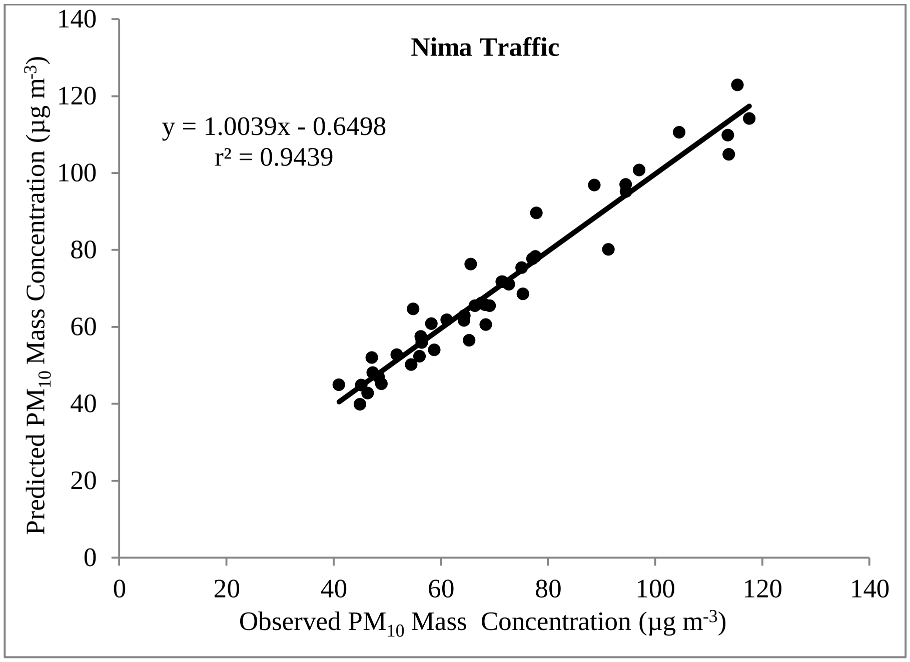


Figure 4.30 Scatter plots of predicted PM_{10} mass concentrations and measured PM_{10} mass concentrations at NM-T.

Source 1: The first source was identified as sea salt aerosol due to the high loadings of Na and Cl at all five sites. This source contributes 14, 8, 33, 12 and 14% on an average at AD-R, EL-R, JT-R, NM-R, and NM-T, respectively. The source profiles are shown in Figure 4.31 and the source contributions shown in Figure 4.32. Across sites, average contributions of the sea salt source in the PM_{10} were higher at JT-R (26.62 µg m^{-3}) than at the other sites in Accra (3.44 µg m^{-3} - 10.02 µg m^{-3}). As expected, sea salt was more dominant in the James Town/Ussher Town neighbourhood as a result of its proximity to the Atlantic Ocean than in the other three neighbours. Similar to the $PM_{2.5}$ fraction discussed earlier, the highest contribution of this source to PM_{10} occurred in August.

From backward trajectories computed for 17 August 2008, it appears that this source is largely due to the tropical maritime air mass originating from the Atlantic Ocean.

Table 4.15 Average contributions of identified sources to PM_{10} concentrations.

	AD-R	EL-R	JT-R	NM-R	NM-T
Sea Salt	14.23% (7.85 μg m^{-3})	7.68% (3.44 μg m^{-3})	32.50% (26.62 μg m^{-3})	11.69% (5.90 μg m^{-3})	14.38% (10.02 μg m^{-3})
Biomass burning	31.73% (17.50 μg m^{-3})	36.91% (16.50 μg m^{-3})	30.25% (24.78 μg m^{-3})	27.86% (14.06 μg m^{-3})	48.06% (33.49 μg m^{-3})
Solid waste burning	3.11% (1.72 μg m^{-3})	5.21% (2.33 μg m^{-3})	5.10% (4.18 μg m^{-3})	4.83% (2.44 μg m^{-3})	3.54% (2.47 μg m^{-3})
Soil Dust	34.00% (18.75 μg m^{-3})	38.89% (17.39 μg m^{-3})	25.67% (21.03 μg m^{-3})	41.57% (20.98 μg m^{-3})	25.95% (18.09 μg m^{-3})
Resuspended dust	6.13% (3.38 μg m^{-3})	11.31% (5.06 μg m^{-3})	6.48% (5.31 μg m^{-3})		
Traffic/Industry	10.80% (5.96 μg m^{-3})			14.05% (7.09 μg m^{-3})	8.07% (5.63 μg m^{-3})

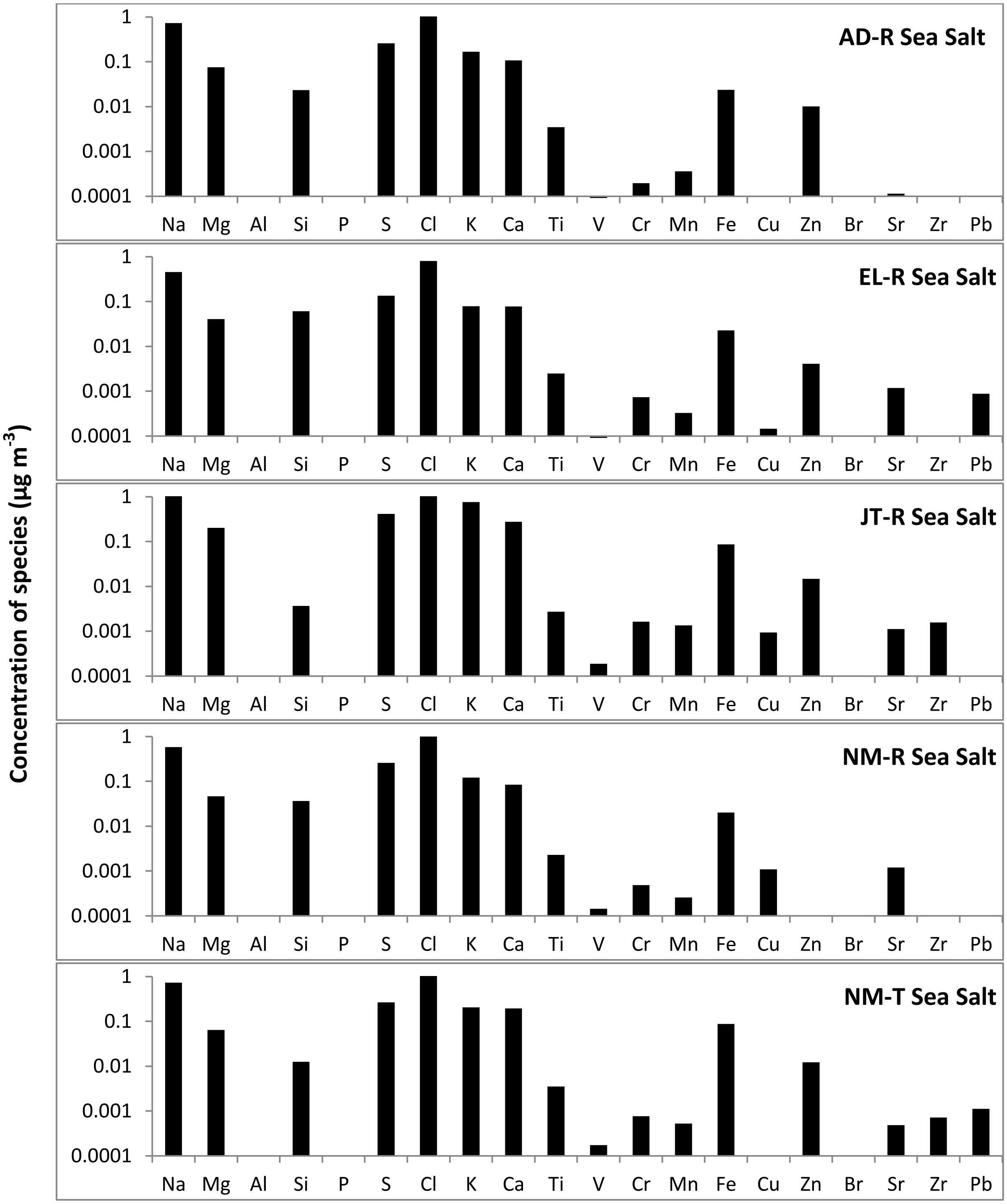


Figure 4.31 PM_{10} source profiles for sea salt factors.

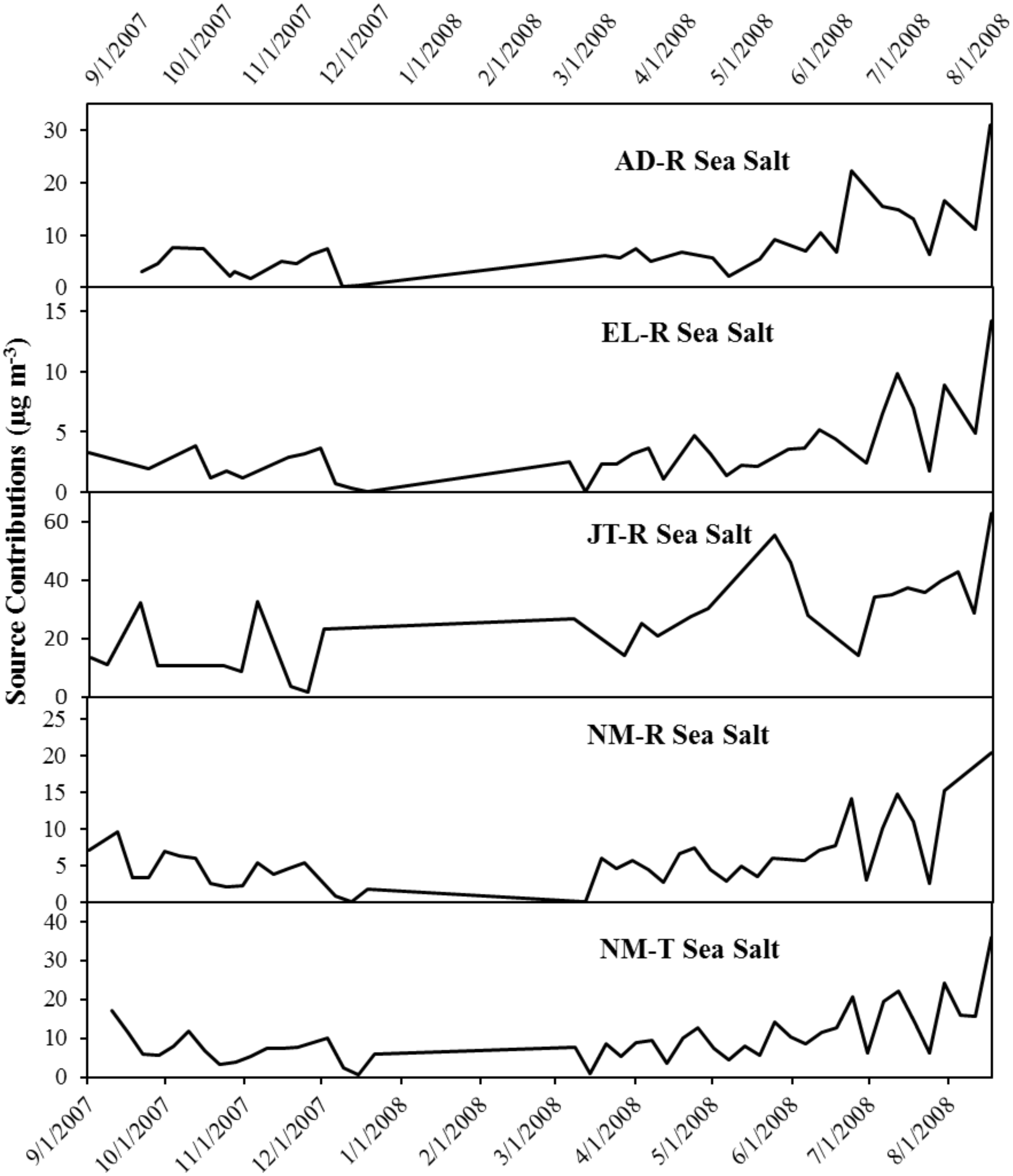


Figure 4.32 Time series of PM_{10} source contributions for sea salt factors.

Source 2: A biomass burning source was identified at all sites largely by the presence of high loadings of potassium (K) in the estimated source profiles as shown in Figure 4.33. This source accounted for 31.7, 36.9, 30.3, 27.9 and 48.1% of the apportioned PM_{10} mass at Ad-R, EL-R, JT-R, NM-R and NM-T, respectively.

Biomass burning is a major component of PM_{10} in all the five neighbours. Relatively elevated source contributions were observed during the dry season as shown in Figure 4.34. This could be attributed to long-range transport of particles from wild bushfires, clearing or preparation land for farming by the process of burning.

Source 3: A source with high loadings for Br and Pb and minor quantities of crustal species was identified at the 5 sites in Accra. This source can be attributed to solid waste burning (Vehlow et al., 2003; Nnoroma and Osibanjo, 2008). The source profiles and source contributions for this source are shown in Figure 4.35 and Figure 4.36, respectively. Similar sources were found in the $PM_{2.5}$ fractions at all the sites. The burning of solid waste is common in residential and open areas in the city of Accra. The solid waste burning source accounted for 3.1%, 5.2%, 5.1%, 4.8% and 3.5% of the total PM_{10} mass measured at AD-R, EL-R, JT-R, NM-R and NM-T, respectively. The source contributions for solid waste burning show no seasonal variations.

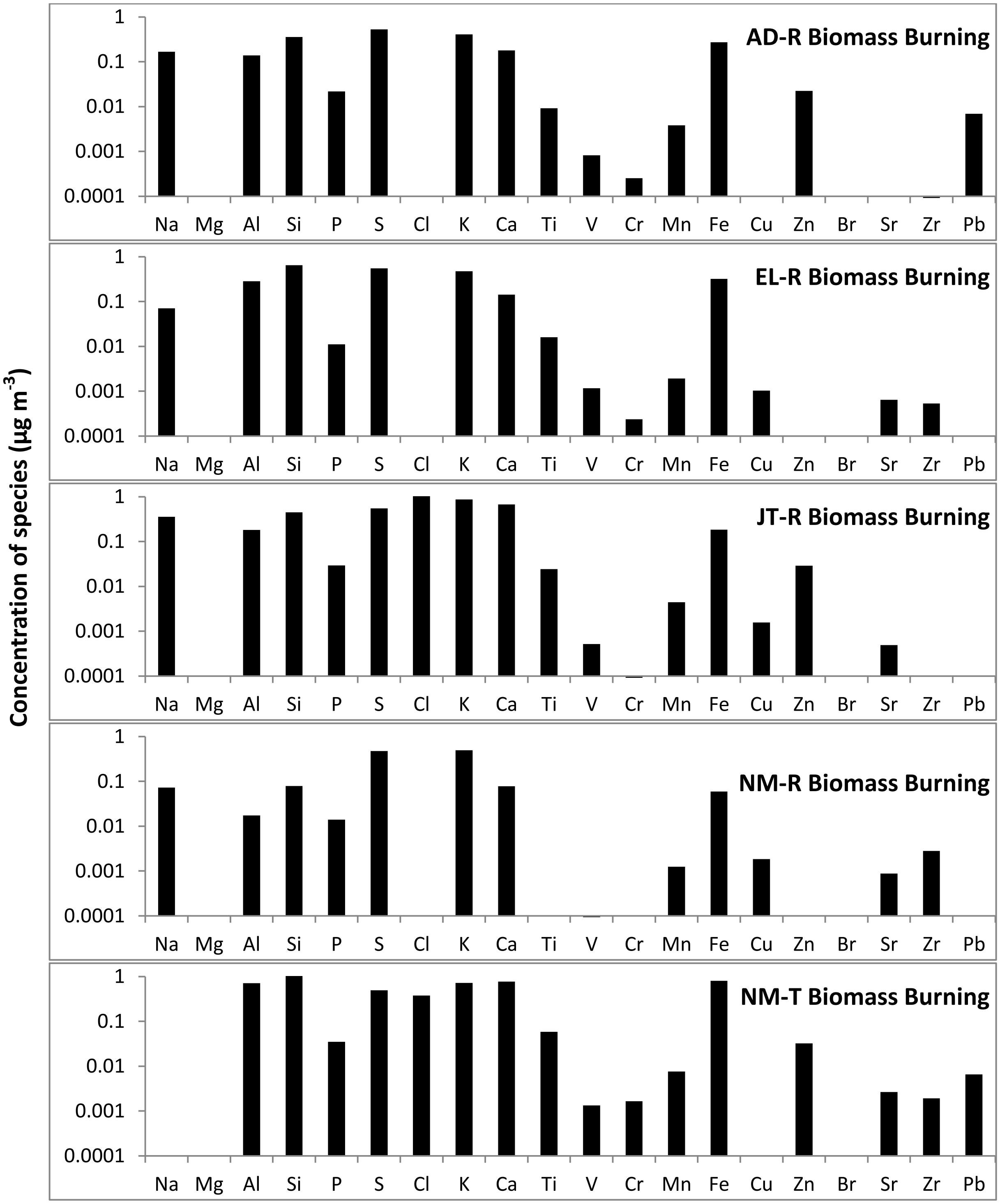


Figure 4.33 PM$_{10}$ source profiles for biomass burning factors.

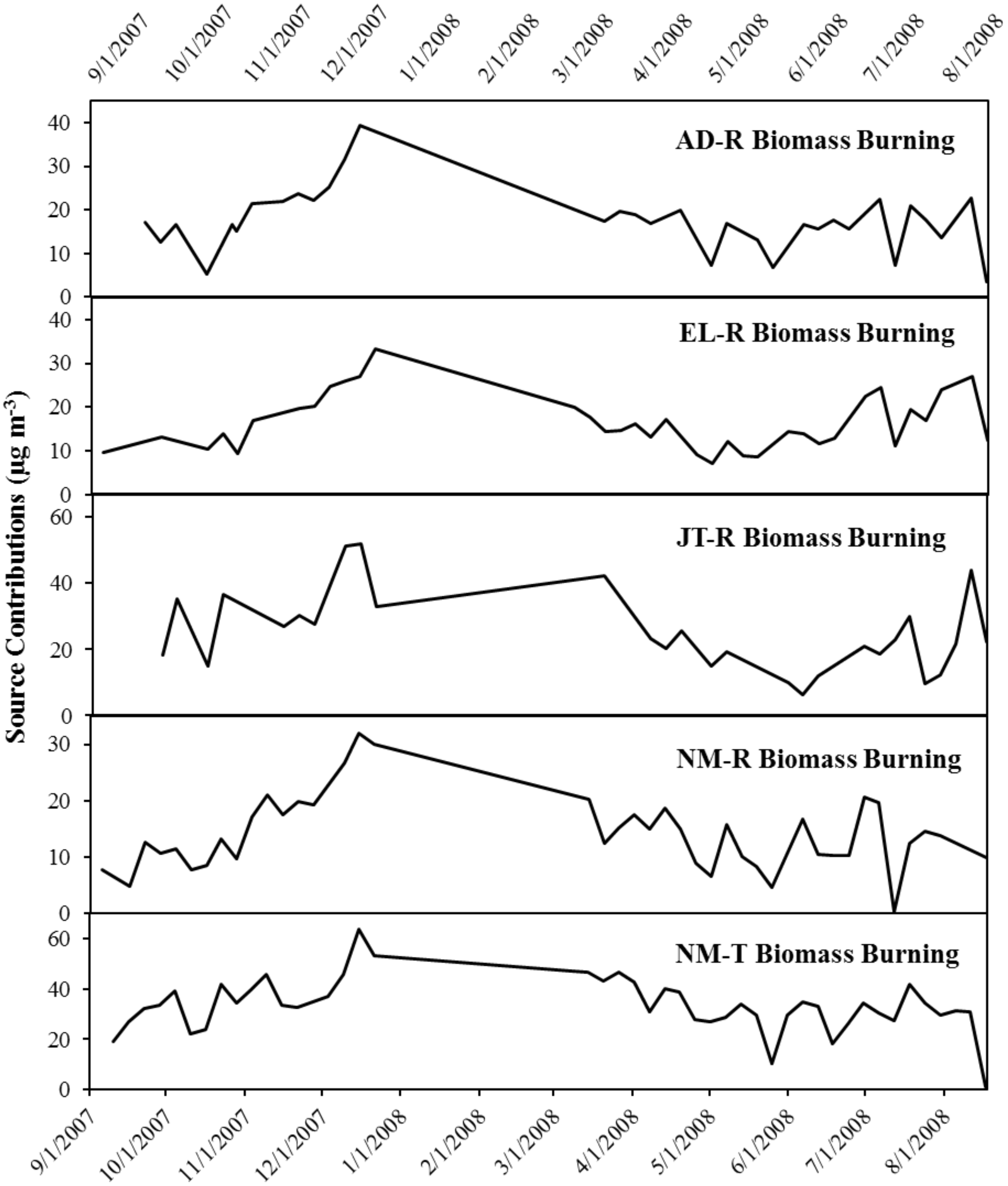


Figure 4.34 Time series of PM_{10} source contributions for biomass burning factors.

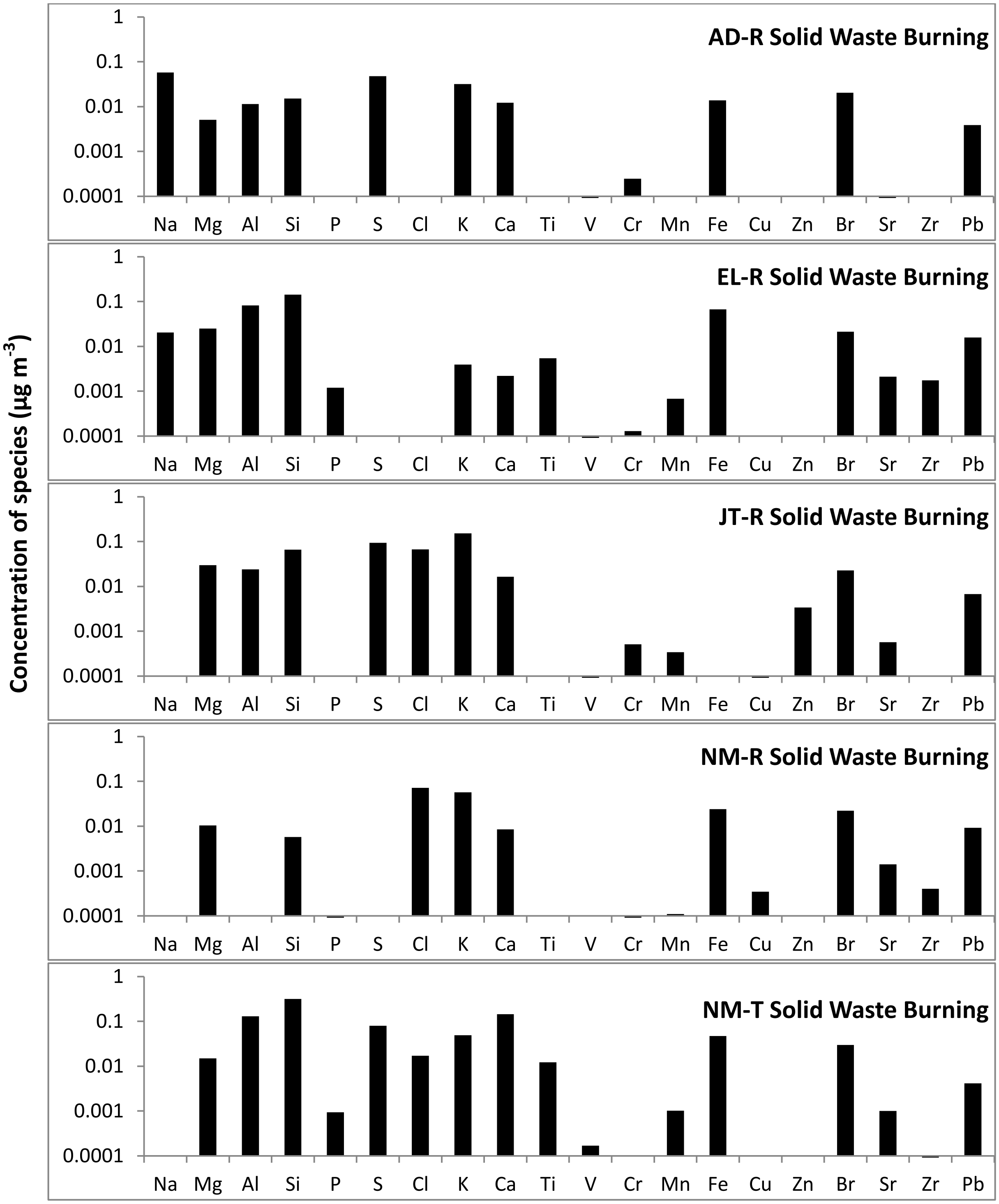


Figure 4.35 PM_{10} source profiles for solid waste burning factors.

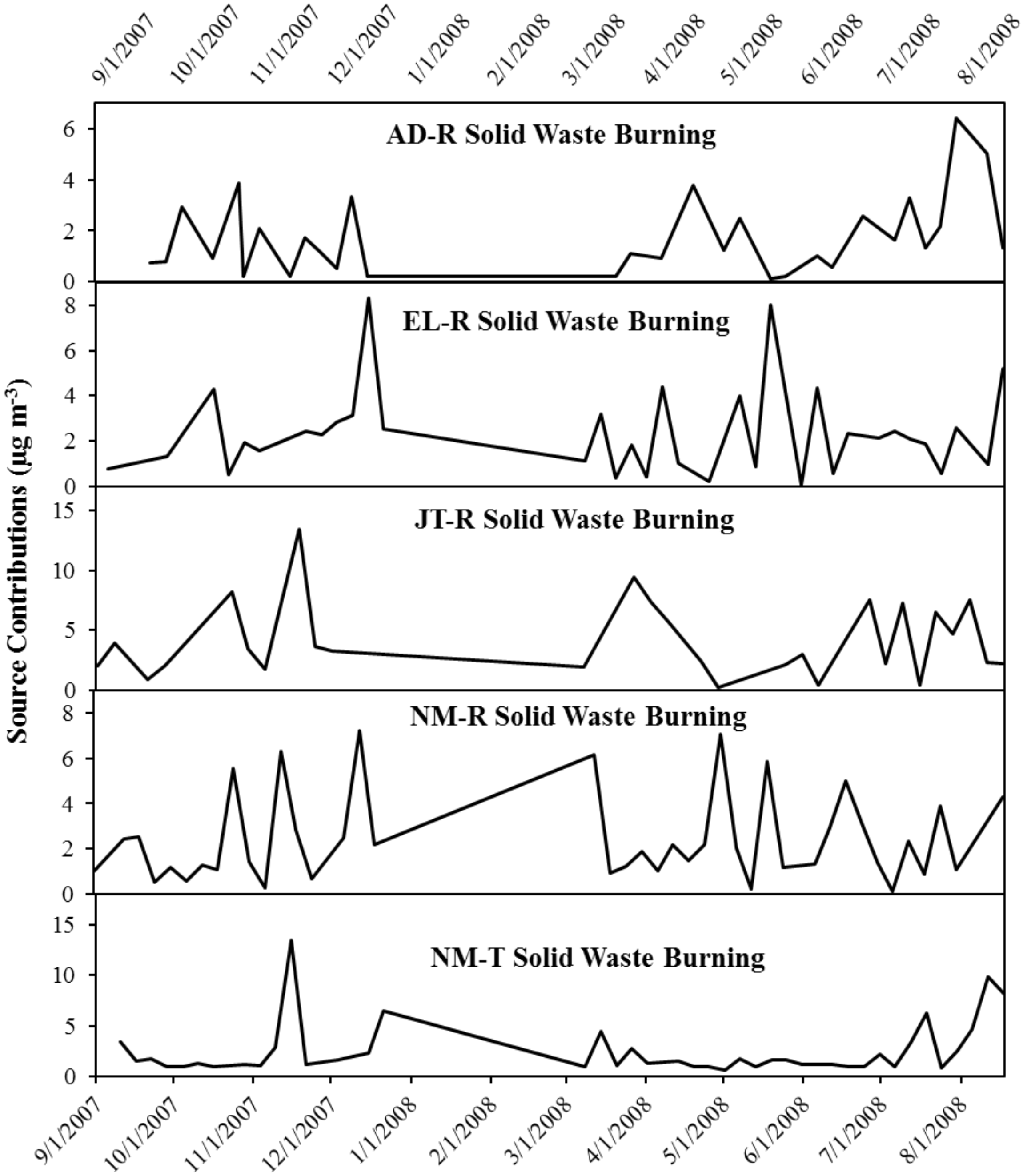


Figure 4.36 Time series of PM_{10} source contributions for solid waste burning factors.

Source 4: The fourth source at all the five sites in Accra was identified as soil dust based on the high loadings of Mg, Al, Si, Ca, Ti, Mn and Fe in the source profiles (Figure 4.37). The contribution of soil dust to total PM_{10} varies from 26-42% and is therefore a significant contributor to PM_{10}. In addition as expected, the contribution of soil dust in PM_{10} is greater than in $PM_{2.5}$ since large diameter particles such as those found in soil dust are expected to be big contributors to PM_{10}. In Accra, soil dust contributes significantly to both $PM_{2.5}$ and PM_{10}.

The source contributions of the soil dust source for the five sites showed high peaks on 9th December 2007, 20th March 2008 and 13th April 2008 (Figure 4.38). In order to understand the source region of the soil dust particles, backward trajectories of the air mass movement on these dates were constructed at heights of 500, 1500 and 3000 m above ground level over 96 h using NOAA HYSPLIT (Draxler and Rolph, 2003), and the result displayed as Figure 4.39 showed that the source contributions on these days had similar backward trajectories originating from both local and long-range transported dust.

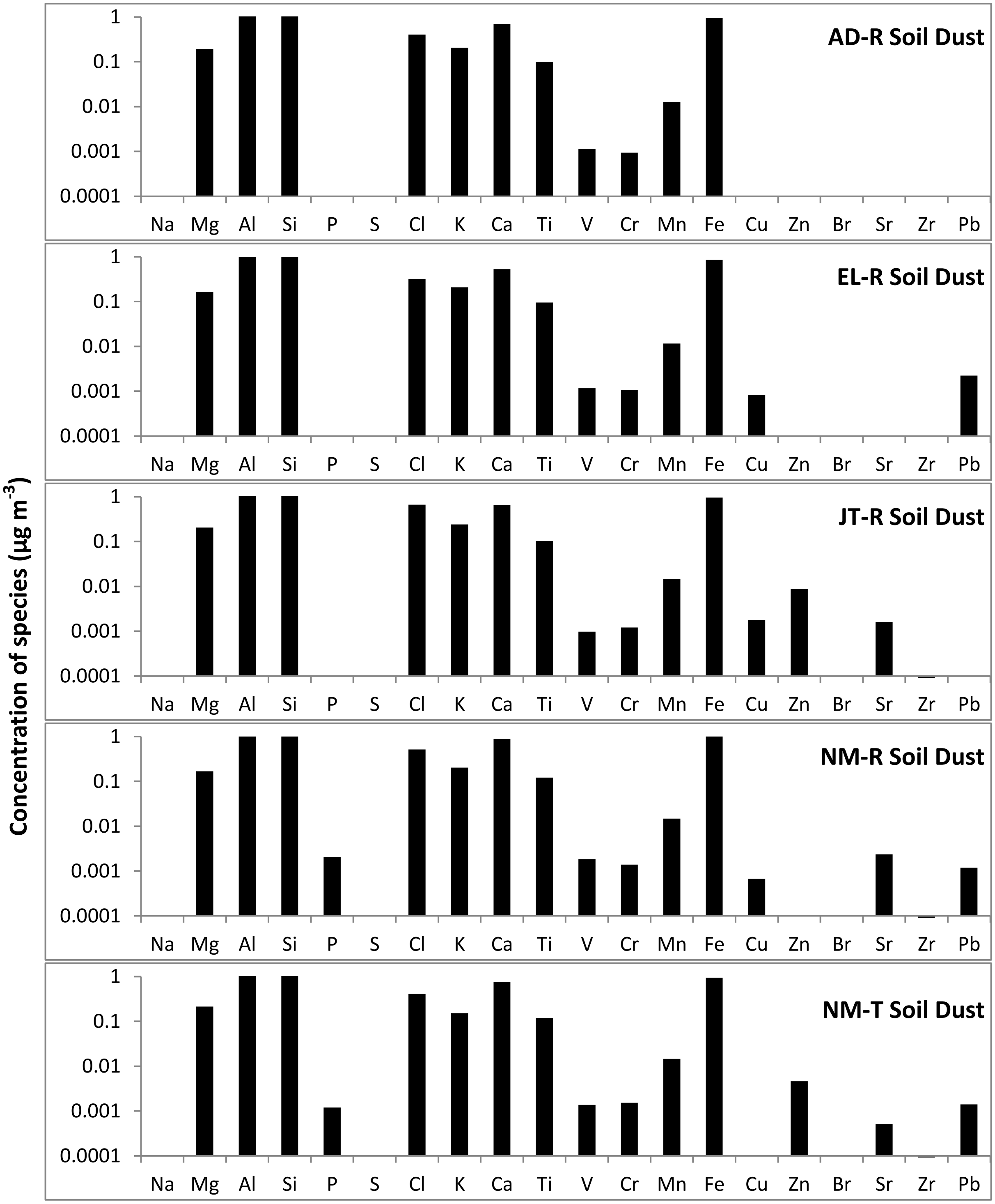


Figure 4.37 PM$_{10}$ source profiles for soil dust factors.

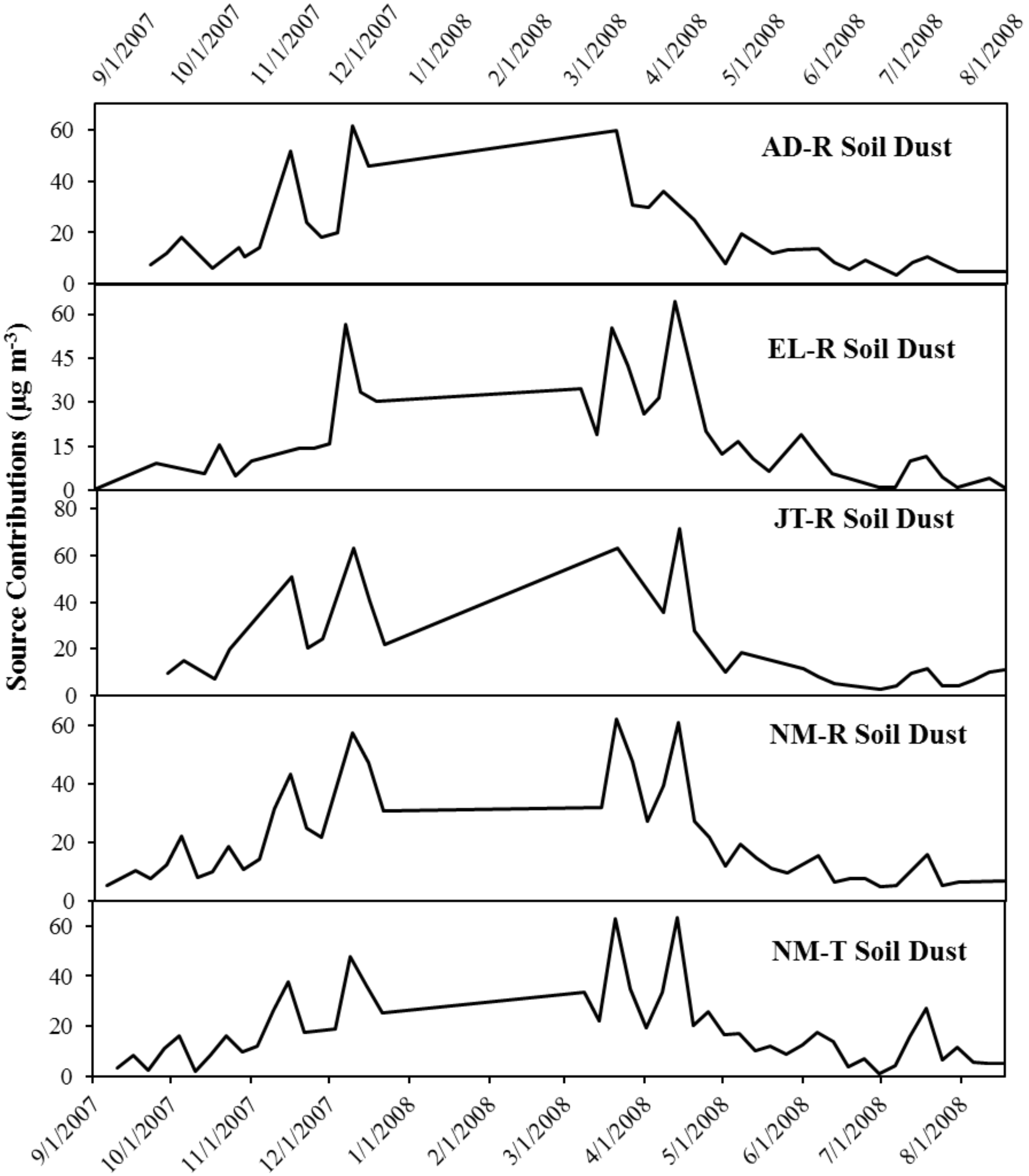


Figure 4.38 Time series of PM_{10} source contributions for soil dust factors.

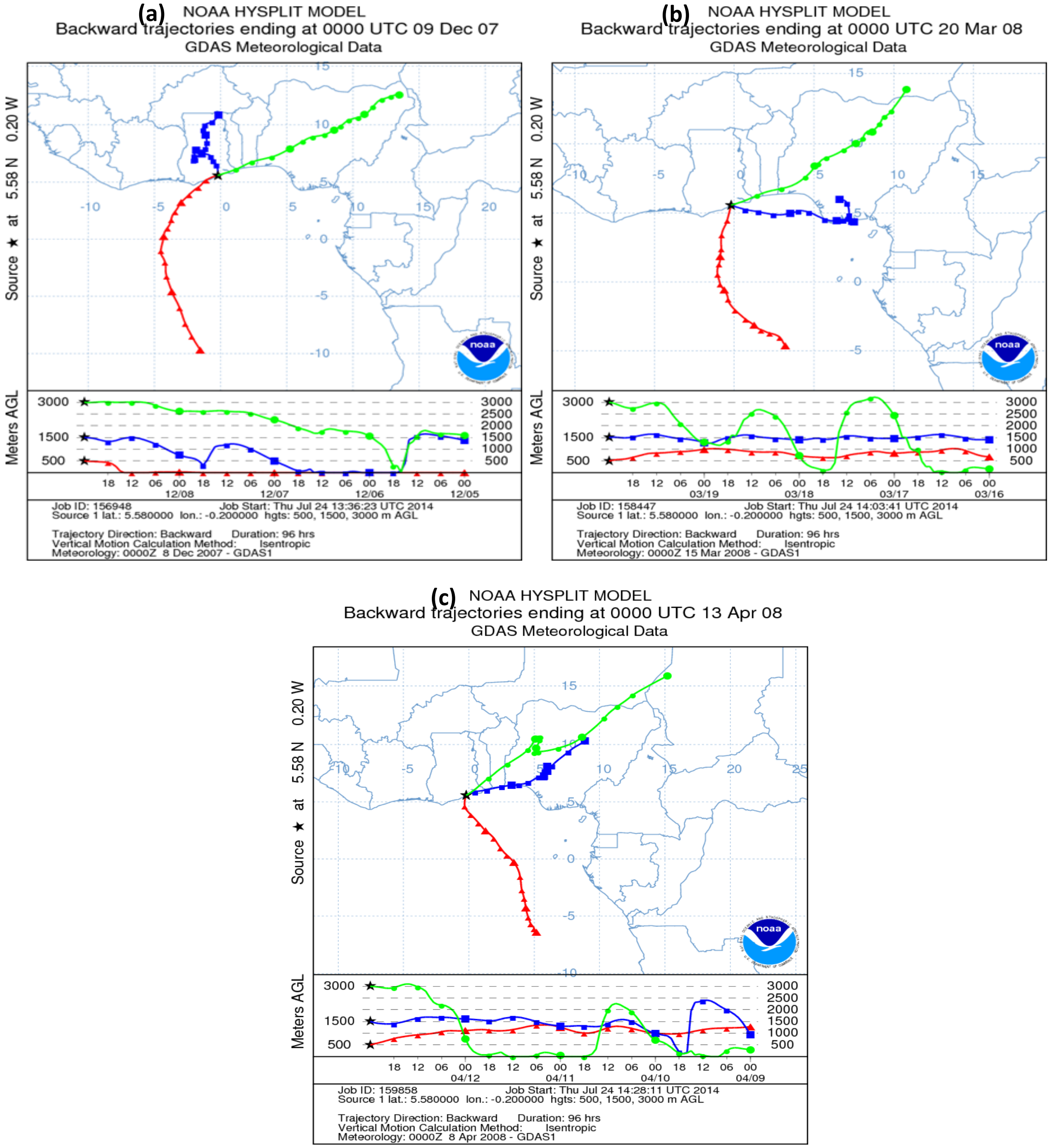


Figure 4.39 NOAA HYSPLIT model of air mass trajectories over Accra (location shown in star★) on (a) 9th December 2007, (b) 20th March 2008 and (c) 13th April 2008. Backward trajectory was derived from the NOAA website: www.arl.noaa.gov/ready/

Source 5: The same resuspended dust source like that found in the $PM_{2.5}$ size range was identified for the PM_{10} fraction. The fifth source has significant loadings of Al, Si, K, Ti, Zn and Fe. It appeared to be a mixture of a resuspension of mineral dust or traffic related particles. This source was identified at AD-R, EL-R and JT-R but not at NM-R and NM-T. The resuspended dust source contributed 6.1, 11.3 and 6.5% to PM_{10} mass at AD-R, EL-R and JT-R respectively. The source profiles and source contributions for this source are shown in Figure 4.40 and Figure 4.41, respectively. It was expected that source contributions for this source would be higher in the PM_{10} fraction than the $PM_{2.5}$ size range. However, with the exception of the EL-R site, the resuspended dust PM_{10} source contributions were lower in the other two neighbourhoods. It is not clear why this occurred, continuous monitoring could be able to explain this occurrence. Time series plots for PM_{10} showed higher concentrations in November, December and April, the dry season period.

Source 6: The sixth source contributed about 10.8, 14.1 and 8.1% of the PM_{10} mass concentrations at AD-R, NM-R and NM-T. PMF model did not resolve this source for EL-R and JT-R sites. The sixth source had high concentrations Cr, Cu, Zn and Pb. These were the key indicator elements for industry and traffic emission sources attributed to wear of brake linings and tires as well as from lubricating oils (Sternbeck *et al.*, 2002). This source was identified as traffic/industry source and is similar to that in the $PM_{2.5}$ fraction. The traffic/industry source was mixed with loadings from crustal elements (Al, Si, Ca and Ti) and biomass combustion emissions (K). Time series plots (Figure 4.43) also show similar variations like the $PM_{2.5}$ fractions discussed earlier.

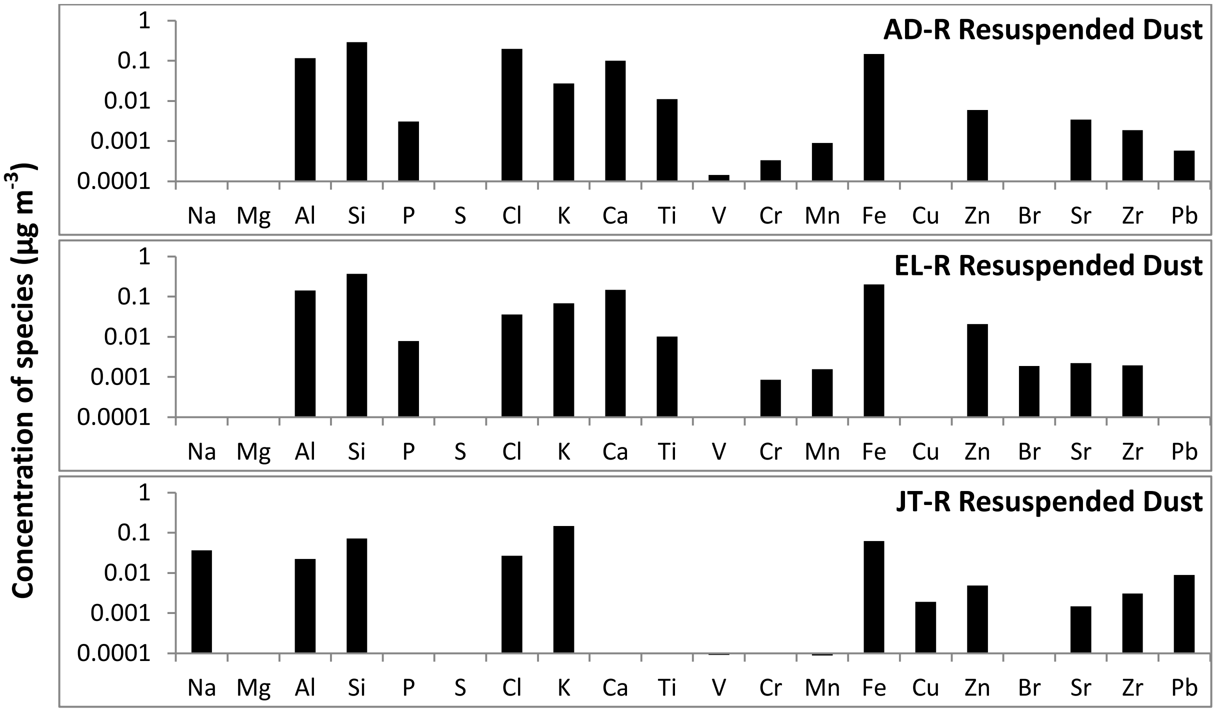


Figure 4.40 PM$_{10}$ source profiles for resuspended dust factors.

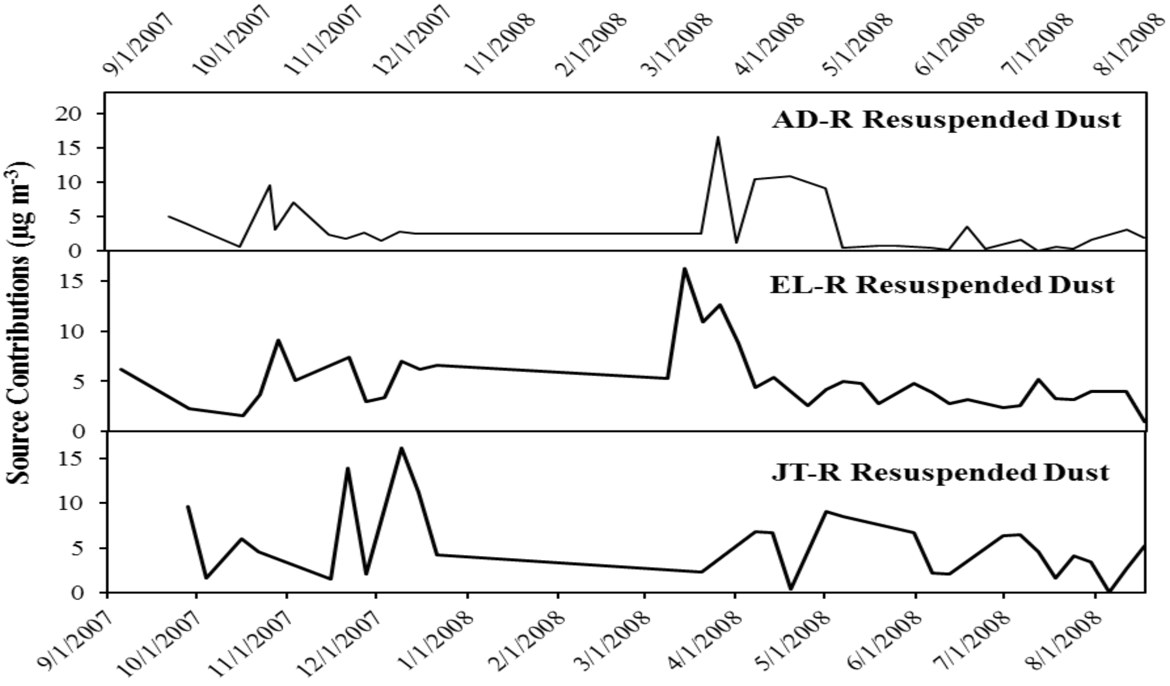


Figure 4.41 Time series of PM$_{10}$ source contributions for resuspended dust factors.

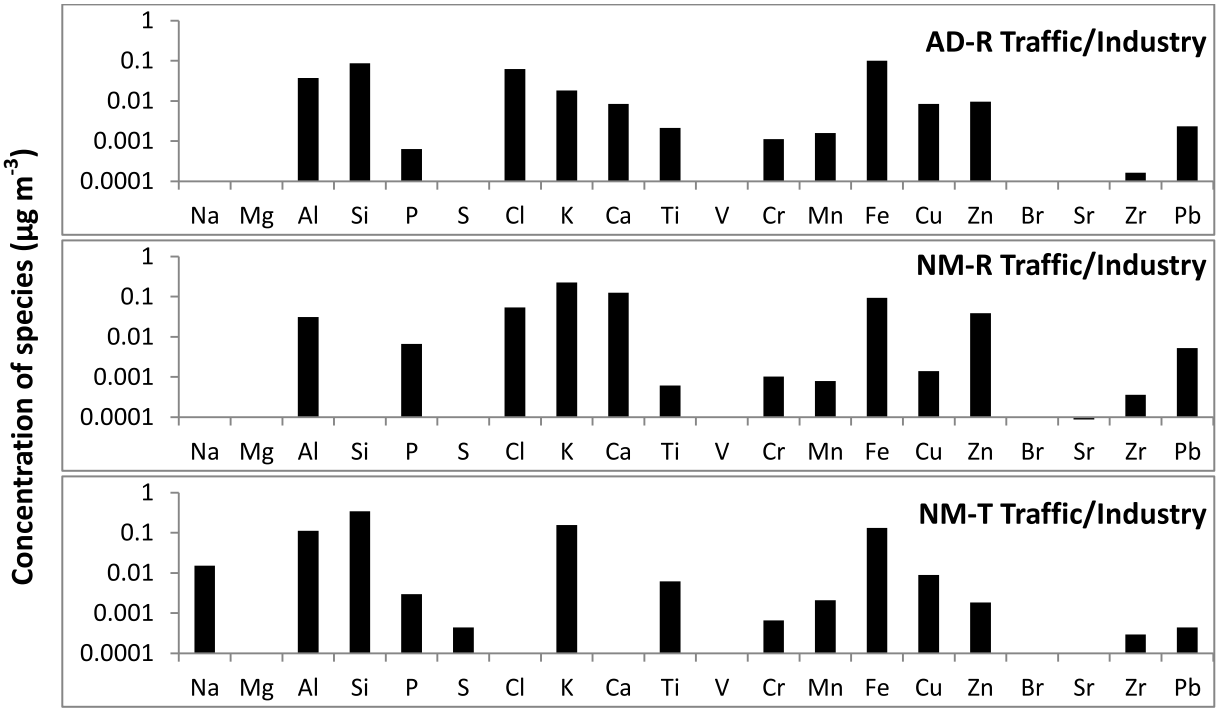


Figure 4.42 PM$_{10}$ source profiles for traffic/industry factors.

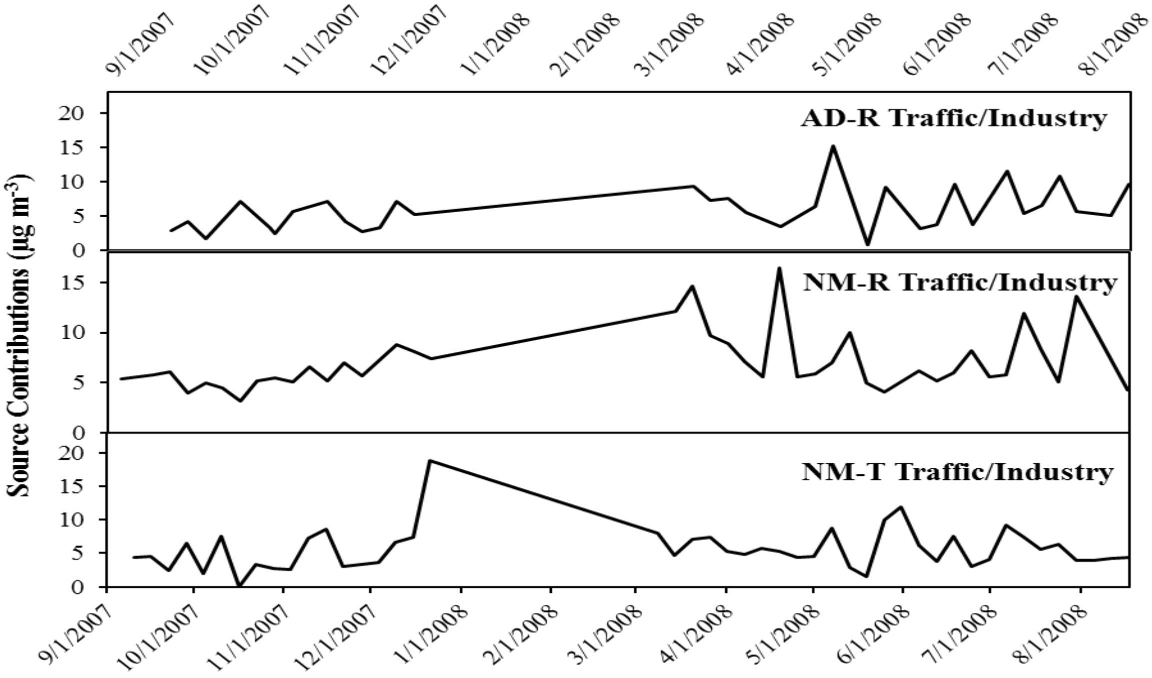


Figure 4.43 Time series of PM$_{10}$ source contributions for traffic/industry factors.

4.5.2 HARMATTAN SEASON

The Harmattan data for the five sites were pooled to increase the sample size. This was carried out after observing that during the non-Harmattan period source profiles were similar across sites but source contributions varied (Zhou *et al.*, 2013). When PMF was applied to the pooled data for the Harmattan period, five sources in both the $PM_{2.5}$ and PM_{10} size fractions were resolved by the model. The five sources identified in both fractions were Sea Salt, Biomass Burning, Soil Dust, Solid Waste Burning and Resuspended Dust. The source profile for the $PM_{2.5}$ and PM_{10} fractions are shown in Figure 4.44 and Figure 4.46, respectively. The corresponding source contributions for $PM_{2.5}$ and PM_{10} are respectively displayed in Figure 4.45 and Figure 4.47. The five sources accounted for 6.6, 44.3, 38.4, 0.4, and 44.3% respectively of the total $PM_{2.5}$ mass. They also accounted for 9.3, 23.1, 59.0, 3.3, and 5.3.0% respectively of total PM_{10} mass.

The first source identified by the PMF model in $PM_{2.5}$ and PM_{10} was sea salt. This source had the highest mass fractions of sodium (Na) and chlorine (Cl). In source apportionment studies conducted in coastal areas, Guo *et al.* (2009) and Ofosu *et al.* (2012) identified a similar source with dominant Na and Cl in the source profiles and classified it as sea salt. The sea salt source contributed more to the PM_{10} mass concentration (25.8 $\mu g\ m^{-3}$) as compared to $PM_{2.5}$ (9.3 $\mu g\ m^{-3}$) during this period.

The second source with high loadings of sulphur (S) and potassium (K) in both $PM_{2.5}$ and PM_{10} was attributed to biomass combustion. This source also reflects regional or long-range transport. The source contributions were relatively high throughout the Harmattan period. It was rather surprising that biomass burning source contributed 4 times more mass concentration to PM_{10} (63.97 µg m^{-3}) than to $PM_{2.5}$ (14.6 µg m^{-3}). Continuous monitoring of PM during the Harmattan season may provide reasons for this anomaly.

The third source includes most of the crustal elements with high concentrations of Mg, Al, Si, K, Ca, Ti, Mn and Fe. These elements are the major constituents of airborne soil and usually make an important contribution to PM_{10}. As expected, soil dust contribution to PM_{10} (166.67 µg m^{-3}) was 3 times more than that to $PM_{2.5}$ (54.1 µg m^{-3}).

The fourth source with large contributions from bromine (Br) and lead (Pb) was identified as solid waste burning. $PM_{2.5}$ and PM_{10} source contributions do not show any significant variations. This source had the lowest contributions to the two PM size fractions; 0.55 µg m^{-3} to $PM_{2.5}$ and 9.2 µg m^{-3} to PM_{10}, respectively. Solid waste burning source was not a significant contributor to PM during this period.

The fifth source was characterized by high loadings of Al, Si, K, Ca, V, Ti, Cr, Mn, Fe, Cu, Zn and Pb. It was attributed to resuspended dust source and it contributed 44.3% (62.3 µg m^{-3}) of $PM_{2.5}$ mass and 5.3% (14.71 µg m^{-3}) of PM_{10} mass, respectively. The high contribution to $PM_{2.5}$ is probably because many roads are unpaved and there is traffic congestion throughout the city.

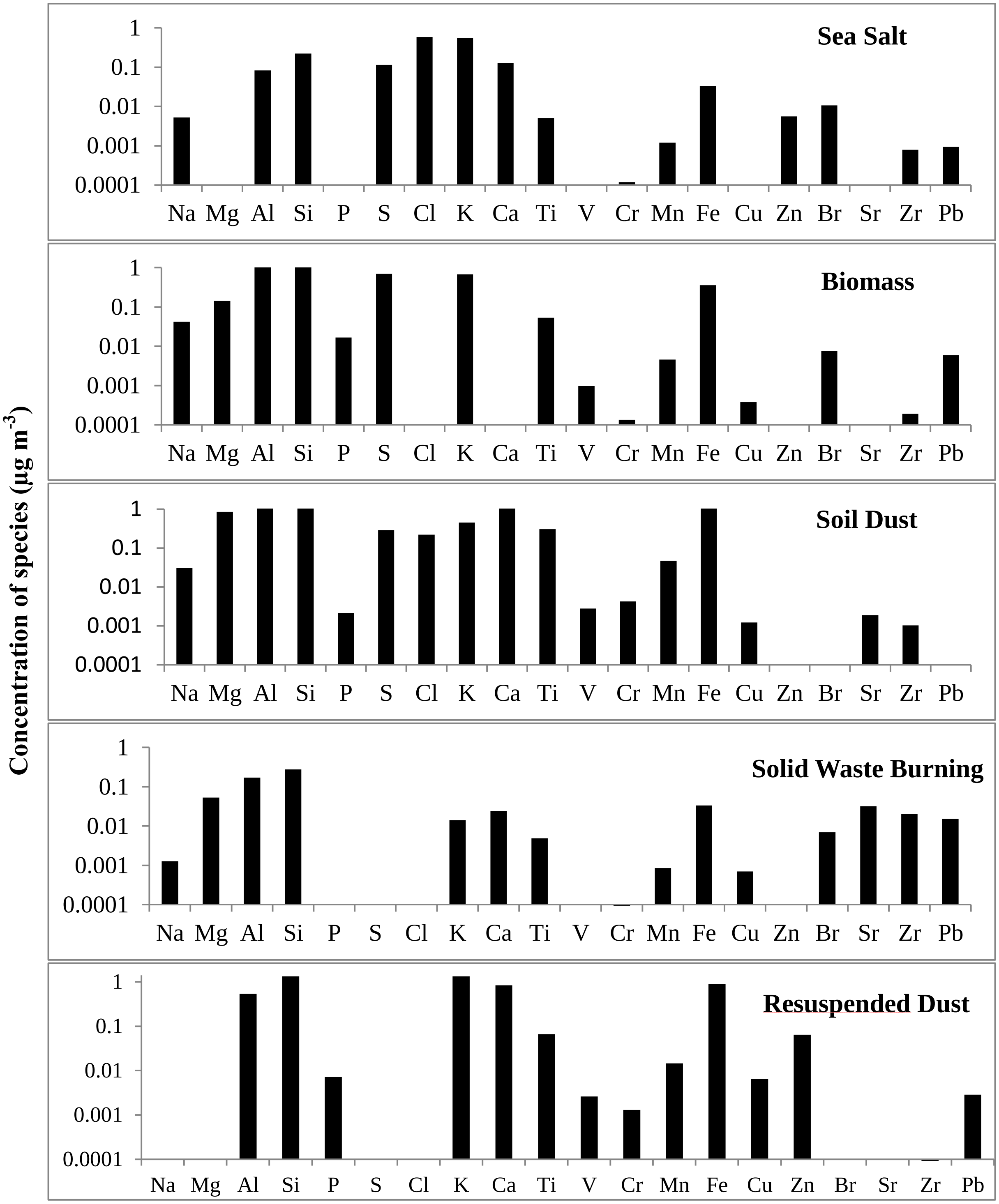


Figure 4.44 $PM_{2.5}$ source profiles for peak Harmattan months (25th December 2007 to 7th February 2008).

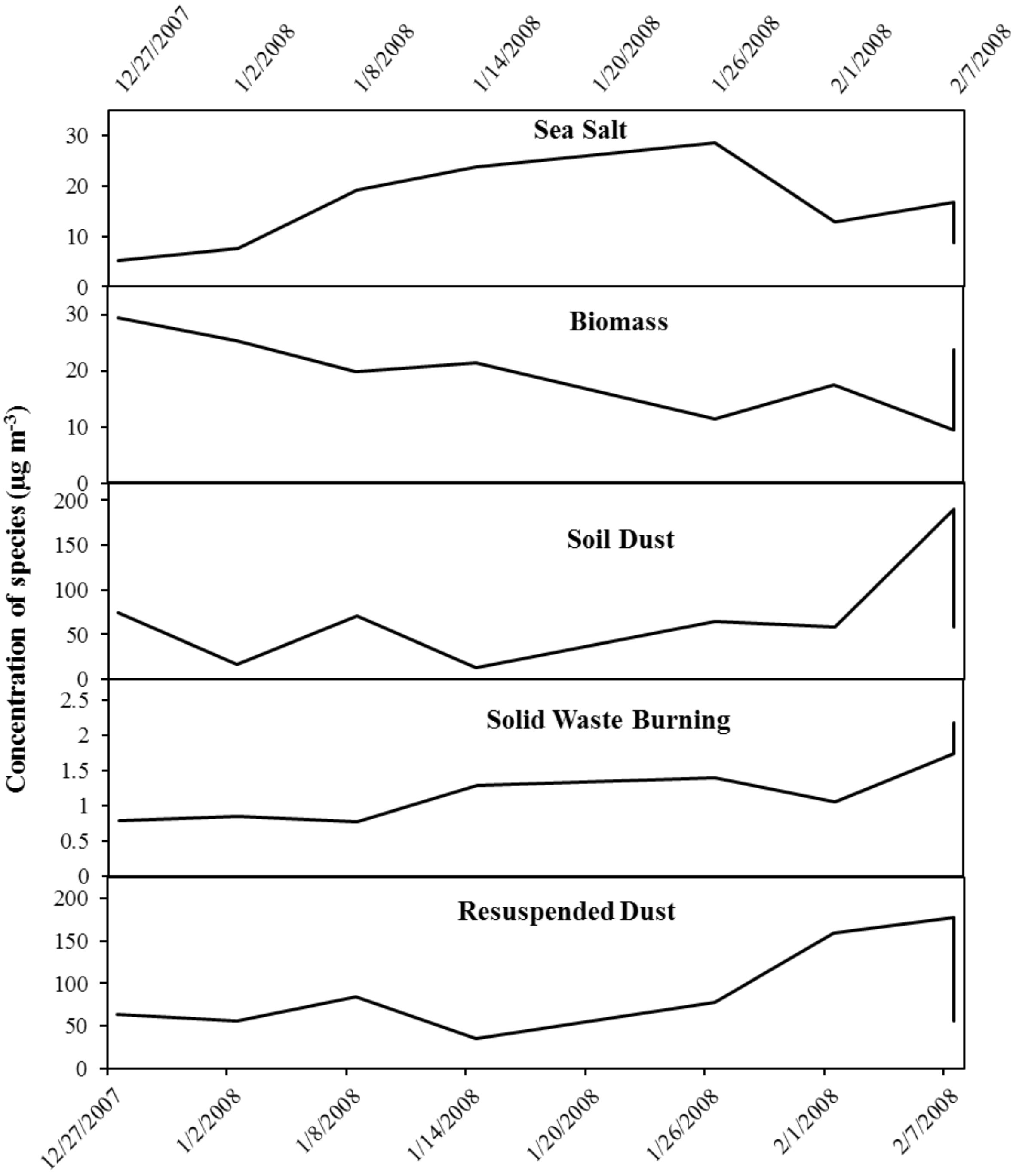


Figure 4.45 Time series of $PM_{2.5}$ source contributions for peak Harmattan months (25th December 2007 to 7th February 2008).

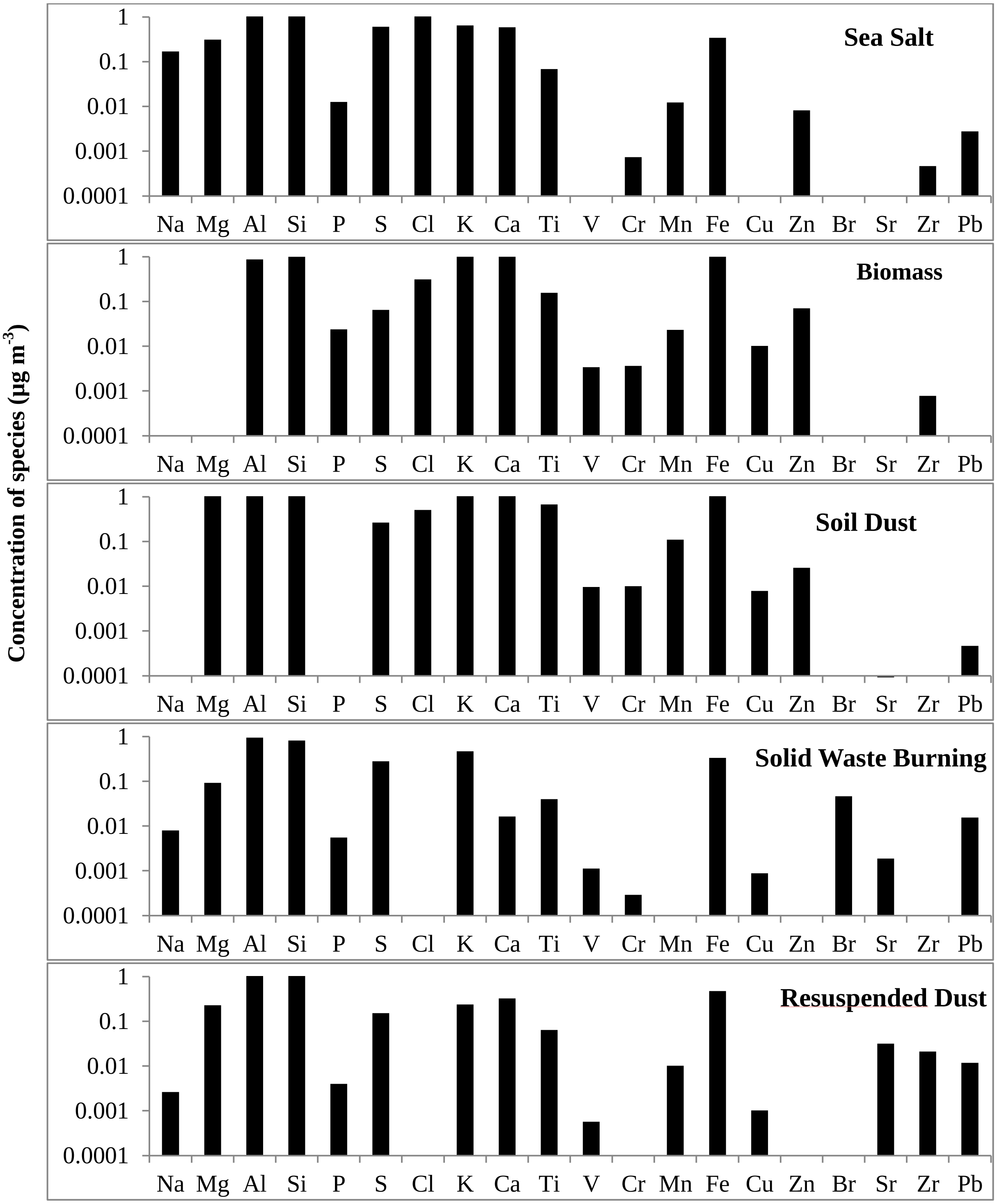


Figure 4.46 PM$_{10}$ source profiles for peak Harmattan months (25th December 2007 to 7th February 2008).

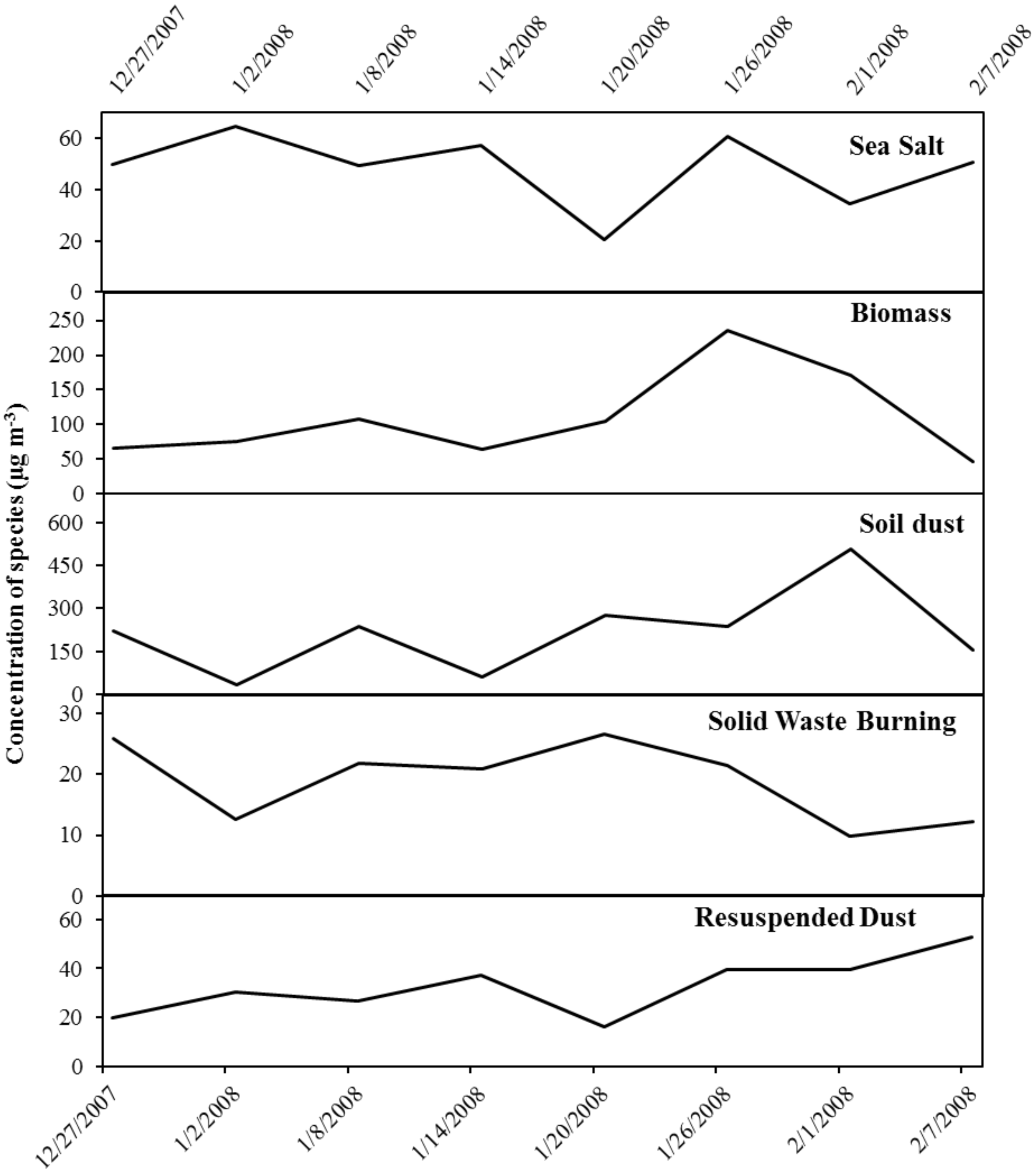


Figure 4.47 Time series of PM_{10} source contributions for peak Harmattan months (25th December 2007 to 7th February 2008).

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This work has investigated the levels, elemental composition and sources of ambient particulate matter from five different receptor sites in four locations, which span from poor to wealthy neighbourhoods in Accra, Ghana. To our knowledge, this is one of the first studies to examine the chemical composition and sources of air pollution in multiple neighbourhoods in a city in a developing country in a year-long campaign which accounts for seasonal differences; data from sub-Saharan Africa, the world's fastest urbanizing region are even more limited. Particulate matter in two size fractions, $PM_{2.5}$ and PM_{10} were determined at all sites between September 2007 and August 2008 by simultaneous 48 h measurement every six days.

The mean mass concentration values for $PM_{2.5}$ obtained at the five sites during the study period were 50.4 µg m^{-3}, 45.9 µg m^{-3}, 74.8 µg m^{-3}, 48.3 µg m^{-3} and 57.5 for AD-R, EL-R, JT-R, NM-R AND NM-T, respectively. The mean mass PM_{10} mass concentration values were 108.2 µg m^{-3}, 96.9 µg m^{-3}, 134.8 µg m^{-3}, 93.9 µg m^{-3} and 111.9 µg m^{-3}at AD-R, EL-R, JT-R, NM-R and NM-T, respectively. These levels are all substantially higher than the WHO, USEPA and EU air quality standards. These results are consistent with the few studies in sub-Saharan Africa such as in urban Addis Ababa that found PM_{10} levels in the range of 40 to 100 µg m^{-3} and in South Africa that measured $PM_{2.5}$ and PM_{10} levels of 86 and 97 µg m^{-3} respectively.

Outside the Harmattan period, the mean annual $PM_{2.5}$ and PM_{10} at neighbourhood sites ranged from 22 to 49 µg m^{-3}, respectively. $PM_{2.5}$ and PM_{10} during the Harmattan period (late December 2007 to early February 2008) were found to be 5 times higher than non-Harmattan period. Harmattan period results revealed that Harmattan dust contributes significantly to ambient particulate pollution.

EDXRF technique was used to identify a total of 21 elements ranging from Al – Pb from the loaded filters. Between-neighbourhood and within-neighbourhood differences in the concentration of many trace element species were observed in this study. These differences could be related to specific local or regional sources affecting the receptor sites. During non-Harmattan months, the three most abundant PM_{10} crustal species at the five sites were Si (5736 to 4002 ng m^{-3}), Al (1654 to 2591 ng m^{-3}), and Fe (1291 to 2034 ng m^{-3}). During the Harmattan months these same crustal species in PM_{10} were highly elevated, Si (31467 to 37526 ng m^{-3}), Al (11599 to 14234 ng m^{-3}) and Fe (8119 to10121 ng m^{-3}).

During the non-Harmattan period between 49% and 55% of PM_{10} mass was found in the fine of $PM_{2.5}$ fraction at the various sites. During Harmattan period, it was observed that about 50% to 53% of PM_{10} mass was found in $PM_{2.5}$ fraction. Elemental species such as K, Cu, Zn, Br and Pb found to have 60% or more of their mass in the fine fraction. These elements are mainly anthropogenic in origin and could originate from sources such as biomass burning, solid waste burning, motor vehicles emissions and industrial emissions.

Enrichment factor results of $PM_{2.5}$ and PM_{10} chemical components for all sites in Accra indicate that elements of anthropogenic origin such as Zn, S, Cl, Br and Pb were highly enriched with respect to crustal elements.

With the exception of temperature which shows a positive relationship with $PM_{2.5}$, the other weather parameters (rainfall, relative humidity and wind speed) had a negative relationship during the study period. However, these relationships were weak and not significant during the period of study.

The receptor model PMF was used to identify sources and their contributions to ambient airborne particulate matter at the five sites in Accra. During non-Harmattan months, PMF resolved for both $PM_{2.5}$ and PM_{10} six sources for AD-R and five sources for EL-R, JT-R, NM-R and NM-T, respectively. Sea salt, biomass burning, solid waste burning and soil dust were ubiquitous sources and were identified at the all five sites. Resuspended dust was identified at three sites. Traffic/industry emissions were identified as a source at three sites near traffic routes. It was not possible to separate of motor vehicle emissions from traffic into diesel and gasoline vehicle contributions due to the lack of data on elemental carbon and organic carbon. In general, anthropogenic related sources were found to be dominant in all neighbourhoods with the exception of East Legon. Contributions of pollutant from natural sources were 27, 56, 34, 32, and 46% at AD-R, EL-R, JT-R, NM-R and NM-T, respectively. Contributions from anthropogenic sources were 73, 44, 66, 68, and 54% at AD-R, EL-R, JT-R, NM-R and NM-T, respectively.

PMF model identify five sources in both $PM_{2.5}$ and PM_{10} pooled data. The five sources were sea salt, biomass burning, soil dust, solid waste burning and resuspended dust. These sources were similar to those resolved during non-Harmattan period at all the sites but much higher contributions from crustal sources during Harmattan as there had been in other months.

5.2. RECOMMENDATIONS

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

- Permanent PM monitoring stations are established at rural, urban and industrial areas to conduct regular monitoring of key indicator pollutants.
- Short duration studies are routinely implemented to estimate $PM_{2.5}/PM_{10}$ ratio for different cities and seasons.
- Black carbon analysis is conducted in future studies in these neighbourhoods to understand their levels and health effects.
- Attention is given to land use and agriculture policies in addition to wildfire management. This is with respect to the finding that there are contributions from regional long-range transport of particulate matter due to wildfire and the annual bush burning that take place in preparation for the farming period.
- Set up effective source-based control strategies and policy on the role of urban biomass burning.
- Regulate the importation of over-aged second hand vehicles and engines by limiting their numbers or through taxation.

- Low-emission mass transportation system is established to decongest the roads, reduce air pollution and fuel consumption.
- Increase community awareness and education on the effect of air pollution as far as particulate matter are concerned.

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APPENDIX A

Table A1: Comparison between measured and PMF calculated $PM_{2.5}$ concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at AD-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
$PM_{2.5}$ Mass (µg m^{-3})	27.29	27.63	0.89	1.2
Elements				
Na	222.16	243.68	0.81	8.8
Mg	79.74	103.19	0.40	22.7
Al	519.06	532.08	0.99	2.4
Si	1132.97	1189.98	0.99	4.8
P	15.09	15.42	0.74	2.2
S	663.33	662.28	0.95	0.2
Cl	242.89	246.54	0.99	1.5
K	568.67	585.63	0.87	2.9
Ca	241.89	242.20	0.97	0.1
Ti	33.05	33.14	0.99	0.3
V	1.10	1.36	0.27	18.9
Cr	1.28	1.67	0.09	23.0
Mn	6.68	6.81	0.96	1.9
Fe	370.15	364.51	0.99	1.5
Cu	4.58	4.66	0.95	1.8
Zn	35.19	37.08	0.78	5.1
Br	14.00	14.49	0.93	3.4
Sr	3.59	4.47	0.36	19.7
Zr	2.81	3.43	0.29	18.0
Pb	12.82	14.25	0.67	10.0

Table A2: Comparison between measured and PMF calculated $PM_{2.5}$ concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at EL-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
$PM_{2.5}$ **Mass (µg m^{-3})**	21.98	22.26	0.92	1.24
Elements				
Na	186.85	220.83	0.49	15.39
Mg	126.45	144.28	0.71	12.36
Al	620.74	643.31	0.99	3.51
Si	1341.27	1430.32	0.98	6.23
P	13.80	14.26	0.86	3.24
S	632.79	638.95	0.94	0.96
Cl	144.61	145.24	0.99	0.44
K	602.54	619.18	0.90	2.69
Ca	245.24	246.60	0.99	0.55
Ti	48.45	49.19	0.99	1.52
V	0.85	0.90	0.68	6.06
Cr	0.98	1.22	0.14	20.02
Mn	8.66	9.31	0.71	6.96
Fe	426.87	411.95	0.99	3.62
Cu	1.40	1.97	0.09	28.82
Zn	12.26	17.60	0.00	30.34
Br	21.46	21.64	1.00	0.83
Sr	2.49	3.43	0.22	27.29
Zr	1.38	2.48	0.19	44.52
Pb	9.69	11.28	0.38	14.12

Table A3: Comparison between measured and PMF calculated $PM_{2.5}$ concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at JT-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
$PM_{2.5}$ **Mass (µg m^{-3})**	48.85	49.30	0.88	0.92
Elements				
Na	420.91	455.63	0.86	7.62
Mg	148.93	165.69	0.39	10.12
Al	671.00	688.92	1.00	2.60
Si	1476.88	1553.64	0.99	4.94
P	16.80	17.93	0.17	6.26
S	799.67	833.33	0.88	4.04
Cl	1408.42	1442.96	0.95	2.39
K	1831.38	1840.75	0.90	0.51
Ca	372.07	380.41	0.95	2.19
Ti	41.97	42.43	1.00	1.08
V	0.97	1.04	0.59	6.50
Cr	1.19	1.39	0.31	14.06
Mn	7.61	7.92	0.96	4.01
Fe	407.33	399.89	0.99	1.86
Cu	4.59	4.60	0.98	0.40
Zn	38.89	44.15	0.17	11.93
Br	19.69	19.92	0.98	1.17
Sr	4.34	5.05	0.24	14.09
Zr	2.92	3.46	0.17	15.81
Pb	11.11	11.87	0.59	6.40

Table A4: Comparison between measured and PMF calculated $PM_{2.5}$ concentrations (in ng m^{-3}) except for PM (in μg m^{-3}) at NM-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
$PM_{2.5}$ **Mass (μg m^{-3})**	26.78	27.27	0.73	1.83
Elements				
Na	217.42	271.01	0.62	19.77
Mg	104.58	131.99	0.29	20.76
Al	550.51	569.41	0.99	3.32
Si	1191.70	1258.44	0.98	5.30
P	12.42	13.23	0.53	6.09
S	606.20	622.38	0.92	2.60
Cl	354.68	359.07	0.99	1.22
K	815.22	842.66	0.73	3.26
Ca	277.81	282.13	0.96	1.53
Ti	36.02	35.80	1.00	0.60
V	0.72	0.80	0.50	10.26
Cr	0.86	1.08	0.23	20.57
Mn	5.42	5.60	0.96	3.29
Fe	370.12	361.32	0.99	2.44
Cu	5.21	5.29	0.96	1.48
Zn	22.87	27.65	0.13	17.31
Br	17.65	20.50	0.73	13.89
Sr	3.59	4.65	0.16	22.65
Zr	1.47	2.10	0.19	29.77
Pb	12.34	13.50	0.58	8.53

Table A5: Comparison between measured and PMF calculated $PM_{2.5}$ concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at NM-T site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
$PM_{2.5}$ **Mass (µg m^{-3})**	33.23	34.04	0.79	2.38
Elements				
Na	152.85	181.10	0.57	15.60
Mg	76.92	90.20	0.65	14.72
Al	776.89	795.17	1.00	2.30
Si	1597.07	1701.65	0.98	6.15
P	17.11	17.69	0.80	3.28
S	650.16	661.65	0.96	1.74
Cl	376.51	378.97	0.99	0.65
K	899.13	929.89	0.57	3.31
Ca	434.54	450.53	0.88	3.55
Ti	54.04	54.11	0.99	0.13
V	0.95	1.02	0.63	6.64
Cr	1.16	1.40	0.19	17.30
Mn	7.99	8.23	0.93	2.92
Fe	539.81	536.69	0.98	0.58
Cu	4.82	4.95	0.97	2.68
Zn	29.00	32.08	0.08	9.61
Br	16.89	16.94	0.99	0.28
Sr	2.14	2.89	0.48	26.19
Zr	1.58	1.96	0.51	19.57
Pb	12.28	14.67	0.60	16.29

Table A6: Comparison between measured and PMF calculated PM_{10} concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at AD-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
PM_{10} **Mass (µg m^{-3})**	55.14	55.65	0.97	0.91
Elements				
Na	959.38	984.60	0.96	2.56
Mg	272.62	287.18	0.92	5.07
Al	1627.32	1654.45	1.00	1.64
Si	4016.63	4137.18	0.99	2.91
P	25.41	25.92	0.90	1.99
S	838.21	861.83	0.91	2.74
Cl	2026.10	2030.75	0.98	0.23
K	857.41	886.20	0.92	3.25
Ca	1113.91	1118.34	0.97	0.40
Ti	124.97	125.60	0.99	0.50
V	2.17	2.28	0.79	4.94
Cr	3.10	3.26	0.54	4.97
Mn	19.15	19.55	0.99	2.01
Fe	1505.08	1491.33	0.97	0.92
Cu	8.45	8.50	0.98	0.55
Zn	48.24	52.86	0.29	8.74
Br	20.42	20.48	1.00	0.30
Sr	3.65	3.68	0.98	0.96
Zr	2.11	2.19	0.93	3.61
Pb	13.74	18.92	0.22	27.36

Table A7: Comparison between measured and PMF calculated PM_{10} concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at EL-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
PM_{10} **Mass (µg m^{-3})**	44.71	45.00	0.97	0.64
Elements				
Na	545.03	569.90	0.96	4.36
Mg	229.67	248.34	0.93	7.52
Al	1830.21	1834.19	1.00	0.22
Si	4176.72	4282.65	0.99	2.47
P	20.22	21.76	0.39	7.07
S	689.03	694.63	0.97	0.81
Cl	1165.27	1160.59	0.98	0.40
K	832.26	850.76	0.94	2.17
Ca	900.53	910.85	0.98	1.13
Ti	129.04	129.32	0.99	0.22
V	2.48	2.57	0.76	3.44
Cr	3.02	3.14	0.56	3.90
Mn	16.16	16.54	0.99	2.31
Fe	1459.67	1462.86	0.94	0.22
Cu	1.99	2.49	0.10	20.01
Zn	24.96	25.12	0.99	0.67
Br	23.04	28.28	0.67	18.54
Sr	6.17	7.28	0.41	15.33
Zr	4.22	4.73	0.43	10.80
Pb	18.99	20.06	0.91	5.31

Table A8: Comparison between measured and PMF calculated PM_{10} concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at JT-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
PM_{10} **Mass (µg m^{-3})**	81.92	82.42	0.94	0.60
Elements				
Na	1940.70	1965.98	0.95	1.29
Mg	439.68	455.07	0.94	3.38
Al	1707.95	1720.22	1.00	0.71
Si	4225.87	4310.29	1.00	1.96
P	29.53	30.21	0.96	2.26
S	1059.66	1114.95	0.64	4.96
Cl	4910.24	4929.92	0.96	0.40
K	2173.59	2215.20	0.84	1.88
Ca	1617.07	1641.68	0.97	1.50
Ti	129.84	130.12	0.99	0.21
V	1.82	1.94	0.69	6.22
Cr	3.44	3.51	0.64	2.09
Mn	20.59	20.81	0.99	1.03
Fe	1298.71	1291.06	0.99	0.59
Cu	6.26	7.25	0.33	13.64
Zn	60.99	67.07	0.29	9.06
Br	22.84	22.72	1.00	0.50
Sr	5.26	6.04	0.29	12.84
Zr	4.68	5.16	0.51	9.33
Pb	15.74	16.08	0.96	2.09

Table A9: Comparison between measured and PMF calculated PM_{10} concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at NM-R site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
PM_{10} **Mass (µg m^{-3})**	50.47	50.87	0.94	0.78
Elements				
Na	656.98	686.73	0.96	4.33
Mg	224.80	248.35	0.86	9.48
Al	1655.98	1679.48	1.00	1.40
Si	3895.90	4001.70	0.98	2.64
P	22.71	23.65	0.66	3.97
S	732.61	750.36	0.94	2.37
Cl	1699.05	1696.07	0.98	0.18
K	1101.36	1111.18	0.91	0.88
Ca	1181.10	1182.53	0.97	0.12
Ti	124.66	124.10	0.99	0.45
V	2.08	2.14	0.83	2.78
Cr	2.93	3.10	0.48	5.77
Mn	17.17	17.42	0.99	1.45
Fe	1369.62	1346.08	0.98	1.75
Cu	5.36	6.31	0.14	15.05
Zn	39.03	39.33	0.98	0.78
Br	22.23	25.01	0.74	11.11
Sr	5.90	6.97	0.35	15.26
Zr	3.64	5.00	0.14	27.24
Pb	15.66	17.45	0.47	10.28

Table A10: Comparison between measured and PMF calculated PM_{10} concentrations (in ng m^{-3}) except for PM (in µg m^{-3}) at NM-T site for studied chemical species.

Species	PMF modelled	Measured	r^2	Uncertainty
PM_{10} **Mass (µg m^{-3})**	69.69	70.30	0.94	0.86
Elements				
Na	742.92	761.69	0.97	2.46
Mg	293.49	307.89	0.92	4.68
Al	2573.85	2590.71	0.99	0.65
Si	5650.19	5736.35	0.99	1.50
P	40.10	41.25	0.82	2.80
S	841.37	884.95	0.73	4.92
Cl	2133.14	2152.32	0.95	0.89
K	1283.18	1317.76	0.73	2.62
Ca	1869.12	1919.56	0.92	2.63
Ti	200.13	202.73	0.96	1.28
V	3.05	3.09	0.82	1.55
Cr	4.61	4.76	0.68	3.19
Mn	25.73	26.11	0.98	1.46
Fe	2020.19	2033.75	0.97	0.67
Cu	8.92	8.97	1.00	0.50
Zn	51.02	53.96	0.51	5.44
Br	29.98	30.01	1.00	0.09
Sr	4.68	5.94	0.21	21.30
Zr	3.04	4.34	0.09	29.85
Pb	13.73	15.19	0.28	9.61