



**Research group “Tropospheric Aerosol Research and Nuclear Microanalysis”
Department of Analytical Chemistry, Ghent University**

**Physico-Chemical Characterisation of Atmospheric Aerosols in
Tanzania, with Emphasis on the Carbonaceous Aerosol
Components and on Chemical Mass Closure**

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**A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy (Ph.D) in Science: Chemistry**

Promoter: Prof. Dr. Willy Maenhaut

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To the best of my knowledge and belief, this thesis contains no material which has been
accepted (previously published) for the award of any other diploma or degree in any
learning institution or University

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*This thesis is dedicated to my son Macaureus, my wife Judith, parents, sisters and
brothers, for their love, kindness and endless support*

Illustrations on the covers:

Front cover:

The pictures show the two sites where ambient aerosol samples were collected in Tanzania

Upper-left: a busy street canyon in the city centre of Dar es Salaam

Upper-right: the samplers on the second-floor balcony of the YWCA building located along Azikiwe Street at Posta Mpya, Dar es Salaam

Lower-left: the western foothill of Uluguru Mountain ranges in Morogoro where the main campus of Sokoine University of Agriculture is located

Lower-right: the samplers mounted on a roof at the main campus of Sokoine University of Agriculture

Back cover:

Some of the instruments used in this research work

Upper-left: the old thermal-optical transmission (TOT) instrument

Upper-right: the new thermal-optical transmission (TOT) instrument

Lower-left: the ion chromatography (IC) instrument

Lower-right: the total organic carbon (TOC) analyzer

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List of Abbreviations and Acronyms

AD	aerodynamic diameter
ASRS	Anion Self-Regenerating Suppressor
BC	black carbon
CCN	cloud condensation nuclei
comm.	communality
comp.	component
CSRS	Cation Self-Regenerating Suppressor
D	Dar es Salaam
DL	detection limit
DMS	dimethylsulphide
D_N	variable for indicating day and night (1 for day, 0 for night)
D _p	particle diameter
EC	elemental carbon
EF	enrichment factor
EU	European Union
FID	flame ionization detector
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IC	ion chromatography
IC _{ws}	inorganic water-soluble carbon
INW	Institute for Nuclear Sciences
IPCC	Intergovernmental Panel on Climate Change
M	Morogoro
max.	maximum
min.	minimum
MSA	methanesulphonic acid
ND	not determined
NDIR	non-dispersive infrared
NEMC	National Environmental Management Council
NN	Nuclepore polycarbonate filters
NOAA	National Oceanic and Atmospheric Administration
NO _x	nitrogen oxides (= NO + NO ₂)
nss	non-sea-salt
NSTL	National Seed Testing Laboratory
OC	organic carbon

OM	organic matter
PC	principal component
PCA	principal component analysis
PIXE	particle-induced X-ray emission
PM	particulate matter
PM10	particulate matter with aerodynamic diameter smaller than 10 µm
PM10(NN)	Gent PM10 stacked filter unit sampler with two Nuclepore filters in series
PM10(Q)	sampler with Whatman QM-A quartz fibre filter and with Gent PM10 inlet
PM10-2	particulate matter with aerodynamic diameter between 2 and 10 µm (coarse PM)
PM2	particulate matter with aerodynamic diameter smaller than 2 µm
PM2.5	particulate matter with aerodynamic diameter smaller than 2.5 µm
PM2.5(Q)	sampler with Whatman QM-A quartz fibre filter and with Gent PM10 inlet
PVDF	Polyvinylidene difluoride
Q	Whatman QM-A quartz fibre filter
RH	relative humidity
SFU	stacked filter unit
SIA	secondary inorganic aerosol
SOA	secondary organic aerosol
stdev	standard deviation
SUA	Sokoine University of Agriculture
SVOCs	semi-volatile organic compounds
TBS	Tanzania Bureau of Standards
TC	total carbon (= OC + EC)
TC _{ws}	total water-soluble carbon
TMA	Tanzania Meteorological Agency
TOC	total organic carbon
TOC _{ws}	total water-soluble organic carbon
TOT	thermal-optical transmission
TSP	total suspended particulates
UGent	Ghent University
UTC	Universal Time, Coordinated
VLIR	Flemish Interuniversity Council
VOCs	volatile organic compounds
WSOC	water-soluble organic carbon
YWCA	Young Women's Christian Association of Tanzania

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CHAPTER 1

INTRODUCTION

1.1 Atmospheric aerosols

Atmospheric aerosols (also referred to as particulate matter, PM) are relatively stable solid and/or tiny liquid particles which are suspended in the ambient air. They arise from natural sources, such as soil dust, sea salt, volcanoes, the vegetation, and natural biomass burning and from a wide variety of anthropogenic sources, such as industrial activities, electricity production, vehicular traffic, man-made biomass burning, agriculture, and households. They can be emitted directly to the atmosphere (primary particles) or arise by gas-to-particle formation from precursor gases (secondary particles). Therefore, atmospheric aerosols are complex mixtures of different chemical species. Their presence is often directly observable by the human eye, such as haze in industrial regions and areas subjected to heavy biomass burning. The sizes of the atmospheric aerosol particles can range from 1 nanometer (nm) to 100 micrometers (μm) in diameter. Most of their mass is in the size range from about 0.1 to 10 μm .

Atmospheric aerosol particles can be divided into two classes reflecting their major formation mechanisms. These classes are primary and secondary, whereby the primary particles are mostly present in the coarse size fraction and the secondary particles mostly in the fine fraction [Raes et al., 2000]. The coarse fraction includes particles greater than 2 μm aerodynamic diameters (AD), which are mostly injected directly to the atmosphere by mechanical processes or from natural sources. The fine fraction (particles with AD less than 2 μm) contains mainly particles, which arise from gas-to-particle conversion, whereby gases such as sulphur dioxide (SO_2), nitric oxide and nitrogen dioxide (NO_x), and volatile organic compounds (VOCs) are oxidized and condensed.

In the global atmosphere, the size distribution of the aerosol particles is highly variable, but generally presents itself as a superposition of more or less distinguishable modes. Each of these modes can be represented by a log-normal distribution. Therefore, four modes can be seen in the particle size distributions of atmospheric aerosols. These, as shown in Figure 1.1, include the “Nucleation mode” (particles with diameter (D_p) $< 0.01 \mu\text{m}$); the “Aitken mode” (particles with $0.01 < D_p < 0.1 \mu\text{m}$ diameter); the “Accumulation mode” ($0.1 < D_p < 1 \mu\text{m}$), and the “coarse mode” ($1 < D_p < 10 \mu\text{m}$). However, the modes result from specific emissions and atmospheric processes. The

nucleation mode is the result of recent nucleation events involving formation of new particles from precursor gases. The Aitken mode results from condensation on, and self-coagulation of nucleation mode particles, as well as from primary emissions during high temperature combustion. The nucleation and Aitken modes contain the largest number of particles, but not much of the total mass burden.

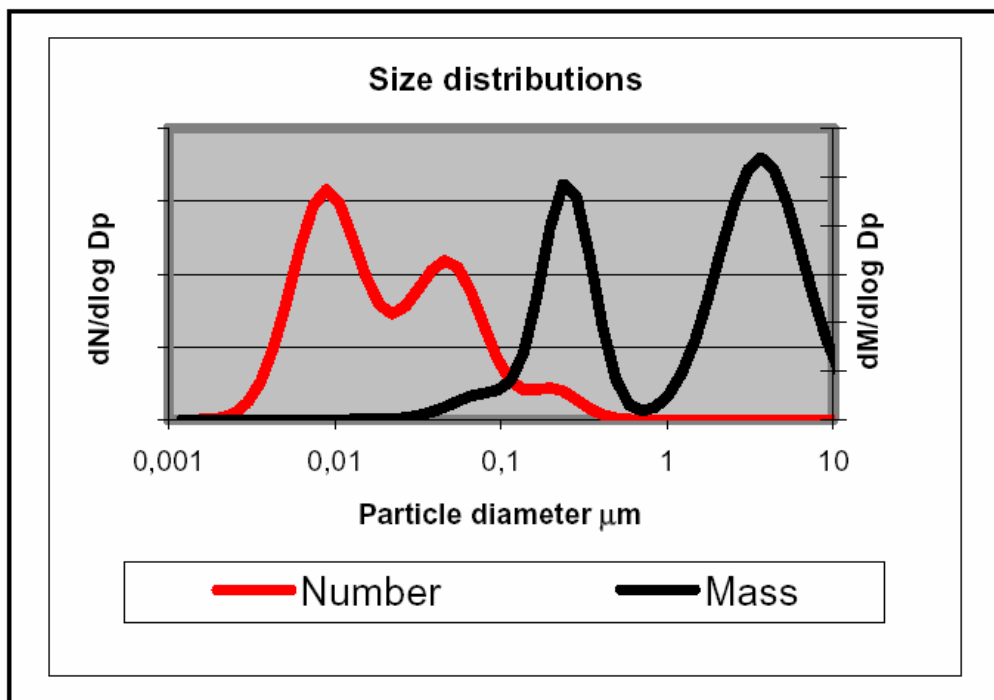


Figure 1.1. Sketch of the number and mass size distributions of the atmospheric aerosol.

On the other hand, the accumulation mode typically results from coagulation and from the formation of particle mass by in-cloud chemistry. As a large part of the accumulation mode particles is made of soluble material, they constitute efficient cloud condensation nuclei (CCN) and are primarily scavenged from the atmosphere by precipitation processes. Primary emissions from the mechanical break-up of bulk material will contribute to the number of accumulation mode particles as well; however, they will dominate the mass of the coarse mode. Particles in the coarse mode are formed by mechanical processes, such as wind erosion of the Earth surface (soil or mineral dust), the

bubble bursting process in the seas and oceans (sea spray) or volcanic eruptions. Bioaerosols, such as spores, pollen, bacteria, and small fragments of plants and animals, are also in this size range. Although the coarse mode particles rapidly settle out from the air due to their large mass, together with the accumulation mode, they make up most of the atmospheric aerosol mass. Even though primary particles dominate in the coarse mode, secondary particles formed by chemical interaction of gases with primary particles of crustal or marine origin may also be found [Wu and Okada, 1994].

1.2 Sources, production mechanisms, and chemical composition of atmospheric aerosols

The spatial and temporal variability in the size distribution and composition of atmospheric aerosols on regional and global scale are controlled by different types of natural and anthropogenic emission sources. Other factors including regional atmospheric dynamics (responsible for transport and dispersion of pollutants), meteorological conditions, and the presence of gaseous precursors (influencing gas-to-particle conversion) are also important. However, it is difficult to discriminate between the natural and anthropogenic contributions to aerosols such as carbonaceous species, and this is especially so for tropical and subtropical areas [Maenhaut et al., 1996]. Chemical characterisation is widely used to identify the particulate matter components and their natural and anthropogenic origin. The major aerosol types (components) are carbonaceous materials (organic carbon, elemental carbon), sulphate, nitrate, ammonium, sea salt (sodium, chloride), and crustal matter (mineral dust). As the chemical composition and size distribution of the aerosol particles are linked to their origin and formation mechanisms, their natural or anthropogenic origin can be identified by chemical characterisation.

1.2.1 Natural particulate sources

Mineral (soil) dust is a major component of the atmospheric aerosol on a global scale and accounts for a large fraction of the natural primary particulate matter. The

natural mineral dust particles may result from physical and chemical weathering, soil dust re-suspension or long-range transport [Tegen et al., 1997]. Dust deflation occurs when the surface wind speed exceeds a threshold velocity, which is a function of surface roughness, grain size, and soil moisture. On the other hand, the disturbance of such surfaces by human activities can strongly enhance dust mobilisation [Tegen and Miller, 1998]. The main chemical components of mineral dust aerosol are earth crust elements: Si, Ca, Fe, Al, Mg, K, O.

Sodium chloride and sulphates mainly of sodium, magnesium and potassium are the main constituents of sea salt particles. They are generated by various physical processes, especially by bursting of entrained air bubbles during whitecap formation which is strongly dependent on wind speed [Monahan et al., 1986; Despiou et al., 1996].

Primary biogenic sources give rise to bio-aerosols or biological residues, some of which are of potential risk to human health. These aerosols consist mainly of plant debris (cuticular waxes and leaf fragments) and microbial particles such as bacteria and fungi (generated in solid waste recycling and composting processes), viruses, protozoon or algae, pollen and spores. Bacteria and viruses have sizes $<2\ \mu\text{m}$ whereas the fragments of plants and spores exhibit sizes in the coarse fraction [Pósfai and Molnár, 2000].

Volcanic eruptions are significant sources of primary and secondary aerosols; they are sources of primary dust and of gaseous sulphur which forms sulphate aerosol (secondary). However, their contribution to the bulk PM levels in ambient air is limited in time and space [Graf et al., 1997; Andres and Kasgnoc, 1998].

Sulphate, nitrate and organic matter are the main components of the natural secondary aerosols. Natural sulphate aerosols (with the exception of sea-salt sulphate and gypsum dust particles) are produced by chemical reactions in the atmosphere from gaseous precursors. The two main sulphate precursors are SO_2 from volcanoes and dimethylsulphide ($(\text{CH}_3)_2\text{S}$; DMS) from biogenic sources, especially marine plankton. The key controlling variables for the production of sulphate aerosol are the source strength of the precursor substances, the fraction of the precursors removed before conversion to sulphate, and the chemical transformation rates along with the gas-phase and aqueous chemical pathways.

Nitrate is mainly formed by the oxidation of nitrogen oxides, NO_x , of which soil transpiration and lightning are the main natural sources [Price et al., 1997; Roelle et al., 2001]. The amount of nitrate in the aerosol phase is closely tied to the relative abundances of ammonium and sulphate. For example, if ammonia is available in excess of the amount required to neutralise sulphuric acid, ammonium nitrate can form small, radiatively efficient aerosols. The relative humidity and temperature also affect the amount of nitrate [Stelson and Seinfeld, 1982].

The main natural sources of the organic precursors for secondary aerosol formation occur in forested areas, where significant quantities of volatile organic compounds, such as isoprene and monoterpenes, are released during plant transpiration. The oxidation of these organic vapours gives lower vapour pressure gases, which form new particles by nucleation or condense onto pre-existing particles [Claeys et al., 2004].

1.2.2 Anthropogenic particulate sources

Anthropogenic particulate sources are mainly located in urban and industrial environments. With regard to traffic, primary coarse particles originate from the abrasion of brake linings and tyres and re-suspended road dust, whereas fine primary particles (soot and trace elements) are emitted by the vehicle exhaust. Manufacturing of bricks, cement and ceramics, building construction, coal combustion, mining, metallurgy, smelters and waste incineration are among the industrial and technical activities that also produce primary particles. All these aerosol sources have an impact on environmental quality, however, in urban environment, the traffic is especially important. The primary particles associated with some industrial sources (mining, cement, building, bricks) consist mostly of coarse particulate matter of crustal composition. Smelters and waste incinerators emit fine primary particles [Pacyna and Pacyna, 2001]. Coal combustion is a large source of fly ash (primary PM) whose emission has been larger in the past, but currently in most industrialized countries it has been reduced due the progress replacement of coal by other fuels and the use of emission abatement technologies.

Anthropogenic secondary particles include sulphate, nitrate, and organic particles. A large proportion of SO_2 (the gaseous precursor of sulphate) originates from coal

combustion, other industrial activities, and vehicular traffic. The oxidation of SO_2 produces sulphuric acid (H_2SO_4) which is then neutralized by ammonia forming ammonium derivatives (NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$) in the fine size fraction. However, sulphuric acid neutralised by calcium carbonate and sodium chloride can be found in the coarse fraction. Traffic emission in the urban environment and some industrial processes are the main anthropogenic sources of nitrogen oxides, NO_x . Gaseous nitric acid (HNO_3) is formed by the oxidation of NO_x and may be neutralised and transformed into particulate nitrate. Ammonium nitrate is present in the fine mode while calcium nitrate and sodium nitrate (formed by neutralisation of HNO_3 by crustal CaCO_3 and marine NaCl , respectively) occurs in the coarse mode.

1.3 Relevance of atmospheric aerosols

The study of this atmospheric pollutant has increased in recent years due to the understanding of its adverse effects on health [Dockery and Pope, 1996; Künzli et al., 2000; Stieb et al., 2002], and because it became evident that atmospheric aerosols also play an important role in climate change [IPCC, 2007]. Furthermore, aerosol particles influence many atmospheric processes, including cloud formation, precipitation (and consequently the global hydrological cycle) and solar radiation, and play a major role in acidification of clouds, rain and fog [Khoder, 2002; Watson, 2002; IPCC, 2007]. Aerosols are important in atmospheric chemistry, contribute to soiling and corrosion of buildings and structures, and have adverse impacts on the vegetation [Emberson et al., 2001] and on ecosystems [Pio et al., 1998]. Most of the effects are driven by the physical and chemical properties of the aerosols, for example, aerosol size, concentration, and chemical composition, which vary from region to region depending on the sources of the aerosols. Figure 1.2 illustrates the role of atmospheric aerosols in many global processes.

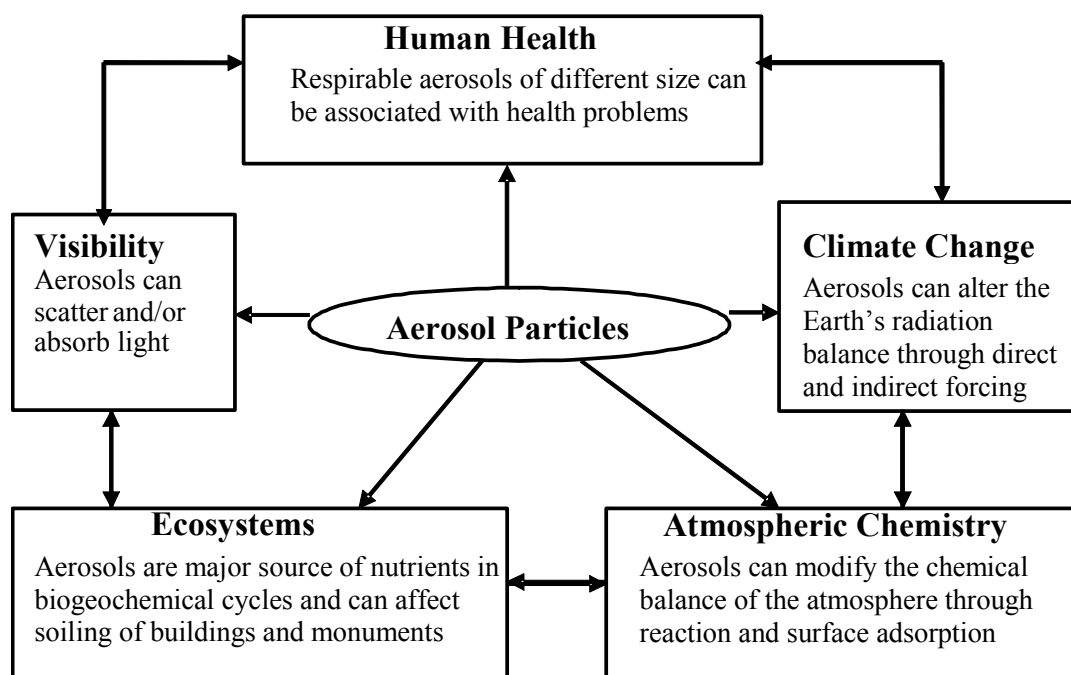


Figure 1.2. Impact of aerosols particles on human health and global processes.

1.3.1 Human health

During the last decade several reports in epidemiological studies showed positive and statistically significant correlation between particulate matter pollution and cardiopulmonary diseases, increased mortality and morbidity [Dockery et al., 1993; Dockery and Pope 1994; Pope 2000; Hauck et al., 2004; Namdeo and Bell, 2005]. The inhalable fraction of PM particles ($<10\ \mu\text{m}$) passing the nose and/or the mouth can accumulate in the respiratory system and is likely to trigger or exacerbate respiratory and cardiovascular diseases [Dockery and Pope, 1996; Pope et al., 2002]. The health effects caused by inhaled particles depend on their size distribution, concentration and chemical composition and on the site at which they deposit within the respiratory system [Hetland et al., 2004]. Although coarse PM has been shown to have a strong potential to induce inflammatory mediators, the effect of PM₁₀ may still largely be caused by fine particles due to their large number or greater surface area [Salma et al., 2002; Villeneuve et al., 2003], and because they contain more toxic elements and species. Studies in the USA

showed that PM₁₀ particles are associated with respiratory responses (effects) and PM_{2.5} fractions are associated with cardiovascular diseases [Wyzga, 2002].

Due to their toxicity trace elements, such as lead, zinc, copper, cadmium, etc., in the form of fine particles are of great concern. Investigators have suggested that trace metals could catalyze the formation of oxidants in the lung which in turn produce tissue damage. Traffic emissions, combustion processes, and industrial processes, such as metal refining, have led to a substantial increase of trace elements in the atmosphere [World Health Organization, 2003].

Mineral dust episodes may cause serious human respiratory health problems because dust particles consist of minerals such as quartz, feldspar, and palygorskite and they also adsorb toxic chemical species [Prospero, 1999]. In addition, volcanic ash can cause pulmonary fibrosis in large doses or over long time exposure [Horwell et al., 2003], whereas occupational exposure to quartz and asbestos has been associated with persistent inflammation, fibrosis and cancer [Schwarze et al., 2002].

1.3.2 Effects on climate

One of the major concerns about aerosol particles is their role in the Earth's climate system. Processes that can interfere with the overall Earth's radiation balance can cause climate change [Seinfeld and Pandis, 1998]. Atmospheric aerosol particles influence the Earth's radiation budget in two ways. Firstly, by scattering and absorbing incoming solar radiation (short-wave radiation) and outgoing terrestrial infrared radiation (long-wave radiation) (direct radiative forcing). Secondly, by influencing the properties and formation processes of clouds (ability to act as cloud condensation nuclei, CCN, and ice nuclei, IN) (indirect radiative forcing) [IPCC, 2007]. In this way, aerosols can affect the concentration and size distribution of cloud droplets. In turn, they can alter the cloud radiative properties, cloud lifetime, the nature and allocation of rain clouds and as a result they interfere with the hydrological cycle [Rosenfeld, 2000; Toon, 2000]. Both direct and indirect radiative forcing has been recognized in recent decades to be of great importance for understanding the observed climate change [IPCC, 2007]. The contributions to radiative forcing from some of the factors influenced by human activities are shown in

Figure 1.3. The values reflect the total forcing relative to the start of the industrial era (about 1750).

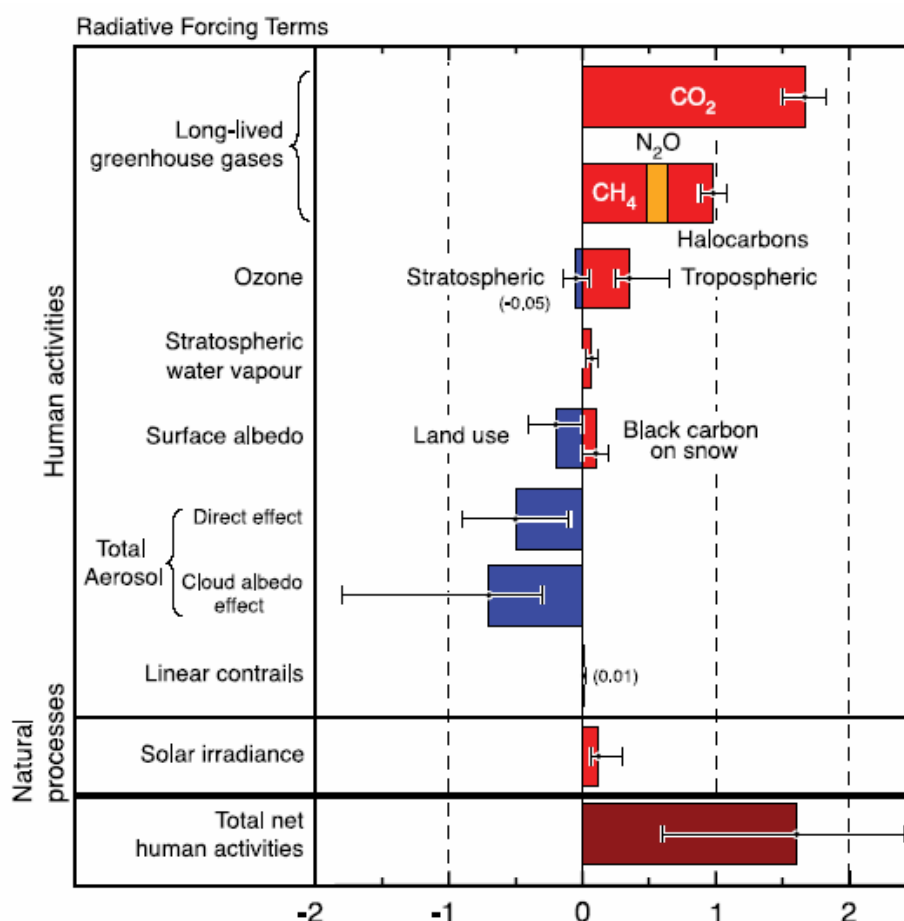


Figure 1.3. Summary of the principal components of the radiative forcing of climate between 1750 and 2005 (source: IPCC [2007]).

1.3.2.1 Direct radiative forcing

The estimated overall direct radiative forcing of aerosol is $-0.50 \pm 0.40 \text{ W m}^{-2}$ [IPCC, 2007]. The radiative effects of aerosols depend on the chemical composition and size of the particles. The estimates of the direct forcing for various aerosol types are given in Table 1.1. Most of the early studies showed that sulphate aerosols are effective at scattering incoming short-wave radiation back to space. However, due to their sizes they have little effect on the out-going long-wave radiation. By reducing the amount of

incoming solar energy, the net direct effect of these small particles is cooling. Organic aerosols generally found in fine particle size range also reduce the amount of incoming solar energy. Due to chemical reactions with gaseous oxidants, the properties of organic aerosols change (aging). An organic coating (non-absorbing) on an absorbing core (soot) increases the absorption of the particle, whereas an organic coating on a hygroscopic core (sulphate) decreases the rate of water up-take by the particle. In many regions the weakening of the radiative forcing of the sulphate aerosol due to reduced emissions will be partially balanced by increases in the radiative forcing of the nitrate aerosol, while the estimated value for organic carbon has remained somewhat the same. On the other hand, black (elemental) carbon is an effective absorber of solar radiation and hence causes a positive forcing (warming) [IPCC, 2007].

The sea-salt aerosol radiative forcing was estimated to be in the range of -0.6 to -2 for low wind speed and in the range of -1.5 to -4 Wm⁻² for high wind speed [Satheesh and Moorthy, 2005]. Mineral dust can also modify the Earth's radiation budget by causing a warming or cooling depending on its concentration, vertical distribution in the atmospheric column, particle size and mineralogy and also albedo and temperature of the underlying surface [Arimoto, 2001; Harrison et al., 2001; Jacobson, 2001].

Table 1.1. Direct radiative forcing estimates for some aerosol types on a global average basis.

Aerosol type	Estimated direct radiative forcing (W m ⁻²)
Sulphate	-0.4 ± 0.2
Organic carbon from fossil fuel	-0.5 ± 0.5
Nitrate	-0.10 ± 0.10
Biomass burning	-0.30 ± 0.12
Black carbon	+0.2 ± 0.15
Mineral dust	-0.3 → +0.1

Source: IPCC [2007]

1.3.2.2 Indirect radiative forcing

The presence of aerosols in the atmosphere has a further indirect impact on the radiation budget as they act as cloud condensation nuclei. It has been proposed that anthropogenic and naturally induced changes in concentration and size of CCN could alter cloud properties [Rosenfeld, 2000]. Increases in the number of CCN with the same cloud water content will result in smaller cloud droplets leading to an increase in cloud's solar reflectance (first indirect effect or cloud albedo effect) and giving a negative radiative forcing. The decreased droplet radius might also decrease the cloud's ability to precipitate, leading to an increased cloud lifetime and causing an additional negative forcing (second indirect effect or cloud lifetime effect). Because the removal rate of aerosols also depends on these cloud processes, the aerosol burden might itself be influenced. Absorption of solar radiation (e.g., by soot particles) has a cooling effect at the surface (negative forcing), but a heating effect in the troposphere which may cause the evaporation of clouds (positive forcing). Probably the cooling effect is larger, but heating the air affects the vertical distribution of temperature (semi-direct effect) and consequently influences the global hydrological cycle [Ramanathan et al., 2001].

Sulphate aerosols appear to act as major CCN. In addition to sulphate, a role in indirect forcing has been proposed for other aerosol types, such as biomass burning, nitrate, mineral dust particles [Dentener et al., 1996; Mallet et al., 2003; Sun and Ariya, 2006].

1.3.3 Effects on atmospheric chemistry

Aerosols can be transported in the troposphere over long distances and during this transport the particles have ample opportunity to interact with trace gases (such as ozone, O_3), nitrogen and sulphur containing inorganic gases and also with organic gases [Usher et al., 2003; Krueger et al., 2004]. Therefore, aerosols serve as reaction surfaces in the atmosphere and they may act as sinks for various atmospheric chemical species (Figure 1.4). One of the ways by which chemical reactions involving aerosols could affect large scale atmospheric processes is through the atmospheric oxidant cycle [Arimoto, 2001]. Changes in the oxidizing capacity of the atmosphere are important since oxidants react

with a variety of organic and inorganic compounds, therefore providing a mechanism for a decrease in atmospheric pollutants. Some of the key oxidants in the atmosphere are the OH radical and tropospheric O₃, which has received considerable attention, primarily as a local or regional pollutant.

Through reactions with vapour-phase HNO₃, mineral dust and sea-salt particles can indirectly affect climate by influencing both the number and chemical composition of aerosols. On the other hand their neutralization reactions are important in atmospheric acidity as well [Bardouki et al., 2003]. Reactions of sulphur compounds with mineral dust and sea-salt particles are analogous to those with nitrogen compounds. Their reactions involve heterogeneous processes, and the key variables are pH and particle size distribution [Arimoto, 2001]. In addition, numerous volatile and semi-volatile organic compounds (VOCs and SVOCs, respectively) have a tendency to adsorb onto atmospheric particles [Aymoz et al., 2004]. While aerosols serve as reaction surfaces and act as sinks for various atmospheric chemical species, they are affected by these reactions, their physical and chemical properties - including optical properties, water-solubility and so their effectiveness to serve as cloud condensation nuclei - change. In addition, during their transportation aerosol particles are subjected to repeated wetting and drying cycles in cloud formation and evaporation processes [Raes et al., 2000; Desboeufs et al., 2001].

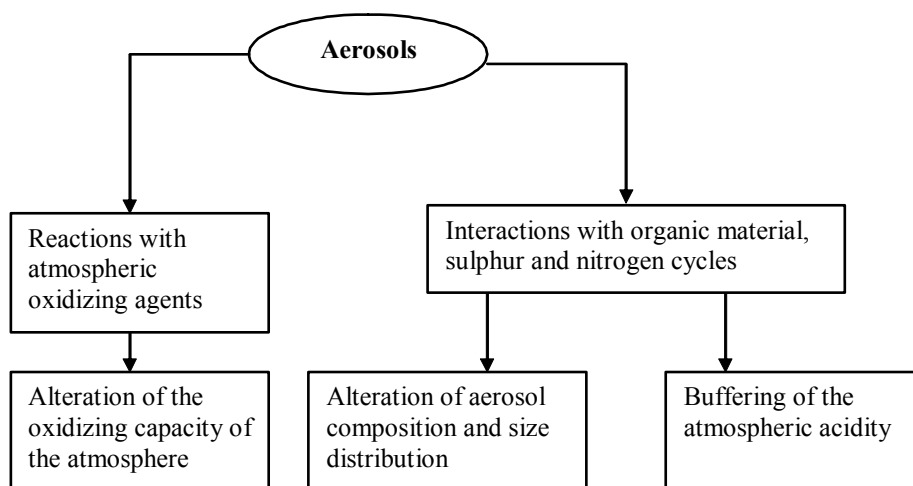


Figure 1.4. Chemical connections between aerosols and other atmospheric constituents [modified from Arimoto, 2001].

1.3.4 Visibility

Research on visibility impairment by atmospheric aerosol pollution has been carried out in different parts of the world [Day and Malm, 2001; Colls, 2002; Doyle and Dorling, 2002; Molnar et al., 2007]. Visibility reduction is generally related most closely to scattering by sulphate, organic and nitrate aerosols, and adsorption and/or scattering by elemental carbon. Aerosol particles that are illuminated by a beam of light scatter and absorb light and thereby reduce the intensity of the beam (extinction). The extinction characteristics of aerosols are important for elaborating the effect of aerosols on visibility. The scattering is most efficient for those particles which are in the same size range as the incoming solar radiation. The visual impact of atmospheric aerosols comes mostly from particles in the size range from 0.1 to 2 μm ; outside this range particles have little effect on light extinction or visibility, because the particle extinction efficiency decreases rapidly for small particles [Watson, 2002]. The relative humidity is also an important factor as it affects the size of the particles, and a significant reduction in visibility occurs if the relative humidity increases from 50 to 90% [Husar et al., 2000].

1.3.5 Effects on ecosystems

In addition to the impacts of aerosols on human health, climate, atmospheric chemistry, and visibility, atmospheric particles may have significant effects on ecosystems and soiling of buildings. Deposition of acidic pollutants (e.g., acid rain, nitrate and sulphate aerosols, gaseous NO_2 and SO_2) damages forests and aquatic ecosystems (e.g., lakes) and also affects agriculture as a consequence of soil acidification [Baker et al., 2003]. On the other hand, atmospheric particles transported to distant places and subsequently deposited on the Earth surface may have an impact on the biogeochemical cycles of some elements, such as K, Fe, Ca, N or P [Jickells et al., 2005].

In the urban environment, aerosol particles can damage paints and building materials and the deterioration of monument surfaces results in costly reconstruction. The deterioration is caused by the reaction of acidic species with stone (e.g., limestone) followed by soiling of surfaces, and by blackening as a result of soot deposition [Pio et al., 1998].

1.4 Literature survey of aerosol studies in Africa

Tanzania is one of the tropical developing countries in Africa that experiences a continuous increase of environmental pollution as a result of increasing urbanization, industrialization, agriculture, mining, and human population. Tanzania, like most of the developing countries, lacks mechanisms to enforce laws and regulations controlling the production, importation, handling, use and disposal of wastes and the emission of pollutants. For example, the law banning the global use of environmentally unfriendly chemicals, such as leaded gasoline, is rarely enforced and often violated [NEMC, 1996]. As a result of such violations, together with other pollutants, the environmental pollution is becoming enormous.

In different parts of the world (e.g., Europe) many scientific data on the characterisation of aerosols in various environments have been published [Putaud et al., 2004; Van Dingenen et al., 2004; and references therein]. In contrast, very few data are available from Africa and Tanzania in particular. Chemical characteristics of particulate matter have been studied in Kenya [Gatari et al., 2001; Gatebe et al., 2001; Gatari and Boman, 2003], Ethiopia [Etyemezian et al., 2005], Algeria [Yassaa et al., 2001], the Democratic Republic of Congo, DRC (former Zaire), and Rwanda [Maenhaut and Akilimali, 1987], South Africa [Maenhaut et al., 1996; Piketh et al., 2002], Botswana [Chimidza and Moloi 2000; Jayaratne and Verma 2001; Moloi et al., 2002] and Zimbabwe [Marufu et al., 1997, 1999; Nyanganyura et al., 2007]. These aerosol studies in Africa reported that soil, biomass burning, and savanna fires are major sources of atmospheric aerosols [Ludwig et al., 2003]. For example, Maenhaut and Akilimali [1987] pointed out that soil dust and biomass burning were important aerosol sources in Kinshasa, DRC, and Butare, Rwanda. In Dar es Salaam (Tanzania), Koleleni [2002] and Bennet et al. [2005] measured PM mass and elemental composition between 1996 and 2001; some of their data are summarized in Table 1.2.

Table 1.2. Mean concentrations of the PM10 mass ($\mu\text{g}/\text{m}^3$) and of elements (ng/m^3) for Dar es Salaam (literature sources are indicated in the table).

Elem	October 1996 [Koleleni, 2001]			April 1997 [Koleleni, 2001]			May 2001 [Bennet et al., 2005]		
	Fine	Coarse	Coarse+Fine	Fine	Coarse	Coarse+Fine	Fine	Coarse	Coarse+Fine
PM	ND	ND	ND	ND	ND	ND	ND	ND	40
S	306	402	708	ND	ND	ND	ND	ND	ND
Cl	ND	ND	ND	85	380	465	520	2700	3220
K	110	180	290	290	44	334	350	330	680
Ca	79	580	659	30	300	330	120	4200	4320
Ti	2.3	5	7.3	ND	ND	ND	5.1	65	70.1
Mn	30	29	59	ND	ND	ND	2.3	21	23.3
Fe	52	73	125	15	35	50	31	470	501
Ni	ND	ND	ND	ND	ND	ND	1.2	0.8	2
Cu	15	14	29	7.3	55	62.3	2.4	2.7	5.1
Zn	7.7	7.7	15.4	13	33	46	19	24	43
Br	18	19	37	3.1	19	22.1	22	6.7	28.7
Rb	ND	ND	ND	ND	ND	ND	ND	0.8	0.8
Sr	1.1	1.3	2.4	2.6	2.7	5.3	ND	9.2	9.2
Pb	70	52	122	14	77	91	39	14	53

ND – not determined.

1.5 Overview of atmospheric pollution in Tanzania

Tanzania is the biggest among the East African countries and it is located between latitude 1° and 12°S and longitude 29° and 41°E . It has a total area of 945,087 square kilometres (sq km), out of which 886,037 sq km is land and 59,050 sq km is inland water. The population of Tanzania is about 36,588,225 million (2004 estimate), with a growth rate of 1.95%, birth rate of 39 birth/1000 population, and death rate of 17.45 death/1000 population per year [URL: <http://www.tanzania.go.tz>].

In Tanzania air quality studies are regularly undertaken for temporal or rapid assessment. In addition, such studies are being carried out in fragmentation and the results are not integrated and easily accessible. Therefore, monitoring of air pollution

(e.g., atmospheric aerosols) is required to establish trends in the already identified problematic areas and intervention is urgently needed to mitigate potential environmental and health risks.

In recent years the increasing number of motor vehicles, which is characteristic of many cities, has led to increasing emissions of pollutants that contribute to public health problems. Reports on urban air quality by Othman [1996] and NEMC [1996] have shown that Dar es Salaam (inhabitants: 3 million) experiences the same problems of air pollution by motor vehicles as urban areas in other parts of the world. A rapid increase in the number of vehicles (10–15% per year, [Ministry of Works, 1999]) and widespread construction activities exacerbate Dar es Salaam's air pollution problems because the tall buildings hinder the dispersion of air pollutants. Mbuligwe and Kassenga [1997] concluded that the air pollution problem in Dar es Salaam should not be neglected. Also Kitilla [1999] commented that Dar es Salaam, being the centre for socio-economic activities of Tanzania, is of interest to investigate its air quality. In the absence of relevant data and information, the extent of the atmospheric pollution problem in Tanzania is not known. Generally its air quality may be low, but it is serious in some localised areas like in cities, where many sources of pollution such as increased traffic volume and industrial activities exist. Within the frame of air quality monitoring capacity building project in Dar es Salaam, the Dar es Salaam Municipal Council, the National Environmental Management Council (NEMC) and the Tanzania Bureau of Standards (TBS) conducted a pilot study from January 2005 to June 2006 to provide information on the levels of PM mass and particulate lead (Pb) and thus to give an indication of urban air quality in Tanzania. However, no results were available till the writing of this thesis.

1.6 Motivation for the study

Concern about atmospheric particulate pollution in urban regions is growing worldwide [Cachier et al., 2005]. Urbanization, industrialization, economic growth and associated increase in energy demands and use of fossil fuels have resulted in a profound deterioration of urban air quality, particularly in developing countries like Tanzania. In

recent years Tanzania is characterised by an increased economic growth and population so that it also has to tackle increased pollution problems.

Aerosol science has an important place in environmental analysis and atmospheric chemistry due to the fact that aerosol particles have adverse effects on human health and play an essential role in climate change and air pollution (the quality of the environment). The interest has focused on the composition of the particles and on the size distribution of the PM and its components.

With the increasing epidemiological evidence for significant health impacts of PM pollution, measurement of particle characteristics has taken a new urgency in the last decades. A number of countries have established or reviewed their national air quality standards for PM concentrations and for specific pollutants in ambient air so as to protect public health. In response to this the Tanzanian commissions dealing with environmental issues have revised environmental laws and tried to establish standards for a number of pollutants including PM₁₀. However, until now no standards were established for TSP, PM₁₀, or PM_{2.5} levels in Tanzania, and the values for PM in this study will be compared to EU standards. The EU standards are based on daily and annual limit values for PM₁₀ levels [EU Directive, 1999].

Very little information is currently available on atmospheric aerosol levels and composition in Tanzania. The few published studies dealt with concentrations of particulate elements for fine and coarse fractions in Dar es Salaam, for which the collections were done between 1996 and 2001 [Koleleni, 2002; Bennet et al., 2005], and their results are summarized in Table 1.2 above. In order to evaluate and to reduce the impacts of aerosols, any program aimed at controlling the levels of PM requires knowledge on the size distribution, chemical composition and sources of particles. For these reasons, fine (PM_{2.5}, PM₂), coarse (PM₁₀₋₂), and PM₁₀ particles were collected at two sites in Tanzania, at a busy street site in the centre of Dar es Salaam (Posta Mpya) and at Sokoine University of Agriculture (SUA) in Morogoro. The collections at the two sites allowed us to look at the contrasts in atmospheric aerosol levels and composition between a much polluted urban site and a site representative for the rural environment of Tanzania. Aerosol collections were conducted over the wet and the dry seasons from May 2005 through May 2006. In order to determine the current PM levels and composition,

which could serve as a reference for further studies in this developing country, the chemical components measured were carbonaceous materials, inorganic water-soluble ions, and elements.

The chemical characteristics (composition) of aerosols, sampling artifacts, source apportionment, chemical mass closure, the influence of meteorological processes and their comparison at two eastern sites of Tanzania are addressed in this study. The specific questions and objectives are:

- Which are the major contaminants in aerosols at the urban site of Dar es Salaam and at the rural site of Morogoro and what are their concentrations?
- How important are the artifacts in the measurement of the particulate mass and of the organic carbon and how can we check the reliability of the results?
- How important are seasonal variations, especially between the dry and wet season?
- Is the PM₁₀ mass explained by the measured aerosol components and which are the major sources of the aerosols sampled at Dar es Salaam and Morogoro?

As mentioned before, some of these points have been well addressed in studies performed in locations in Europe, the USA, and Asia. However, no such studies have been conducted in Tanzania.

1.7 Structure of the thesis

This study is made up of seven chapters. Chapter 1 gives an overview of the characteristics of atmospheric aerosols including the definition of atmospheric aerosol, classification of aerosol types and their sources (both natural and anthropogenic). The impacts of aerosols on human health, climate, atmospheric chemistry, visibility, and ecosystems are also discussed. A brief literature survey is given of aerosol studies conducted so far in Africa, and the motivations and objectives for this study are indicated. This last section of chapter 1 describes the structure of the thesis.

Chapter 2 gives an overview of the experimental techniques and methods used for this study. Chapter 3 describes the evaluation and assessment of artifacts in the measurement of the PM mass and OC for the three field campaigns conducted at both study sites. Chapters 4 and 5 present the ambient levels and chemical composition of

PM10 aerosols during the wet and dry season campaigns at Morogoro and Dar es Salaam, Tanzania, respectively. Chapter 6 discusses the aerosol chemical mass closure and aerosol sources at the two sites in Tanzania. General conclusions, recommendations and need for future are given in Chapter 7. A list of publications and oral and poster presentations can be found in the Appendix.

CHAPTER 2

EXPERIMENTAL

2.1 Description of sampling sites

Ambient aerosol samples were collected at two sites located in the eastern part of Tanzania (Figure 2.1) between May 2005 and May 2006. One of the sites was in a busy street canyon situated in the city centre of Dar es Salaam and can be classified as kerbside site [Van Dingenen et al., 2004]. The second site was located at the main campus of Sokoine University of Agriculture (SUA) in Morogoro about 200 km west from Dar es Salaam. The samplings were done at the two sites one after the other; during campaigns in wet and dry seasons the samplings at Dar es Salaam followed those in Morogoro. The meteorological parameters were continuously monitored at both sites.

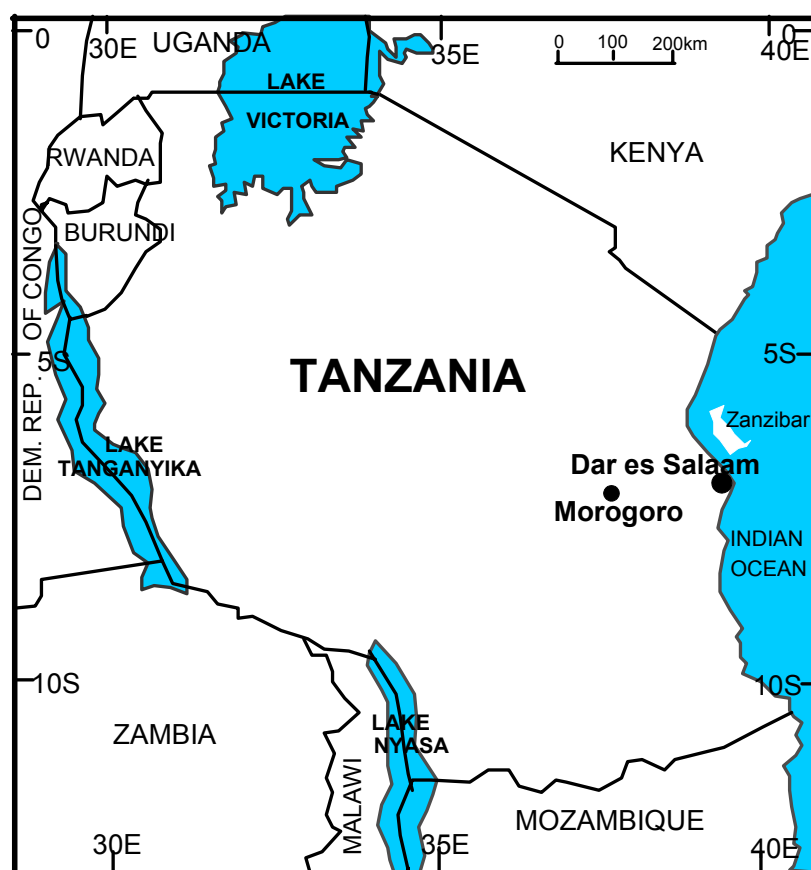


Figure 2.1. Location of the sampling sites in Tanzania.

2.1.1 Morogoro site

Morogoro town is a small town (287,000 inhabitants, 2007 estimate) located at an altitude of about 500 – 600 m above sea level. The sampling station in Morogoro was located about 3 km south of the town centre on the western foothill of Uluguru Mountain ranges, which rise to 2648 meters above the mean sea level. The instruments were mounted on a roof approximately 6 m above ground level at the main campus of Sokoine University of Agriculture, SUA (6°49'S, 37°39'E, altitude 526 m above sea level (a.s.l.)) (Figure 2.2a). The surrounding of this site is purely a residential area and it is far from major road systems; however, a small 2-line paved road at a distance of 40 m is on its western side. The site is also characterised by small-scale agricultural fields (horticulture and cereals crops growing) and open fenced cattle grazing fields. The main local emission sources therefore are soil, road and agricultural dust, and biomass burning, mainly for domestic cooking and peat fires. During the sampling period meteorological data (Table 2.3) were collected by the Tanzanian Meteorological Agency (TMA) at SUA meteorological observatory 600 m from the site.

(a) SUA-Main Campus, Morogoro



(b) Azikiwe Street, Posta Mpya-Dar es Salaam



Figure 2.2. Location of the two sampling stations.

2.1.2 Dar es Salaam site

Dar es Salaam, the economical capital of Tanzania is located on a coastal flat area at the Indian Ocean. It is the country's primary city and the undisputed administrative, commercial, industrial, and transportation centre. Oil refinery, cement production, and metal processing are among the industrial activities in the city. Dar es Salaam with a population of over 3 million (2007 estimate) has over half of the country's heavy industries and nearly 600,000 vehicles within its boundaries [Personal contact, 2007].

In Dar es Salaam, the aerosol sampling was conducted on the second-floor balcony (about 10 m above the ground level, see Figure 2.2b) of the Young Women's Christian Association of Tanzania (YWCA) building (6°48'S, 39°17'E, altitude 4 m a.s.l.), which is located along one of the major paved roads (Azikiwe street) in the city centre (Posta Mpya). The street is characterised by a length of 900 m and a width of about 20 to 25 m and is sided by multi-storey buildings. This site can be classified as a kerbside site according to Van Dingenen et al. [2004]. Most of the daytime period the street is extremely busy with vehicular traffic, business men (Machinga), and also pedestrians. The car congestion ratio and the traffic volume in this part of the street is about 1.26 and 25,000 cars per 24 h, respectively, with a proportion of commuter buses (commonly known as Daladala) of ~78%, which operate within the city [Ministry of Works, 1999]. At this sampling site, traffic, sea spray and ships from the harbour, and cooking in domestic houses and restaurants, and other commercial activities, such as industry and transportation, are the main local sources. Meteorological data (see Table 2.3) were measured at about 2 km from the sampling site during the sampling periods.

2.2 Aerosol collections

2.2.1 Aerosol samplers

At both sites, depending on the campaign, two or three low-volume filter samplers were used in parallel to collect aerosol particles: "Gent"-type PM₁₀ stacked filter unit (SFU) sampler (PM₁₀(NN)) [Maenhaut et al., 1994; Hopke et al., 1997] with coarse (Apiezon-coated) and fine Nuclepore polycarbonate filters (pore sizes 8 and 0.4 µm,

respectively); “Gent”-type PM10 filter holder (PM10(Q)) with two quartz fibre filters (Whatman QM-A) in series; and a PM2.5 filter holder (PM2.5(Q)) also with two Whatman QM-A quartz fibre filters. The samplers operated at a flow rate of 17 L/min. At this flow rate the coarse filter of the SFU sampler collects the particles with aerodynamic diameter (AD) between 2 and 10 μm , while the fine filter collects the size fraction $<2 \mu\text{m}$ AD. The (PM2.5(Q)) sampler was deployed only during the 2006 wet season campaign in Morogoro and during the dry season 2005 and the wet season 2006 campaigns in Dar es Salaam.

Quartz fibre filters can adsorb volatile organic compounds (VOCs) causing positive artifacts when measuring the PM mass and particulate OC. On the other hand, semi-volatile organic compounds (SVOCs) in aerosols may partially evaporate during sampling resulting in negative artifacts [Turpin et al., 2000; Mader et al., 2003; Hitzenberger et al., 2004]. Some studies suggest that quartz fibre filters may cause larger positive artifacts than negative ones [Mader et al., 2003; Fan et al., 2004]. Therefore, in order to assess and correct for this problem in aerosol collection, the tandem filter method (with two quartz fibre filters in series) was used. The quartz fibre filters were pre-fired at 550 °C for 24 h before use. All filters used in this study had a diameter of 47 mm. Field blank filter samples were taken by placing the filters in the samplers and allowing air flow through the filters for 10 seconds.

2.2.2 Sampling periods

At each site and during each sampling campaign, the aerosol collection was carried out continuously with all samplers operated in parallel. Table 2.1 presents an overview of the samplings. In Morogoro, the 24-hour collections started at 8.30 am and at 8.00 am (local time, UTC + 3) during the 2005 wet season and 2006 wet season campaigns, respectively. The 12-hour samplings during the dry season campaign in 2005 started at 7.00 am for the daytime samplings and at 7.00 pm for the nighttime samplings. The campaigns in Dar es Salaam followed the Morogoro campaigns for each of the wet or dry seasons, as can be seen from Table 2.1. At Dar es Salaam, the 24-hour collections during the 2005 wet season campaign started at 8.30 am. The 12-hour samplings during

the 2005 dry season campaign were done over daytime and nighttime with start at 6.30 am and 6.30 pm, respectively, and during the 2006 wet season campaign, the exchange of filters was done at 7.00 am and 7.00 pm, respectively. For both sites 3 field blanks were collected with each sampler during the 2005 wet season campaign and 7 field blanks during the 2005 dry and 2006 wet season campaigns.

Table 2.1. Overview of the samplings at Morogoro and Dar es Salaam during the various campaigns.

Sampling campaign	Sampling period	Samplers deployed	Collection time per sampling (hours)	Number of parallel samplings
Morogoro (6°49'S, 37°39'E, 526 m a.s.l.)				
2005 wet	4 May – 17 May	PM10(NN), PM10(Q)	24	13
2005 dry	11 July – 11 August	PM10(NN), PM10(Q)	24 or 12	9 + 42*
2006 wet	13 March – 11 April	PM10(NN), PM10(Q), PM2.5(Q)	24	29
Dar es salaam (6°48'S, 39°17'E, 4 m a.s.l.)				
2005 wet	19 May – 4 June	PM10(NN), PM10(Q)	24	16
2005 dry	16 August – 17 September	PM10(NN), PM10(Q), PM2.5(Q)	12	64
2006 wet	14 April – 12 May	PM10(NN), PM10(Q), PM2.5(Q)	12	55

*The first 9 samplings were 24-hour collections, whereas the subsequent 42 samplings were 12-hour collections.

From each campaign at both sites, the exposed filters and field blanks were placed into polycarbonate Petrislide dishes and kept frozen at -20 °C during storage (to limit losses of volatile components) and transported cool to the Institute for Nuclear Sciences, INW (Ghent, Belgium) for analysis.

2.3 Aerosol chemical analysis

In this study bulk analyses are done, including determination of the PM mass, organic carbon (OC) and elemental carbon (EC), (and black carbon, BC), water-soluble organic carbon (WSOC), water-soluble inorganic species, and major, minor, and trace elements. The aerosol components were measured with techniques and methods, which

were already used by the research group “Tropospheric Aerosol Research and Nuclear Microanalysis” of the Department of Analytical Chemistry (UGent). The techniques include gravimetry [Maenhaut, 1996], a light reflectance technique [Maenhaut, 1996], a thermal-optical transmission (TOT) method [Maenhaut et al., 2004a], a total organic carbon analyzer (TOC) [Viana et al., 2006], ion chromatography (IC) [Maenhaut et al., 2002], and particle-induced X-ray emission (PIXE) [Maenhaut, 1996; Maenhaut and Cafmeyer, 1998].

It should be noted that the reported atmospheric concentrations for the PM_{2.5} and PM₁₀ mass, carbonaceous species, water-soluble ions, and elements were corrected for field blanks. For the PM₁₀(NN) sampler the data from the coarse and fine filters were added in order to obtain PM₁₀ data.

2.3.1 Determination of PM mass

To obtain the PM mass concentration, the field blanks and actual samples were weighed before and after sampling with a Mettler-Toledo microbalance model MT5 (sensitivity 1 µg). Before weighing, the filters were conditioned at relative humidity of 50% and a temperature of 20 °C for 24 h and the weighings were done under these conditions. An anti-static ionisator was used to eliminate possible static electricity on the Nuclepore filters. The uncertainty (in µg) on the net mass of a filter sample for PM mass determinations was derived from repeated weighings of blank and exposed filters on several days. Then the mass uncertainty (in µg) was converted into mass concentration uncertainty by dividing it by the average volume of air sampled daily. In this study the uncertainty (1 standard deviation) of the PM mass determinations is estimated to be 5 µg for the Nuclepore polycarbonate filters and 30 µg for the Whatman QM-A quartz fibre filters [Hitzenberger et al., 2004].

2.3.2 Analysis of carbonaceous species

All quartz fibre filters were analysed for organic carbon (OC), elemental carbon (EC), and total carbon (TC; with $TC = OC + EC$) by a thermal-optical transmission

(TOT) technique [Birch and Cary, 1996] and for water-soluble organic carbon (WSOC) using a Total Organic Carbon Analyzer, TOC-V CPH from Shimadzu.

2.3.2.1 OC and EC analysis

OC, EC and TC were determined from a 1.5 cm² portion of each quartz fibre filter with a TOT analyzer from Sunset Lab following the Ghent standard (quartz program) thermal evolution protocol [Schmid et al., 2001; Maenhaut et al., 2004b].

The analysis proceeds in two stages. In the first stage, the sample is heated stepwise to 250, 500, 650, and 900 °C in a non-oxidizing pure helium atmosphere. In the second stage, after cooling the sample to 600 °C, a mixture of 98% helium and 2% oxygen is introduced and the temperature is increased stepwise to 900 °C. The evolved carbon in each stage is immediately oxidized to carbon dioxide (CO₂) using a plug of MnO₂ at 860 °C, reduced to methane (CH₄) over a Ni-firebrick in the presence of H₂, and then quantified using a flame ionization detector (FID). Details of the temperature program are given in Table 2.2. During the stepwise heat treatment of the filter punch, laser light (of 670 nm) is continuously transmitted through the punch and the light transmission is continuously monitored, so that it is possible to correct for the artifact EC that is formed by charring during pyrolysis of organic material in the first stage. When the transmission through the punch reaches the same value as at the start of the analysis, the OC/EC split point is set and the carbon measured up to then is considered as OC, whereas the carbon measured after the split point is considered as EC. TC is determined as the sum of OC and EC. At the end of every analysis run, the response of the FID is monitored by injecting automatically a fixed known quantity of methane as an internal standard to calculate the carbon results.

Table 2.2. The Ghent Standard (ST) temperature program used in this study.

Gas	He						He/O ₂			
Duration (s)	60	50	60	100	50	5	30	30	40	75
Temp (°C)	250	500	650	900	0	600	600	700	850	900

The uncertainty in the OC, EC, and TC measurements is provided for every individual filter sample by the calculation software provided with the Sunset Lab instrument used. The uncertainty is made up of a constant part (which is $0.2 \mu\text{g C/cm}^2$ for OC and EC and $0.3 \mu\text{g C/cm}^2$ for TC) and of a variable part, which amounts to 5% of the OC, EC or TC mass loading. It is well-known that OC and EC are operationally defined and that different methods may give different results for OC and EC, although the results are generally comparable for TC [Schmid et al., 2001; Chow et al., 2001]. For quality assurance, a five-point calibration was performed prior to the analysis of the field samples. A control standard was analysed daily before and after analysis of a series of samples using a standard sucrose solution that was prepared by dissolving highly pure sucrose (Aldrich Chemical Co.) in Millipore Simplicity water.

Black carbon (BC) is the principal light-absorbing component in atmospheric aerosols. BC analyses were done for Nuclepore polycarbonate filter samples. They were based on the measurement of the light intensity which was reflected from the sample. The light reflectance measurements were performed with a commercial smoke stain reflectometer (Diffusion Systems Ltd, London, UK, model 43). The instrument was calibrated with the aid of over 100 Nuclepore filter samples, for which the BC black loading (in $\mu\text{g/cm}^2$ of filter) had been determined by Andreae using an instrument and a procedure that were described by Andreae [1983] and Andreae et al. [1984].

2.3.2.2 WSOC analysis

Water-soluble organic carbon (WSOC) was determined from one or two punches of 1.5 cm^2 from each quartz fibre filter [Viana et al., 2006]. The filter punches were placed into a 15 mL polystyrene tube, 5 mL Millipore Simplicity water was added and the tube was hand-shaken for about 5 min, after which it was allowed to stand for 30 min. The sample extract was filtered through a syringe filter (PVDF with $0.2 \mu\text{m}$ pore size) and the filtered extract was analysed for water-soluble total carbon (TC_{WS}) and inorganic carbon (IC_{WS}) using a TOC-V CPH Shimadzu instrument. Total water-soluble organic carbon was calculated by difference between total water-soluble carbon and inorganic water-soluble carbon ($\text{TOC}_{\text{WS}} = \text{TC}_{\text{WS}} - \text{IC}_{\text{WS}}$), and was used as WSOC. For each sample

analysis, at least three replicate injections were made. The detection limit of the TC measurements was 2 µgC.

For the TC determination 150 µL of the extract is injected into a combustion tube maintained at 680 °C. The process involves catalytic (high sensitivity) burning in oxygen. The catalyst endorses the redox reaction. The reaction time is prolonged to 5 min or less in the combustion tube to oxidise all the organic species to carbon dioxide (CO₂). The evolved carbon dioxide is transported by a constant flowing carrier gas (O₂) to a Non-Dispersive Infrared (NDIR) detector cell for quantification. For the IC analysis, 150 µL of the extract is injected in the IC reaction vessel. The sample is then acidified (pH <3) with ortho-phosphoric acid to convert all carbonates to carbon dioxide, which is quantified by the NDIR detector. The instrument was calibrated every week and control standard solutions were prepared from potassium hydrogen phthalate, KHC₈H₄O₄, for TC_{WS} and a mixture of sodium bicarbonate and sodium carbonate for IC_{WS}. Each day before and after sample analysis, TC and IC control standard solutions were tested.

2.3.3 Analysis for water-soluble ionic species

All the coarse and fine Nuclepore polycarbonate filters from the PM10(NN) SFU sampler were analysed by ion chromatography (IC) for major water-soluble inorganic ions using a Dionex 4500i instrument with a PC based AutoIon (AI-450) data acquisition and analysis system. IC is widely used for the measurement of inorganic ions in aerosols since it offers advantages in terms of sensitivity and multiple analyte determination in a single assay [McMurry, 2000; Wilson et al., 2002]. One half of each Nuclepore polycarbonate filter was placed in a 15 mL polystyrene tube and extracted ultrasonically with 5 mL or 10 mL of Millipore Simplicity water for 1 hour. For the determination of the anions (i.e., methanesulphonate (MSA⁻), NO₂⁻, Br⁻, SO₄²⁻, NO₃⁻, Cl⁻), an IonPac AG12A guard column and IonPac AS12A (4 mm) analytical column were employed, and a buffer of 2.7 mM sodium carbonate/0.3 mM sodium bicarbonate (isocratic) was used as a mobile phase (eluent) at a flow rate of 1 mL min⁻¹. The cations (i.e., Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were measured with IonPac CG12 guard column and IonPac CS12 (4 mm) analytical column, and 20 mM methanesulphonic acid, MSA, (isocratic) was used as mobile phase (eluent) at a flow rate of 1 mL min⁻¹ [Maenhaut et al., 2002]. ASRS Ultra II

and CSRS Ultra II auto-suppressors were applied for anions and cations, respectively, operating in auto-suppression mode and a conductometric detector was used. For the measured inorganic anions and cations the detection limit was close to 1 ng/m³.

The injection of the extracts to the IC instrument was done manually using a 1 mL syringe and through a membrane filter unit with a pore size of 0.22 µm (Millipore Corporation, USA), the volume of the sample loop was 100 µL. To check the quality of the IC analysis, measurement and evaluation of standard solutions and calibrations were made regularly. Laboratory blanks were processed and analysed simultaneously with the real samples and field blanks to monitor possible contamination.

2.3.4 Analysis for elements

In addition to carbonaceous materials and water-soluble inorganic ions, also major, minor, and trace elements, including heavy metals, are important constituents of atmospheric aerosols. Particle-induced X-ray emission (PIXE) spectrometry is one of the most commonly used micro-analytical techniques for elemental analysis of aerosols [Maenhaut and Malmqvist, 2001]. The greatest advantages of PIXE in atmospheric aerosol research are its excellent sensitivity and capabilities as being a multi-element non-destructive technique, with a wide range of elements (all elements from Na to U). It has also the advantage of being of relatively low cost, the small sample size requirement, the low absolute detection limits, the speed of the analysis, and preservation of the filter for additional analyses. PIXE is able to provide concentration data for many key elements of various aerosol types that are essential for source identification work and for application of receptor models for source apportionment. However, it has the disadvantage that light elements, such as C, N, H and O, cannot be determined [Maenhaut and Cafmeyer, 1998]. A large number of studies on the elemental concentration of atmospheric aerosols using the PIXE technique have been reported [Maenhaut and Malmqvist, 2001].

In this study, one quarter of each Nuclepore polycarbonate filter was used to determine the elemental composition by PIXE. Up to 28 elements between Na and Pb were measured [Maenhaut, 1996; Maenhaut and Cafmeyer, 1998]. However, it should be noted that the data for the lightest elements (Na and Mg) are not very reliable because of

severe X-ray attenuation. The PIXE analysis of the samples was carried out using a compact isochronous cyclotron, installed at the Institute for Nuclear Sciences (INW) of Ghent University, Belgium. An incident proton beam of 2.4 MeV was used; the diameter of the beam at the specimen was 8 mm, the beam current up to 150 nA and the preset charge up to 100 μC . The X-rays emerging from the specimen were detected with a Si(Li) detector, and for all measurements a so-called "funny filter" [Maenhaut and Raemdonck, 1984] was placed in front of the detector. After passage through the specimen, the beam was dumped in a Faraday cup for charge integration (proton dose measurement). The PIXE spectra were analysed with the non-linear least squares fitting program AXIL-84 [Maenhaut and Vandenhaute, 1986]. The PIXE set-up had been calibrated as described by Maenhaut and Raemdonck [1984].

2.4 Local meteorology and air mass source regions

The temporal and spatial variability of the PM and its components are influenced by meteorological parameters such as rainfall, temperature, relative humidity, and air flow patterns [Bardouki et al., 2003]. Aerosol particles are removed from the air by a combination of wet (precipitation scavenging) and dry deposition processes. Wet deposition occurs in rain events; it is a process, which is rather independent on the particle size, although larger and smaller particles can be removed sequentially during a single rain event. In contrast, dry deposition is a continuous process in which the fall-out of aerosol particles is strongly determined by particle size [Özsoy and Saydam, 2000]. Long-range transport of air masses has an impact upon the aerosol composition at a sampling site, as it brings in particles from distant source areas. Air mass backward trajectories are useful to determine possible sources of aerosol particles and have been extensively used in the literature [Brankov et al., 1998; Cape et al., 2000].

2.4.1 Meteorology

The climate of Tanzania is mainly tropical on the coast and temperate inland. It is characterised by a warm, humid wet season and a somewhat colder dry season. In the

eastern part of the country, the rainfall is mainly bimodal, with two rainy seasons. The 'short rains' or '*Vuli*' last from October to December and the 'long rains' or '*Masika*' extend from March through June (the wet season). A dry season (July-September) separates the 'short rains' and 'long rains' and is characterised by the lack of precipitation. The wet and the dry seasons can be distinguished due to the passage of the inter-tropical convergence zone, with the north-east East-African monsoon between March and October, and the south-east East-African monsoon between October and March [Trewartha, 1961].

Morogoro experiences a sub-humid tropical climate characterised by an annual average rainfall of 870 mm, which ranges between 610 and 1180 mm. It has a mixture of cool and warm temperature, ranging between 16 and 28 °C in the cold dry season and 21 and 31 °C in the warm wet season. The average relative humidity is 63–88% in March through May (the wet season) and 46–82% from July to September (the dry season). The annual mean temperature is 25 °C and the relative humidity is, on average, 80% in the morning and 61% in the afternoon.

Despite its proximity to the equator, Dar es Salaam enjoys a pleasant warm climate. The annual mean temperature is 26 °C ranging from 22 to 31 °C (annual mean minimum and maximum temperature, respectively) based on a 33-year period of 1971-2003. From July to September are the driest months. The annual average relative humidity is 96% in the morning and 67% in the afternoon. The main rainy season, which occurs between March and May, is responsible for 80% of the annual average rainfall of 1100 mm in Dar es Salaam.

Table 2.3. Average (or total amount) of meteorological parameters and ranges during the three sampling periods in Morogoro and Dar es Salaam [TMA, 2007].

Parameter	Morogoro			Dar es Salaam		
	Min	Max.	Total/Mean	Min.	Max.	Total/Mean
2005 wet season						
Precipitation (mm)	0	3.3	6.2	0	28	102
Relative humidity (%)	73	87	81 ± 4	59	82	65 ± 11
Temperature (°C)	23	26	25 ± 0.8	26	29	28 ± 0.59
Wind speed (m/s)	0	1.6	0.5 ± 0.5	0	5.9	4.1 ± 1.7
Pressure (mmHg)	953	956	955 ± 0.9	1015	1020	1015 ± 0.93
2005 dry season						
Precipitation (mm)	0	0.23	0.23	0	1.9	5
Relative humidity (%)	50	86	69 ± 11	47	76	60 ± 9
Temperature (°C)	21	25	23 ± 6	24	27	25 ± 0.9
Wind speed (m/s)	0	3.6	1.3 ± 1.0	3	7	5 ± 1
Pressure (mmHg)	956	960	958 ± 0.97	1015	1019	1017 ± 1
2006 wet season						
Precipitation (mm)	0	39	248	0	113	306
Relative humidity (%)	72	90	83 ± 5	69	86	79 ± 4.5
Temperature (°C)	21	27	26 ± 1.2	23	28	26 ± 1.2
Wind speed (m/s)	0	2.5	0.6 ± 0.5	1.1	4.4	3 ± 0.85
Pressure (mmHg)	950	954	952 ± 0.95	1004	1007	1006 ± 0.97

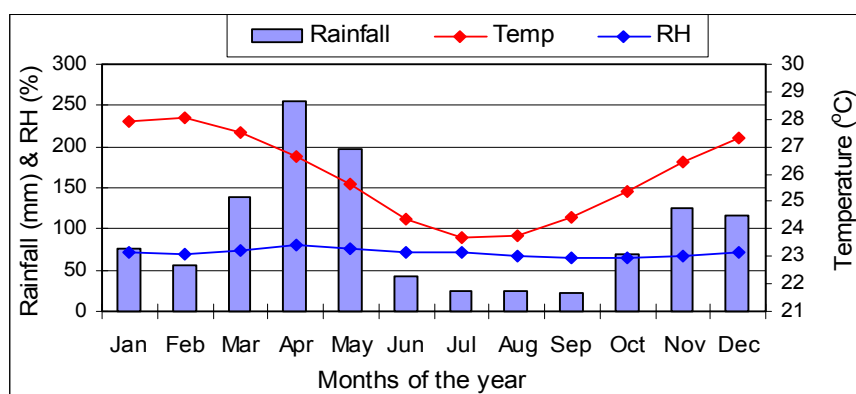


Figure 2.3. Monthly average of atmospheric temperature (°C), relative humidity (RH, in %) and rainfall (mm) for the 33-year period 1971-2003 in Dar es Salaam.

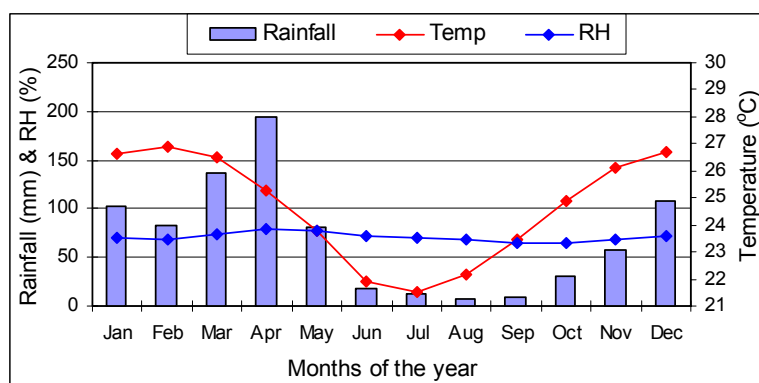
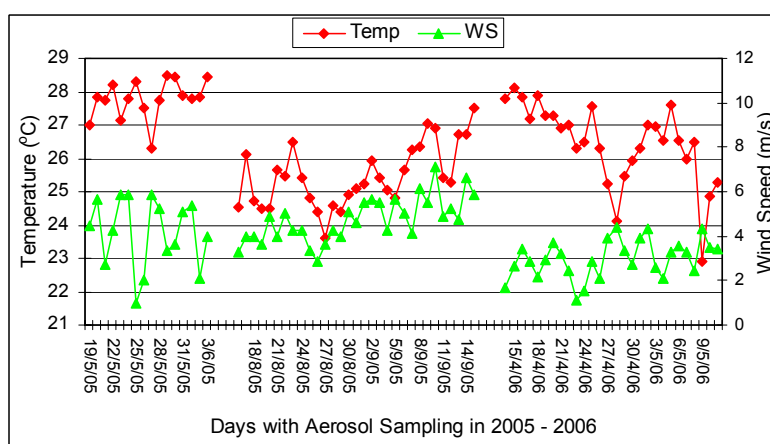
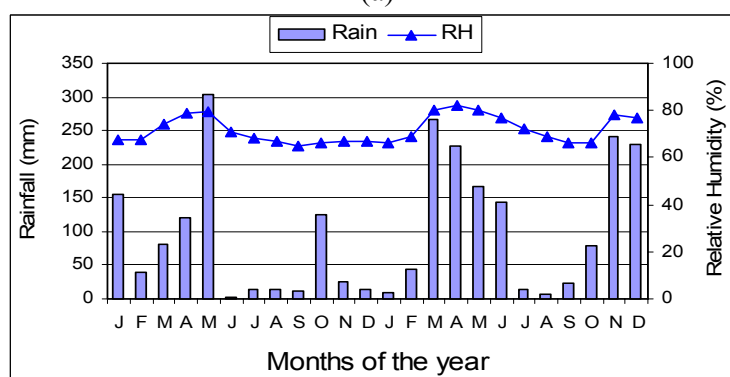


Figure 2.4. Monthly average of atmospheric temperature ($^{\circ}\text{C}$), relative humidity (RH, in %) and rainfall (mm) for the 32 years period 1973-2004 in Morogoro.



(a)

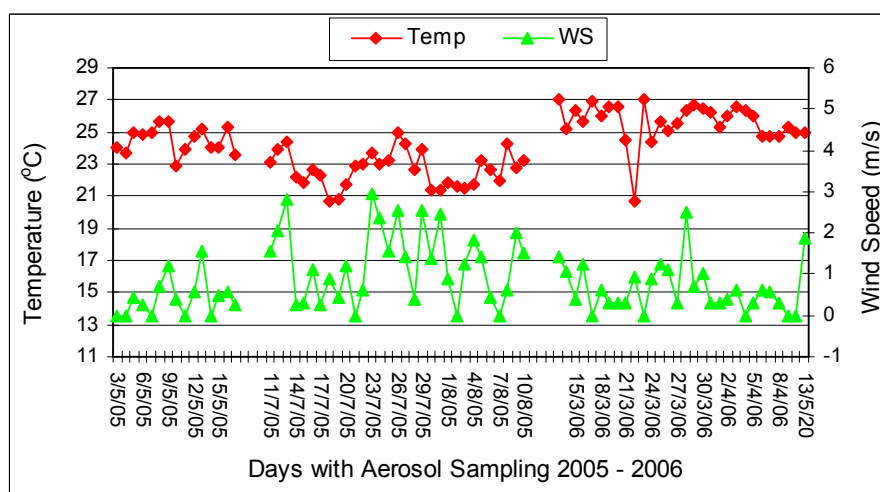


(b)

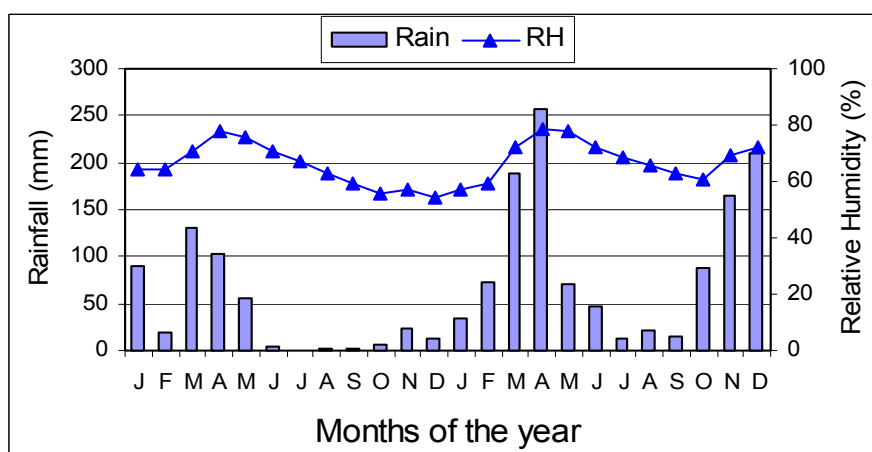
Figure 2.5. (a) Daily average temperature ($^{\circ}\text{C}$) and wind speed (m/s) recorded for days with aerosol sampling at Dar es Salaam and (b) Relative humidity (RH, in %) and precipitation (mm) recorded for all days in 2005 and 2006 in Dar es Salaam [TMA, 2007].

Since meteorological conditions influence the aerosol PM concentration, the wet (March - May) and the dry (July - September) seasons were investigated separately for each site. Data for relative humidity and precipitation (Figures 2.5b and 2.6b) are given for all days of the years because the atmospheric aerosol levels are highly controlled by the relative humidity and precipitation of the days before sampling. The average values for temperature and wind speed are presented only for the days with aerosol sampling (Figures 2.5a and 2.6a).

During this study, a seasonal cycle of local precipitation was observed for both sites; the seasonal mean values (see Table 2.3) were similar to the seasonal mean rainfall values calculated over the 30-year period. For Morogoro, it was, however, rather dry during the 2005 wet season campaign. The local ambient temperature also exhibited a seasonal cycle with highest temperatures during the wet season and lowest temperatures during the dry season.



(a)



(b)

Figure 2.6. (a) Daily average temperature ($^{\circ}\text{C}$) and wind speed (m/s) recorded for days with aerosol sampling at Morogoro and (b) Relative humidity (RH, in %) and precipitation (mm) recorded for all days in 2005 and 2006 in Morogoro [TMA, 2007].

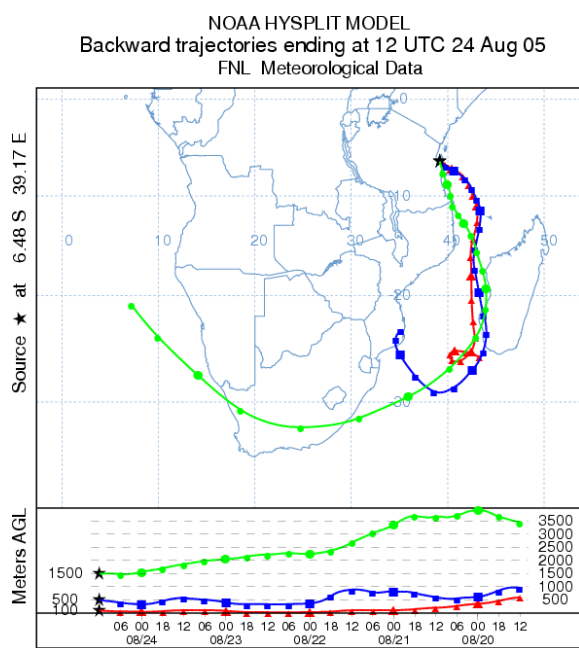
2.4.2 Air Mass Climatology

Measurements of the PM and its constituents, whether as part of a long-term monitoring or of a short-term intensive campaign, show that concentrations vary on time scales from days to years. Some of these variations can be related to seasonal changes in the transport of the chemical constituents or their precursors and seasonal variation in

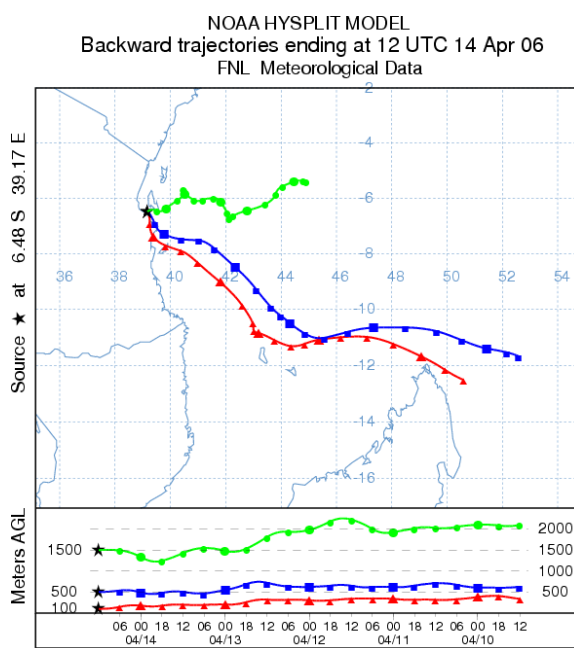
meteorological parameters. But the daily variability is closely related to the immediate history of the air before arriving at the sampling site. Therefore, there are two main approaches for the categorisation of the measured data to understand the different processes which contribute to the changes in aerosol chemical composition. These include the levels of the concentration and the origin of the sampled air. The former is represented by extreme events, such as the highest and the lowest detected concentrations over the study period. The second approach relies on some measure of the direction and past history of the air mass arriving at the sampling site.

Air masses during their motion can be loaded with particles and gases from natural (dust, volcanic eruptions, sea spray) and anthropogenic (smelters, motor vehicle exhausts, industrial and agricultural activities) sources. Backward air mass trajectories are useful to determine possible sources of aerosol particles and have been successfully used in the field of aerosol science [Brankov et al., 1998; Cape et al., 2000; Lelieveld et al., 2002]. To examine the effect of long-range transported air masses on PM and aerosol components, air mass back trajectory analyses were performed daily for both sites during the sampling periods (May 2005 – May 2006) using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPPLIT version 4) [Draxler and Rolph, 2003] utilizing the Final Model Run (FNL) meteorological data set. Five-day isentropic backward trajectories were computed for arrival levels of 100, 500, and 1500 m above ground level (agl) at 00:00 and 12:00 UTC arrival times for night and daylight periods, respectively.

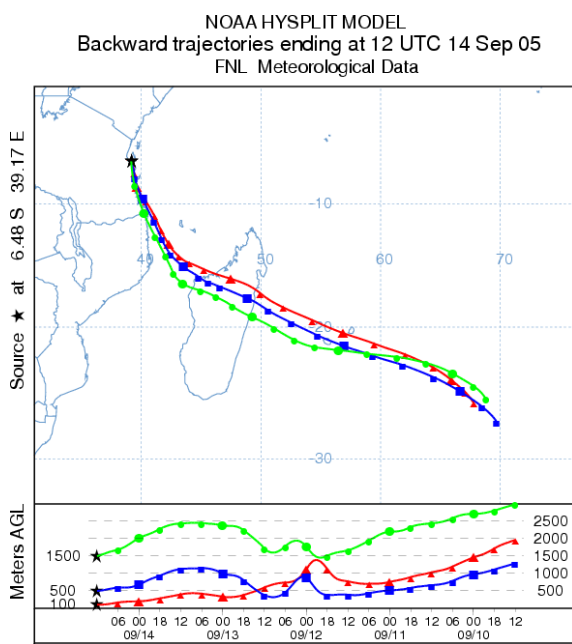
The daily air mass back trajectories for Dar es Salaam and Morogoro were categorized into four different sectors at the arrival levels of 100, 500, and 1500 m agl (see Figures 2.7 and 2.8). The allocated sectors were T1 (Oceanic); T2 (Oceanic, over Madagascar); T3 (Madagascar and/or oceanic over continental, mainly through Mozambique and Tanzania) and T4 (Continental, over Tanzania, Mozambique, South Africa). Allocation to a particular sector was made using criteria similar to those used by Traub et al. [2003].



(a)



(d)



(c)

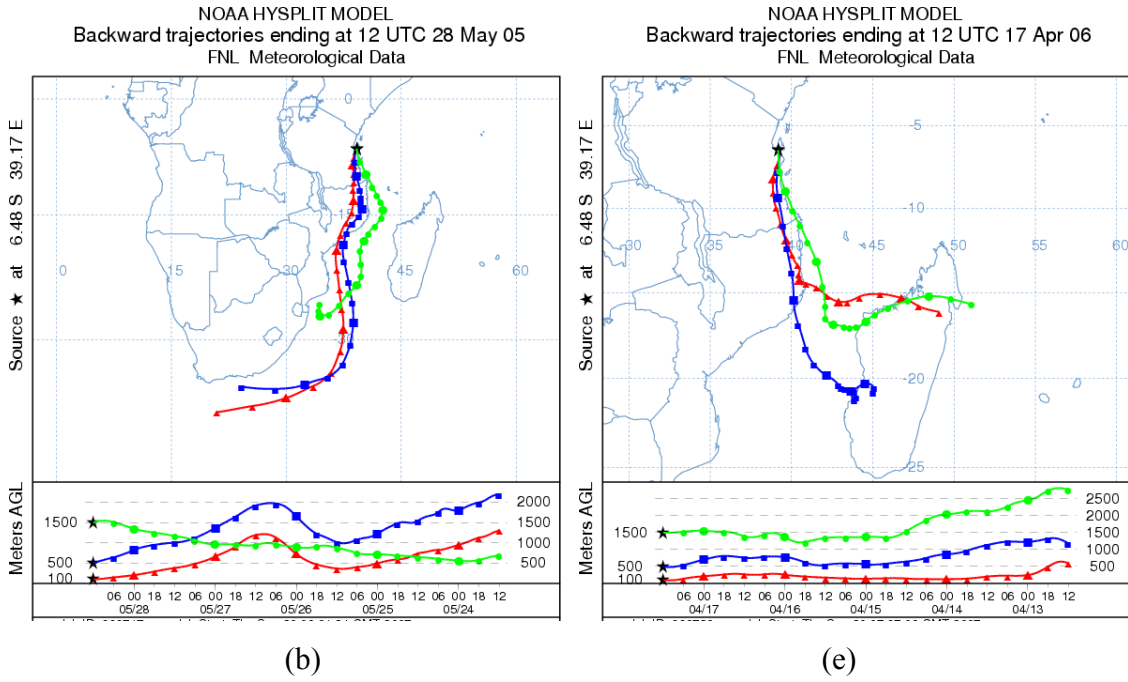
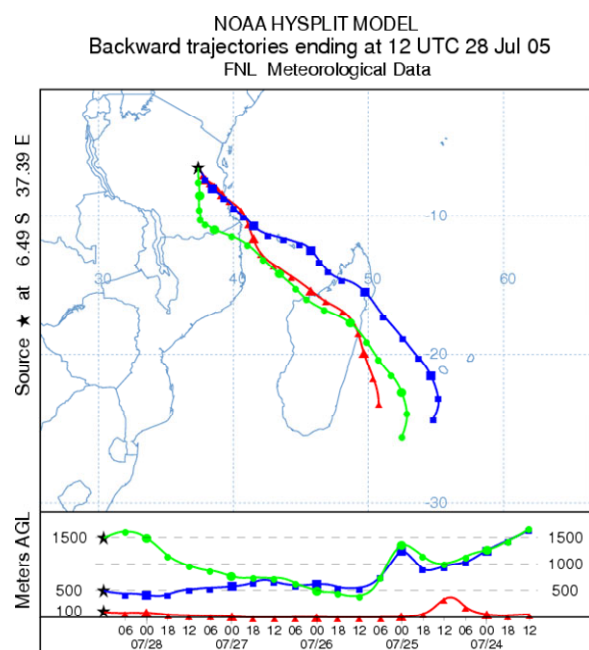
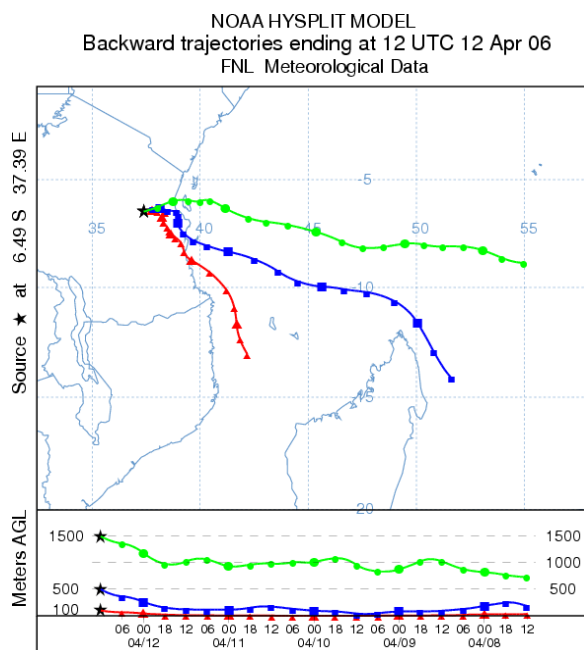


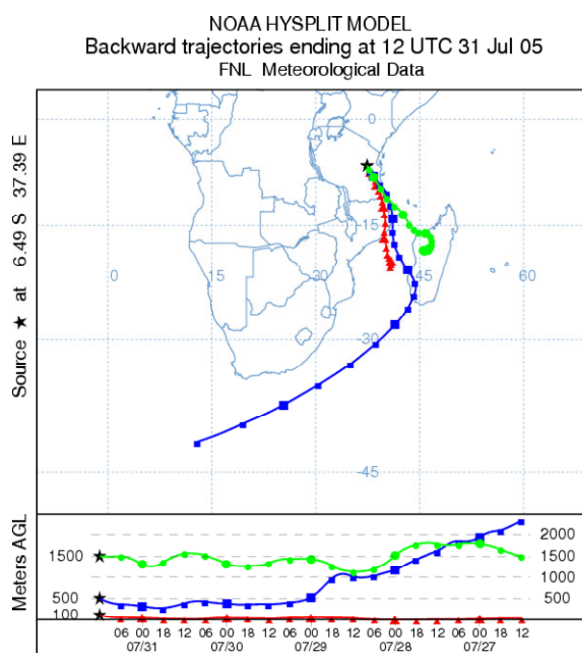
Figure 2.7. Typical examples of five-day back trajectories for air masses arriving at Dar es Salaam during the sampling campaigns. In (a) and (d) mainly oceanic origin-T1; (c) oceanic origin over Madagascar-T2; (b) and (e) oceanic or Madagascar origin over continental-T3.



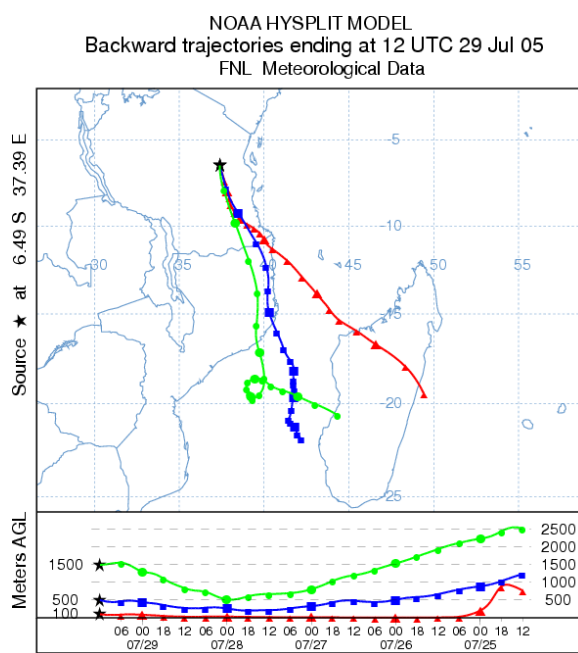
(a)



(e)



(b)



(d)

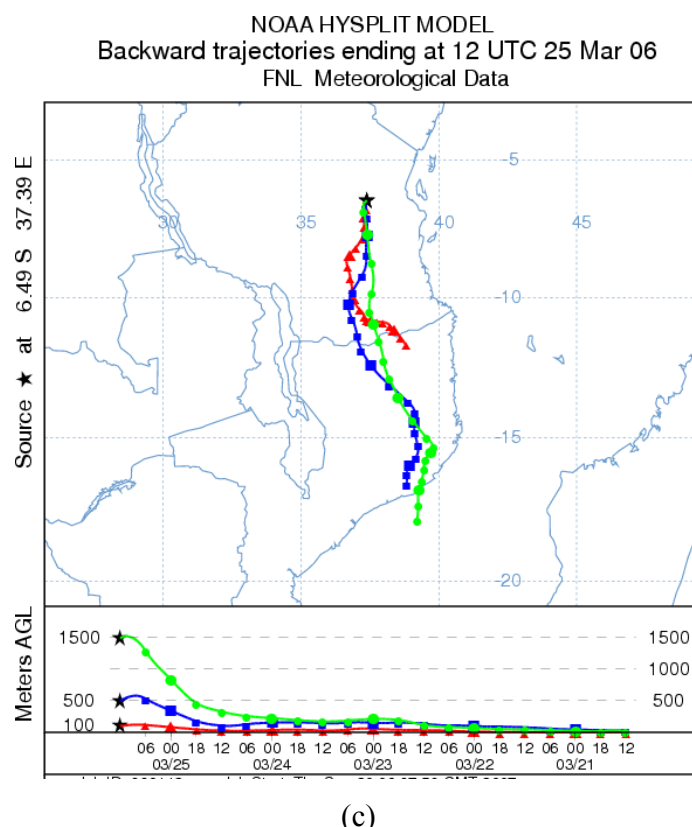


Figure 2.8. Typical examples of five-day back trajectories for air masses arriving at Morogoro during the sampling campaigns. In (e) mainly oceanic origin-T1; (a) oceanic origin over Madagascar-T2; (b) and (d) oceanic or Madagascar origin over continental-T3; (c) Continental origin-T4.

Table 2.4 presents a summary of the seasonal airflow characteristics for Dar es Salaam and Morogoro, expressed as percentage (%) of daily air mass back trajectories arriving from each of the defined four sectors for each of the three arrival levels. The airflow at each of the sites was somewhat different for the three arrival levels, in particular for Dar es Salaam. At this site, T2 was the most frequent arrival sector in the 2005 campaigns, followed by T3, whereas this order was reversed in the 2006 campaign. At Morogoro, T3 was most common in the two wet season campaigns, followed by T2 during the 2005 wet season and by T1 in the 2006 wet season; in the 2005 dry season campaign, T2 was most common, followed by T3. When comparing the data of the two sites, it appears that there is a fair similarity between both for the 2005 dry season and 2006 wet season campaigns, but that there is a substantial difference for the 2005 wet

season, with T2 most common at Dar es Salaam and T3 clearly most common at Morogoro.

Table 2.4. Summary of airflow characteristics (given as percentage frequency) at Dar es Salaam and Morogoro for four air mass sectors at three arrival levels agl during the sampling campaigns.

Dar es Salaam					Morogoro			
2005 wet season								
	T1	T2	T3	T4	T1	T2	T3	T4
1500 m	13	51	19	17	0	33	67	0
500 m	19	54	21	6	0	30	69	1
100 m	11	49	39	1	0	16	80	4
2005 dry season								
	T1	T2	T3	T4	T1	T2	T3	T4
1500 m	5	68	24	3	0	60	34	6
500 m	5	70	23	2	0	50	39	11
100 m	4	67	26	3	0	51	37	12
2006 wet season								
	T1	T2	T3	T4	T1	T2	T3	T4
1500 m	10	27	54	9	34	10	51	5
500 m	11	25	60	4	23	19	56	2
100 m	6	19	64	11	24	20	53	3

CHAPTER 3

EVALUATION AND ASSESSMENT OF ARTIFACTS IN THE MEASUREMENT OF THE PARTICULATE MASS AND ORGANIC CARBON

3.1 Introduction

As stated before, in Tanzania till to date, limit values for PM₁₀ mass are lacking. The EU Directive 1999/30/EC established annual and daily limit values for PM₁₀ starting from 2001, and provided a standard procedure for the measurement of this atmospheric pollutant based on air filtration through quartz fibre filters. However, the collection of PM on filters has been proved to be subject to a number of artifacts, such as adsorption and loss of certain compounds depending on the type of filter, the chemical species, and the ambient conditions [Jacobson et al., 2000; Turpin et al., 2000; Mader et al., 2003; ten Brink et al., 2004]. The use of sampling techniques other than the European reference method in order to prevent or minimize the effect of such artifacts may also result in non-comparable data, as they involve different filter types (filter material and diameter) which also exert an influence on the PM collection [Hitzenberger et al., 2004].

One of the main PM chemical components affected by sampling artifacts is the carbon fraction. Sampling errors related to the interaction of semi-volatile and volatile organic species with the filter substrate or the particles collected on it cause the volatilization of particulate-phase organics from the sample or the adsorption of gas-phase organics onto the filter or onto the already collected particles [Turpin et al., 2000]. These errors result in negative and positive artifacts, respectively, although positive artifacts are considered to prevail [Jacobson et al., 2000; Turpin et al., 2000]. The influence of these artifacts on PM levels can be highly significant as carbonaceous aerosols may represent up to 70% of the fine PM mass [Turpin et al., 2000].

Three sampling campaigns were devised during the 2005 wet and dry seasons and the 2006 wet season at two sites (Dar es Salaam and Morogoro) in Tanzania. During the monitoring periods two or three different sampling devices were simultaneously used. These included PM₁₀(Q) and PM_{2.5}(Q) low-volume samplers. The aim of the present study was to evaluate and assess the influence and magnitude of the sampling artifacts concerning PM and the organic carbon fraction, furthermore to evaluate to which extent the PM, OC, and WSOC levels obtained in the various seasons at the two sites may be compared.

3.2 Assessment of artifacts in the measurement of PM mass

The mean PM₁₀ and PM_{2.5} mass levels and mean back/front filter ratios obtained from the quartz fibre filters for the sampling periods are shown in Table 3.1. The highest mean PM₁₀ and PM_{2.5} mass levels (front filter data) were obtained during the dry season campaign, and this for both sites, and the lowest ones during the 2006 wet season campaign, especially in Morogoro. Averaged over all samples from the three campaigns, the PM₁₀ mass levels were 31% higher at Dar es Salaam than in Morogoro. For PM_{2.5} (and the 2006 wet season), the mean mass level was 12% higher at Dar es Salaam than in Morogoro.

For the PM₁₀ quartz fibre filter samples from Dar es Salaam, the mass on the back filter was, on average, 5% of that on the front filters. For the PM₁₀ quartz fibre filter samples from Morogoro, the mass on the second filter was, on average, 9%, 3% and 11% of that on the first filter during the 2005 wet season, 2005 dry season, and 2006 wet season campaigns, respectively. This suggests that approximately 3–11% of the PM₁₀ mass collected on the front quartz fibre filters at both sites may be due to positive artifacts. These artifacts may be related to the absorption or adsorption of gaseous carbonaceous species, inorganic species, or water vapour on the filter substrate. The fact that the back/front filter ratio was (at least for Morogoro) larger in the wet season campaigns than in the 2005 dry season campaign could imply that the adsorption of water vapour on the filters is partly responsible for the mass collected on the filters.

Table 3.1. Mean concentrations and standard deviations ($\mu\text{g}/\text{m}^3$) of the PM₁₀ and PM_{2.5} mass and OC obtained with the PM₁₀ and PM_{2.5} low-volume samplers with two quartz fibre filters, and mean back/front filter ratios and standard deviations.

		Morogoro			Dar es Salaam		
		Front filter	Back filter	Back/front filter ratio	Front filter	Back filter	Back/front filter ratio
2005 wet							
PM ₁₀ (Q)	PM	28 ± 13	2.0 ± 1.1	0.09 ± 0.10	51 ± 20	2.2 ± 1.0	0.05 ± 0.02
	OC	7.8 ± 2.2	1.0 ± 0.4	0.13 ± 0.04	13 ± 3	0.72 ± 0.18	0.06 ± 0.02
2005 dry							
PM ₁₀ (Q)	PM	49 ± 13	1.2 ± 2.0	0.03 ± 0.04	76 ± 32	3.3 ± 2.9	0.05 ± 0.05
	OC	12 ± 3	0.70 ± 0.32	0.06 ± 0.05	17 ± 7	1.1 ± 0.4	0.07 ± 0.03
PM _{2.5} (Q)	PM	ND	ND	ND	25 ± 8	2.4 ± 2.2	0.09 ± 0.09
	OC	ND	ND	ND	8.7 ± 2.5	0.70 ± 0.30	0.08 ± 0.03
2006 wet							
PM ₁₀ (Q)	PM	14 ± 13	1.9 ± 2.1	0.11 ± 0.14	51 ± 28	0.4 ± 3.8	0.01 ± 0.08
	OC	4.5 ± 0.9	0.42 ± 0.23	0.09 ± 0.05	12 ± 6	0.74 ± 0.34	0.06 ± 0.03
PM _{2.5} (Q)	PM	7.3 ± 4.0	0.98 ± 1.12	0.13 ± 0.16	18 ± 11	0.8 ± 4.3	0.03 ± 0.23
	OC	2.8 ± 1.0	0.33 ± 0.20	0.11 ± 0.06	6.8 ± 3.9	0.38 ± 0.38	0.05 ± 0.06

ND - not determined.

The PM₁₀ mass concentration data of the PM₁₀(Q) and PM₁₀(NN) samplers were also compared with each other. The ratio of the front filter PM₁₀(Q) mass concentration to the PM₁₀(NN) mass concentration (sum of coarse + fine) was calculated for each sample pair and these ratios were then averaged for each site and each campaign. The resulting average concentration ratios and associated standard deviations are given in Table 3.2. The mean ratios are close to 1.0 for the 2005 wet season campaign at the two sites, but for the 2005 dry and 2006 wet season campaigns, ratios larger than 1.0 are found. For these latter campaigns, the mass concentrations obtained from the front Whatman QM-A quartz fibre filters were thus higher than those derived from the Nuclepore polycarbonate filters. Other studies [e.g., Maenhaut et al., 2002; Hitzenberger

et al., 2004; Maenhaut et al., 2005] also found larger PM₁₀ data from Whatman QM-A front filters than from Nuclepore polycarbonate filters. This is attributed to positive artifacts (adsorption of VOCs and inorganic gaseous compounds) by the quartz fibre filters (as evidenced by the positive PM mass data for the back filters, see Table 3.1) and/or to loss of semi-volatile aerosol components from the Nuclepore filters.

Table 3.2. Mean PM₁₀(Q)/PM₁₀(NN) mass ratios and associated standard deviation for Morogoro and Dar es Salaam during three campaigns.

Season	Morogoro	Dar es Salaam
2005 wet	1.02 ± 0.14	1.01 ± 0.08
2005 Dry	1.06 ± 0.11	1.15 ± 0.11
2006 Wet	1.18 ± 0.17	1.13 ± 0.15

3.3 Influence of sampling artifacts for carbonaceous aerosols

Table 3.1 also gives the mean OC concentrations for the front and back filters and the mean ratios of the back filter relative to the front filter (EC was not detected on the back filter). The mean front filter OC concentrations were higher during the dry season than the wet season campaigns at both sites. The same was observed for the mean back filter OC concentrations. The OC on the second filter was assumed to be mainly due to adsorption of volatile organic compounds, VOCs (positive artifact). When compared to the PM data above, it appears that the back OC concentration represents, on average, 40%, 36%, and 18% of the back filter PM₁₀ mass for the 2005 wet season, 2005 dry season, and 2006 wet season campaigns at Dar es Salaam. The corresponding percentages for Morogoro are 52%, 28%, and 32%. This indicates that the adsorption of carbonaceous compounds on the back filter is for a substantial part (about one third) responsible for the artifact in PM. The mean back to front filter ratio for OC in PM₁₀ was 6–7% in Dar es Salaam and 6–13% in Morogoro. For PM_{2.5} (and the 2006 wet season campaign), it was 5% in Dar es Salaam and 11% in Morogoro. Thus, the percentage OC on the back filter (and the positive artifact) was somewhat larger for Morogoro than for Dar es Salaam. This suggests that there were relatively more volatile organics at the rural site.

In conclusion, the artifacts (based on the back to front filter ratios) for PM and OC sampling were not large. For PM₁₀, approximately 6% of the PM and OC mass in Dar es Salaam and 3–11% of the PM mass and 6–13% of the OC mass in Morogoro may be due to artifacts.

The mean front filter WSOC/OC ratios in PM₁₀ measured at the rural site (Morogoro) and the kerbside site (Dar es Salaam) in the 2005 wet and dry season and the 2006 wet season campaigns are given in Table 3.3. The mean WSOC/OC ratios were similar at the two sites in Tanzania during the 2006 wet season campaign. The contribution of WSOC to OC mass was larger at Morogoro (36% and 42%) than at Dar es Salaam (26% and 29%) in the 2005 wet and dry season campaigns. In Dar es Salaam, the mean WSOC/OC ratios were similar in all three campaigns, while in Morogoro it was larger in the 2005 wet and dry season campaigns (the former was rather dry). It seems that the different meteorological conditions did not affect the WSOC (and OC) concentrations very much, so the explanation could be that the main sources of WSOC (and OC) were close to the site. At Dar es Salaam, vehicular traffic was probably an important source. As vehicles emit mainly less water-soluble compounds, for which it takes some time to be oxidized to more water-soluble forms, the WSOC/OC ratio was smaller at the kerbside site than at the rural site.

With regard to the larger WSOC/OC ratios at Morogoro in the dry season, at European sites [Kleefeld et al., 2002; Viana et al., 2006], similar observations were made. They are likely due to stronger photochemical oxidation processes forming oxygen containing functional groups (increasing water solubility) in the dry season and to enhanced wet depositional losses of WSOC relative to the insoluble carbon in the wet season.

Table 3.3. Mean front filter WSOC/OC ratios (%) in PM10 during three campaigns in Tanzania.

Site	2005 wet season	2005 dry season	2006 wet season
Morogoro	36 ± 4	42 ± 7	31 ± 5
Dar es Salaam	26 ± 3	29 ± 9	28 ± 9

3.4 Comparison of sampling artifacts for OC with other studies

The percentage OC on the back filter, relative to the OC on the front filter, [OC(back)/OC(front)] for Morogoro and Dar es Salaam was compared with studies in Europe, whereby the same PM2.5 and PM10 tandem filter samplers were used as in this work. The studies in Europe [Maenhaut and Claeys, 2007] were conducted in Ghent (Belgium), Barcelona (Spain), Amsterdam (The Netherlands), Bily Kriz (Czech Republic), and Budapest and K-pusztá (Hungary). Bily Kriz and K-pusztá are rural background sites and the other European sites are urban sites. For PM2.5, the mean [OC(back)/OC(front)] percentages at the European sites ranged from 3.2 to 17% and higher percentages were observed for summer campaigns than for winter campaigns. In Tanzania, the PM2.5 back filter OC represented, on average, 8% and 5% of the front filter OC at the Dar es Salaam kerbside during the 2005 dry and 2006 wet season campaigns, respectively; the corresponding percentage for the 2006 wet season campaign at Morogoro was 11%. For PM10, the mean [OC(back)/OC(front)] percentages were 5.3-13% at the various European sites; in Tanzania, the mean percentages were 6-7% in Dar es Salaam and 6-13% in Morogoro. Overall, the results for the Tanzanian sites are thus rather similar to these for the European sites. However, whereas at the European sites (and for PM2.5) larger back filter OC percentages (and thus larger positive artifacts) were observed during summer than during winter, at the Tanzanian sites there was little difference between the data from the different campaigns (both for PM2.5 and PM10). On the other hand, as indicated above, there is some difference between the data from Morogoro and Dar es Salaam, and the positive artifacts are somewhat larger for the rural Morogoro site.

3.5 Comparison of WSOC/OC ratios with other studies

Our results for the front filter WSOC/OC ratio can be compared with those for European cities, such as Ghent, Barcelona, and Amsterdam, where also sampling campaigns were performed in different seasons [Viana et al., 2006, 2007b]. However, it should be noted that the meteorological conditions, in particular temperature, are quite different between the Tanzanian and European sites. For the European sites, there was a large difference in temperature between the summer and winter seasons, except at Barcelona, where this difference was less pronounced. At Morogoro, the daily mean minimum and maximum temperatures were 14 and 31 °C in the 2005 dry season campaign and 23 and 26 °C and 21 and 27 °C in the 2005 and 2006 wet season campaigns; the corresponding data for Dar es Salaam were 24 and 27 °C in the 2005 dry season campaign and 26 and 29 °C and 23 and 28 °C in the wet season campaigns. For the European sites, the daily mean minimum and maximum temperatures were 11 and 20 °C in summer and 2 and 7 °C in winter in Ghent, 20 and 30 °C in summer and 9 and 14 °C in winter in Barcelona, and 14 and 21 °C in summer and 1 and 6 °C in winter in Amsterdam.

The WSOC/OC ratios were relatively similar at the Dar es Salaam and Amsterdam sites (26–29% in Dar es Salaam and 34% in Amsterdam). The mean WSOC/OC ratio in Morogoro showed an increase from the wet season to the dry season (31% to 42%). The higher dry-season ratio was similar to those obtained in Ghent during summer and winter (40–42%) and to the summertime ratio in Barcelona (43%), while the lower wet-season ratio was similar to the wintertime ratio in Barcelona (33%) and also to the ratios obtained for Amsterdam. The small differences in the percentage contribution of WSOC to the OC at the different sites may to some extent be due to seasonal differences. In the dry season in Tanzania and during summertime at the European sites there is enhanced photochemical oxidation of the particulate OC and this leads to more WSOC.

3.6 Conclusions

The measurement of PM, OC, and WSOC in atmospheric aerosols is a complex issue due to the influence of positive and negative artifacts. The artifacts related to the adsorption and/or volatilization of carbonaceous species were studied. The adsorption or loss of semi-volatile species is influenced by the sampling face velocity, the filter type and diameter.

The evaluation of sampling artifacts for the low-volume samplers showed that at most 13% of the PM mass (and usually less than 10%) collected on the front filter of the samplers with the quartz fibre filters may be due to positive artifacts. The OC mass concentration on the back filters for Dar es Salaam represented approximately 6% of the front filter concentration, while for Morogoro, it was somewhat larger (from 6% to 13%, on average). In PM₁₀, the back filter OC mass accounted on average for one third of the back filter PM mass.

As indicated above, it is generally assumed that the artifacts for OC with quartz fibre filters are mainly positive (i.e., due to adsorption of VOCs on the filters) and that artifact-free particulate OC data with a tandem quartz fibre filter set-up, as used in this study, can be obtained by subtracting the OC on the back filter from that on the front filter. In the subsequent chapters, unless indicated otherwise, back-filter corrected OC data will therefore be used. As to EC, since it was absent on the back filter (as was expected for a primary aerosol species), the data reported or used in the subsequent chapters are always without back-filter correction. With regard to TC, the sum of back-filter corrected OC and front filter EC will be used (unless indicated otherwise). Although there is certainly some positive artifact in the PM mass and WSOC data derived from the quartz fibre filters, the uncorrected data derived from the front filters will be employed in the subsequent chapters, because the PM mass and WSOC data for the back filters had a large associated uncertainty (which was much larger than that for OC, EC or TC). The PM mass data derived from the Nuclepore filters may also not be free from artifacts (in this case negative artifacts), but the PM mass determination for such filters has a much smaller uncertainty than for quartz fibre filters. For aerosol chemical mass closure calculations, the PM mass data from the Nuclepore filters were therefore used.

CHAPTER 4

AMBIENT LEVELS AND CHEMICAL COMPOSITION OF PM₁₀ AEROSOLS DURING THE WET AND THE DRY SEASON CAMPAIGNS AT MOROGORO, TANZANIA

4.1 Introduction

This chapter is dedicated to the study of ambient levels and chemical composition of PM₁₀ aerosols during the wet and the dry season campaigns in Morogoro, Tanzania. At first the levels of the different aerosol components in the PM₁₀ fraction are described. These include PM₁₀ mass, OC, EC, WSOC, inorganic ions, and elements. Also the time series, enrichment, and the correlation for selected aerosol species are calculated and discussed. In section 4.8 the influence of meteorology on the concentration of the PM mass, carbonaceous species, and major inorganic ions is discussed. Then, in section 4.9, the relationship between OC and EC with indicators of pollution elements is described so as to explain the possible sources for OC and EC. Finally, conclusions are given in section 4.10.

4.2 Levels of different aerosol components

In this research work, 13, 51 and 29 sets of PM₁₀ samples were collected at Morogoro during 2005 wet, 2005 dry, and 2006 wet season sampling campaigns, respectively. The concentrations of the PM mass, carbonaceous species, inorganic water-soluble ions, and major, minor, and trace elements were determined. The median concentrations and concentration ranges of the PM₁₀ mass and the determined components are shown in Table 4.1.

Table 4.1. Median concentrations and concentration ranges in the PM10 size fraction at Morogoro. Data for the PM mass, BC, TC, OC, EC, and WSOC are in $\mu\text{g}/\text{m}^3$; for all other species in ng/m^3 . Ions, elements, and BC were obtained from PM10(NN); TC, OC, EC, and WSOC from PM10(Q).

	2005 wet season [N = 13]		2005 dry season [N = 51]		2006 wet season [N = 29]	
	Median	(min. – max.)	Median	(min. – max.)	Median	(min. – max.)
Data in $\mu\text{g}/\text{m}^3$						
PM(NN)	23	(15 – 49)	45	(28 – 77)	13	(8.2 – 25)
PM(Q)	25	(12 – 56)	47	(29 – 90)	15	(10 – 28)
BC	2.5	(1.5 – 3.3)	5.5	(2.7 – 12)	1.7	(1.2 – 3.2)
TC	7.0	(4.3 – 12)	12	(6.8 – 29)	4.4	(2.9 – 6.9)
OC	6.5	(4.0 – 11)	11	(6.4 – 26)	3.9	(2.7 – 6.0)
EC	0.46	(0.25 – 0.76)	0.82	(0.16 – 2.6)	0.51	(0.26 – 0.90)
WSOC	2.7	(1.5 – 4.5)	5.1	(2.7 – 19)	1.4	(0.86 – 2.4)
Data in ng/m^3						
Ammonium	150	(60 – 340)	230	(72 – 1420)	121	(43 – 390)
Nitrate	430	(240 – 630)	1530	(490 – 4800)	182	(68 – 850)
Sulphate	770	(460 – 1070)	1850	(970 – 5800)	410	(130 – 1500)
Na (IC)	410	(240 – 650)	1020	(230 – 2200)	131	(11 – 730)
Mg (IC)	85	(43 – 109)	150	(64 – 300)	31	(12 – 110)
Al	660	(230 – 2500)	1260	(560 – 2700)	400	(120 – 1160)
Si	1320	(500 – 4600)	2500	(1200 – 5200)	740	(230 – 2100)
P	32	(25 – 61)	38	(23 – 78)	34	(21 – 52)
S	350	(230 – 470)	690	(420 – 2000)	173	(93 – 600)
Cl	390	(180 – 610)	860	(200 – 1920)	92	(DL – 680)
Cl (IC)	370	(168 – 650)	1060	(173 – 2500)	110	(22 – 790)
K	470	(320 – 720)	1580	(760 – 3600)	189	(110 – 350)
K (IC)	270	(210 – 410)	1310	(600 – 3800)	120	(76 – 210)
Ca	530	(172 – 2000)	960	(440 – 2100)	250	(100 – 900)
Ca (IC)	600	(169 – 2000)	950	(430 – 2100)	280	(120 – 1060)
Ti	60	(23 – 230)	111	(48 – 240)	35	(10 – 100)
V	1.4	(DL – 6.2)	2.2	(DL – 6.6)	0.62	(DL – 2.7)
Cr	DL	(DL – 4.2)	1.6	(DL – 3.9)	DL	(DL – 1.8)
Mn	8.6	(5.4 – 29)	15	(8.7 – 33)	4.7	(1.4 – 14)
Fe	610	(240 – 2400)	1110	(500 – 2400)	370	(110 – 1110)
Ni	0.50	(DL – 2.1)	0.80	(DL – 2.5)	0.27	(DL – 1.1)
Cu	1.3	(0.61 – 3.5)	2.0	(DL – 11)	0.89	(0.35 – 3.6)
Zn	5.7	(4.0 – 15)	12.6	(DL – 29)	4.4	(2.2 – 9.7)
Ga	0.49	(DL – 2.5)	1.1	(DL – 2.7)	0.25	(DL – 1.4)
As	DL	(DL – 1.0)	DL	(DL – 1.7)	DL	(DL – 0.59)
Se	DL	(DL – 0.37)	DL	(DL – 0.58)	DL	(DL – 0.30)
Br	1.6	(DL – 3.1)	7.5	(DL – 19)	DL	(DL – 2.1)
Rb	DL	(DL – DL)	1.2	(DL – 4.4)	DL	(DL – DL)
Sr	2.9	(1.3 – 7.2)	5.1	(2.0 – 12)	1.2	(DL – 3.3)
Ba	5.9	(DL – 17)	9.7	(DL – 23)	DL	(DL – 7.0)
Pb	1.5	(DL – 4.4)	DL	(DL – 6.3)	DL	(DL – 0.98)

DL - detection limit; IC - ion chromatography.

4.2.1 PM mass

As can be seen from Table 4.1, the highest median and maximum concentrations for the PM₁₀ mass were obtained during the 2005 dry season campaign and the lowest median and minimum during the 2006 wet season campaign. The average contributions of fine (PM₂) particulate mass to the PM₁₀ mass during the three campaigns were 35 ± 9 , 49 ± 9 , and 37 ± 6 % for the 2005 wet, 2005 dry, and 2006 wet seasons, respectively, indicating that most of the PM₁₀ mass was in the coarse size fraction. The variations in ambient PM₁₀ levels observed during the campaigns resulted from variations in sources strengths and in meteorological conditions, such as mixing height and precipitation. The main sources of the PM₁₀ mass at this rural site are expected to be primary sources, i.e., soil dust dispersal and biomass burning, but gas-to-particle conversion processes may also contribute.

Since there are no standard limits for TSP, PM₁₀ or PM_{2.5} levels in Tanzania, the data from this work are compared to EU standards. In the EU the daily limit concentration for PM₁₀ mass is $50 \mu\text{g}/\text{m}^3$, which cannot be exceeded more than 35 times per year, and the yearly average concentration (based on daily measurements) is $40 \mu\text{g}/\text{m}^3$ [EU Directive, 1999]. In Morogoro, the daily PM₁₀ concentrations exceeded the daily EU standard 2 times during the 2005 wet season campaign (note that this season was rather dry) and 17 times during the 2005 dry season campaign.

The levels of the PM₁₀ mass at the rural background site of Morogoro are in line with the levels at rural sites in Europe, as reported in the European aerosol phenomenology study [Van Dingenen et al., 2004]. Our data are also comparable to the few available other data sets for eastern and southern Africa [Nyanganyura et al., 2007]. For the remote site of Rukomechi in northern Zimbabwe, median PM₁₀ mass concentrations of $8 \mu\text{g}/\text{m}^3$ and $23 \mu\text{g}/\text{m}^3$ were obtained for the wet and the dry seasons, respectively [Nyanganyura et al., 2007], which are lower than the data for Morogoro.

4.2.2 Carbonaceous aerosols

It appears further from Table 4.1 that the concentrations of BC, TC, OC, EC, and WSOC in PM₁₀ at Morogoro were higher during the 2005 dry season campaign and lowest during the 2006 wet season campaign. This is in line with what was found for the PM₁₀ mass. BC was mainly associated with the fine size fraction: of the PM₁₀ BC, 78 ± 6 , 86 ± 7 , and 82 ± 5 % was, on average, in the PM_{2.5} aerosol in the 2005 wet season, 2005 dry season, and 2006 wet season campaigns, respectively. In the 2006 wet season campaign, besides PM₁₀(Q) samples, PM_{2.5}(Q) were also taken and analysed for OC, EC, and WSOC; the average percentages of PM₁₀ OC, EC, and WSOC in the fine (PM_{2.5}) size fraction were 58 ± 8 , 84 ± 11 , and 88 ± 16 %, respectively.

There are very few literature data available for carbonaceous species in Africa, and data for OC and WSOC are completely lacking for Tanzania. Data for complete seasonal cycles are also rare; however, other interesting studies over shorter periods exist. More studies of carbonaceous species have been done in Europe, as reported by Putaud et al. [2004]. The data of the present study can be compared with the few available data sets for eastern and southern Africa. Gatari et al. [2001] reported an average TC level of 7 ± 1 $\mu\text{g}/\text{m}^3$ for the rural site of Meru in Kenya. This average is similar to the median TC data in Morogoro (4.4 - 12 $\mu\text{g}/\text{m}^3$).

The mean percentages (relative to the front filter PM mass, OC, or TC) of front filter OC, WSOC, EC, and TC in PM₁₀ and PM_{2.5} are shown in Figure 4.1. It can be seen that the PM₁₀ aerosol contained more OC and TC in the wet season campaigns than in the dry season campaign. On average, front filter TC accounted for 31 ± 7 % of the front filter PM₁₀ mass (range: 23–41%) in the 2005 wet season, for 27 ± 5 % (range: 21–51%) in the 2005 dry season, and for 33 ± 10 % (range: 20–62%) in the 2006 wet season. A larger fraction of the OC was water-soluble (WSOC) in the dry season than in the wet season campaigns, and the EC/TC percentage ratio was higher in the 2006 wet season campaign than in the other two campaigns. The EC/TC ratio gives clues on the sources of the carbonaceous aerosol and on the contribution of secondary organic aerosol (SOA). Low EC/TC ratios may indicate that there is a large contribution of SOA or that the carbonaceous aerosol originates mainly from biogenic aerosols and/or biomass burning

[Maenhaut and Claeys, 2007]. Biogenic matter contains no EC, whereas the TC from wood and other biomass burning has typically only around 10% or less EC [Hildemann et al., 1991; Andreae and Merlet, 2001; Fine et al., 2004]. In contrast, there is much more EC in the carbonaceous aerosol from traffic. Figure 4.1 further shows that, for the 2006 wet season and the PM_{2.5} size fraction, the OC/PM and the WSOC/OC percentage ratios were, on average, 38 ± 11 % and 45 ± 8 %, respectively. The percentages ranged from 15 to 72% for OC/PM and from 31 to 63% for WSOC/OC. The mean EC/TC percentage in PM_{2.5} was 14 ± 4 % (range: 8–23%), while the mean percentage of TC in PM_{2.5} was 44 ± 12 % (range: 19–83%).

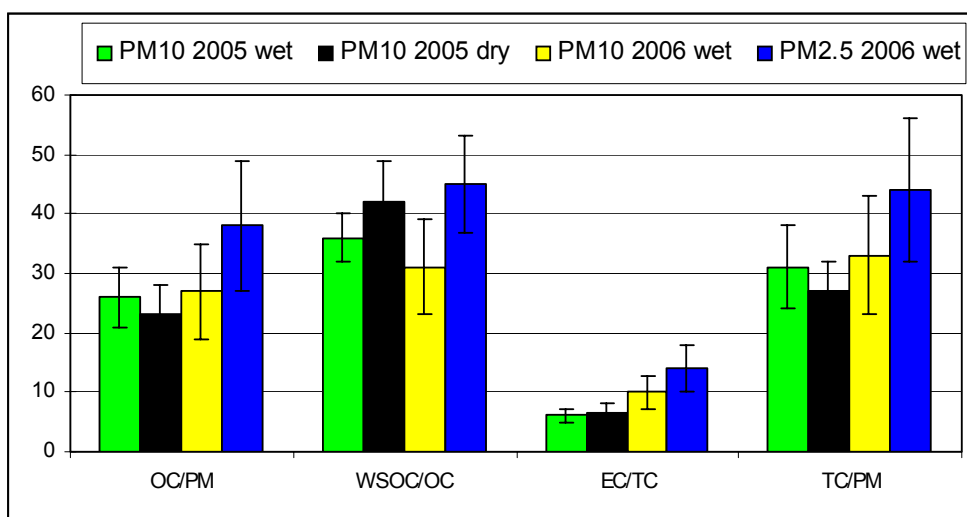


Figure 4.1. Mean percentage ratios (and associated standard deviations) for OC/PM, WSOC/OC, EC/TC, and TC/PM for the PM₁₀ and PM_{2.5} front filter PM(Q) samples from Morogoro.

Since OC is both of primary and secondary origin, whereas EC is exclusively a primary aerosol component, EC has often been used as a tracer of primary OC [Turpin and Huntzicker, 1991]. The statistical analysis indicated that there is to some extent a correlation between PM₁₀ EC and OC ($r^2 = 0.66$ for 93 samples). This correlation seems to indicate that there is a certain homogeneity in the sources of carbonaceous matter and in the contribution of SOA to OC at the Morogoro site. However, when split up per

campaign, there was clearly a difference in the relationships between PM10 OC and EC, as shown in Figure 4.2. The correlation between OC and EC is moderate for the 2005 wet ($r^2 = 0.60$) and dry ($r^2 = 0.70$) season campaigns, but poor for the 2006 wet season ($r^2 = 0.29$). Furthermore, there is a large difference in the slopes of the regression lines (of OC on EC) between the 2005 wet (0.99) and the dry (7.0) season campaigns, which suggests that there a large fraction of the OC was SOA in the latter campaign. In contrast, in the 2005 wet season campaign, the OC seems to have been mostly primary carbon.

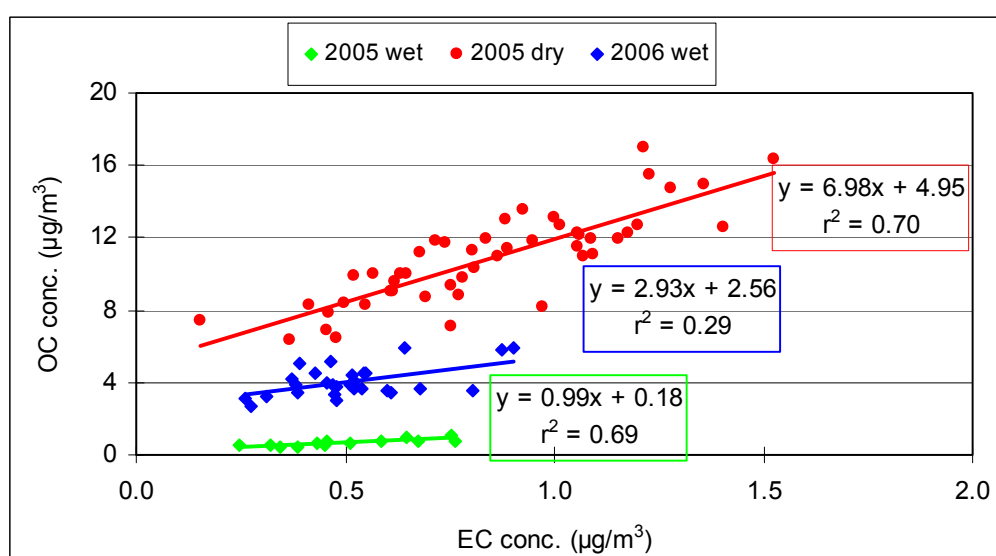


Figure 4.2. Relationship between OC and EC in PM10 during the dry and the wet season campaigns in Morogoro.

4.2.3 Major, minor and trace elements

Table 4.1 shows that the differences in concentrations of many major, minor, and trace elements between the 3 campaigns followed the same patterns as the differences for the PM10 mass and the carbonaceous components. All elements had their lowest median concentration in the 2006 wet season campaign. The medians of Al, Si, P, S, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Br, Rb, Sr, and Ba were highest in the 2005 dry season campaign, while those for Pb were highest in the 2005 wet season campaign. Arsenic and Se were below the detection limit in all 3 sampling campaigns.

That all elements have their lowest medians in the 2006 wet season campaign is mainly ascribed to the increased precipitation in that campaign; besides, the soil is wetter so that there is less dispersal of soil dusts and there is also less biomass burning in the wet than in the dry season. There are several possible reasons for the elevated concentrations of the elements in the dry season: (1) There is much biomass burning in this season. (2) There are temperature inversions, so that the air is not diluted. (3) It is very dry, with little or no rain at all, so wash-out of particles by wet deposition is weak. (4) With little vegetation, a larger contribution from soil dust dispersal can be expected in the dry season.

The elemental concentration data for Morogoro can be compared with those of other studies in eastern Africa. The levels of the measured elements (except Zn) are about a factor of 6 higher than those reported by Gatebe et al. [2001] for aerosol samples from a rural site on the slope of Mount Kenya and a factor of 3 – 10 higher than for aerosols from Rukomechi, a rural site in Zimbabwe [Nyanganyura et al., 2007]. In contrast, the levels at Morogoro are lower by a factor of 2 – 14 for elements such as Si, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, and Pb than those reported for traditional villages of Serowe in Botswana [Moloi et al., 2002].

4.2.4 Ionic components

Like for most other species, discussed so far, higher concentrations in PM₁₀ were also observed for the ions in the dry season campaign. The differences between the dry and the wet seasons can again be attributed to the differences in meteorological conditions.

The median SO_4^{2-} concentration in the 2005 dry season campaign was 2.4 and 4.5 times higher than in the 2005 and 2006 wet season campaigns, respectively. A similar situation is observed for nitrate. The median for NO_3^- in the 2005 dry season was 3.6 times higher than in the 2005 wet season and 8.5 times higher than in the 2006 wet season. Thus, the difference between seasons is even more pronounced for nitrate than for sulphate. The partition of NO_3^- between the gas phase and particulate phase depends strongly on temperature (T), relative humidity (RH), and ammonia concentration, and

larger particulate nitrate concentrations are expected at low temperature and high RH. There was no dramatic seasonal difference in RH, whereas the temperature was lowest in the dry season. Thus, the larger nitrate levels in this season are expected. On the other hand, biomass burning is an important source of NO_x , the precursor gas of nitrate, and enhanced biomass burning in the dry season may be responsible for the elevated nitrate levels then. The median for particulate NH_4^+ is also higher in the dry than in the wet season. This may be due to enhanced ammonia levels then. Unfortunately, no data for the gases SO_2 , NO_x , and NH_3 are available for the 3 campaigns.

The medians for Ca^{2+} , Na^+ , Mg^{2+} , K^+ , and Cl^- are higher in the dry than in the wet season campaigns. The highest median for K^+ in the dry season campaign is expected, as K^+ is a good indicator for biomass burning, which is most enhanced in the dry season. K^+ was higher in the 2005 wet season than in the 2006 wet season campaign, which is in accordance with the fact that the 2005 wet season campaign at Morogoro was rather dry.

When compared to literature data for rural sites in Europe, it appears that the levels in PM_{10} of SO_4^{2-} , NO_3^- , and NH_4^+ are substantially lower at Morogoro than at the European rural sites [Putaud et al., 2004; Ocskay et al., 2006].

4.3 Time series of the PM mass and selected aerosol species

The time series of the PM mass and selected aerosol species and elements in the PM_{10} , fine or coarse size fractions for the 2005 dry season campaign in Morogoro is shown in Figure 4.3. Whereas the concentrations of the PM_{10} mass and OC are quite constant, the levels of the other components, and especially that of fine ammonium, show quite some variability.

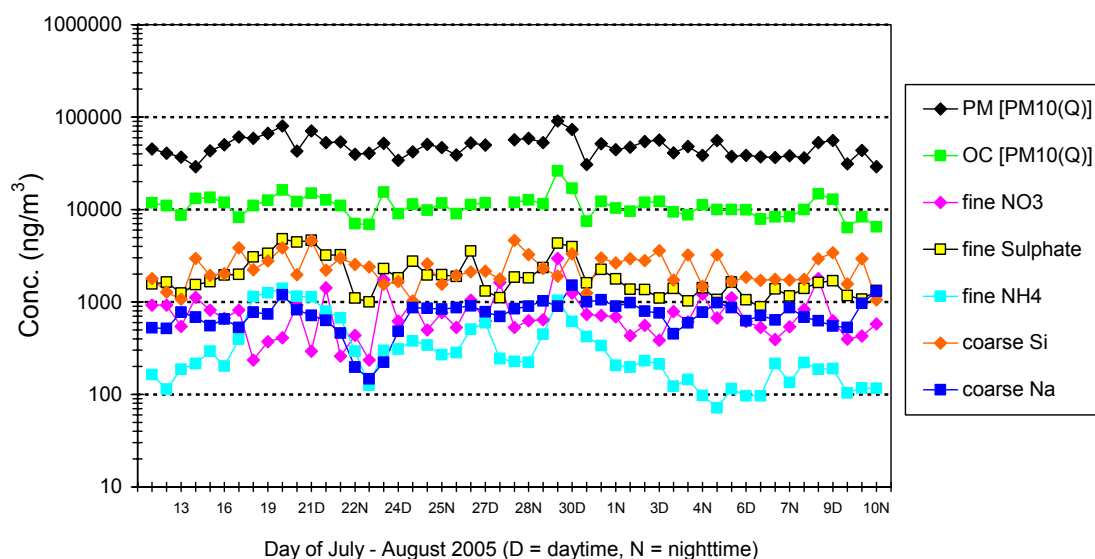


Figure 4.3. Time series of the PM mass and selected aerosol species and elements in the PM10, fine or coarse size fractions at Morogoro during the 2005 dry campaign.

4.4 Fine to PM10 ratios

Average fine to PM10 concentration ratios were calculated for the PM mass, OC, EC, BC, ammonium, nitrate, nss-sulphate, and various elements; the results are shown in Figure 4.4. The average PM₂(NN)/PM₁₀(NN) concentration ratios and associated standard deviations for the PM mass were 0.35 ± 0.09 , 0.49 ± 0.09 , and 0.37 ± 0.06 for the 2005 wet, 2005 dry, and 2006 wet season campaigns, respectively. The higher PM₂/PM₁₀ ratio for the PM mass in the dry season may be due to a larger contribution from pyrogenic aerosol, which is known to be mostly associated with fine particles. Figure 4.4 further shows that OC, EC, ammonium, non-sea-salt (nss) sulphate (and nss S), and some anthropogenic metals were mainly present in the fine size fraction. The crustal elements (Al, Si, Ca, Ti, Mn, and Fe) and the sea-salt elements (Na, Mg, Cl, Sr) were predominantly associated with the coarse size fraction. Cu and Zn were also mainly associated with the coarse particles. K (a well-known indicator for biomass burning) was mostly associated with the fine particles (in contrast to Ca), as was, for example, also

noted in the SAFARI-92 campaign [Maenhaut et al., 1996]. This suggests that biomass burning was important in Morogoro, especially in the 2005 dry season campaign, when around 80% of the PM₁₀ K was in the PM₂ size fraction.

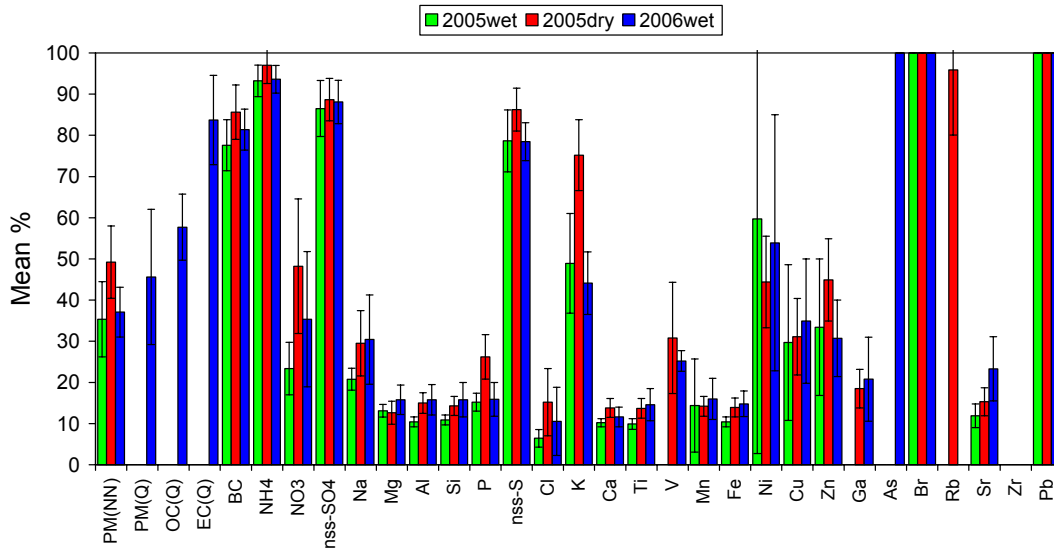


Figure 4.4. Mean percentage and associated standard deviation of the PM₁₀ aerosol in the fine (PM₂ or PM_{2.5}) size fraction for the PM mass, OC, EC, BC, ammonium, nitrate, nss-sulphate, and various elements at Morogoro for the three campaigns.

4.5 Crustal enrichment factors

Median crustal enrichment factors (EFs) for the various elements in the coarse and fine size fractions were calculated relative to the average crustal rock composition of Mason and Moore [1982], with Fe as reference element:

$$EF = (X_{PM}/Fe_{PM})/(X_{crust}/Fe_{crust})$$

where X_{PM} and Fe_{PM} are the concentrations of the measured element and Fe in the aerosol, while X_{crust} and Fe_{crust} are the concentrations of the measured element and Fe in average crustal rock composition of Mason and Moore [1982]. The calculated EFs are shown in Figure 4.5; for BC the ratio to Fe (instead of the EF) is shown. Interestingly,

there is little difference in the crustal EFs between the different campaigns, and this for each of the two size fractions. For the coarse size fraction and all campaigns, most elements have crustal EFs that are very close to one, thus suggesting that they are attributable mainly to soil dust dispersal. With the exception of Al, Cl, and Ca, which are slightly more enriched in the coarse fraction, all elements exhibit higher EFs in the fine fraction in all campaigns. For the strongly enriched elements (EFs > 10 in the fine size fraction) like S, Cl, Zn, Br, and Pb, and also for BC an anthropogenic (pyrogenic) origin can be suggested [Maenhaut et al., 1996].

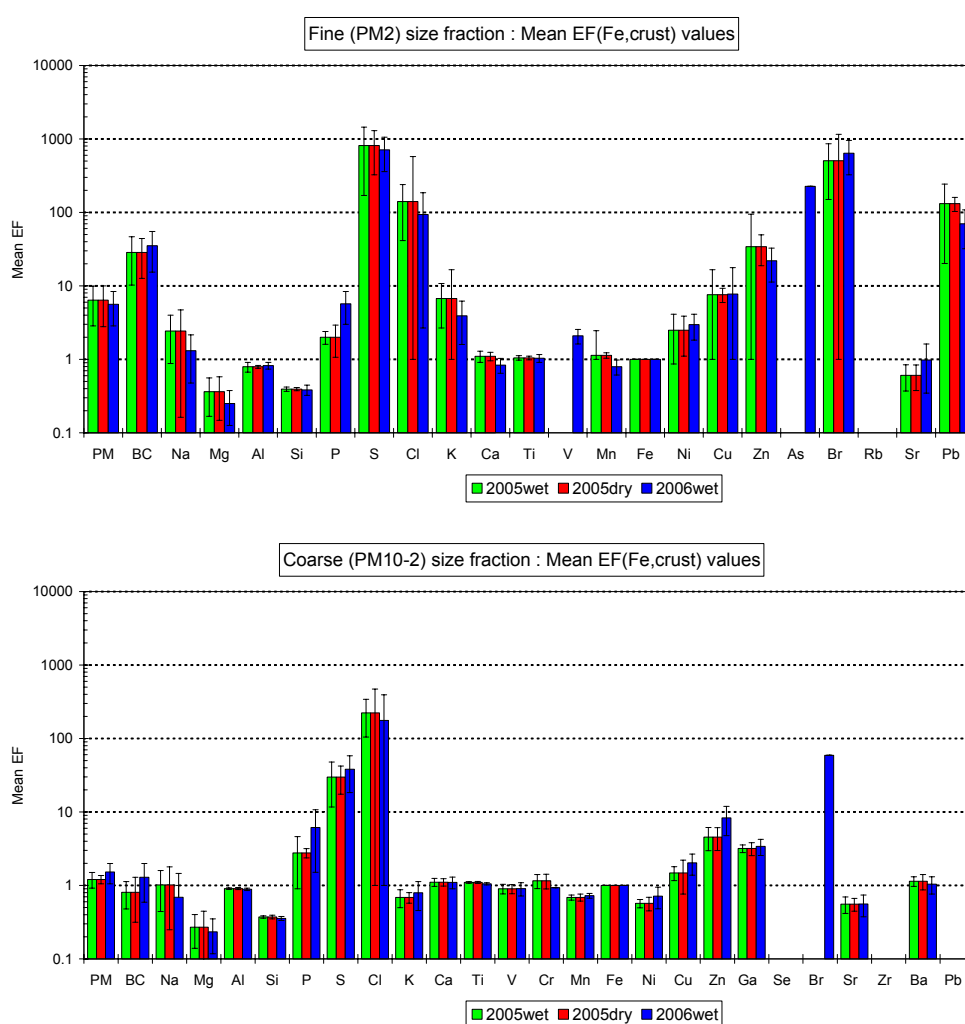


Figure 4.5. Mean crustal enrichment factors, calculated relative to the average rock composition of Mason and Moore [1982] for the **fine** and **coarse** size fraction aerosols in Morogoro. The error bars denote 1 standard deviation.

4.6 Concentration ratios of cationic and anionic species

Table 4.2. Medians (and ranges) of ratios between various equivalent concentrations in the fine and coarse size fractions.

Species	Fine size fraction		Coarse size fraction	
	Median	Range	Median	Range
2005 wet				
cations/anions	1.44	(1.12 – 1.85)	2.56	(1.24 – 5.45)
NH ₄ ⁺ /cations	0.35	(0.22 – 0.71)	0.01	(0.003 – 0.04)
Na ⁺ /cations	0.19	(0.10 – 0.32)	0.32	(0.11 – 0.42)
Mg ²⁺ /cations	0.04	(0.02 – 0.07)	0.12	(0.05 – 0.14)
K ⁺ /cations	0.24	(0.17 – 0.38)	0.03	(0.02 – 0.07)
Ca ²⁺ /cations	0.04	(0.00 – 0.33)	0.55	(0.37 – 0.81)
NO ₃ ⁻ /anions	0.10	(0.04 – 0.18)	0.26	(0.19 – 0.33)
SO ₄ ²⁻ /anions	0.84	(0.74 – 0.93)	0.17	(0.12 – 0.29)
Cl ⁻ /anions	0.05	(0.02 – 0.08)	0.55	(0.22 – 0.63)
Cl ⁻ /Na ⁺	0.18	(0.12 – 0.29)	0.69	(0.52 – 0.79)
2005 dry				
cations/anions	1.30	(1.12 – 1.64)	2.01	(1.21 – 5.45)
NH ₄ ⁺ /cations	0.22	(0.07 – 0.71)	0.002	(0.00 – 0.06)
Na ⁺ /cations	0.21	(0.07 – 0.36)	0.36	(0.09 – 0.55)
Mg ²⁺ /cations	0.02	(0.005 – 0.067)	0.12	(0.07 – 0.16)
K ⁺ /cations	0.45	(0.17 – 0.62)	0.04	(0.02 – 0.08)
Ca ²⁺ /cations	0.08	(0.02 – 0.23)	0.48	(0.24 – 0.81)
NO ₃ ⁻ /anions	0.23	(0.05 – 0.43)	0.27	(0.01 – 0.44)
SO ₄ ²⁻ /anions	0.69	(0.39 – 0.93)	0.16	(0.11 – 0.32)
Cl ⁻ /anions	0.08	(0.01 – 0.26)	0.54	(0.24 – 0.82)
Cl ⁻ /Na ⁺	0.26	(0.07 – 1.21)	0.79	(0.39 – 1.09)
2006 wet				
cations/anions	1.34	(1.05 – 1.59)	3.14	(1.28 – 8.09)
NH ₄ ⁺ /cations	0.59	(0.37 – 0.79)	0.02	(0.01 – 0.12)
Na ⁺ /cations	0.11	(0.03 – 0.19)	0.17	(0.02 – 0.48)
Mg ²⁺ /cations	0.03	(0.01 – 0.05)	0.09	(0.06 – 0.13)
K ⁺ /cations	0.13	(0.06 – 0.36)	0.06	(0.02 – 0.16)
Ca ²⁺ /cations	0.12	(0.04 – 0.32)	0.63	(0.38 – 0.82)
NO ₃ ⁻ /anions	0.09	(0.06 – 0.21)	0.29	(0.14 – 0.40)
SO ₄ ²⁻ /anions	0.86	(0.69 – 0.94)	0.22	(0.09 – 0.58)
Cl ⁻ /anions	0.03	(0.00 – 0.09)	0.43	(0.12 – 0.56)
Cl ⁻ /Na ⁺	0.19	(0.00 – 0.79)	0.70	(0.45 – 2.91)

Various equivalent concentration ratios were calculated for the water-soluble inorganic species, including the ion balance (expressed as the ratio of total cation equivalents to total anion equivalents), the ratios of individual cations to the total cations and of individual anions to the total anions, and the Cl^-/Na^+ ratio. The median ratios and ranges for the fine and coarse size fractions for each of the three campaigns are given in Table 4.2. The median ion balance ratios are all larger than 1.0; they range from 1.30 to 1.44 for the fine size fraction and from 2.01 to 3.14 for the coarse size fraction. It should be indicated that carbonates were not measured by IC; these missing carbonates are thought to be largely responsible for the observed deviation from 1.0. If we assume that all the Ca^{2+} is present as CaCO_3 and recalculate the ion balances with Ca^{2+} excluded, then the new median ion balance ratios range from 1.17 to 1.25 for the fine size fraction and from 1.02 to 1.22 for the coarse fraction. These new medians are all fairly close to 1.0. That Ca^{2+} may be present as CaCO_3 is not an unreasonable supposition, as limestone soils often contribute substantially to the mineral dust aerosol.

Table 4.2 further shows that SO_4^{2-} is by far the most prominent anion and that NH_4^+ is the main cation in the fine size fraction; in the coarse fraction, Cl^- and Ca^{2+} are the main anionic and cationic species. As just indicated, Ca^{2+} may be present as CaCO_3 . With regard to Cl^- , this may be mainly be derived from sea salt. To examine this, the Cl^-/Na^+ equivalent ratios of Table 4.2 can be compared with the ratio of 1.18 for sea water [Brewer, 1975]. The median Cl^-/Na^+ ratios range from 0.18 to 0.26 for the fine size fraction and from 0.69 to 0.79 for the coarse size fraction. All these medians are substantially lower than the sea-water ratio. Not all Na^+ at the Morogoro site may originate from sea salt, though. There is also Na in mineral dust. Actually, the crustal EF for coarse Na is near 1 (see Figure 4.5), so that the low Cl^-/Na^+ coarse medians may well be due to the contribution from mineral dust Na. It should be noted here that at locations where there is virtually no contribution from sea salt, one often sees crustal EFs for Na of lower than 1 (sometimes even below 0.5), indicating that the EF of 1 as seen in Figure 4.5 does not imply that all the Na is fully derived from mineral dust. As to the fine size fraction, the mean crustal EFs for Na are in two of the three campaigns about 2, suggesting that at least half of the fine Na may be coming from non-crustal sources, such as sea salt. Even taking this into account, we would never arrive at Cl^-/Na^+ ratios that

approach that in sea water. It is well-known, though that Cl may be lost from the fine sea-salt aerosol because of reactions with acidic gases and acidic aerosol species [e.g., Graedel and Keene, 1995] both in the atmosphere and during the actual sampling.

The medians and ranges of the molar ratios of ammonium to sulphate and nitrate are given in Table 4.3. As indicated above, in the fine size fraction, SO_4^{2-} is by far the most prominent anion and NH_4^+ is the main cation. In the neutralization of the precursor gases H_2SO_4 and HNO_3 by NH_3 gas and the formation of particulate compounds, H_2SO_4 is neutralized [first to NH_4HSO_4 , then to $(\text{NH}_4)_2\text{SO}_4$] before the neutralization of HNO_3 takes place. Only in the case of an ammonia-rich environment will the H_2SO_4 and HNO_3 be fully converted to the ammonium salts [Seinfeld and Pandis, 1998]. It follows from the data in Table 4.3 that there was insufficient NH_4^+ to fully neutralize H_2SO_4 to $(\text{NH}_4)_2\text{SO}_4$, in the fine size fraction, during the 2005 dry season campaign, but that there was nearly sufficient NH_4^+ for this neutralization in the wet season campaigns, especially in the 2006 wet season campaign. H_2SO_4 and sulphate in the atmosphere are formed through homogeneous gas phase and heterogeneous gas/particle phase oxidation of SO_2 . The atmospheric lifetime of fine sulphate is in the order of several days [Seinfeld and Pandis, 1998], so it can be transported far away from the sources of the SO_2 . With regard to the sulphate in the coarse size fraction, this is to some extent primary (e.g., derived from sea salt) and in part secondary (formed from SO_2). Table 4.3 indicates that a substantial fraction of the coarse sulphate may have been present as NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ during the two wet season campaigns, but that there was very little of these ammonium salts in the 2005 dry season campaign. The neutralizing cations for coarse sulphate in this latter campaign must therefore have been alkali and/or earth alkali metals (e.g., Ca^{2+}).

Fine particulate nitrate is formed by homogeneous gas phase oxidation of nitrogen oxides (NO_x) to gaseous nitric acid, which is followed by the reaction with gaseous ammonia to form highly volatile NH_4NO_3 . The distribution of NH_4NO_3 between the gas phase and particle phases depends mainly upon meteorological conditions (temperature and relative humidity) [Stelson and Seinfeld, 1982], on the aerosol composition, and on the acidity of the particles. As indicated above, the chemical reaction between sulphuric acid and ammonia is the preferred chemical reaction in the atmosphere [see also Baek et al., 2004]. As there was insufficient NH_4^+ in the fine fraction to fully neutralize the fine

sulphate, the formation of particulate NH_4NO_3 was inhibited and most of the NO_3^- may have been in the gas phase (as HNO_3). However, gaseous nitric acid may react with alkaline particles, which are mainly present in the coarse size fraction, such as sea salt and soil particles [Pakkanen, 1996] and thereby be converted into coarse nitrate. It is therefore not surprising that more than half of the PM10 nitrate was present in the coarse size fraction (see Figure 4.4), whereas PM10 ammonium and sulphate were predominantly associated with the fine aerosol.

Table 4.3. Medians (and ranges) of molar ratios of NH_4^+ to SO_4^{2-} and NO_3^- in the fine and coarse size fractions.

Species	Fine size fraction		Coarse size fraction	
	Median	Range	Median	Range
2005 wet				
$\text{NH}_4^+/\text{SO}_4^{2-}$	1.48	0.91 – 2.06	0.61	0.27 – 2.04
$\text{NH}_4^+/(2\text{SO}_4^{2-})$	0.74	0.46 – 1.03	0.30	0.14 – 1.32
$\text{NH}_4^+/(2\text{SO}_4^{2-} + \text{NO}_3^-)$	0.60	0.36 – 0.91	0.07	0.04 – 0.14
2005 dry				
$\text{NH}_4^+/\text{SO}_4^{2-}$	0.92	0.45 – 1.97	0.09	0.0 – 1.71
$\text{NH}_4^+/(2\text{SO}_4^{2-})$	0.46	0.22 – 0.99	0.04	0.0 – 0.17
$\text{NH}_4^+/(2\text{SO}_4^{2-} + \text{NO}_3^-)$	0.34	0.12 – 0.93	0.01	0.0 – 0.21
2006 wet				
$\text{NH}_4^+/\text{SO}_4^{2-}$	1.84	1.37 – 2.58	0.79	0.31 – 4.32
$\text{NH}_4^+/(2\text{SO}_4^{2-})$	0.91	0.68 – 1.29	0.40	0.16 – 2.16
$\text{NH}_4^+/(2\text{SO}_4^{2-} + \text{NO}_3^-)$	0.84	0.61 – 1.08	0.14	0.04 – 0.88

4.7 Comparison of PIXE and IC data for S, Cl, K, and Ca

The elements S, Cl, K and Ca were measured by both IC and PIXE. A comparison of the data from the two techniques allows us to examine which fraction of the element was water-soluble (for S which fraction was present as water-soluble SO_4^{2-}) and at the same time to evaluate to some extent the reliability of the analytical data obtained by the two methods. The comparison between the IC and PIXE data was done in terms of ratios

IC/PIXE; furthermore, for each campaign and size fraction the regression line of the IC data (in ng/m^3) on the PIXE data (also in ng/m^3) was calculated. The IC SO_4^{2-} data were converted into $\text{SO}_4^{2-}\text{-S}$ data for these calculations. The mean ratios and associated standard deviations for the fine and coarse size fractions of each campaign and the regression equations and their r^2 -values are given in Table 4.4. The data for Cl in the fine size fraction are left out from this Table as the PIXE analysis of fine Cl suffered from large blank corrections (from Cl in the Nuclepore filters), so that the fine Cl PIXE data were not very reliable. For the three remaining elements in the fine size fraction, the mean IC/PIXE ratios are all larger than 0.75 (with the exception of Ca in the 2005 wet season campaign). Furthermore, the slopes of the regression equations lie between 0.76 and 1.09 and all r^2 -values are larger than 0.76. This all indicates that the fine S, K and Ca were highly water-soluble, that the S was mainly present as water-soluble $\text{SO}_4^{2-}\text{-S}$, and that both the IC and PIXE data seem to be reliable, with the exception of Ca in the 2005 wet season campaign. From looking at the scatter plot of fine IC Ca versus fine PIXE Ca for this campaign, it appeared that although there was a fairly nice correlation, several IC Ca data were negative (actually 5 out of the 13 data points). The blank correction for Ca in IC was quite substantial and it seems that it was incorrectly too high for fine Ca in this campaign. As to fine K, its crustal EF was well above 1 (see Figure 4.5), indicating that the fine K originated predominantly from non-crustal sources, most likely biomass burning. K is present in the biomass burning aerosol as water-soluble salts (mainly KCl), so that it is not surprising that the fine K in our samples is also highly water-soluble.

As to the coarse size fraction, Ca is equally water-soluble as for the fine size fraction. Also coarse Cl is mainly water-soluble, as would be expected if it is predominantly derived from sea salt. S and in particular K are, however, less water-soluble in the coarse size fraction than in the fine. Coarse K has a crustal EF of somewhat less than 1 (see Figure 4.5), suggesting that it is entirely derived from mineral dust; K in soils is associated with various minerals and many of these are not soluble in water. As to S in the coarse size fraction, although sulphate is a main contributor to it, coarse S may also originate from primary biogenic particles, which are insoluble in water. In one study during the wet (non biomass burning) season in the Amazon basin in Brazil, it was found

that most of the S during night was not soluble in water and this was attributed to the association with primary biogenic particles [Graham et al., 2003].

Table 4.4. Mean IC/PIXE ratios (and standard deviation), regression equations of IC on PIXE data (both in ng/m^3) and r^2 for S, Cl, K, and Ca in the fine and coarse size fractions.

Element	Fine size fraction			Coarse size fraction		
	Mean ratio	Regression equation	r^2	Mean ratio	Regression equation	r^2
2005 wet						
S	0.75 ± 0.06	$y = 0.83x - 53.40$	0.96	0.61 ± 0.09	$y = 0.43x + 47.96$	0.33
Cl				0.95 ± 0.09	$y = 0.98x - 11.48$	0.93
K	0.85 ± 0.05	$y = 1.09x - 56.01$	0.97	0.33 ± 0.10	$y = 0.12x + 46.65$	0.68
Ca	0.10 ± 0.77	$y = 1.01x - 47.68$	0.78	1.09 ± 0.13	$y = 1.00x + 44.31$	0.99
2005 dry						
S	0.94 ± 0.23	$y = 0.94x - 12.07$	0.89	0.85 ± 0.13	$y = 0.87x - 10.57$	0.89
Cl				1.10 ± 0.21	$y = 1.05x + 39.86$	0.82
K	1.03 ± 0.22	$y = 1.01x + 13.21$	0.91	0.42 ± 0.10	$y = 0.27x + 49.01$	0.45
Ca	0.82 ± 0.16	$y = 0.76x + 7.61$	0.76	1.06 ± 0.15	$y = 0.93x + 110.36$	0.88
2006 wet						
S	0.84 ± 0.17	$y = 0.76x + 34.02$	0.92	0.51 ± 0.18	$y = 0.99x - 67.04$	0.96
Cl				0.63 ± 0.77	$y = 0.99x + 37.73$	0.94
K	0.81 ± 0.16	$y = 0.79x + 0.27$	0.87	0.52 ± 0.14	$y = 0.10x + 43.83$	0.07
Ca	1.10 ± 0.31	$y = 0.77x + 7.55$	0.82	1.22 ± 0.22	$y = 1.06x + 27.73$	0.96

4.8 Influence of meteorology on the concentration of the PM mass and other aerosol components

4.8.1 Impact of meteorology on the PM mass

Many studies have indicated that the PM₁₀ mass concentrations in the ambient air are affected by various meteorological factors such as temperature, wind speed, rainfall, and relative humidity [Rajkumar and Chang, 2000]. The daily average meteorological parameters (wind speed, cumulative precipitation, temperature, and relative humidity)

were obtained from the Tanzania Meteorological Agency (SUA-station) and are summarized in Table 2.3 of Chapter 2.

The daily average wind speed ranged from 0.0 to 3.6 m/s. The winds were predominantly blowing from the south-east for most of the sampling periods. The daily average temperature ranged from 14 °C to 31 °C. The daily mean relative humidity ranged from 50% to 90%, with the lower value typically recorded in the dry season. The cumulative precipitation varied from nearly zero during the 2005 wet and 2005 dry season campaigns to 248 mm during the 2006 wet season campaign. The correlations of the PM10 mass concentrations with different meteorological parameters were examined.

4.8.1.1 Relationship with precipitation

The PM10 mass concentration was systematically low during precipitation events (Figure 4.6). It never exceeded 20 $\mu\text{g}/\text{m}^3$ when the daily precipitation was higher than 5 mm.

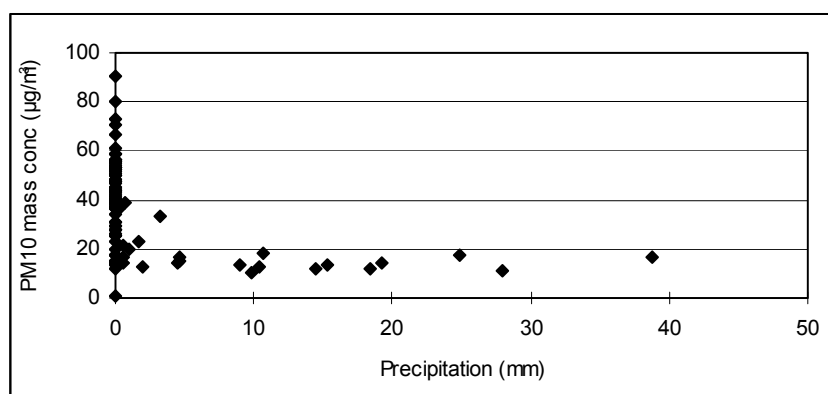


Figure 4.6. Relationship between PM10 mass and total daily cumulative precipitation.

4.8.1.2 Relationship with temperature

The variation of PM10 mass concentration with temperature is shown in Figure 4.7. The concentrations were higher at low temperatures (below about 24 °C) and high temperature (above about 27 °C), and reached a minimum for temperatures between 24 and 27 °C. One could make a number of assumptions to explain this observation. The rise

in concentration at low temperatures could be due to more frequent inversion events. The altitude of the site (526 m above sea level), as well as the morphology of the foothill of the Uluguru Mountain ranges, make that the site is rather sensitive to the phenomenon of temperature inversion. The higher PM₁₀ mass concentrations at higher temperatures might be caused by more intense formation of secondary aerosols.

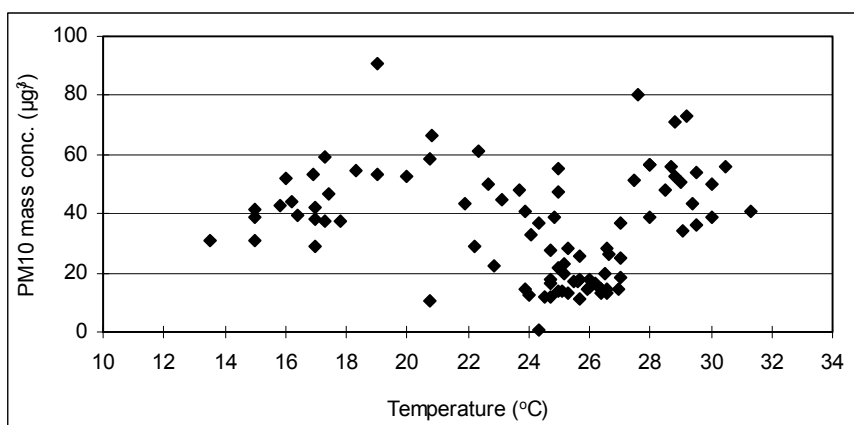


Figure 4.7. Relationship between PM₁₀ mass and daily mean temperature.

4.8.1.3 Relationship with wind speed

The influence of the wind speed (Figure 4.8) is less clear than that of the meteorological parameters discussed above. Low wind speeds inhibit dilution whereas large wind speeds lead to increased soil dust mobilisation. It seems that the effects of decreased dilution and increased soil dust mobilisation were roughly of equal importance.

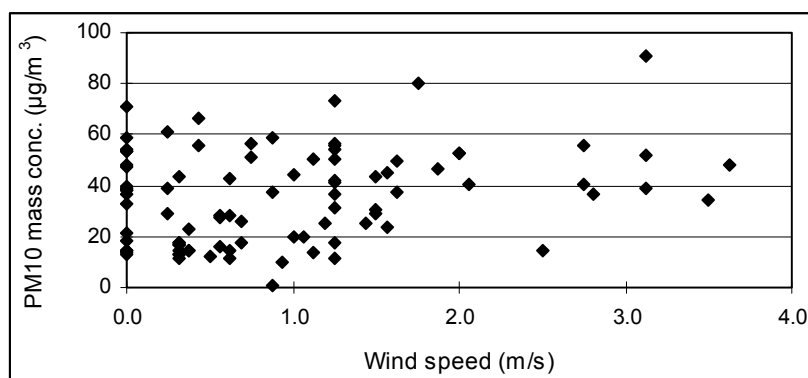
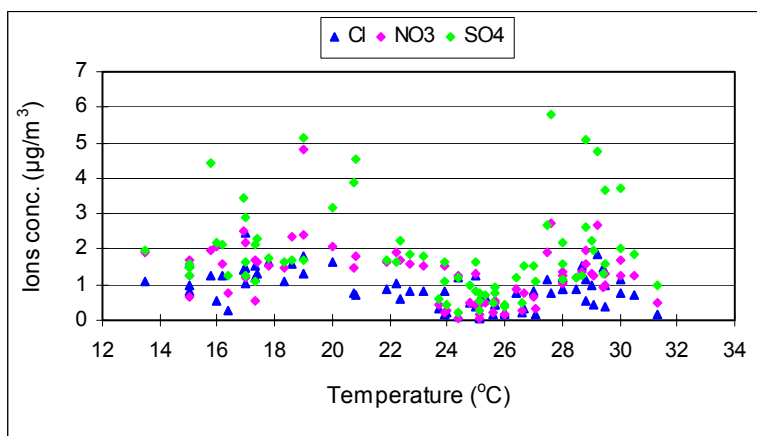


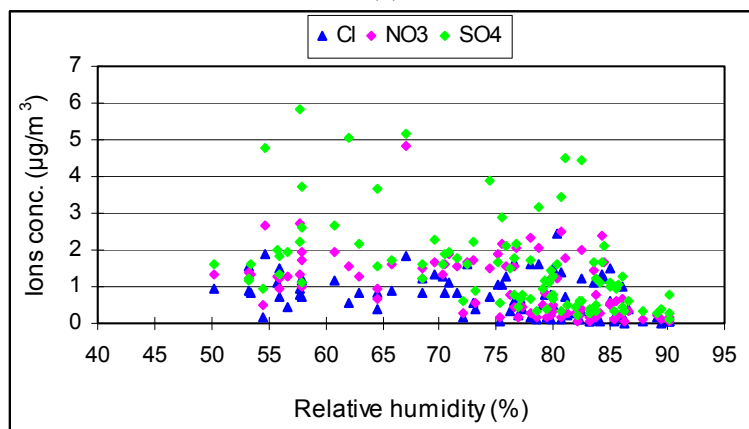
Figure 4.8. Relationship between PM₁₀ mass and daily mean wind speed.

4.8.2 Impact of temperature and relative humidity on anion concentrations

The relationship between the atmospheric concentrations in PM10 of the anions and temperature and relative humidity was examined. To do this, the data were selected excluding rainy periods and classified according to ambient temperature and relative humidity levels. The sensitivity of particulate SO_4^{2-} , NO_3^- , and Cl^- concentrations to changes of temperature and relative humidity is shown in Figure 4.9. There was virtually no dependence on relative humidity, while a temperature dependence could be found. The change in particulate SO_4^{2-} , NO_3^- , and Cl^- concentrations with temperature resembles the change for the PM10 mass: lower levels at temperatures between 23 and 27 °C.



(a)



(b)

Figure 4.9. Relationship between the atmospheric concentration of the anions and (a) temperature and (b) relative humidity.

4.8.3 Impact of meteorology on the carbonaceous species

It was already indicated (i.e., in Figure 4.1) that the front filter OC/PM and WSOC/OC ratios are different in the dry and wet season campaigns. This suggests that there is some impact of the meteorological parameters on the carbonaceous components. Here, the relationships of the front filter OC/PM, WSOC/OC, and EC/TC ratios in PM₁₀ with precipitation and temperature are considered.

4.8.3.1 Relationship with precipitation

The relationship between the concentration ratios of front filter OC/PM, WSOC/OC, and EC/TC in PM₁₀ with precipitation in Morogoro is presented in Figure 4.10. For the OC/PM and EC/TC ratios, no effect of precipitation is visible. In contrast, for WSOC the highest ratios were obtained when there was no precipitation. The lower WSOC/OC ratios during days with precipitation may reflect the preferential removal of WSOC from the organic aerosol by rain.

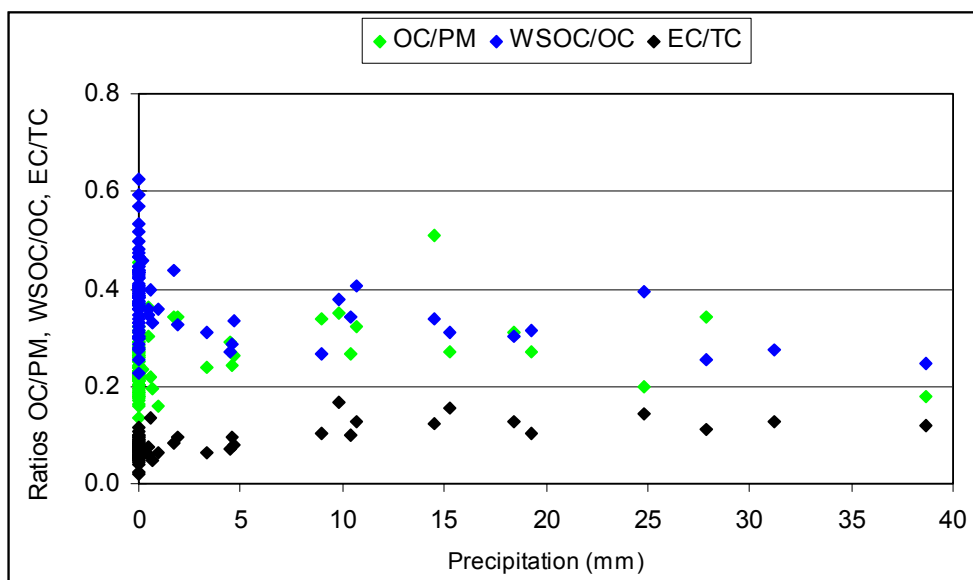


Figure 4.10. Relationship of carbonaceous species and precipitation.

4.8.3.2 Relationship with temperature

Figure 4.11 shows the variation for the front filter OC/PM, WSOC/OC, and EC/TC ratio in PM₁₀ with temperature for Morogoro. It is hard to detect trends in the data. For the WSOC/OC ratio there seem to be lower values in the temperature range of 23-27 °C than at lower and higher temperatures. This may be due to a larger contribution of SOA, which is more water-soluble than primary OC, at low and high temperatures. At low temperatures, semi-volatile organics may partition into the particulate phase (and contribute to SOA), whereas at high temperatures enhanced photochemical oxidation may give rise to SOA.

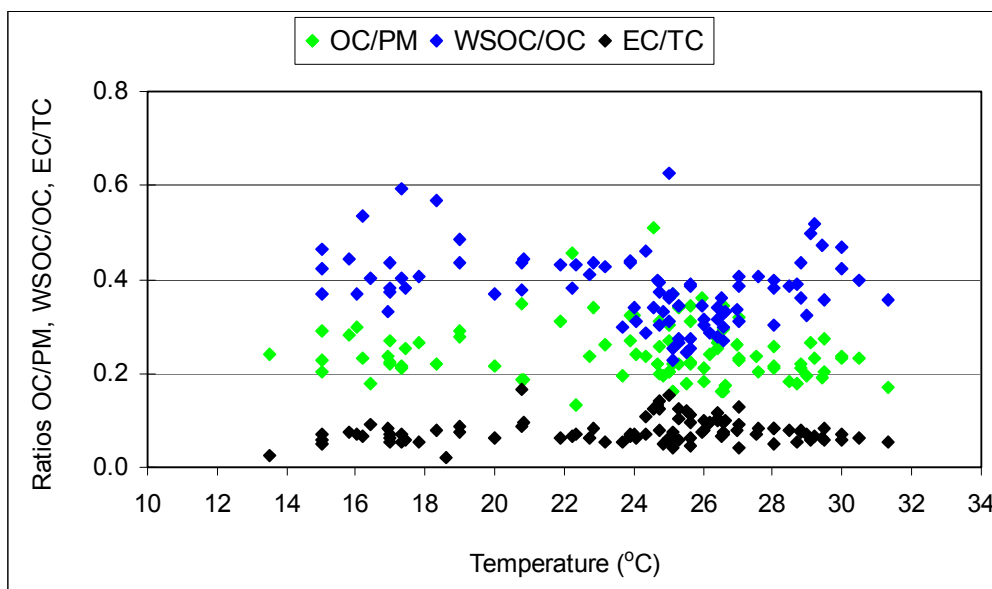


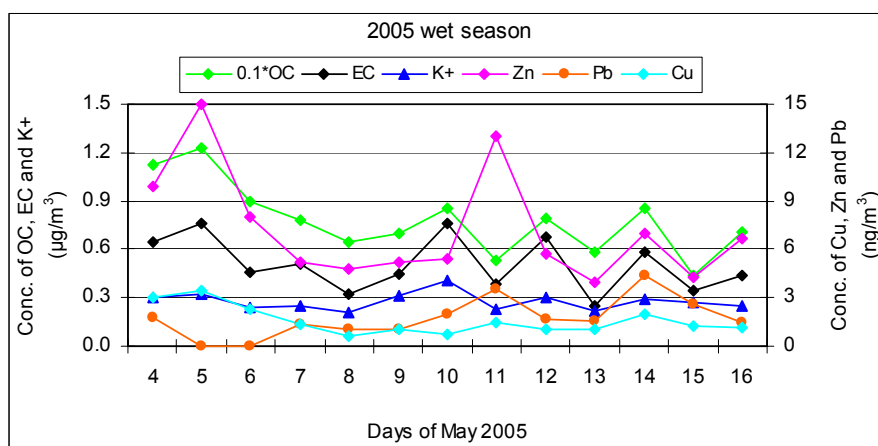
Figure 4.11. Relationship between the carbonaceous species and temperature.

4.9 Relationship between OC, EC, K⁺ and selected anthropogenic elements

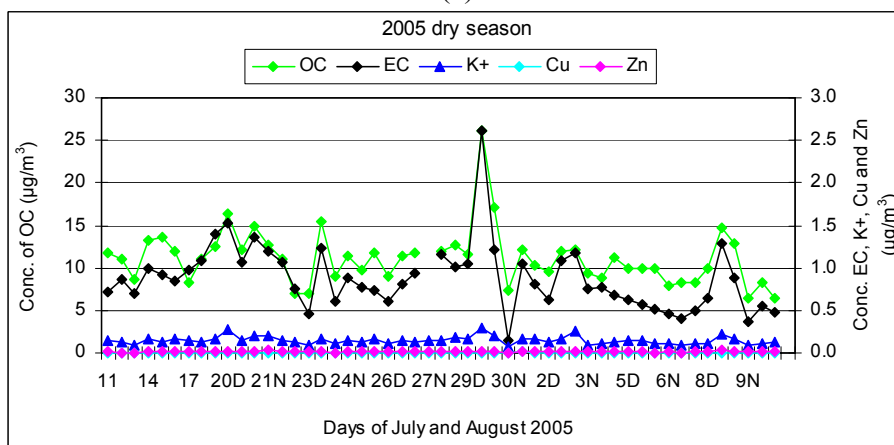
The relationship between OC and EC and selected anthropogenic elements in PM₁₀ was examined in order to identify potential sources of OC and EC in Morogoro. The time series of the elements, K⁺, Cu, Zn, and Pb and of OC and EC during three sampling campaigns is shown in Figure 4.12. As indicated before, EC is essentially

emitted directly from the combustion of fossil fuels and/or biomass [Song et al., 2001]. Water-soluble potassium is known as a tracer of biomass combustion, whereas Cu, Zn and Pb are usually related to vehicular traffic, waste incineration, and industrial sources [Gao et al., 2002]. There was a fair correlation between OC and Cu ($r^2 = 0.60$) in the 2005 wet season campaign, while there was no correlation ($r^2 < 0.08$) in the 2005 dry and 2006 wet season campaigns. The square of the correlation coefficient (r^2) between OC and K^+ was 0.26, 0.34, and 0.48 for the 2005 wet, the 2005 dry, and the 2006 wet season campaigns, respectively. EC was well correlated with K^+ during the 2005 wet and the dry season campaigns ($r^2 = 0.66$ and 0.75 , respectively), but poorly ($r^2 = 0.38$) during the 2006 wet season campaign.

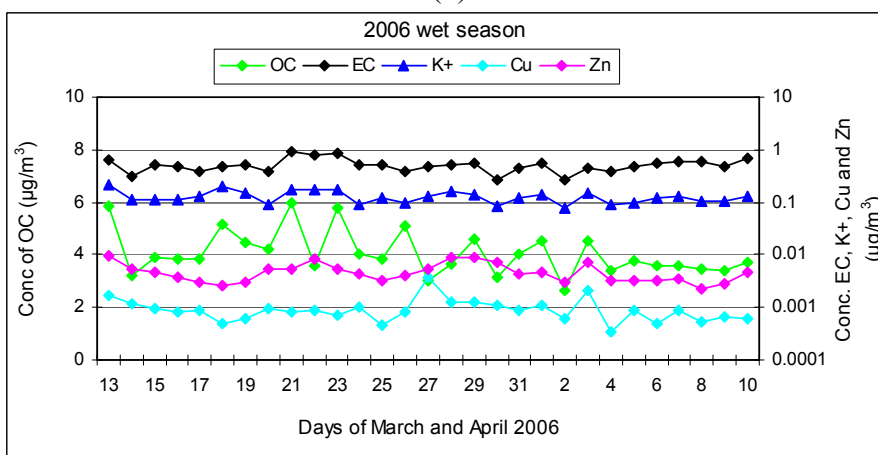
It is impossible to draw real conclusions from these various correlations. However, it is thought that in the rural area of Morogoro OC and EC come mostly from burning of wood for domestic cooking during the wet season, while in the dry season the two carbonaceous components are derived from the burning of agricultural wastes and from wood and charcoal burning for cooking. It should be noted that traffic was not important at the Morogoro site. A further analysis on the sources of the OC will be given in Chapter 6.



(a)



(b)



(c)

Figure 4.12. Time series of OC, EC, K⁺, Cu, Zn, and Pb during the three campaigns.

4.10 Conclusions

Three aerosol sampling campaigns were conducted at a rural site at the main campus of the university in Morogoro, Tanzania, between May 2005 and April 2006. These were the first aerosol measurements performed in Morogoro. The atmospheric concentrations of the PM mass, carbonaceous species, water-soluble inorganic ions, and elements were determined. The median levels of the PM₁₀ mass for the 2005 wet season, 2005 dry season, and 2006 wet season campaigns were 23, 45, and 13 $\mu\text{g}/\text{m}^3$ and the average contributions of fine fraction to the PM₁₀ mass during the three campaigns were 35, 49, and 37%, respectively. Large concentration differences were observed between the wet and the dry seasons for most aerosol constituents, with highest levels during the dry season.

The OC concentration in PM₁₀ ranged from 4.0 to 11 and from 2.7 to 6.0 $\mu\text{g}/\text{m}^3$ during the wet season campaigns and from 6.4 to 26 $\mu\text{g}/\text{m}^3$ during the dry season campaign. Lower median EC concentrations were observed in the two wet season campaigns (0.46 and 0.51 $\mu\text{g}/\text{m}^3$) than in the dry season campaign (0.82 $\mu\text{g}/\text{m}^3$). Similarly to OC and EC, the WSOC levels showed a seasonal difference with maximum in the 2005 dry and minimum in the 2006 wet season; WSOC ranged from 0.86 to 19 $\mu\text{g}/\text{m}^3$. Also the sulphate and ammonium concentrations were higher during the dry season campaign than in the wet season campaigns; these two species were highly correlated with each other in the fine particles ($r^2 = 0.82$), consistent with their occurrence as NH_4HSO_4 , and $(\text{NH}_4)_2\text{SO}_4$ in the fine aerosol.

CHAPTER 5

CHEMICAL COMPOSITION OF ATMOSPHERIC AEROSOLS AT A KERBSIDE IN DAR ES SALAAM, TANZANIA: SEASONAL VARIATIONS AND SOURCES

5.1 Introduction

The objective of this chapter is to describe the chemical characteristics of the atmospheric aerosols, their seasonal evolutions, and sources in Dar es Salaam. The first sections of this chapter give details of the levels of PM, inorganic water-soluble ions, elements, and carbonaceous materials. Their seasonal evolutions, fine to PM10 ratios, and the correlations between various aerosol components are also described. Furthermore, other sections explain the sources of certain main elements and aerosol components and finally the dependence of the PM mass and other aerosol components on meteorology is discussed.

5.2 PM10 mass

The median concentrations (and concentration ranges) for the PM mass, BC, carbonaceous components, water-soluble inorganic ions, and major, minor, and trace elements (all for PM10) in the three campaigns are given in Table 5.1. The highest levels for most of the measured components were observed during the 2005 dry season campaign and the lowest ones during the 2006 wet season campaign. Furthermore, and as expected, the levels were higher at the Dar es Salaam kerbside than at the rural Morogoro site (see Chapter 4, Table 4.1). For example, for the PM10 mass the median levels in the three campaigns (2005 wet, 2005 dry, and 2006 wet season) were 46, 58, and 40 $\mu\text{g}/\text{m}^3$ at Dar es Salaam versus 23, 45, and 13 $\mu\text{g}/\text{m}^3$ at Morogoro.

In an earlier study conducted in May 2001 in Dar es Salaam, Jonsson et al. [2004] obtained an average PM10 mass concentration of 40 $\mu\text{g}/\text{m}^3$. As described earlier, there is no ambient PM10 standard in Tanzania; however, the results from this study can be compared to the EU limit values. The average PM10 mass concentration in each of the three campaigns in Dar es Salaam is similar or higher than the daily EU PM10 limit value of 50 $\mu\text{g}/\text{m}^3$ in ambient air [EU Directive, 1999]. Actually, at this kerbside site, the daily PM10 concentration exceeded the daily EU standard 7 times during the 2005 wet season campaign, 38 times during 2005 dry season campaign, and 19 times during the 2006 wet season campaign. When compared with PM10 data for kerbside sites in Europe, as

reported in the European aerosol phenomenology study [Van Dingenen et al., 2004], the results for PM₁₀ mass in Dar es Salaam are slightly higher than at the Europe sites.

5.3 Major, minor, and trace elements

As is commonly observed in elemental analyses of PM samples, the concentrations of the heavy metals are lower than those for the elements of crustal origin (Al, Si, Ca). Nevertheless, some typical anthropogenic metals, such as Zn and Pb, exhibited 20 - 70 times higher median PM₁₀ levels at Dar es Salaam than at Morogoro, suggesting strong local sources for these elements in Dar es Salaam. The levels of Zn and Pb were also quite variable at this site (note the ranges in Table 5.1), which suggests that the impact from the local sources varied with change in wind direction. The Dar es Salaam site also showed very strong day / night differences for the crustal elements (Al, Si, Ca, Ti and Fe). This was particularly obvious in the 2005 dry season campaign. For example, during this campaign, the average ratio of the PM₁₀ level during the day to that during the subsequent night (D/N concentration ratio) was 3.3 ± 1.0 (N = 31) for Al, Si, and Fe. In contrast, the D/N ratio for the sea-salt elements, Na and Cl was 0.7 ± 0.4 and 1.1 ± 0.4 , respectively; for Zn it was 0.52 ± 0.55 and for Pb 0.78 ± 0.70 . This indicates that the day/night differences for the crustal elements are not due to differences in boundary layer height between day and night, as the latter should also have affected the D/N ratio for the sea-salt elements and heavy metals. Actually, at sites where there are changes in boundary layer height between night and day, one normally observes a shallow boundary layer (and thus higher concentrations) during the night. The day/night difference for the crustal elements can be attributed to resuspended road dust by vehicular traffic, which is more intense during the day. It can be seen from Table 5.3 that in the coarse size fraction there was a good correlation between the crustal elements and, for example, BC, Cu, OC, and EC, for which traffic can be expected to be an important source.

Table 5.1. Median concentrations and concentration ranges in the PM₁₀ size fraction in Dar es Salaam. Data for the PM mass, BC, TC, OC, EC, and WSOC are in $\mu\text{g}/\text{m}^3$; for all other species in ng/m^3 . BC, ions, and elements were obtained from PM₁₀(NN); TC, OC, EC, and WSOC from PM₁₀(Q).

	2005 wet season [N = 16]		2005 dry season [N = 64]		2006 wet season [N = 55]	
	Median	(min. – max.)	Median	(min. – max.)	Median	(min – max)
Data in $\mu\text{g}/\text{m}^3$						
PM(NN)	46	(23 – 98)	58	(23 – 130)	40	(12 – 105)
PM(Q)	57	(33 – 95)	62	(23 – 150)	46	(15 – 118)
BC	9.3	(8 – 14)	11	(4.7 – 17)	9.7	(5.3 – 26)
TC	16	(11 – 24)	17	(8.3 – 36)	14	(6.2 – 52)
OC	11	(7 – 18)	14	(6.3 – 27)	9.5	(3.9 – 34)
EC	4.3	(3.3 – 8.3)	4.4	(1.6 – 8.8)	4.3	(2.1 – 18)
WSOC	3.4	(2.1 – 4.3)	4.1	(1.8 – 12)	3.2	(1.2 – 5.1)
Data in ng/m^3						
Ammonium	94	(18 – 700)	107	(4.9 – 1400)	48	(0 – 680)
Nitrate	750	(230 – 1050)	820	(330 – 2800)	340	(76 – 960)
Sulphate	2100	(900 – 3400)	2500	(1340 – 7300)	1440	(270 – 3400)
Na (IC)	1570	(420 – 2600)	3000	(1170 – 6900)	880	(110 – 3500)
Mg (IC)	220	(65 – 330)	420	(220 – 910)	130	(24 – 440)
Al	410	(52 – 1230)	620	(170 – 1920)	460	(14 – 1780)
Si	1500	(189 – 4100)	1990	(550 – 6300)	1640	(51 – 6100)
P	45	(25 – 91)	47	(DL – 160)	49	(14 – 87)
S	960	(470 – 1440)	1080	(580 – 2800)	700	(170 – 1430)
Cl	2100	(670 – 4000)	3900	(1200 – 9200)	1490	(130 – 5300)
Cl (IC)	2400	(650 – 4700)	5100	(1280 – 11300)	1500	(150 – 5800)
K	620	(450 – 820)	790	(340 – 1820)	510	(190 – 1610)
K (IC)	480	(360 – 660)	650	(290 – 1450)	320	(120 – 1450)
Ca	4000	(420 – 12600)	4600	(1140 – 16900)	4000	(150 – 15400)
Ca (IC)	3800	(560 – 7700)	6500	(1600 – 14900)	4300	(350 – 13000)
Ti	45	(4.2 – 160)	65	(16 – 200)	49	(1.3 – 180)
V	1.7	(DL – 7.1)	0.87	(DL – 10)	DL	(DL – 16)
Cr	0.81	(DL – 3.9)	1.7	(DL – 9.0)	DL	(DL – 4.9)
Mn	16	(4.6 – 45)	24	(4.7 – 79)	17	(0.85 – 63)
Fe	410	(88 – 1080)	500	(141 – 1700)	420	(36 – 1520)
Ni	1.6	(0.51 – 3.7)	1.5	(DL – 7.3)	1.2	(DL – 7.3)
Cu	5.5	(2.5 – 8.8)	7.5	(2.0 – 21)	6.3	(0.50 – 39)
Zn	370	(26 – 1150)	270	(22 – 3200)	86	(7.5 – 3500)
Ga	1.0	(DL – 2.7)	1.3	(DL – 4.7)	0.86	(DL – 3.3)
As	1.2	(DL – 4.3)	1.6	(DL – 31)	DL	(DL – 6.7)
Se	DL	(DL – 2.2)	1.6	(DL – 11)	DL	(DL – 2.3)
Br	11	(4.0 – 19)	12	(3.3 – 36)	5.0	(DL – 33)
Rb	DL	(DL – 3.0)	DL	(DL – 5.3)	DL	(DL – 1.7)
Sr	8.4	(1.6 – 22)	11	(1.9 – 35)	7.6	(DL – 34)
Ba	DL	(DL – 9.7)	DL	(DL – 30)	DL	(DL – 136)
Pb	58	(12 – 230)	110	(1.9 – 1090)	17	(DL – 340)

DL - detection limit; IC - ion chromatography.

5.4 Carbonaceous aerosols

Table 5.1 shows that there were differences for BC, TC, OC, EC, and WSOC between the three campaigns, with highest median in the 2005 dry season and lowest one in the 2006 wet season. BC from the smoke stain reflectometer is substantially larger than the EC data from the TOT method, as was also found in several other studies [e.g., Guyon et al., 2003]. The mean BC/EC ratios and the associated standard deviations in PM₁₀ were 2.18 ± 0.34 , 2.46 ± 0.40 , and 2.32 ± 0.55 for the 2005 wet, 2005 dry, and 2006 wet season campaigns, respectively. Nevertheless, there was a good correlation between both parameters over all samples ($r^2 = 0.86$). The levels of the carbonaceous species at the Dar es Salaam kerbside site are in line with the levels observed at kerbside sites in Europe, as reported in the European aerosol phenomenology study [Putaud et al., 2004]. Our data can also be compared with the few available other data sets for eastern and southern Africa. Gatari et al. [2001] reported average TC levels of $16 \pm 3 \mu\text{g}/\text{m}^3$ for the city of Nairobi (Kenya). These averages are surprisingly similar to the median TC data ($14 - 17 \mu\text{g}/\text{m}^3$) in Dar es Salaam.

The mean mass ratios of the carbonaceous components in the front filters of the PM₁₀(Q) samples are given in Table 5.2. Overall, there is little difference between the three campaigns for the various ratios. The EC/TC ratio is lower in the 2005 dry season campaign than in the two wet season campaigns. This may be due to an increased contribution from SOA in the dry season. The EC/TC ratios for Dar es Salaam are substantially larger than these for Morogoro (see Figure 4.1). This is in line with the much larger EC/TC ratios for traffic sites than for rural sites

Table 5.2 also gives the mean ratios of the carbonaceous components in the front filters of the PM_{2.5}(Q) samples. It appears that the average OC/PM and the WSOC/OC percentage ratios in the PM_{2.5} size fraction were similar for the 2005 dry and 2006 wet season campaigns. The percentage ratios for the two campaigns ranged from 13 to 67% for OC/PM and from 17 to 58% for WSOC/OC. The mean EC/TC and TC/PM percentage ratios in PM_{2.5} were higher during the 2006 wet season than in the 2005 dry season campaign. The EC/TC ratio ranged from 19 to 54% for the two campaigns, whereas the percentage of TC in PM_{2.5} varied from 20 to 96%.

Table 5.2. Mean percentage ratios (and associated standard deviations) for OC/PM, WSOC/OC, EC/TC, and TC/PM for the PM10 and PM2.5 front filter PM(Q) samples from Dar es Salaam.

Ratio	Size fraction	2005 wet	2005 dry	2006 wet
		Mean $\pm$ stdev	Mean $\pm$ stdev	Mean $\pm$ stdev
OC/PM	PM10	26 $\pm$ 6	23 $\pm$ 5	24 $\pm$ 6
	PM2.5	ND	34 $\pm$ 7	36 $\pm$ 12
WSOC/OC	PM10	26 $\pm$ 3	29 $\pm$ 9	28 $\pm$ 9
	PM2.5	ND	34 $\pm$ 10	35 $\pm$ 7
EC/TC	PM10	27 $\pm$ 5	22 $\pm$ 3	29 $\pm$ 6
	PM2.5	ND	29 $\pm$ 5	38 $\pm$ 7
TC/PM	PM10	37 $\pm$ 10	29 $\pm$ 7	35 $\pm$ 11
	PM2.5	ND	48 $\pm$ 8	59 $\pm$ 17

5.5 Water-soluble ionic components

Table 5.1 further shows that the median concentration for most cations and for the anions Cl^- , NO_3^- , and SO_4^{2-} are lowest in the 2006 wet season campaign and highest in the 2005 dry season campaign. A notable exception is Ca^{2+} with lowest median for the 2005 wet season campaign. The dominant aerosol components among the anions and cations are chloride and calcium, respectively. Both clean marine air masses and precipitation scavenging effects due to rain caused the low concentrations during the 2006 wet season campaign. In the 2005 dry season campaign, the air masses originated mainly from the southern African subcontinent (i.e., Mozambique, Malawi, Zimbabwe, and South Africa) and this, combined with the dry and cold weather, gave rise to high aerosol concentrations.

The charge equivalent ion balance, expressed by the ratio of the sum of cation equivalents to the sum of anion equivalents, was calculated for each individual sample. The median ratios (and ranges) were 2.63 (1.61-4.46), 2.50 (1.20-5.73) and 3.35 (1.15-8.65) for the 2005 wet, 2005 dry and the 2006 wet season campaigns, respectively. Figure 5.1 shows the relationship between the total cation equivalents against the total anion

equivalents in PM₁₀ data from the entire study period. The slope of the regression equation of the total cation data (in neq/m³) on the total anion data (neq/m³) is 2 and the r^2 -value is 0.52. This indicates that the total equivalent cation concentration was larger than that of the anions. The difference between cations and anions is attributed to the presence of carbonate, which was not analysed. This is discussed in more detail below (see section 5.10).

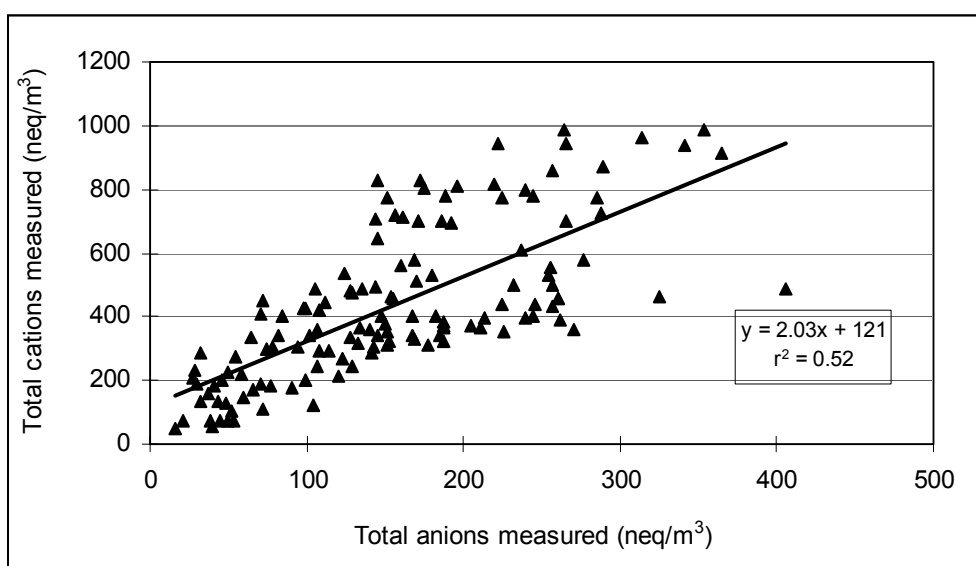


Figure 5.1. Relationship between total cations and anions in PM₁₀ (N = 135) for Dar es Salaam during the study period.

5.6 Time series of the PM mass and selected aerosol species

The time series of PM mass and selected aerosol species and elements in the PM₁₀, fine or coarse size fractions at Dar es Salaam as a function of sampling time is shown in Figure 5.2. For the PM₁₀ mass, PM₁₀ OC, coarse Si (an indicator for mineral dust), and fine NH₄⁺ there is a pronounced day/night difference, with for the PM₁₀ mass, OC and Si highest concentrations during the daytime and for NH₄⁺ highest concentrations during the night. For NO₃⁻ there is occasionally also a day/night variation, with higher levels at night, but it is much weaker than for NH₄⁺. In contrast, for coarse Na (an indicator for sea salt) and for fine sulphate no diurnal variation can be noted. The lower

levels for NH_4^+ and NO_3^- during daytime are a reflection of the transfer of ammonium nitrate and of the ammonium in other salts from the particulate phase to the vapour phase during the warm day. The high levels of Si, OC, and as a consequence also of the PM during the day indicate that there is an important extra source for these components during daytime, which disappears at night. Undoubtedly, this extra daytime source is traffic, which gives rise to airborne road dust (and thus Si) and to OC because of tailpipe emissions.

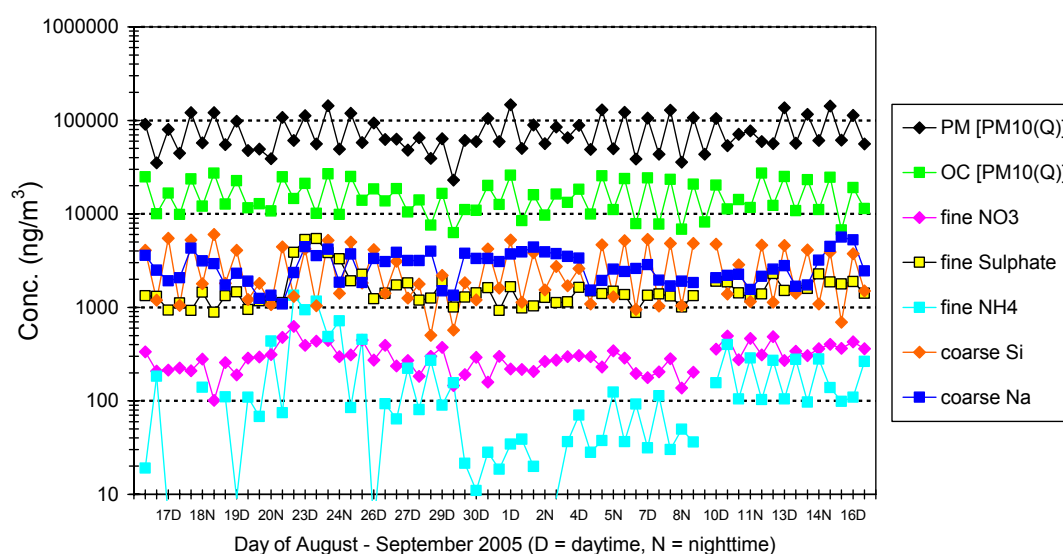


Figure 5.2. Time series of the PM mass and selected aerosol species and elements in the PM10, fine or coarse size fractions at Dar es Salaam during the 2005 dry season campaign.

5.7 Fine to PM10 ratios

The average percentages of the PM10 mass in the fine (PM2) size fraction during the three campaigns (2005 wet, 2005 dry, and 2006 wet season) were 31 ± 11 , 27 ± 8 , and 32 ± 13 % at Dar es Salaam, indicating that most of the PM10 mass was in the coarse size fraction, similarly to Morogoro. However, the PM2/PM10 ratios for the PM mass were smaller here than in Morogoro, especially in the 2006 dry season campaign.

Figure 5.3 shows the average percentage (and associated standard deviation) of the PM₁₀ aerosol in the fine (PM₂ or PM_{2.5}) size fraction for the PM mass, OC, EC, BC, ammonium, nitrate, nss-sulphate, and several elements in each of the three campaigns. As expected, the crustal and sea-salt elements were even more associated with the coarse size fraction (for the crustal elements typically about 90%) than was the case for the PM mass; also P and Cu were mainly in the coarse fraction. In contrast, OC, EC, BC, non-sea-salt (nss) SO₄²⁻ (and nss-S), K, V, and Pb were mostly associated with the fine size fraction, suggesting that these species and elements originated mainly from anthropogenic high-temperature sources and/or gas-to-particle conversion. Still other elements, such as Ni, had about equal percentages in the two size fractions.

As at Morogoro, K was mostly associated with the fine particles (in contrast to Ca). A similar phenomenon was noted at sites that were highly impacted by biomass burning, such as in SAFARI-92 [Maenhaut et al., 1996]. This suggests an impact from biomass burning also here.

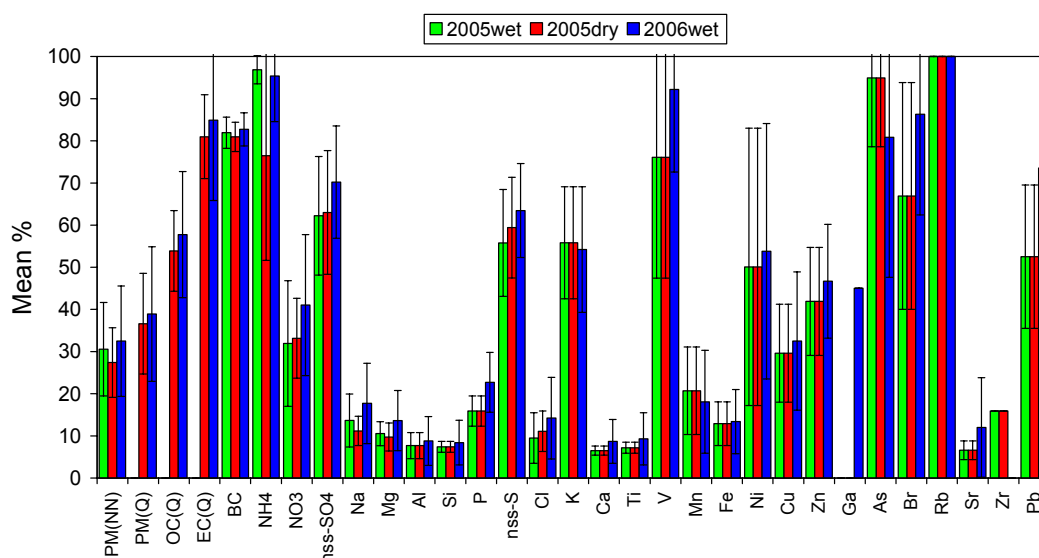


Figure 5.3. Mean percentage and associated standard deviation of the PM₁₀ aerosol in the fine (PM₂ or PM_{2.5}) size fraction for the PM mass, OC, EC, BC, ammonium, nitrate, nss-sulphate, and various elements at Dar es Salaam for the three campaigns.

5.8 Crustal enrichment factors and sources of the elements

5.8.1 Crustal enrichment factors

The crustal enrichment factors (EFs) of the various elements for Dar es Salaam were calculated in the same way as these for Morogoro, (Chapter 4, section 4.5), thus relative to the average crustal rock composition of Mason and Moore [1982] and with Fe as crustal reference element. For elements with an EF close to unity, soil dust (or other crustal matter, such as road dust) is the predominant source. If the EF is over 5, the element would have a significant contribution from non-crustal sources.

The average EFs for the various elements in each of the three campaigns are shown in Figures. 5.4 and 5.5 for the fine and coarse size fractions, respectively. Interestingly, the EFs for the Dar es Salaam kerbside aerosol resemble those for the Morogoro rural site (see Figure 4.5) for most of the elements. Most elements in the coarse size fraction at Dar es Salaam have EFs very close to one, thus suggesting that they are mainly attributable to soil dust dispersal and road dust re-suspension. In contrast to what was the case at Morogoro, Ca exhibits high EFs in both size fractions at Dar es Salaam. This is attributable to enrichment of the local soil (and road dust) at this site with limestone soil. The enrichments for Na and Cl are due to the fact that these elements have sea-salt as their major source. Several elements, including S, K, V, Ni, Cu, Zn, As, Br, Rb, and Pb have high to very high EFs in the fine size fraction, which suggests that they were mainly of anthropogenic origin. Interestingly, some of these enriched elements, i.e., V, Ni, As, and Pb, have significantly higher EFs at the Dar es Salaam kerbside than at the Morogoro rural site suggesting that their sources were within the city, such as traffic.

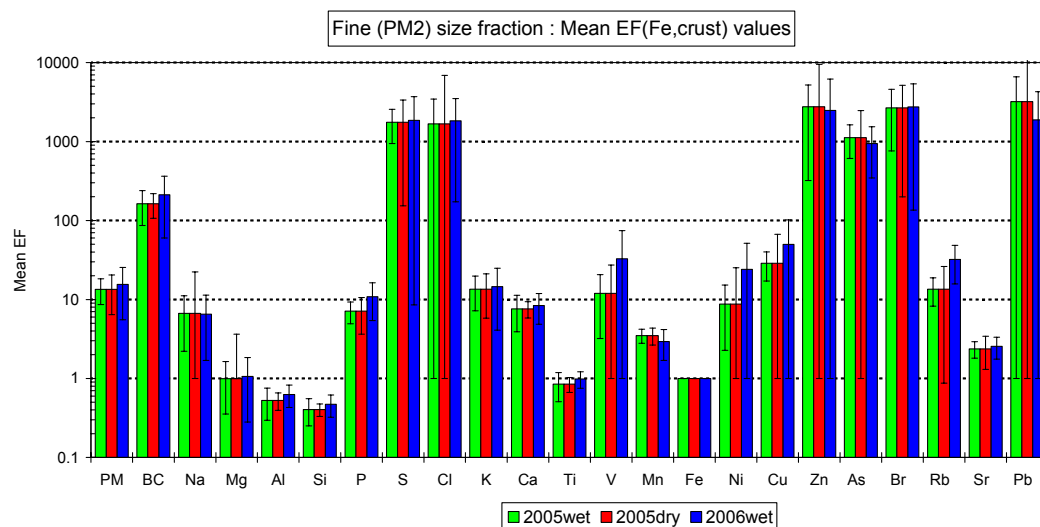


Figure 5.4. Mean crustal enrichment factors, calculated relative to the average crustal rock composition of Mason and Moore's [1982], for the **fine (PM2)** size fraction aerosols. The error bars denote 1 standard deviation. The data for BC are ratios to Fe instead of EFs.

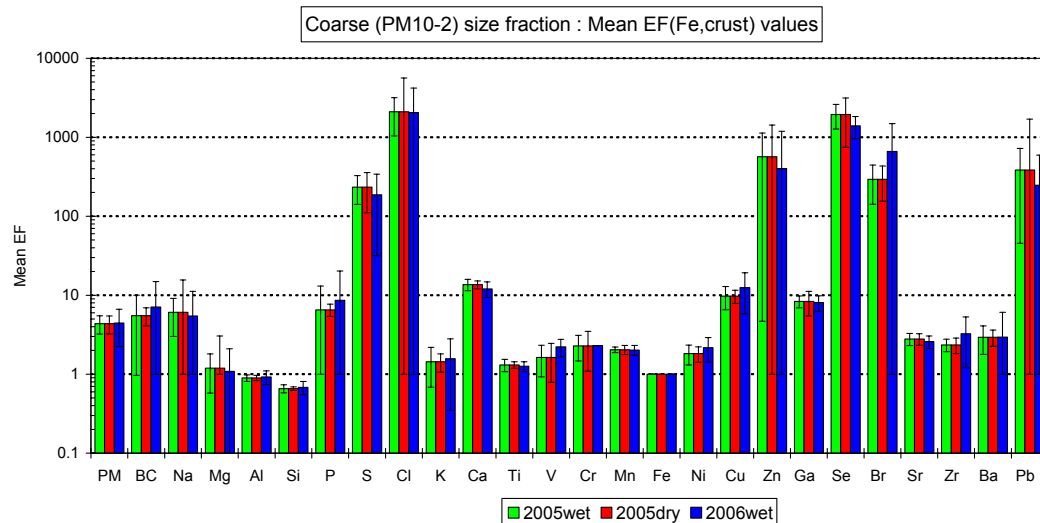


Figure 5.5. Mean crustal enrichment factors, calculated relative to the average crustal rock composition of Mason and Moore's [1982], for the **coarse (PM10-2)** size fraction aerosols. The error bars denote 1 standard deviation. The data for BC are ratios to Fe instead of EFs.

5.8.2 Sources of certain elements and aerosol components

From the concentrations of the crustal elements, the concentration of the crustal aerosol component was calculated for each campaign (see Section 6.2.7). The crustal component accounted for about one third of the PM₁₀ mass. A large fraction of the crustal component is undoubtedly due to resuspended road dust, particularly during the daytime, when the concentrations of the crustal elements and traffic intensity were much greater than during the night. During the 2005 dry season campaign, the concentration of the crustal component in PM₁₀ was, on average, 35 $\mu\text{g}/\text{m}^3$ during the daytime and only 10 $\mu\text{g}/\text{m}^3$ during the night; for comparison, the sea-salt concentration (calculated from Na and Cl, Section 6.2.6) was very similar during day and night (on average, around 9 - 10 $\mu\text{g}/\text{m}^3$). It is therefore reasonable to assume that the day/night concentration difference of 25 $\mu\text{g}/\text{m}^3$ for the crustal matter component is essentially due to road dust. The difference between the average daytime and nighttime PM₁₀ mass concentrations in the same 2005 dry season campaign was 49 $\mu\text{g}/\text{m}^3$, of which 25 $\mu\text{g}/\text{m}^3$ came thus from crustal matter. The remaining 24 $\mu\text{g}/\text{m}^3$ is likely also partly related to traffic and may to a large extent consist of carbonaceous matter.

To elucidate the sources of the various elements at Dar es Salaam, crustal enrichment factors (Figures 5.4 and 5.5) and pairwise correlation coefficients were calculated and various scatter plots were constructed. Potassium was substantially enriched in the fine size fraction, on average, around 10, which is similar as observed at African sites that were heavily impacted by biomass burning and where the pyrogenic aerosols accounted for a large fraction of the PM mass [Maenhaut et al., 1996]. This suggests that biomass burning (in this case for cooking) was also a main contributor to the PM mass at the Dar es Salaam site and in particular to the organic fraction of the PM. Fine V and fine Ni were highly correlated with each other at Dar es Salaam (r^2 ranged from 0.74 to 0.76 for the different campaigns) and their concentration ratio was around 2, which is consistent with residual oil burning as a source for these elements. BC and coarse Cu were highly correlated with the crustal elements, suggesting that they were related to traffic sources. For BC, automotive exhaust emissions, in particular from diesel trucks, are undoubtedly important. That also Cu comes from traffic is not unexpected, as

abrasion of brake linings wear is a well-known source for this element. Also coarse Zn and fine Pb are in cities often related to traffic, with tire wear and leaded gasoline as important sources, respectively [Ruellan and Cachier, 2001; Salma and Maenhaut, 2006]. However, neither Zn nor Pb was strongly correlated with the crustal elements (or with any other element) at Dar es Salaam; besides, the ratio of non-sea-salt Br to Pb was much lower than in particulate emissions from leaded gasoline. It is therefore thought that Zn and Pb originated from industrial emissions and possibly also re-suspended contaminated road dust, and that different industries were responsible for the two elements. For Pb this could be a battery industry and for Zn several metal processing industries, which are all located within 10 km from the sampling site.

5.9 Correlation between various aerosol components

The correlation matrix for the PM mass, BC, various elements, water-soluble ions and OC and EC in the fine and the coarse particle fractions of the 2005 dry season campaign is given in Table 5.3. This campaign was selected due to the higher sample size.

Most elements and species exhibit strong correlations in the coarse size fraction and somewhat weaker ones in the fine size fraction. This suggests that many elements and species originate predominantly from the same source, i.e., traffic and the associated resuspended road dust.

In the fine particles, a higher correlation was observed for SO_4^{2-} and NH_4^+ suggesting that these species are associated in ambient air. The carbonaceous species OC and EC showed a correlation with BC and most of the crustal elements, such as Al, Si, Ca, Ti, and Fe, indicating that they may be associated with traffic and resuspended road dust as explained above. Furthermore, a significant correlation is found between NH_4^+ and K^+ ; and for the typical sea salt elements (Na^+ , Mg^{2+} , Cl^-) in the fine size fractions.

As for the coarse particles, a strong correlation coefficient between Na^+ and Cl^- ($r = 0.97$) and Mg^{2+} and Cl^- ($r = 0.91$) was found as shown in Table 5.3, meaning that these three chemical species share the same source at the Dar es Salaam sampling site. The source of these species appears to be dust and sea salt aerosol that is transported from the

Indian Ocean about 1 km to the East side of the sampling site. Most of the crustal elements (Al, Si, Ca, Ti, Mn, Fe and Sr) have a good correlation with each other. Significant correlations exist between OC, EC and the pollution elements (Ni and Cu) with crustal sources elements. Also a good correlation was found for coarse K^+ and SO_4^{2-} ($r = 0.82$) and coarse Ca^{2+} and SO_4^{2-} ($r = 0.69$). The correlation between Ni and Cu in the coarse size fraction was $r = 0.90$; and both of them were also strong correlated with typical crustal elements, BC, OC, EC, K^+ , and the PM mass. This all could be related to the resuspension from road dusts caused by moving vehicles and exhaust gas.

Table 5.3. Correlation matrix for the PM mass, BC, selected elements, water-soluble ions, and OC and EC in the fine (PM_{2.5}, PM_{2.5} for OC and EC) size fraction (upper diagonal triangle) and in the coarse (PM_{10-2.5}; PM_{10-2.5} for OC and EC) size fraction (lower diagonal triangle) in Dar es Salaam during the 2005 dry season campaign. Correlation coefficients that are larger than 0.75 are indicated in bold.

	PM	BC	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Br	Sr	Pb	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	OC	EC	
PM																													
BC	0.92	0.71	0.57	0.61	0.43	0.63	-0.21	0.87	0.54	0.58	0.56	0.63	0.13	0.10	-0.04	0.26	0.53	-0.02	-0.11	-0.08	-0.26	0.86	0.48	0.59	0.47	0.42	0.80	0.51	
Al	0.97	0.92	0.73	0.76	0.50	0.12	-0.13	0.57	0.79	0.74	0.65	0.80	-0.04	0.26	-0.12	-0.03	0.56	-0.11	-0.34	-0.24	-0.36	0.52	0.75	0.03	-0.03	-0.16	0.81	0.92	
Si	0.97	0.92		0.99	0.59	0.06	-0.41	0.47	0.96	0.97	0.80	0.97	-0.08	0.08	-0.34	-0.16	0.78	-0.08	-0.45	-0.32	-0.60	0.43	0.94	0.03	-0.05	-0.15	0.82	0.70	
P	0.90	0.87	0.99		0.63	0.08	-0.35	0.50	0.97	0.98	0.81	0.98	-0.02	0.12	-0.30	-0.12	0.76	-0.08	-0.42	-0.29	-0.55	0.47	0.95	0.05	-0.04	-0.16	0.82	0.73	
S	0.85	0.74	0.77	0.77	0.71	0.17	0.04	0.39	0.67	0.58	0.49	0.66	0.17	0.26	-0.12	0.15	0.51	0.09	0.02	0.12	-0.19	0.37	0.64	0.13	-0.01	-0.17	0.48	0.47	
Cl	0.20	0.06	0.03	0.04	-0.02	0.49	-0.30	0.75	-0.02	0.06	0.03	0.09	0.44	-0.02	-0.12	0.34	0.13	-0.07	0.26	0.24	-0.14	0.71	-0.10	0.98	0.55	0.87	0.21	-0.08	
K	0.97	0.91	0.97	0.97	0.91	0.85	0.12	-0.40	-0.27	-0.30	-0.06	-0.27	-0.10	0.14	0.64	0.38	-0.30	0.18	0.61	0.55	0.91	-0.37	-0.26	-0.30	-0.21	-0.40	-0.29	-0.05	
Ca	0.97	0.92	0.99	0.99	0.91	0.76	0.08	0.95	0.42	0.46	0.32	0.49	0.15	0.10	-0.30	0.19	0.38	-0.21	-0.08	-0.03	-0.41	0.96	0.35	0.72	0.52	0.59	0.65	0.34	
Ti	0.97	0.91	0.99	0.99	0.94	0.77	0.01	0.98	0.97	0.95	0.79	0.97	-0.03	0.10	-0.27	-0.15	0.71	-0.08	-0.40	-0.26	-0.49	0.39	0.98	-0.06	-0.13	-0.27	0.75	0.76	
Mn	0.96	0.90	0.99	0.99	0.94	0.77	0.03	0.98	0.97	0.99	0.84	0.97	-0.03	0.15	-0.25	-0.06	0.75	-0.03	-0.42	-0.27	-0.52	0.43	0.93	0.04	-0.03	-0.19	0.82	0.73	
Fe	0.98	0.93	0.99	0.99	0.93	0.79	0.06	0.97	0.99	0.99	0.87	0.87	-0.03	0.17	0.12	0.08	0.70	0.08	-0.30	-0.24	-0.24	0.32	0.78	0.00	-0.04	-0.22	0.73	0.66	
Ni	0.93	0.88	0.89	0.89	0.87	0.83	0.43	0.88	0.91	0.88	0.88	0.90	-0.03	0.15	-0.20	-0.06	0.75	-0.02	-0.39	-0.27	-0.48	0.46	0.95	0.05	-0.05	-0.18	0.82	0.77	
Cu	0.94	0.91	0.94	0.94	0.90	0.78	0.11	0.94	0.92	0.94	0.94	0.94	0.90	-0.02	-0.11	0.40	-0.17	-0.25	0.55	0.58	0.08	0.06	-0.05	0.37	0.08	0.42	-0.18	-0.01	
Zn	-0.20	-0.07	-0.23	-0.23	-0.27	-0.10	0.16	-0.21	-0.20	-0.23	-0.21	-0.20	0.03	-0.15	0.06	0.17	0.14	0.04	-0.08	-0.05	0.10	0.10	0.07	-0.01	-0.09	-0.09	0.23	0.25	
Br	0.62	0.61	0.58	0.59	0.50	0.56	0.2	0.59	0.59	0.58	0.58	0.60	0.49	0.66	0.07	0.38	-0.09	0.40	0.12	-0.02	0.56	-0.23	-0.29	-0.14	-0.10	-0.23	-0.14	-0.02	
Sr	0.98	0.91	0.98	0.98	0.92	0.79	0.12	0.95	0.98	0.97	0.97	0.99	0.92	0.92	-0.24	0.61	-0.09	0.14	0.48	0.43	0.46	0.15	-0.19	0.31	0.31	0.18	0.03	-0.10	
Pb	-0.10	-0.04	-0.06	-0.06	-0.09	-0.1	-0.16	-0.09	-0.07	-0.06	-0.07	-0.10	-0.10	-0.08	0.18	-0.10	-0.09	0.04	-0.33	-0.25	-0.49	0.40	0.69	0.13	0.09	-0.01	0.72	0.58	
Na ⁺	0.30	0.10	0.12	0.13	0.08	0.57	0.92	0.21	0.16	0.11	0.12	0.15	0.38	0.18	0.03	0.27	0.22	-0.20	-0.06	-0.17	0.18	-0.21	-0.11	-0.09	0.00	-0.14	0.01	-0.02	
Mg ²⁺	0.40	0.21	0.23	0.24	0.20	0.68	0.88	0.33	0.26	0.22	0.24	0.25	0.47	0.28	-0.04	0.29	0.32	-0.20	0.95	0.97	0.76	-0.11	-0.40	0.26	0.14	0.14	-0.41	-0.38	
Cl ⁻	0.26	0.09	0.06	0.08	0.02	0.49	0.95	0.15	0.12	0.05	0.07	0.10	0.39	0.15	0.13	0.31	0.17	-0.20	0.97	0.91	0.67	-0.08	-0.26	0.23	0.10	0.10	-0.33	-0.29	
K ⁺	0.87	0.78	0.81	0.82	0.80	0.84	0.2	0.90	0.78	0.83	0.83	0.82	0.81	0.82	-0.13	0.62	0.81	0.06	0.33	0.42	0.26	-0.38	-0.48	-0.12	-0.03	-0.16	-0.46	-0.31	
Ca ²⁺	0.93	0.87	0.95	0.95	0.90	0.74	0.05	0.91	0.94	0.95	0.94	0.95	0.87	0.92	-0.26	0.62	0.95	-0.10	0.17	0.26	0.11	0.78	0.33	0.71	0.54	0.60	0.63	0.30	
SO ₄ ²⁻	0.79	0.64	0.69	0.70	0.63	0.95	0.48	0.78	0.68	0.70	0.7	0.71	0.71	0.7	-0.1	0.60	0.72	-0.10	0.63	0.72	0.54	0.82	0.69	-0.14	-0.17	-0.32	0.73	0.75	
NO ₃ ⁻	0.16	0.02	0.18	0.17	0.18	0.32	-0.1	0.25	0.10	0.21	0.19	0.16	-0.03	0.12	-0.23	-0.29	0.14	-0.10	0.13	0.2	-0.06	0.30	0.17	0.44	0.59	0.89	0.17	-0.17	
NH ₄ ⁺	-0.30	-0.30	-0.29	-0.30	-0.22	-0.04	0.25	-0.21	-0.32	-0.28	-0.28	-0.30	-0.18	-0.27	-0.17	-0.18	-0.29	-0.10	0.24	0.28	0.20	-0.11	-0.28	0.01	0.42	0.61	0.29	-0.15	
OC	0.94	0.90	0.95	0.95	0.90	0.76	0.04	0.93	0.93	0.94	0.94	0.95	0.87	0.93	-0.22	0.60	0.94	-0.10	0.15	0.25	0.10	0.82	0.93	0.71	0.17	-0.23	0.02	-0.32	
EC	0.83	0.87	0.81	0.82	0.76	0.68	0.00	0.82	0.81	0.81	0.81	0.83	0.73	0.84	-0.13	0.63	0.82	-0.01	0.08	0.18	0.08	0.74	0.79	0.62	-0.01	-0.34	0.88	0.78	

5.10 Concentration ratios of cationic and anionic species

Table 5.4 shows the median ratios and ranges for the water-soluble inorganic species in the fine and coarse size fractions of each of the three campaigns, similar to Table 4.2 in section 4.6 of Chapter 4. The median ion balances (the ratio of total cation equivalents to total anion equivalents) are all larger than 1.0; they range from 1.33 to 1.49 for the fine size fraction and from 2.85 to 4.18 for the coarse size fraction. As explained before, carbonates were not measured by IC and these missing carbonates are thought to be largely responsible for the observed deviation from 1.0. If we assume that all Ca^{2+} is present as CaCO_3 and recalculate the ion balance with Ca^{2+} excluded, then the new median ion balances range from 0.86 to 0.93 for the fine size fraction and from 0.88 to 0.97 for the coarse fraction. These new medians are all fairly close to 1.0. The assumption that Ca^{2+} may be present as CaCO_3 is quite reasonable, because the local soil in Dar es Salaam contains a lot of limestone; besides, there is limestone mining and cement industry; it should be noted, though that there is also gypsum mining.

It appears from Table 5.4 that SO_4^{2-} and Cl^- are the most prominent anions in the fine and coarse size fraction, respectively; and that Ca^{2+} is the main cationic species in both size fractions. As to the Cl^- , this is presumably mainly derived from sea salt, as the sampling site was only about 1 km from the Indian Ocean. The Cl^-/Na^+ equivalent ratios in Table 5.4 are consistent with a sea spray origin. The median Cl^-/Na^+ ratios for the three field campaigns are in the range of 1.05-1.06 for the coarse size fraction, and thus all quite close to the equivalent ratio of 1.18 for sea water [Brewer, 1975]. In the fine size fraction, the median Cl^-/Na^+ ratios range from 0.54 to 0.99; the fact that these are lower is explained by loss of Cl from the fine sea salt because of reactions with acidic species. It should be noted that although Na^+ at the Dar es Salaam site is likely mainly derived from sea salt, a minor fraction of it may be derived from mineral dust. The crustal EFs for both coarse and fine Na is about 6 (see Figure 5.4 and 5.5), suggesting that 15-20% of the Na originates from mineral dust. The fact that the coarse Cl^-/Na^+ median ratios are somewhat lower than the sea-water ratio is likely due to the contribution of mineral dust Na.

Table 5.4. Medians (and ranges) of ratios between various equivalent concentrations in the fine and coarse size fractions.

Species	Fine size fraction		Coarse size fraction	
	Median	Range	Median	Range
2005 wet				
cations/anions	1.39	(0.89 – 2.46)	3.21	(1.96 – 6.49)
NH ₄ ⁺ /cations	0.11	(0.03 – 0.59)	0.001	(0.00 – 0.006)
Na ⁺ /cations	0.16	(0.09 – 0.33)	0.21	(0.09 – 0.34)
Mg ²⁺ /cations	0.04	(0.02 – 0.08)	0.06	(0.03 – 0.12)
K ⁺ /cations	0.17	(0.10 – 0.40)	0.01	(0.01 – 0.06)
Ca ²⁺ /cations	0.30	(0.11 – 0.71)	0.72	(0.49 – 0.87)
NO ₃ ⁻ /anions	0.10	(0.04 – 0.15)	0.08	(0.04 – 0.16)
SO ₄ ²⁻ /anions	0.67	(0.51 – 0.91)	0.24	(0.15 – 0.36)
Cl ⁻ /anions	0.18	(0.05 – 0.42)	0.66	(0.59 – 0.76)
Cl ⁻ /Na ⁺	0.54	(0.27 – 1.56)	1.05	(0.87 – 1.15)
2005 dry				
cations/anions	1.33	(0.72 – 3.44)	2.85	(1.28 – 6.74)
NH ₄ ⁺ /cations	0.07	(0.00 – 0.59)	0.002	(0.00 – 0.014)
Na ⁺ /cations	0.23	(0.05 – 0.63)	0.26	(0.07 – 0.61)
Mg ²⁺ /cations	0.05	(0.02 – 0.14)	0.07	(0.03 – 0.16)
K ⁺ /cations	0.15	(0.06 – 0.26)	0.01	(0.01 – 0.04)
Ca ²⁺ /cations	0.36	(0.05 – 0.79)	0.66	(0.22 – 0.87)
NO ₃ ⁻ /anions	0.10	(0.05 – 0.18)	0.05	(0.01 – 0.23)
SO ₄ ²⁻ /anions	0.56	(0.30 – 0.88)	0.17	(0.11 – 0.42)
Cl ⁻ /anions	0.31	(0.02 – 0.61)	0.76	(0.37 – 0.86)
Cl ⁻ /Na ⁺	0.99	(0.23 – 2.96)	1.06	(0.74 – 1.25)
2006 wet				
cations/anions	1.49	(0.90 – 3.40)	4.18	(0.99 – 15.34)
NH ₄ ⁺ /cations	0.07	(0.00 – 0.80)	0.00	(0.00 – 0.09)
Na ⁺ /cations	0.17	(0.03 – 0.39)	0.15	(0.02 – 0.47)
Mg ²⁺ /cations	0.04	(0.01 – 0.09)	0.04	(0.02 – 0.13)
K ⁺ /cations	0.14	(0.04 – 0.46)	0.01	(0.01 – 0.08)
Ca ²⁺ /cations	0.50	(0.04 – 0.78)	0.78	(0.37 – 0.95)
NO ₃ ⁻ /anions	0.09	(0.02 – 0.19)	0.07	(0.03 – 0.12)
SO ₄ ²⁻ /anions	0.64	(0.42 – 0.92)	0.19	(0.12 – 0.51)
Cl ⁻ /anions	0.22	(0.02 – 0.43)	0.71	(0.29 – 0.83)
Cl ⁻ /Na ⁺	0.78	(0.25 – 2.91)	1.06	(0.55 – 2.78)

The medians and ranges of the molar ratios of ammonium to sulphate and nitrate are given in Table 5.5. As indicated above, in the fine size fraction, SO_4^{2-} is the most prominent anion and Ca^{2+} is the main cation. It can be observed from the table that fine NH_4^+ was insignificant in all campaigns and completely absent in the coarse size fraction. Therefore, Ca^{2+} being the main cationic species in fine fraction, is the main neutralizing cation for fine sulphate forming particulate CaSO_4 . Table 5.5 also indicates that a substantial fraction of the coarse Cl^- may have been present as CaCl_2 during the three campaigns. The chloride in the coarse size fraction at this site is to a large extent derived from sea salt. As discussed above, there was insufficient NH_4^+ in the fine fraction, so that the formation of particulate NH_4NO_3 was inhibited and most of the NO_3^- may have been in the gas phase (as HNO_3). However, gaseous nitric acid may have reacted with Ca particles and thereby be converted into $\text{Ca}(\text{NO}_3)_2$. This can also be observed in Figure 5.3 where more than half of the PM10 nitrate was present in the coarse size fraction.

Table 5.5. Medians (and ranges) of molar ratios of NH_4^+ to SO_4^{2-} and NO_3^- in the fine and coarse size fractions.

Species	Fine size fraction		Coarse size fraction	
	Median	Range	Median	Range
2005 wet				
$\text{NH}_4^+/\text{SO}_4^{2-}$	0.57	(0.23 – 1.44)	0.03	(0.00 – 0.24)
$\text{NH}_4^+/(2\text{SO}_4^{2-})$	0.28	(0.11 – 0.72)	0.01	(0.00 – 0.12)
$\text{NH}_4^+/(2\text{SO}_4^{2-} + \text{NO}_3^-)$	0.24	(0.09 – 0.67)	0.01	(0.00 – 0.05)
2005 dry				
$\text{NH}_4^+/\text{SO}_4^{2-}$	0.45	(0.00 – 2.33)	0.12	(0.01 – 2.01)
$\text{NH}_4^+/(2\text{SO}_4^{2-})$	0.22	(0.00 – 1.16)	0.06	(0.00 – 1.00)
$\text{NH}_4^+/(2\text{SO}_4^{2-} + \text{NO}_3^-)$	0.18	(0.00 – 0.94)	0.03	(0.00 – 0.32)
2006 wet				
$\text{NH}_4^+/\text{SO}_4^{2-}$	0.37	(0.00 – 1.86)	0.00	(0.00 – 1.22)
$\text{NH}_4^+/(2\text{SO}_4^{2-})$	0.18	(0.00 – 0.93)	0.00	(0.00 – 0.61)
$\text{NH}_4^+/(2\text{SO}_4^{2-} + \text{NO}_3^-)$	0.16	(0.00 – 0.91)	0.00	(0.00 – 0.48)

5.11 Comparison of PIXE and IC data for S, Cl, K and Ca

As described in section 4.7 (Chapter 4), the concentration of the elements S, Cl, K and Ca was measured by both IC and PIXE, so that the data from the two techniques can be compared to estimate which fraction of the elements is water-soluble and to assess the reliability of the two techniques. Table 5.6 presents the mean IC/PIXE ratios (and standard deviations) and the regression equations of IC on PIXE data (and associated r^2) for the fine and coarse size fractions in each of the three campaigns. In the fine size fraction, the mean IC/PIXE ratios are all larger than 0.73. In addition, the slopes of the regression equations lie between 0.71 and 1.54 (except for K in the 2006 wet season campaign) and all r^2 -values are larger than 0.71. These indicate that the fine S, Cl, K and Ca were considerably water-soluble, and that both IC and PIXE provided reliable data for the four elements. As to fine K, its crustal EF was on average around 10 (see Figure 5.4), indicating that the fine K at Dar es Salaam originated mainly from non-crustal sources, most likely biomass burning.

As to the coarse size fraction, the mean IC/PIXE ratios are all larger than 0.65 (except for K), the slopes of the regression equations lie between 0.57 and 1.17, and all r^2 -values are larger than 0.87. These indicate that the coarse S, Cl and Ca were substantially water-soluble. That coarse Cl is highly water-soluble is expected as it is predominantly derived from sea salt at the Dar es Salaam site. S and especially K are less water-soluble in the coarse size fraction than in the fine. As to coarse K, its crustal EF was on average around 1 (see Figure 5.5), suggesting that coarse K is mainly derived from mineral dust.

Table 5.6. Mean ratios (and standard deviation), regression equations and r^2 for the comparison of PIXE and IC data (both in ng/m^3) for S, Cl, K, and Ca in the fine and coarse size fractions.

Element	Fine size fraction			Coarse size fraction		
	Mean ratio	Regression equation	r^2	Mean ratio	Regression equation	r^2
2005 wet						
S	0.75 ± 0.06	$y = 0.85x - 111.72$	0.99	0.67 ± 0.10	$y = 0.83x - 185.25$	0.97
Cl	1.69 ± 0.75	$y = 1.54x - 4.97$	0.97	1.03 ± 0.13	$y = 1.11x - 102.46$	0.96
K	0.95 ± 0.04	$y = 0.93x + 4.39$	0.97	0.63 ± 0.13	$y = 0.41x + 52.75$	0.88
Ca	1.18 ± 0.28	$y = 1.20x - 15.52$	0.99	0.92 ± 0.19	$y = 0.57x + 1166.22$	0.94
2005 dry						
S	0.78 ± 0.08	$y = 0.85x - 95.85$	0.96	0.80 ± 0.09	$y = 0.94x - 224.92$	0.91
Cl	3.05 ± 4.18	$y = 0.95x - 201.65$	0.83	1.21 ± 0.15	$y = 1.17x + 142.85$	0.90
K	0.96 ± 0.13	$y = 0.88x + 27.15$	0.93	0.63 ± 0.20	$y = 0.49x + 48.38$	0.80
Ca	1.13 ± 0.14	$y = 1.26x - 49.25$	0.97	1.19 ± 0.22	$y = 0.77x + 1876.17$	0.88
2006 wet						
S	0.73 ± 0.17	$y = 0.71x + 12.76$	0.75	0.65 ± 0.13	$y = 0.83x - 118.29$	0.95
Cl	1.60 ± 2.66	$y = 0.82x + 94.07$	0.71	1.02 ± 0.18	$y = 1.10x - 59.50$	0.95
K	0.81 ± 0.18	$y = 0.62x + 49.35$	0.73	0.52 ± 0.21	$y = 0.48x + 2.63$	0.59
Ca	1.60 ± 1.57	$y = 1.34x - 54.12$	0.81	1.19 ± 0.56	$y = 0.64x + 1202.89$	0.87

5.12 Effect of meteorology on the PM mass and various aerosol components

The influence of meteorological parameters, including temperature, precipitation, wind speed, and relative humidity, on the PM mass and various aerosol components was evaluated. The 2005 dry season campaign was cool and dry with a mean daily maximum temperature of 27 °C and a total precipitation of 5 mm; during the 2006 wet season campaign the weather was hot and wet with a mean daily maximum temperature of 28 °C and a total precipitation of 306 mm; the 2005 wet season campaign was rather dry compared to the 2006 wet season campaign. The ambient temperature in Dar es Salaam during the three campaigns was minimum in August 2005 (about 20 °C) and reached a maximum in May 2005 (about 33 °C). The concentrations of the PM mass and OC were clearly influenced by the meteorology; higher levels were observed during the dry season

campaign than in the wet season campaigns. In the wet season, there is substantial removal of aerosol particles by wet deposition, whereas in the dry season soil dust dispersal is enhanced (because of dry soils) and there is an increased possibility for photochemical formation of aerosol particles from their gaseous precursors.

5.13 Conclusions

This chapter provides a substantial number of data on the concentration levels of many aerosol constituents in Dar es Salaam. For many constituents there were clear seasonal trends, with higher concentration during the dry season than the wet campaigns. Based on the temporal variation of the concentrations, EFs and correlations of the various constituents, their sources (mainly traffic but also biomass burning) could be identified.

CHAPTER 6

AEROSOL CHEMICAL MASS CLOSURE AND AEROSOL SOURCES AT TWO SITES IN TANZANIA

6.1 Introduction

Chemical mass closure for atmospheric aerosols involves a combination of the results for the various measured species and elements and is nowadays commonly done in a chemical characterisation of aerosols. Chemical mass closure aims to examine to which extent the gravimetric PM mass can be reconstructed on the basis of the masses of the measured chemical species (or components) for the desired size fraction.

There are numerous examples of aerosol chemical mass closure studies [e.g., Maenhaut et al., 2002; Matta et al., 2003; Putaud et al., 2004; Maenhaut and Claeys, 2007]. Even when the important aerosol components (carbonaceous compounds, inorganic ions, and elements) are measured, a complete mass closure is rarely obtained [Maenhaut et al., 2002; Harrison et al., 2003; Tsyro, 2005]. This is due to the fact that water is not measured and that this component may account for 10 to 20% of the gravimetric PM mass at the relative humidity of 50% at which the weighing is done.

Although aerosol chemical mass closure does not provide a real complete source apportionment, it gives information on the contributions of some major natural and anthropogenic components, such as sea salt and secondary inorganic aerosols (SIA), which are generally included in the mass closure calculations.

6.2 Aerosol chemical mass closure

In this study, aerosol chemical mass closure calculations were performed separately for the fine (PM₂), coarse (PM₁₀₋₂), and PM₁₀ size fractions for each campaign at each of the two sites (rural and kerbside). As gravimetric PM mass data, the data derived from the Nuclepore filter samples were always used. For reconstructing the gravimetric PM mass, eight aerosol types (or components) were considered, as described below:

6.2.1 Organic aerosol

Thermal methods, including TOT, provide OC data in terms of carbon mass, but the organic matter also contains other elements, such as H and O. Therefore, the OC data have to be converted to data for organic matter (OM) using an OC-to-OM conversion factor, which represents the ratio of the total weight of organic aerosols to the weight of carbon atoms in the organic molecules. Conversion factors, ranging from 1.2 to 1.8 are used to do so [Seinfeld and Pandis, 1998] and for urban aerosols, a factor of 1.4 has very commonly adopted [Turpin et al., 2000]. In recent years, a lot of research has been done on the conversion factor. It has become clear that there is no unique factor, which is generally applicable for all sites [e.g., Turpin and Lim, 2001; Bardouki et al., 2003; Russell, 2003]. Turpin and Lim [2001] suggested using an OC-to-OM conversion factor of 1.6 ± 0.2 for urban aerosols and of 2.1 ± 0.2 for nonurban aerosols. In this study, we adopted a conversion factor of 1.6 for the urban kerbside site at Dar es Salaam and of 1.8 for the rural site in Morogoro. The OC data used were corrected OC data, obtained by subtracting the back filter OC from the front filter OC for the tandem quartz fibre filter samples. It was thus assumed that the back filter OC was totally due to positive sampling artifacts (i.e., adsorption of VOCs), that the positive artifacts were the same for the front and back filters, and that there were essentially no negative artifacts.

6.2.2 Elemental Carbon

Although EC data are sometimes converted to data for elemental matter (EM) using a factor of 1.1 [e.g., Yttri et al., 2007], here the EC data obtained by TOT for the front quartz fibre filters were used as such in the mass closure calculation.

6.2.3 Ammonium

Ammonium was obtained by ion chromatography (IC) from the coarse and fine filters of the PM₁₀(NN) samples and the data were used as such.

6.2.4 Non-sea-salt (nss) sulphate

Non-sea-salt (nss) sulphate was derived from the sulphate data obtained by IC. A correction was made for the sulphate that is associated with sea salt. The latter sulphate was estimated by multiplying the IC Na^+ data by the sulphate/Na ratio of 0.252 in bulk sea water [Riley and Chester, 1971]. It was thus assumed that all the Na^+ originated from sea salt. The correction was largest for the coarse size fraction of the samples collected during the 2005 dry season campaign at Dar es Salaam, i.e., on average about 50%. For the fine size fraction, the correction was, on average, smaller than 10% for each campaign at each of the two sites.

6.2.5 Nitrate

Nitrate was obtained from the IC analysis of the coarse and fine filters of the PM₁₀(NN) samples. Similarly as for ammonium, the nitrate data were used as such.

6.2.6 Sea salt

Several approaches have been used in the literature for estimating the sea salt component. The simplest is to base it on the Na concentration in the aerosol. Since the mass percentage of Na in pure sea salt is equal to 30.61% [Miller et al., 1972], the concentration of the sea salt in the aerosol is then obtained as:

$$[\text{Sea salt}] = 3.267 \times [\text{Na}] \quad [6.1]$$

It is implicitly assumed here that all the Na in the aerosol comes from sea salt and that the sea-salt component in the aerosol still has the same composition as the sea salt that is emitted by the oceans.

However, chlorine loss from sea salt is a common phenomenon in the atmosphere, especially for the fine particles [e.g., Graedel and Keene, 1995]. In our data sets, the Cl^-/Na^+ mass ratio was only close to the ratio of 1.81 in bulk sea water [Riley and Chester

1971] for the coarse size fraction at Dar es Salaam; for the fine size fraction at this site and for both size fractions at Morogoro substantial lower Cl^-/Na^+ ratios were obtained, indicating important chlorine loss. Therefore, by, using equation 6.1, the sea-salt component would be overestimated. To take the chlorine loss into account, one can estimate the sea-salt component from the Na and Cl data for the aerosol as follows [Virkkula et al., 1999]:

$$[\text{Sea salt}] = [\text{Cl}] + 1.4486 \times [\text{Na}] \quad [6.2]$$

where 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water [Riley and Chester 1971]. Use of equation [6.2] implicitly assumes that all the Cl and Na in the aerosol is from sea salt.

In this work, use was made of equation [6.2] and of the Na^+ and Cl^- concentrations obtained by IC for the coarse and fine filters of the PM10(NN) samples.

6.2.7 Crustal matter

Also for the estimation of crustal matter several approaches are available. A common method is to estimate it from the Al concentration in the aerosol, thereby making use from the Al concentration of 8.13% in the average crustal rock composition of Mason and Moore [1982]. This requires that the Al data for the aerosol are of excellent quality, such as is the case when Al is measured by instrumental neutron activation analysis (INAA). In PIXE and other X-ray emission analysis techniques, the Al determination suffers to some extent from matrix effects, including particle size effects. On the other hand, the X-ray emission techniques provide concentrations for several typical crustal elements. When using such techniques, it is therefore recommended to base the estimation of crustal matter component on several typical crustal elements. In the US IMPROVE program [URL: <http://vista.cira.colostate.edu/IMPROVE/>], where X-ray emission techniques are used to determine the crustal elements, the crustal matter component is estimated as follows:

$$[\text{Crustal matter}] = 1.16 (1.90 [\text{Al}] + 2.15 [\text{Si}] + 1.41 [\text{Ca}] + 1.67 [\text{Ti}] + 2.09 [\text{Fe}]) \quad [6.3]$$

where the factor 1.16 is to compensate for the exclusion of MgO, Na₂O, K₂O, and H₂O from the crustal mass calculation and [Al], [Si], etc. are the concentrations of the element Al, Si, etc. in the aerosol. Equation 6.3 has been used by several authors [e.g., Chan et al., 1997; Maenhaut et al. 2002] and is also used in the present work. The concentrations of the various crustal elements were obtained by PIXE of the coarse and fine filters of the PM₁₀(NN) samples.

6.2.8 Elements

PIXE provided concentrations for several other elements besides data for the major crustal elements. Therefore, “elements” was included as an eighth component in the mass closure calculation. This last component was calculated as the sum of the mass of all non-crustal/non-sea salt elements measured by PIXE (S and K were excluded from this sum).

6.2.9 Unexplained mass

The sum of the above eight aerosol components is called the reconstructed PM mass. This mass may differ from the gravimetric PM mass, since there are uncertainties involved with the gravimetric PM mass determination and with the measurement of the various species and elements in the aerosol and also with the estimation of certain components (especially OM) from the measured species. The difference between the gravimetric PM mass and the reconstructed mass is called the unexplained mass. This difference may be positive or negative, but is generally negative when the sum of the above eight components is used, because H₂O is not included in the calculation, except for that associated with crustal matter.

6.3 Aerosol chemical mass closure results for the three campaigns at Morogoro and Dar es Salaam

Figure 6.1 shows the average absolute concentrations of the eight aerosol types (components) and of the unexplained mass in PM10 for each of the three campaigns at Morogoro and Dar es Salaam. The percentage contributions of the eight aerosol types and of the unexplained mass to the average gravimetric PM10 mass are given in Table 6.1. The absolute concentrations of the PM10 mass, crustal matter, sea salt, and EC (and also the percentages for sea salt and EC) are substantially larger for the Dar es Salaam kerbside than for the Morogoro rural site. For sea salt, this is of course due to the proximity of the Dar es Salaam kerbside to the Indian Ocean. The higher absolute levels for crustal matter and EC at Dar es Salaam are attributed to the much larger impact from road traffic there, with more resuspended road dust and larger soot emissions.

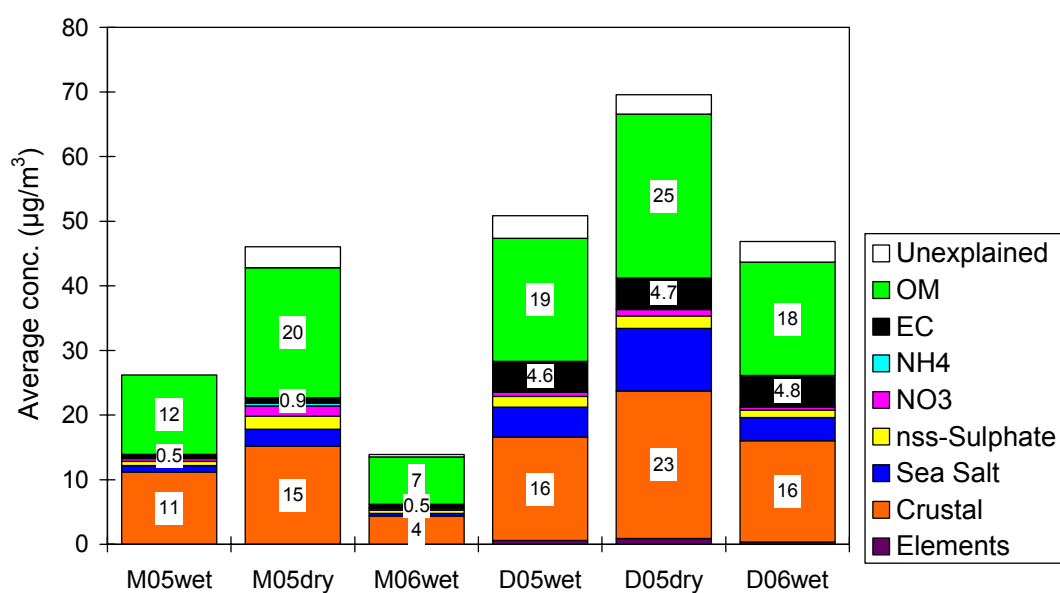


Figure 6.1. Average concentrations of 8 aerosol types in PM10 and of the unexplained gravimetric PM10 mass during the 2005 wet, 2005 dry, and 2006 wet season campaigns at Morogoro and Dar es Salaam. OM was calculated as 1.8 OC for Morogoro and as 1.6 OC for Dar es Salaam.

Table 6.1. Percentage attribution of the mean gravimetric PM10 mass concentration to eight aerosol types (components) for each of the three campaigns in Morogoro and Dar es Salaam.

Species	Morogoro			Dar es Salaam		
	05wet	05dry	06wet	05wet	05dry	06wet
OM	48	44	53	37	36	37
EC	1.99	1.91	3.7	9.0	6.7	10.3
Ammonium	0.66	0.84	1.18	0.34	0.27	0.21
Nitrate	1.63	3.4	1.66	1.31	1.43	0.93
Nss-sulphate	2.5	4.5	3.7	3.3	2.8	2.5
Sea salt	4.0	5.6	2.7	9.1	13.9	7.7
Crustal matter	44	33	32	32	33	33
Other elements	0.05	0.05	0.05	1.14	1.29	0.75
Unexplained	-2.8	7.1	2.7	6.9	4.3	6.9

With regard to the aerosol chemical mass closure for the separate fine and coarse fractions, full calculations could only be made for the campaigns when also the PM2.5 sampler with quartz fibre filters was deployed, thus for the 2005 dry season campaign at Dar es Salaam and for the 2006 wet season campaigns at both sites. The average absolute concentrations of the eight aerosol types and of the unexplained mass in PM2 and PM10-2 for these campaigns are given in Table 6.2 and the percentage contributions of the eight aerosol types and of the unexplained mass to the average gravimetric PM2 and PM10-2 mass are shown in Figure 6.2.

It is clear that OM is the dominant aerosol type in the fine size fraction for both sites and that crustal matter and OM are the major components in the coarse fraction. Noteworthy is further the large percentage contribution of EC to the fine PM mass at the Dar es Salaam kerbside, again emphasizing the large impact from fossil fuel combustion (especially traffic) at this site.

Table 6.2. Average concentrations (in $\mu\text{g}/\text{m}^3$) in PM₂ and PM₁₀₋₂ of the 8 aerosol types and of the unexplained gravimetric mass during the 2005 dry season campaign at Dar es Salaam and during the 2006 wet season campaigns at the two sites. OM was calculated as 1.8 OC for Morogoro and as 1.6 OC for Dar es Salaam.

Species	PM ₂			PM ₁₀₋₂		
	D05dry	D06wet	M06wet	D05dry	D06wet	M06wet
OM	10.3	8.0	3.6	15.0	9.5	3.8
EC	3.3	3.6	0.39	1.39	1.26	0.12
Ammonium	0.17	0.10	0.15	0.02	0.00	0.01
Nitrate	0.30	0.16	0.06	0.69	0.28	0.17
Nss-sulphate	1.22	0.80	0.44	0.72	0.37	0.07
Sea salt	1.09	0.44	0.06	8.6	3.1	0.31
Crustal matter	1.68	1.31	0.68	21	14.4	3.7
Other elements	0.46	0.17	0.00	0.43	0.19	0.00
Unexplained	-1.52	-1.45	-0.32	4.5	4.6	0.70

The sums (in percent) of the eight included components are for PM₁₀ and the fine size fraction close to 100%. There is a somewhat larger difference from 100% for the coarse size fraction, but considering the uncertainties involved in estimating some of the components, even for that size fraction, the mass closure is quite good.

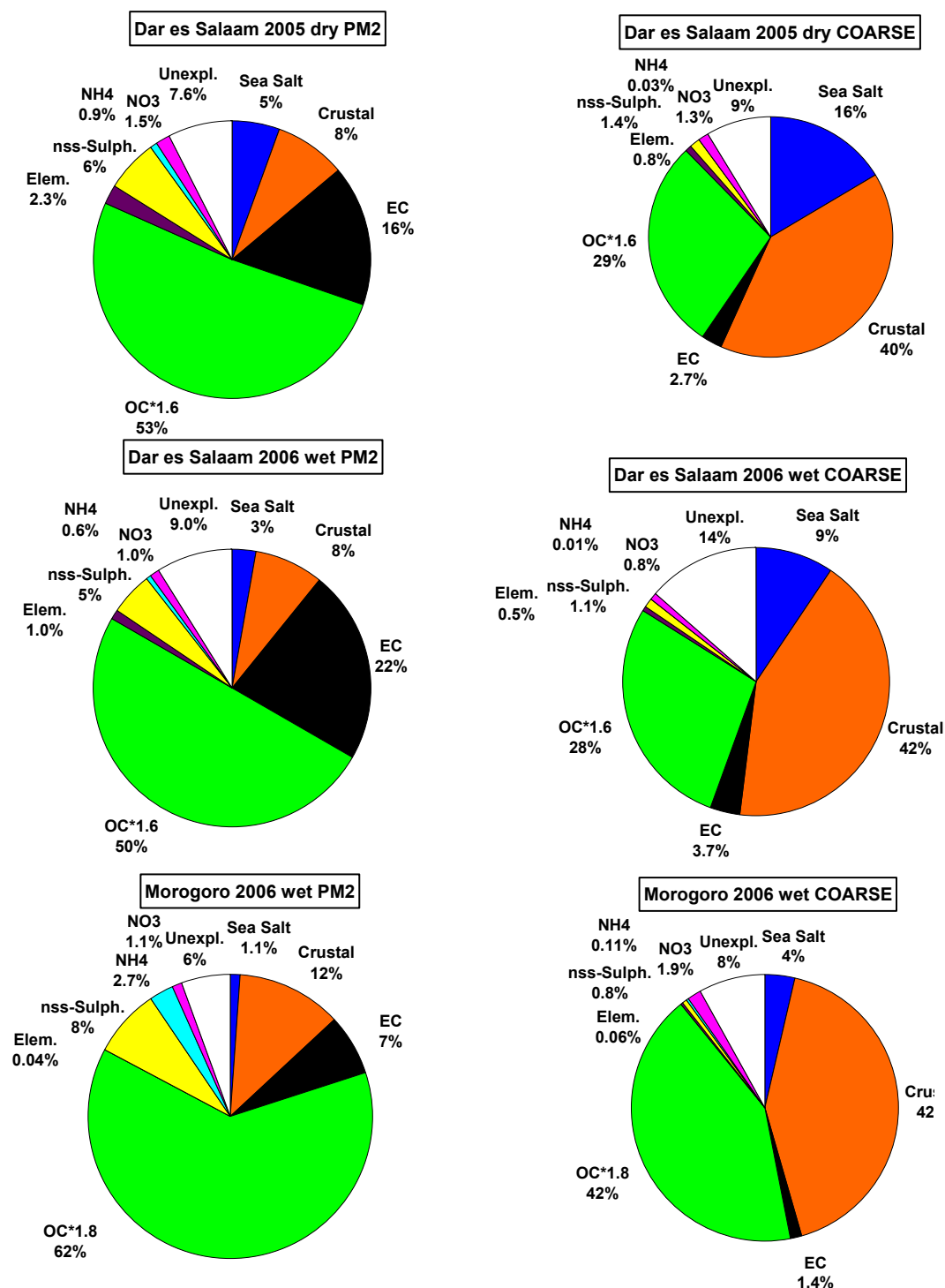


Figure 6.2. Percentage attribution of the mean gravimetric PM₂ and PM₁₀₋₂ mass concentration to eight aerosol types (components) for the 2005 dry season campaign at Dar es Salaam and the 2006 wet season campaigns.

6.4 Aerosol chemical mass closure: Comparison with other locations

The aerosol chemical mass closure results for the two Tanzanian sites can be compared with those obtained in the European aerosol phenomenology exercise [Putaud et al., 2004] and in subsequent studies in Europe [e.g., Maenhaut et al., 2005; Viana et al., 2007a]. The largest difference resides in the much lower contribution of SIA in Tanzania. Whereas the higher temperatures may play a role for the lower nitrate percentages, other explanations have to be invoked for the lower percentages of nss-sulphate. They indicate that the emissions of the precursor gas SO₂ on the regional scale are substantially lower for the Tanzanian sites than they are for European sites, as is also evident from the GEIA emission inventory [see <http://geiacenter.org/> and, e.g., Verma et al., 2006].

Table 6.3 compares the percentage results for the Dar es Salaam kerbside with those for selected urban sites in Europe [Maenhaut and Claeys, 2007]. The species and elements at these sites were determined with the same techniques as used in the present study. It appears that the percentage contributions of OM, EC, and crustal matter of Dar es Salaam are remarkably similar to those for the Budapest kerbside.

Table 6.3. Percentage contribution to the gravimetric PM₁₀ mass of various aerosol types at selected urban locations in Europe and at the Dar es Salaam kerbside.

Aerosol component	Budapest ¹	Ghent ¹		Dar es Salaam	
	Spring 2002	Winter 2004	Summer 2004	2005 Dry	2006 Wet
OM	34	26	25	36	37
EC	8.6	2.8	5.4	6.7	10.3
Ammonium	2.6	13.9	7.3	0.27	0.21
Nitrate	4.5	22	13.2	1.43	0.93
Nss-Sulphate	7.4	12.0	12.5	2.8	2.5
Sea salt	1.57	9.3	11.0	13.9	7.7
Crustal matter	37	11.2	11.9	33	33
Other elements	0.62	0.36	0.16	1.29	0.75
Unexplained	3.8	2.6	13.0	4.3	6.9

¹Maenhaut and Claeys [2007].

6.5 Sources of the OC at Morogoro and Dar es Salaam

Various approaches can be used for source identification and apportionment. Besides sophisticated approaches such as chemical mass balance and multivariate receptor modelling techniques, also the use of simple tracers can be quite valuable. Here, use was made of non-crustal, non-sea-salt K to apportion the OC to biomass burning and other sources. Non-crustal, non-sea-salt K is considered a good indicator for biomass burning and it is reasonable to assume that it derives nearly exclusively from this source in Tanzania. Particulate OC at the two sites may originate from several sources, with for the rural site of Morogoro, biomass burning and primary and secondary biogenic organic matter as likely sources. At the Dar es Salaam kerbside, the OC is thought to originate essentially from automotive emissions and biomass burning.

Andreae and Merlet [2001] reviewed the emissions of trace gases and aerosols from biomass burning and provided emission factors for many pyrogenic species that are emitted from various types of biomass burning, including (1) savanna and grassland, (2) tropical forest, (3) extratropical forest, (4) biofuel burning, (5) charcoal making, (6) charcoal burning, and (7) agricultural residues. For all these burning activities, with the exception of charcoal making, emission factors for particulate OC and K are available. Although charcoal making may be a source of OC at the two sites, because of the absence of emission factor data, it was not further considered in the analysis. Of the remaining activities, biofuel burning, charcoal burning, and to a lesser extent agricultural residues are thought to be possible contributors to the K and OC at Morogoro, whereas at Dar es Salaam, only charcoal burning is thought to be important.

From the data given in Table 2 of Andreae and Merlet [2001], OC/K mass ratios of 76, 9, and 12 can be calculated for the emissions of biofuel burning, charcoal burning, and agricultural residues, respectively. Since only two tracers (i.e., K and OC) were included in the analysis, the contributions from only 2 sources could be estimated. Biofuel burning and charcoal burning were retained as sources for the Morogoro site, and for Dar es Salaam charcoal burning and automotive emissions were included. The average percentage apportionments of the OC to the two retained sources for each of the three campaigns at each of the sites are given in Table 6.4. The apportionments were

done on a sample by sample basis and the individual percentages were then averaged over all samples for each campaign and each site. Very consistent results were obtained for Dar es Salaam, both on a sample by sample basis (as can be seen from the associated standard deviations) and from campaign to campaign. For Morogoro, there is a large difference between the results from the 2005 dry season campaign and the two wet season campaigns. It is hard to indicate the reasons for this behaviour. It may well be that there was a substantial contribution to the OC at Morogoro from the non-included natural biogenic/biological aerosol. The results for Morogoro should therefore be considered with great caution and further research is needed on the sources of OC for this site. For the Dar es Salaam kerbside, where the contribution from natural biogenic/biological aerosol should be very minor, the apportionment results are thought to be much more reliable.

Table 6.4. Mean percentage attribution of the OC to two sources for the campaigns in Morogoro and Dar es Salaam.

Morogoro	2005wet	2005dry	2006wet
	mean $\pm$ stdv	mean $\pm$ stdv	mean $\pm$ stdv
Biofuel burning	80 $\pm$ 15	14 $\pm$ 33	93 $\pm$ 9
Charcoal burning	20 $\pm$ 15	86 $\pm$ 33	7 $\pm$ 9

Dar es Salaam	2005wet	2005dry	2006wet
	mean $\pm$ stdv	mean $\pm$ stdv	mean $\pm$ stdv
Traffic	68 $\pm$ 13	73 $\pm$ 9	70 $\pm$ 12
Charcoal burning	32 $\pm$ 13	27 $\pm$ 9	30 $\pm$ 12

6.6 Receptor modelling by Principal Component Analysis

6.6.1 Introduction

In this study, Principal Component Analysis (PCA) was applied to the fine and coarse size fraction data sets from the 2005 dry season campaign at Dar es Salaam. Briefly, PCA makes use of an eigenanalysis of the correlation matrix of the data set, after

which a limited number of principal components (PCs) and their associated eigenvectors are retained and a rotation of the matrix with retained eigenvectors is carried out [Thurston and Spengler, 1985; Maenhaut and Cafmeyer, 1987]. The most commonly used rotation is the VARIMAX rotation of Kaiser [1958] and this rotation was also used here. The original and rotated eigenvectors contain the original and rotated PC loadings and are the correlation coefficients between the variables and the PCs. The sum of the squares of all loadings within a PC gives the variance in the data set explained by the particular PC, whereas the sum of the squares of the loadings over all PCs for each variable is the communality for the particular variable, which is the variance explained for that variable. In a good PCA, the retained PCs should explain about 90% or more of the total variance in the data set and the communality for each variable should be 0.8 or larger. A delicate decision in PCA is to decide on the number of PCs to retain. Several criteria have been proposed to make this decision, but it is common to retain all PCs that explain at least one unit of variance after the rotation [Maenhaut and Cafmeyer, 1987]. This criterion was also used here.

6.6.2 Aerosol source identification

The identification and “naming” of the VARIMAX rotated PCs in terms of aerosol sources (or source types) is based on the loadings for the various variables within each PC. For example, if a PC has high (>0.7) or better very high (>0.9) loadings for several crustal elements (e.g., Al, Si, Ti, Fe), then it is clearly a crustal matter or soil dust component. Similarly, if it has high or very high loadings for Na and Cl, then it is a sea-salt component. A high loading for K suggests that the PC is likely associated with biomass burning, and so on.

6.6.3 PCA on the fine size fraction data set from the 2005 dry season campaign at Dar es Salaam

Twenty-six variables, i.e., PM, BC, OC, EC, NH_4^+ , NO_3^- , SO_4^{2-} , Na (IC), Mg (IC), Al, Si, S, Cl, Cl(IC), K, K(IC), Ca, Ca (IC), Ti, Mn, Fe, Cu, Zn, Br, Pb, and D_N,

were included for the PCA on the fine size fraction data set from the 2005 dry season. The variable D_N stands for the day/night character of the samples and was set equal to 1 for the daytime samples and equal to 0 for the nighttime samples. The VARIMAX rotated PCA resulted in seven PCs, for which the loadings are given in Table 6.5. The seven components explained 89% of the variance in the data set. The first component (Comp 1) is very highly loaded with the crustal elements Al, Si, Ca [and Ca (IC)], and Fe and is clearly a crustal component. However, OC, EC, and BC are also highly loaded on it, as are the D_N variable and Mn. Comp 1 is therefore also associated with the daytime and with emissions from traffic. It seems to represent a mixture of road dust and traffic exhaust. Comp 2 is very highly loaded with the secondary inorganic species NH_4^+ and SO_4^{2-} , and also with S; besides, K [and Ca (IC)] is highly correlated with this component. The high loading for K indicates that this component contains biomass burning aerosol. Also the secondary component SO_4^{2-} may in part be associated to biomass burning. The third component has very high loadings for Na (IC) and Mg (IC) and high loadings for Cl [and Cl (IC)]. It represents undoubtedly sea salt. The final four components are unique components, since only one element or species is highly or very highly loaded on each of them. The metallic components Zn, Cu, and Pb represent likely different pollution sources within Dar es Salaam. For Zn several metal processing industries such as metallurgical factories, alloy industries, galvanizing activities in industries, and galvanized parts of heating appliances could be the sources and for the Pb the battery industry could be the main source. The last (nitrate) component is a secondary component, whereby the precursor NO_x may predominantly have originated from automotive emissions. Energy production and refineries may also have contributed to this component.

Table 6.5. VARIMAX rotated PC matrix for the fine (PM₂ or PM_{2.5}) samples from the 2005 dry season campaign at Dar es Salaam. High (>0.7) and very high (>0.9) loadings are indicated in bold.

Variable	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5	Comp 6	Comp 7	Comm.
	Crustal and traffic	Secondary & biomass burning	Sea spray	Zn	Cu	Pb	Secon- dary	
PM	0.61	0.68	-0.01	0.21	0.06	-0.06	0.25	0.95
OC	0.82	0.25	-0.21	0.07	0.16	-0.02	0.35	0.93
EC	0.81	-0.09	-0.16	0.24	0.25	-0.21	0.04	0.85
BC	0.83	0.13	-0.13	0.19	0.24	-0.28	0.06	0.90
NH ₄	-0.29	0.90	-0.06	-0.15	-0.05	-0.02	0.09	0.93
NO ₃	-0.09	0.56	0.06	-0.08	-0.07	0.08	0.78	0.95
SO ₄	-0.05	0.97	0.12	-0.09	-0.02	0.06	0.00	0.97
Na (IC)	-0.29	0.13	0.93	-0.02	-0.09	-0.05	-0.03	0.97
Mg (IC)	-0.17	0.10	0.94	-0.14	-0.06	-0.14	-0.05	0.97
Al	0.95	0.09	-0.18	-0.16	-0.04	0.06	0.01	0.98
Si	0.96	0.09	-0.16	-0.17	-0.01	0.02	-0.02	0.98
S	0.01	0.98	0.13	-0.05	-0.02	0.04	-0.02	0.97
Cl	-0.13	-0.36	0.70	0.56	0.11	0.01	-0.03	0.95
Cl (IC)	-0.36	-0.21	0.76	0.41	0.09	0.09	0.03	0.94
K	0.44	0.80	-0.06	-0.06	0.11	-0.21	0.20	0.94
K (IC)	0.41	0.79	-0.10	0.01	0.08	-0.21	0.23	0.91
Ca	0.97	-0.02	-0.12	-0.13	-0.03	-0.04	-0.06	0.97
Ca (IC)	0.95	-0.09	-0.12	-0.16	-0.06	-0.06	-0.06	0.97
Ti	0.95	0.07	-0.17	-0.14	0.03	0.06	-0.00	0.96
Mn	0.87	0.05	-0.05	0.22	-0.04	0.20	-0.01	0.85
Fe	0.98	0.09	-0.12	-0.07	0.01	0.05	-0.03	0.98
Cu	0.16	0.02	0.03	0.04	0.95	0.08	-0.02	0.94
Zn	-0.14	-0.12	0.15	0.89	0.02	0.30	-0.04	0.93
Br	-0.01	0.29	0.58	0.25	0.20	0.27	0.24	0.66
Pb	-0.02	-0.10	-0.05	0.24	0.07	0.85	0.04	0.81
D_N	0.85	-0.03	-0.03	-0.14	0.32	-0.18	-0.09	0.88
Variance	10.2	5.2	3.4	1.8	1.3	1.2	1.0	
% Var.	37.6	19.2	12.7	6.5	4.7	4.6	3.7	

6.6.4 PCA on the coarse size fraction data set from the 2005 dry season campaign at Dar es Salaam

For the coarse size fraction data set from the 2005 dry season campaign at Dar es Salaam 27 variables were included in the PCA, i.e., the same variables as for the fine data set, but without Br, and in addition P and Sr. Five PCs were retained, which explained 90% of the total variance of the data set. The VARIMAX rotated PC loadings are given in Table 6.6. Several variables are very highly or highly loaded on the first component, which seems to be the coarse fraction counterpart of Comp 1 in the fine size fraction. That Cu is also very loaded on this component may be due to the contribution from brake lining wear in automobiles. It is well-known that this process is an important source of coarse Cu at kerbsides [e.g., Salma and Maenhaut, 2006; and references therein]. The high loading of SO_4^{2-} and S on Comp 1 is unexpected and an appropriate explanation for this is not available. Comp 2 is very highly loaded with Na (IC), Mg (IC), Cl and Cl (IC) and represents sea salt, similarly as Comp 3 in the fine size fraction. The third coarse component is very highly loaded with NO_3^- and to some extent also with NH_4^+ . It clearly stands for secondary inorganic aerosol. The final two coarse components are unique components with Zn and Pb and they are undoubtedly the counterparts of the same components in the fine size fraction.

Table 6.6. VARIMAX rotated PC matrix for the coarse samples from the 2005 dry season campaign at Dar es Salaam. High (>0.7) and very high (>0.9) loadings are indicated in bold

Variable	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5	Comm.
	Crustal and traffic	Sea spray	Secondary	Zn	Pb	
PM	0.97	0.22	0.02	0.01	0.01	0.99
OC	0.96	0.06	0.04	-0.06	0.03	0.93
EC	0.87	0.03	-0.13	0.02	0.07	0.78
BC	0.94	0.05	-0.09	0.08	0.02	0.90
NH ₄	-0.34	0.27	0.63	-0.29	-0.01	0.67
NO ₃	0.16	-0.02	0.94	-0.02	-0.07	0.92
SO ₄	0.70	0.55	0.35	0.09	0.03	0.92
Na (IC)	0.09	0.97	0.10	-0.01	-0.05	0.97
Mg (IC)	0.20	0.94	0.19	-0.03	-0.08	0.96
Al	0.99	0.03	0.02	-0.06	-0.00	0.98
Si	0.99	0.04	0.01	-0.05	-0.00	0.99
P	0.94	-0.08	0.06	-0.07	-0.14	0.93
S	0.77	0.51	0.25	0.09	0.04	0.92
Cl	-0.01	0.97	-0.07	0.06	-0.03	0.95
Cl (IC)	0.04	0.99	-0.07	0.04	-0.01	0.98
K	0.97	0.13	0.12	-0.01	-0.00	0.98
K (IC)	0.83	0.25	0.23	0.05	0.19	0.85
Ca	0.98	0.08	-0.06	-0.04	-0.01	0.96
Ca (IC)	0.95	0.07	-0.00	-0.10	-0.05	0.93
Ti	0.99	0.01	0.06	-0.05	0.00	0.99
Mn	0.99	0.03	0.05	-0.03	-0.01	0.97
Fe	0.99	0.06	0.01	-0.03	0.01	0.98
Cu	0.96	0.11	-0.02	0.01	-0.01	0.93
Zn	-0.19	0.08	-0.15	0.93	0.11	0.95
Sr	0.97	0.13	-0.02	-0.08	-0.02	0.97
Pb	0.00	-0.13	-0.07	0.10	0.98	0.98
D_N	0.87	0.07	-0.09	-0.13	-0.07	0.80
Variance	16.7	4.6	1.7	1.1	1.1	
% Variance	59.6	16.4	6.0	3.8	3.8	

6.7 Conclusions

A comprehensive chemical aerosol characterisation was carried out at a kerbside site in downtown Dar es Salaam and at a rural site in Morogoro in three sampling campaigns. For reconstituting the gravimetric PM, eight aerosol components were considered. Organic matter and crustal matter were the dominant aerosol types in the PM₁₀ size fraction; they explained, on average, 37 and 33%, respectively, of the PM mass at Dar es Salaam. The crustal matter at this site is undoubtedly mostly resuspended road dust. At Morogoro the PM₁₀ aerosol consisted mainly of organic matter (48%) and crustal matter (36%).

Using non-crustal, non-sea-salt K as an indicator for biomass burning it was attempted to estimate the contribution from two different biomass burning sources to the OC at Morogoro, but the results were not very satisfactory. For Dar es Salaam, the OC was apportioned to its contributions from charcoal burning and traffic. It appeared that, on average, around 70% of the OC originated from traffic and 30% from charcoal at this site.

Principal component analysis with VARIMAX rotation was applied to the separate fine and coarse size fraction data sets from the 2005 dry season campaign in Dar es Salaam. Five components were identified for the coarse size fraction, i.e., an important mixed road dust / traffic component, sea salt, a secondary nitrate component, and Zn and Pb components, which are attributed to different local pollution sources. The same five components were also present in the fine size fraction, but the latter fraction also contained a biomass burning component and a separate Cu component.

CHAPTER 7

GENERAL CONCLUSIONS, RECOMMENDATIONS AND NEEDS FOR FUTURE

7.1 General conclusions

In areas of rapid urbanization, such as Africa, measurement of aerosols and understanding their sources can be a valuable tool for urban planners to mitigate potential negative effects. Air pollution in many African cities is neither monitored nor controlled, and there are no long-term records of pollution levels and impacts. For Tanzania very little information is currently available on atmospheric aerosol levels and composition. In order to obtain an idea of the current levels of the fine, coarse, and PM₁₀ particulate matter and its composition, which could serve as a reference for further studies in this developing country, aerosol collections were conducted at Dar es Salaam and Morogoro in Tanzania during three sampling campaigns (two campaigns in 2005 and one in 2006). The main questions and objectives of the study were: (1) Which are the major contaminants in aerosols at the urban site of Dar es Salaam and at the rural site of Morogoro and what are their concentrations? (2) How important are the artifacts in the measurement of the particulate mass and of the organic carbon and how can we check the reliability of the results? (3) How important are seasonal variations, especially between the dry and wet season? (4) Is the PM₁₀ mass explained by the measured aerosol components and which are the major sources of the aerosols sampled at Dar es Salaam and Morogoro?

To address the above questions, PM_{2.5} and PM₁₀ filter holders and a “Gent” PM₁₀ stacked filter unit (SFU) sampler were deployed. The samples were analysed by several techniques to obtain a comprehensive aerosol characterisation and various approaches, including relation of the data to meteorological parameters, crustal enrichment factor calculations, and correlation and principal component analyses, were used to assist in the data interpretation. With regard to question (1), it appeared that organic matter and crustal matter were the major aerosol components at both sites. At the urban site of Dar es Salaam, also sea salt, elemental carbon, and certain heavy metals, such as Zn and Pb, were important. Furthermore, the PM mass levels were substantially higher at the urban site of Dar es Salaam than at the rural site of Morogoro. At Dar es Salaam, the average PM₁₀ mass concentration in each of the three campaigns was similar or higher than the daily EU PM₁₀ limit value of 50 µg/m³ for ambient air. As to question

(2), the sampling artifacts for the PM and OC were assessed by resorting to the tandem quartz fibre filter approach, and for the PM, also by collecting simultaneously samples with Nuclepore polycarbonate filters and with quartz fibre filters. The back to front filter ratio for the mass of the PM and OC in the quartz fibre filter samples was typically smaller than 0.10 for the Dar es Salaam site and somewhat larger (but typically below 0.15) for the Morogoro site. The PM₁₀ mass derived from the front quartz fibre filter samples was somewhat larger than that obtained from the Nuclepore polycarbonate filter samples, up to, on average, 18% for the 2006 wet season campaign at Morogoro. Similar findings on the artifacts for the PM and OC were obtained at various European sites [Maenhaut and Claeys, 2007]. Intercomparison of the data obtained by IC and PIXE for the elements S, Cl, K, and Ca allowed us to determine what fraction of the element was water-soluble and to assess the accuracy of the IC and PIXE results. Overall, the results of these intercomparisons were quite satisfactory. With regard to question (3), the concentration of the various measured aerosol components at Morogoro and Dar es Salaam showed clear seasonal trends with highest level during the 2005 dry season campaign and lowest level during the 2006 wet season campaign. As to question (4), the gravimetrically measured PM mass was compared with the reconstituted mass, which was obtained on the basis of the measured aerosol constituents; thus a so-called aerosol chemical mass closure was made. In this mass reconstruction, eight aerosol components were considered and overall very good mass closure was obtained. Organic matter and crustal matter were the dominant aerosol types in the PM₁₀ size fraction, but their sources were somewhat different at the two sites. Anthropogenic biomass/biofuel burning was a major contributor to the OM at both sites, but in Dar es Salaam there was also an important contribution to the OM from road traffic, especially during the daytime. The crustal matter at Morogoro is thought to originate essentially from soil dust dispersal. This source process undoubtedly also contributed to the crustal matter at Dar es Salaam, but in addition, during the daytime there was a major contribution at this site from road dust resuspension. At Dar es Salaam, there was also a substantial impact from industrial sources for some metallic elements, such as Zn and Pb.

A quantitative understanding of the source contributions to the ambient particulate levels is needed to develop emission control strategies. The results of this study will be

very useful for the environmental management of particulate concentrations that violate the standard limits (to be developed) in the country. However, Tanzania needs a quick action to introduce continuous PM monitoring stations in various sites within the country so as to improve air quality studies, control and assessment.

7.2 Recommendations

- I recommend community awareness and education on the effect of air pollution as far as the aerosol particles are concerned. The pollution of particulate matter can lead to serious health effects and climate change.
- More research is desirable because of poor knowledge of PM components and their sources.
- The establishment of PM monitoring stations in different locations in the country, including in rural, urban or industrial areas is recommended.
- I also recommend the establishment of PM₁₀ limit values for the country.

7.3 Needs for future

Some important aspects may not have been given full consideration due to the limited financial capacity of this study. For instance, more meaningful results could be obtained by conducting a field campaign during the entire period of the season (dry or wet season). Furthermore, some important meteorological data to interpret the separate daytime and nighttime data were lacking. Thus, it is essential that detailed meteorological data are available. Furthermore, there is definitely a need for year-round monitoring of the PM mass levels in a number of carefully chosen locations throughout the country. In a first stage, such monitoring would be welcome at a few sites in Dar es Salaam. In a later stage, the monitoring could be complemented with intensive campaign-type studies, whereby the major aerosol components are measured using techniques that are similar to those used in this study. The requested techniques are not highly complicated or sophisticated: a thermal-optical technique for measuring OC and EC, ion chromatography for the water-soluble species, and an energy-dispersive X-ray fluorescence instrument for

the crustal elements and various heavy metals would do the job. Campaign-type studies are also needed to further examine the contribution of biomass burning, in particular of biofuel to the PM levels. Biofuel is extensively used for cooking and heating in Africa and also in other continents (e.g., Asia) and may be a major contributor to the PM in many locations. Finally, further work is required to quantify, where necessary, the effects of PM on human health in Tanzania.

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SUMMARY

Three aerosol sampling campaigns were conducted at two sites in Tanzania, during different seasons from May 2005 through May 2006. The sites were in Dar es Salaam and in Morogoro, about 200 km to the west of Dar es Salaam. In Dar es Salaam, the aerosol sampling was conducted on the second-floor balcony of the Young Women's Christian Association of Tanzania (YWCA) building at Azikiwe Street in Posta Mpya, while the sampling station in Morogoro was located on the western foothill of Uluguru Mountain and the instruments were mounted on a roof at the main campus of Sokoine University of Agriculture (SUA). The aim of the project was to characterise the ambient atmospheric aerosols with emphasis on carbonaceous components and on chemical mass closure at the two sites. A Gent PM10 stacked filter unit (SFU) sampler with sequential Nuclepore polycarbonate filters, providing coarse (2-10 μm diameter) and fine (<2 μm) size fractions, and PM2.5 and PM10 tandem filter samplers with two pre-fired Whatman QM-A quartz fibre filters in series were deployed. Depending upon the season and the location, either 24-hour collections or separate daytime and nighttime samplings were performed. The samples were analysed for the particulate matter (PM) mass, total carbon (TC), organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), black carbon (BC), major inorganic cationic and anionic species, and 28 elements (from Na to Pb).

To obtain the PM mass, the filters were weighed before and after sampling with a microbalance (sensitivity 1 μg). Before weighing, the filters were conditioned at a relative humidity of 50% and a temperature of 20 $^{\circ}\text{C}$ for 24 h and the weighings were done under these conditions. TC, OC, and EC were determined from a 1.5 cm^2 portion of each quartz fibre filter with a thermal-optical transmission instrument from Sunset Laboratory following the Ghent standard thermal evolution protocol.

WSOC was determined from a punch of 1.5 cm^2 from each quartz fibre filter. The filter punch was placed into a 15 mL polystyrene tube, 5 mL Millipore Simplicity water was added, after which the tube was hand-shaken for about 5 min and allowed to stand for 30 min. The water extract was filtered through a syringe filter and analysed for water-

soluble total carbon and inorganic carbon using a TOC-V CPH Shimadzu instrument. Total water-soluble organic carbon was calculated by difference between total water-soluble carbon and inorganic water-soluble carbon, and was used as WSOC.

One half of each Nuclepore polycarbonate filter was analysed by ion chromatography (IC) for major water-soluble inorganic ions using a Dionex 4500i instrument with a PC based AutoIon (AI-450) data acquisition and analysis system. The filter half was placed in a 15 mL polystyrene tube and extracted ultrasonically with 5 or 10 mL Millipore Simplicity water for 1 hour. For the determination of the anions, an IonPac AG12A guard column and an IonPac AS12A analytical column were employed. The eluent (mobile phase) consisted of a buffer of 2.7 mM sodium carbonate/0.3 mM sodium bicarbonate (isocratic) and the flow rate was 1 mL min⁻¹. The cations were measured with an IonPac CG12 guard column and an IonPac CS12 analytical column; 20 mM methanesulphonic acid (MSA) (isocratic) was used as mobile phase at a flow rate of 1 mL min⁻¹. ASRS Ultra II and CSRS Ultra II auto-suppressors were applied for the anions and cations, respectively, operating in auto-suppression mode, and a conductometric detector was used.

One quarter of the remaining half of each Nuclepore polycarbonate filter was used to determine the elemental composition by particle-induced X-ray emission spectrometry (PIXE). Prior to the PIXE analysis, BC was determined using a simple light reflectance technique. The PIXE analysis of the samples was carried out using a compact cyclotron, installed at the Institute for Nuclear Sciences of Ghent University, Belgium. The measurements were done with an incident proton beam of 2.4 MeV; the beam current at the specimen was typically 150 nA and the integrated beam charge 100 µC. The X-rays emerging from the specimen were detected with a Si(Li) detector.

The measurement of the PM mass, OC, and WSOC for aerosols is subject to both positive and negative sampling artifacts. The artifacts depend to some extent on the type of filter used. Whereas it is generally assumed that positive artifacts prevail with quartz fibre filters, the use of Nuclepore (or Teflon) filters may lead to negative artifacts. The extent of the artifacts with quartz fibre filters was assessed for the PM_{2.5} and PM₁₀ tandem filter set-ups. It appeared that 13% of the PM₁₀ mass collected on the front filter might result from positive artifacts. With regard to PM₁₀ OC, the mass on the back filter

represented approximately 6% of that on the front filter for the Dar es Salaam samples, whereas the corresponding percentage was about 6-13% for the Morogoro samples. This back filter OC mass accounted, on average, only for about one third of the PM mass on the back filters, suggesting that the latter was also influenced by non-carbonaceous components. It should be indicated, though, that OC could be measured with substantially better precision than the PM mass for the quartz fibre filters.

For the rural site at Morogoro the median levels of the PM₁₀ mass for the 2005 wet season, 2005 dry season, and 2006 wet season campaigns were 23, 45, and 13 $\mu\text{g}/\text{m}^3$ and the average contributions of the fine (PM₂) fraction to the PM₁₀ mass during the three campaigns were 35, 49, and 37%, respectively. Most elements were predominantly associated with the coarse size fraction; notable exceptions were non-sea-salt S, K, and Pb, suggesting that they originated mainly from anthropogenic sources. Higher concentrations of most measured aerosol components were observed in the dry season campaign than in the wet season campaigns. This was due to an increased influence from biomass burning and soil dust in the dry season.

At the Dar es Salaam kerbside, there were also seasonal trends for most components, with higher levels in the dry season campaign than in the wet season campaigns. As expected, most aerosol components exhibited higher levels at the Dar es Salaam kerbside than at the rural Morogoro site. Furthermore, the concentrations of most species at Dar es Salaam followed a strong diurnal pattern, with 3-5 times higher levels during the day than during the night. At Dar es Salaam the PM₁₀ mass median levels in the three campaigns (2005 wet, 2005 dry, 2006 wet) were 46, 58, and 40 $\mu\text{g}/\text{m}^3$, respectively. TC accounted for 29% of PM₁₀ mass in the 2005 dry season campaign, whereas in the 2005 and 2006 wet season campaigns, it accounted for 37% and 35% respectively. The EC/TC ratio was lower in the 2005 dry season campaign than in the two wet season campaigns; this may be due to an increased contribution from secondary organic aerosol (SOA) in the dry season. As is commonly found in the elemental analysis of PM samples, the elements of crustal origin (such as Al, Si, Ca) exhibited larger concentrations than the anthropogenic elements. It is noteworthy, though that some typical anthropogenic elements, such as Zn and Pb, exhibited 20 - 70 times higher median PM₁₀ levels at Dar es Salaam than at Morogoro, suggesting strong local sources for these

elements in Dar es Salaam. Relation of the aerosol data to the meteorological data showed that there was some influence of wind speed and of precipitation on the aerosol concentration and composition.

For reconstituting the gravimetric PM mass, eight aerosol types were considered. Organic matter and crustal matter were the dominant aerosol types in the PM₁₀ size fraction; they explained on average 37 and 33% of the PM mass, respectively, at Dar es Salaam. Also at Morogoro the PM₁₀ aerosol consisted mainly of organic matter (48%) and crustal matter (36%).

Using non-crustal, non-sea-salt K as an indicator for biomass burning it was attempted to estimate the contribution from two different biomass burning sources to the OC at Morogoro, but the results were not very satisfactory. For Dar es Salaam, the OC was apportioned to its contributions from charcoal burning and traffic. It appeared that, on average, around 70% of the OC originated from traffic and 30% from charcoal at this site.

Principal component analysis (PCA) with VARIMAX rotation was applied to further identify the sources and source types for the 2005 dry season campaign at Dar es Salaam. Seven components were identified for the fine size fraction, i.e., a mixed crustal/traffic component, a mixed biomass burning/secondary species component, sea spray, three single-element components (i.e., with Zn, Cu, and Pb), and a secondary nitrate component. In the coarse size fraction, only five components were identified; they were the same as for the fine fraction, with the exception of the biomass burning and Cu components.

SAMENVATTING

Er werden drie aerosolmonsternemingscampagnes verricht op twee locaties in Tanzania. De campagnes gingen door in het natte en droge seizoen vanaf mei 2005 tot en met mei 2006. De locaties waren in Dar es Salaam en in Morogoro, ongeveer 200 km ten westen van Dar es Salaam. In Dar es Salaam gebeurde de aerosolmonsterneming op het balkon van de tweede verdieping van het gebouw van de “Young Women’s Christian Association of Tanzania” (YWCA) in de Azikiwe straat in Posta Mpya. In Morogoro was de monsternemingsapparatuur geplaatst op een dak in de hoofdcampus van de “Sokoine University of Agriculture” (SUA); deze locatie ligt aan de westelijke voet van het Uluguru gebergte. Het was de bedoeling van het project de atmosferische aerosolen in de omgevingslucht te karakteriseren en hierbij de nadruk te leggen op de koolstofhoudende componenten en op chemische massa “closure”. Er werden drie verschillende monsternemingsapparaten ingezet, nl. een Gent PM10 “stacked filter unit” (SFU) collector met twee sequentiële Nuclepore polycarbonaatfilters, waardoor het aerosol in grote (2-10 μm diameter) en fijne ($<2 \mu\text{m}$) deeltjesgroottefracties werd gescheiden, en PM2.5 en PM10 tandemfiltercollectoren met twee voorgebakken Whatman QM-A kwartsvezelfilters in serie. Naargelang het seizoen en de locatie, werden ofwel 24-uur collecties of afzonderlijke dag- en nachtcollecties verricht. De monsters werden geanalyseerd voor de deeltjesmassa (PM), totale koolstof (TC), organische koolstof (OC), elementaire carbon (EC), wateroplosbare organische koolstof (WSOC), zwarte koolstof (BC), belangrijke anorganische kationaire en anionaire species en 28 elementen (van Na tot Pb).

De PM werd bepaald door de filters te wegen vóór en na monsterneming met een microbalans (met gevoeligheid van 1 μg). De filters werden vóór de weging gedurende 24 uur geconditioneerd in een lokaal met een relatieve luchtvochtigheid van 50% en een temperatuur van 20 °C en de wegingen zelf gebeurden onder dezelfde voorwaarden. TC, OC en EC werden bepaald door een 1.5 cm^2 sectie van elke kwartsvezelfilter te analyseren met een thermo-optisch transmissie-instrument van Sunset Laboratory en daarbij het standaard Gent thermisch evolutieprotocol aan te wenden.

Voor de bepaling van WSOC werd ook gebruik gemaakt van een 1.5 cm² sectie van elke kwartsvezelfilter. De filtersectie werd in een polystyreenbuis van 15 mL gebracht, er werd 5 mL Millipore Simplicity water toegevoegd en de buis werd gedurende 5 min met de hand geschud, waarna men ze gedurende 30 min liet staan. Het waterextract werd gefiltreerd door een injectiespuitfilter en dan met een TOC-V CPH Shimadzu instrument geanalyseerd voor wateroplosbare totale koolstof en anorganische koolstof. Totale wateroplosbare organische koolstof werd bekomen door de anorganische wateroplosbare koolstof af te trekken van de totale wateroplosbare koolstof, en dit verschil werd aangewend als WSOC.

Eén helft van elke Nuclepore polycarbonaatfilter werd geanalyseerd voor belangrijke wateroplosbare anorganische ionen door middel van ionenchromatografie (IC). Hierbij werd gebruik gemaakt van een Dionex 4500i apparaat met een op een PC-gebaseerd AutoIon (AI-450) data-acquisitie- en analysesysteem. De filterhelft werd in een polystyreenbuis van 15 mL gebracht en gedurende 1 uur ultrasoon geëxtraheerd met 5 of 10 mL Millipore Simplicity water. Voor de bepaling van de anionen werden een IonPac AG12A beschermkolom en een IonPac AS12A analytische kolom aangewend. Het eluent (de mobiele fase) bestond uit een buffer van 2.7 mM natriumcarbonaat/0.3 mM natriumbicarbonaat (isocratisch) en het eluentdebiet was 1 mL min⁻¹. De kationen werden bepaald met gebruik van een IonPac CG12 beschermkolom en een IonPac CS12 analytische kolom; 20 mM methaansulfonzuur (MSA) (isocratisch) werd aangewend als mobiele fase bij een debiet van 1 mL min⁻¹. ASRS Ultra II en CSRS Ultra II autosuppressoren, die werkten in de autosuppressie mode, werden respectievelijk gebruikt voor de anionen en kationen en de metingen gebeurden met een geleidbaarheidsdetector.

Eén kwart van de overblijvende helft van elke Nuclepore polycarbonaatfilter werd aangewend voor de bepaling van de elementaire samenstelling van het aërosol. Hiervoor werd beroep gedaan op deeltjesgeïnduceerde X-straalesspectrometrie (PIXE). Voorafgaand aan de PIXE analyse werd BC bepaald met een eenvoudige lichtreflectietechniek. De PIXE analyse van de monsters werd verricht met een compact cyclotron, dat is geïnstalleerd in het Instituut voor Nucleaire Wetenschappen van de Universiteit Gent. Voor de metingen werd gebruik gemaakt van een invallende

protonenbundel van 2,4 MeV; de bundelstroom op het monster was typisch 150 nA en de geïntegreerde bundelintensiteit 100 μC . De X-straling, die door het monster werd uitgezonden, werd gemeten met een Si(Li) detector.

De bepaling van de PM, OC en WSOC voor aerosolen wordt beïnvloed door zowel positieve als negatieve monsternemingsartefacten. De artefacten zijn in bepaalde mate afhankelijk van het aangewende filtertype. Terwijl algemeen wordt aangenomen dat positieve artefacten overwegen bij kwartsvezelfilters, zijn bij het gebruik van Nuclepore (of Teflon) filters negatieve artefacten mogelijk. De grootte van de artefacten voor de PM_{2.5} en PM₁₀ tandemfilteropstellingen met kwartsvezelfilters werd nagegaan. Het bleek dat 13% van de PM₁₀ massa, die wordt gecollecteerd op de “front” (eerste) filter mogelijks te wijten is aan positieve artefacten. Voor wat de PM₁₀ OC betreft, was de massa op de “back” (tweede) filter ongeveer 6% van deze op de “front” filter voor de monsters van Dar es Salaam; het overeenkomstig percentage voor de monsters van Morogoro was ongeveer 6-13%. De “back” filter OC massa was gemiddeld gezien verantwoordelijk voor ongeveer één derde van de PM op de “back” filters, wat suggereert dat deze laatste ook beïnvloed wordt door niet-koolstofhoudende componenten. Er moet echter worden opgemerkt dat OC met duidelijk betere precisie kon worden bepaald dan de PM voor de kwartsvezelfilters.

Voor de landelijke locatie in Morogoro waren de mediaanwaarden van de PM₁₀ massa in de campagnes van het 2005 natte seizoen, het 2005 droge seizoen en het 2006 natte seizoen respectievelijk 23, 45 and 13 $\mu\text{g}/\text{m}^3$. De bijdrage van de PM in de fijne (PM₂) fractie tot de PM₁₀ massa was gemiddeld 35, 49 en 37%, in de drie campagnes. De meeste elementen waren vooral geassocieerd met de grove deeltjesgroottefractie; belangrijke uitzonderingen waren niet-zeezout S, K en Pb, wat suggereert dat deze drie elementen vooral afkomstig waren van antropogene bronnen. Voor de meeste aerosolcomponenten werden hogere concentraties waargenomen in de campagne van het droge seizoen dan in de twee natte seizoen campagnes. Dit wordt toegeschreven aan een hogere impact van biomassaverbranding en opgewaaid bodemstof tijdens het droge seizoen.

Voor de Dar es Salaam straatzijde locatie werden ook seizoenverschillen waargenomen voor de meeste aerosolcomponenten, met hogere niveaus in de droge

seizoen campagne dan in de natte seizoen campagnes. Zoals verwacht, vertoonden de meeste componenten hogere concentraties op de Dar es Salaam straatzijde locatie dan op de landelijke Morogoro locatie. Verder bleek dat de concentraties van de meeste species in Dar es Salaam een sterk dag-nacht patroon vertoonden, met 3- tot 5-maal hogere niveaus tijdens de dag dan tijdens de nacht. In Dar es Salaam waren de mediaanwaarden voor de PM₁₀ massa in de drie campagnes (2005 nat, 2005 droog, 2006 nat) respectievelijk 46, 58 en 40 $\mu\text{g}/\text{m}^3$. TC was verantwoordelijk voor 29% van de PM₁₀ massa in de 2005 droge seizoen campagne, tegenover respectievelijk 37% and 35% in de 2005 en 2006 natte seizoen campagnes. De EC/TC verhouding was lager in de 2005 droge seizoen campagne dan in de twee natte seizoen campagnes; dit werd mogelijks veroorzaakt door een grotere bijdrage van secundair organisch aerosol (SOA) in het droge seizoen. Zoals over het algemeen wordt waargenomen bij de elementanalyse van aerosolmonsters, kwamen de elementen van aardkorstoorsprong (zoals Al, Si, Ca) in hogere concentraties voor dan de antropogene elementen. Het is waard te vermelden dat bepaalde typische antropogene elementen, zoals Zn en Pb, 20- tot 70-maal hogere mediaanwaarden in PM₁₀ vertoonden in Dar es Salaam dan in Morogoro, wat suggereert dat er sterke lokale bronnen voor deze elementen aanwezig waren in Dar es Salaam. Door de aerosolgegevens in verband te brengen met meteorologische gegevens kon worden besloten dat de windsnelheid en precipitatie een bepaalde invloed hadden op de aerosolconcentratie en –samenstelling.

Om de gravimetrische PM te reconstrueren, werden acht aerosoltypes ingesloten. Organisch materiaal en bodemstofachtig materiaal waren de dominante aerosoltypes in de PM₁₀ deeltjesgroottefractie; ze droegen gemiddeld voor respectievelijk 37 en 33% bij tot de PM₁₀ massa in Dar es Salaam. Ook in Morogoro bestond het PM₁₀ aerosol vooral uit organisch materiaal (48%) en bodemstofachtig materiaal (36%).

Door gebruik te maken van niet-aardkorst, niet-zeezout K als indicator voor biomassaverbranding werd getracht de bijdragen tot de OC te berekenen van twee verschillende types van biomassaverbranding voor Morogoro, maar de resultaten waren niet bevredigend. Voor Dar es Salaam werd de OC toegewezen aan bijdragen van houtskoolverbranding en het verkeer. Het bleek dat voor deze locatie gemiddeld ongeveer 70% van de OC afkomstig was van het verkeer en 30% van houtskoolverbranding.

Principal componentanalyse (PCA) met VARIMAX-rotatie werd aangewend om de bronnen en brontypes nader te onderzoeken voor de 2005 droge seizoencampagne in Dar es Salaam. Voor de fijne deeltjesgroottefractie werden zeven componenten geïdentificeerd, nl. een gemengde bodemstof/verkeerscomponent, een gemengde biomassaverbranding/secundaire species component, zeezout, drie single-element componenten (nl. met Zn, Cu en Pb) en een secundaire nitraatcomponent. In de grove fractie werden slechts vijf componenten geïdentificeerd; het waren dezelfde componenten als voor de fijne fractie met uitzondering van de biomassaverbranding en Cu componenten.

APPENDIX: Curriculum Vitae and Publications**Curriculum Vitae**

Stelyus L. Mkoma was born on the 30th of August 1970 in Dar es Salaam, Tanzania. He married to Judith in May 2000 and they have one son by the name Macaureus. He attended ordinary level studies at Kwirow Secondary School (1986-1989) and advanced level studies at Mzumbe High School (1990-1992, major subjects: Physics, Chemistry and Biology) both located in the Morogoro region. In 1998, he completed his Bachelor of Science with Education (B.Sc. Ed. Hons, in Chemistry, Biology and Education) at the University of Dar es Salaam, Tanzania, and in 2001, he graduated with a Master of Science (M.Sc. in Environmental Sciences) degree also at the University of Dar es Salaam, Tanzania. He served as an education officer at Benjamin William Mkapa High School for 3 years before joining Sokoine University of Agriculture (SUA), Faculty of Science, as an Assistant Lecturer in April 2003. He started his PhD in January 2004 at Ghent University, Institute for Nuclear Sciences, Department of Analytical Chemistry (Ghent, Belgium), in the framework of the VLIR Interuniversity Collaboration Programme with SUA under the supervision of Prof. Dr. Willy Maenhaut. He has papers in preparation for publication in international refereed journals. He has attended and made contributions to international conferences. His research interests are in atmospheric aerosols, climate change and health effects. His permanent address is Faculty of Science, Sokoine University of Agriculture, P.O. Box 3038, Morogoro. Tanzania. E-mail: stelyus@yahoo.com (or: mkoma@suanet.ac.tz)

Publications in international refereed journals

1. S.L. Mkoma, W. Maenhaut, X. Chi, W. Wang, and N. Raes. 2008. Characterisation of PM₁₀ atmospheric aerosols for the wet season 2005 at two sites in Tanzania, East Africa. *Atmospheric Environment*, submitted.

Publications in proceedings of international conferences

1. W. Maenhaut, N. Raes, and S. Mkoma. Atmospheric levels and elemental composition of fine and coarse aerosols during wet and dry season campaigns at two sites in Tanzania. Proceedings of the XI International Conference on PIXE and its Analytical Applications, Puebla, Mexico, May 25-29, 2007, Editors J. Miranda, J.L. Ruvalcaba-Sil and O.G. de Lucio, Universidad Nacional Autónoma de México (2007), Paper PI-28, 4 pages (published on CD-rom). (ISBN: 978-970-32-5115-5).

Abstracts of presentations at international conferences

1. S. Mkoma, X. Chi, W. Wang, N. Raes, and W. Maenhaut. Aerosol chemistry, aerosol chemical mass closure, and aerosol sources at two sites in Tanzania. European Aerosol Conference 2007, Salzburg, Abstract T01A038. (published on CD rom).
2. W. Maenhaut, N. Raes, and S.L. Mkoma. Atmospheric levels and elemental composition of fine and coarse aerosols during the wet and the dry season campaigns at two sites in Tanzania. Eleventh International Conference on PIXE and its Analytical Applications, Puebla, Mexico, May 25-29, 2007, Conference Program and Abstracts, Universidad Nacional Autónoma de México, Lugo-Licon, M.F., Miranda, J., Rodríguez-Fernández, L. and Ruvalcaba-Sil, J.L. (Eds.), p. PI-28.
3. W. Maenhaut, S.L. Mkoma, W. Wang, X. Chi., and N. Raes. Aerosol chemistry and chemical mass closure at two sites in Tanzania. Atmospheric Chemistry at the Interfaces, Cape Town, Sept 2006, Joint IGAC/CACGP/WMO Symposium, 17-22 September 2006, Cape Town, South Africa, p. 313. (published on CD-rom).
4. W. Wang, S.L. Mkoma, M. Viana, X. Chi, J. Cafmeyer, N. Raes, and W. Maenhaut. Aerosol chemical mass closure during 2004 winter and summer sampling campaigns in Ghent, Belgium. Abstracts of the European Aerosol Conference 2005 (EAC 2005), 28 August - 2 September 2005, Ghent, Belgium, Maenhaut, W. (Ed.) 2005, Abstract no. 564. (ISBN: 9080915939).