Continuous Real-Time Measurement of the Chemical Composition of Submicron Aerosol Particles in Kigali City Using Aerosol Chemical Speciation Monitor (ACSM)

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Declaration

I declare that this Dissertation contains my own work except where specifically acknowledged

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ABSTRACT

Three weeks of recording data from 29th April to 20th May, 2018 by Aerosol Chemical Speciation Monitor (ACSM) allowed for identifying, with a precise amount in $\mu g m^{-3}$, the chemical composition of non-refractory submicron aerosol particles (NR-PM_1) emitted in Kigali city.

Results revealed that average cumulative mass concentration of PM_1 during the study period was $0.99 \pm 0.69 \mu g m^{-3}$, and the most abundant component of PM_1 was organic aerosol with 85.57%, followed by ammonium (6.2%), nitrate (5.41%), sulfate (1.59%) and chloride (1.21%). The highest PM_1 concentration was $4.01 \mu g m^{-3}$, whereas its lowest concentration was $0.01 \mu g m^{-3}$.

Source apportionment of OA was carried out by applying positive matrix factorization (PMF) to the ACSM organic aerosol mass spectra. Three sources were identified: Hydrocarbon-like Organic Aerosol (HOA), Oxygenated Organic Aerosol (OOA) and Biomass-Burning Organic Aerosol (BBOA). OOA was the dominant source with an average 49.48% of the OA mass spectra, while HOA and BBOA represented 29.58% and 20.94% respectively.

PMF results analysis indicates that the organic aerosols in kigali city are mainly emitted from the traffic, demostic cooking acitivities (i.e food cooking, meat charboiling and frying) and the oxidation of organic gaseous precursors.

In addition, correlation between PM_1 components mass concentrations and meteorological parameters was studied in this thesis. Three (Org, NO_3 and Chl) among five PM_1 components were strongly correlated with the meteorological parameters.

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KEY WORDS

PM_1 chemical composition, aerosol chemical speciation monitor, positive matrix factorization, organic aerosol

LIST OF SYMBOLS AND ACRONYMS

PM: Particulate matter

D_ρ: Aerodynamic diameter

ρ_P: Unity Density Sphere

PM_x : Particulate Matter with diameter smaller than X µm

PM_1: Particulate Matter with diameter smaller than 1 µm

NR-PM_1: Non-Refractor Particulate Matter with diameter smaller than 1 µm

$PM_{2.5}$: Particulate Matter with diameter smaller than 2.5 µm

PM_{10}: Particulate Matter with diameter smaller than 10 µm

UFP_S: Ultra-Fine Particles

ACSM: Aerosol Chemical Speciation Monitor

AMS: Aerosol Mass Spectrometer

PMF: Positive Matrix Factorization

OA: Organic Aerosol

HOA: Hydrocarbon-like Organic Aerosol

OOA: Oxygenated Organic Aerosol

BBOA: Biomass-Burning Organic Aerosol

BB: Biomass Burning

WHO: World Health Organization

AQG: Air Quality Guideline

TSP: Total Suspended Particulate

REMA: Rwanda Environment Manangement Authority

IPCC: Intergovernmental Panel on Climate Change

BC: Black Carbon

CCN: Cloud Condensation Nuclei

IC: Ice Nuclei

COPD: Chronic Obstructive Pulmonary Diseases

PAN: Peroxyacetylnitrate

LPM: Liters per Minute

ARI: Aerodyne Research Inc

amu: atomic mass unit

UPS: uninterruptible battery backed up supply

CST: College of Science and Technology

UR: University of Rwanda

RF: Response Factor

DMA: Differential Mobility Analyzer

CPC: Condensation Particle Counter

IC: Ion Current

IE: Ionization Efficiency

CE: Collection Efficiency

RIE: Relative Ionization Efficiency

WS: Wind Speed

RH: Relative Himidity

T: Temperature

LT: Local Time

UTC: Universal Time Coordinated

EPA: Environmental Protection Agency

APTI: Air Pollution Training Institute

PBL: Planetary Boundary Layer

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CHAPTER 1: GENERAL INTRODUCTION

1.1. INTRODUCTION

The aerosols, as solid and/or liquid particles suspended in the atmosphere, have significant effects on the Earth's climate, human health and environment. They influence the Earth's climate directly by scattering and absorbing both shortwave solar radiation and longwave terrestrial radiation or indirectly by changing the depth (or thickness) and albedo (amount of light reflected) of the clouds. This way, aerosol particles can contribute to cooling or warming the climate **[1, 2].** The aerosols, especially the fine particles, are closely related to human health because they deposit deep in the respiratory tract and increase respiratory diseases. The ultra-fine particles (UFPs) can penetrate deeply into the pulmonary and nervous systems which results in the pulmonary and cardiovascular diseases, and neurodegenerative disorders **[3-9]**. The aerosol particles can also have many effects on the environment such water acidification, soil eutrophication, atmospheric visibility degradation and stratospheric ozone depletion **[3, 10].** A clear understanding of the chemistry of aerosols in atmosphere is the critical importance for better quantifying these effects **[1].**

The rapid industrialization, motorization and high population density in cities are main causes of high aerosols emission **[11].** Investigation to the aerosol mass and chemical composition of non-refractory submicron aerosol particles (PM_1) using an Aerosol Chemical Speciation Monitor (ACSM), in Kigali-Capital of Rwanda, is the purpose of this study.

The sampling site in this study was selected at College of Science and Technology Campus (1°57'32.5"S, 30°03'53.2"E), University of Rwanda, and the ACSM has been deployed there since 25th January, 2018, on the roof of building approximately 10m above ground level for long-term of monitoring PM_1 components emitted in Kigali City.

The monitoring site was selected as it was located away from emission sources such as direct traffic emissions, and broadly representative of city-wide background conditions. The data considered in the period of 29th April-20th May, 2018 (3 weeks) revealed that 85% of PM_1 was organic aerosol. The remaining fraction was distributed to ammonium, nitrate, sulfate and chloride, with respective percentage of 6.2%, 5.41%, 1.59% and 1.21%.

Further investigation was applied to the PM_1 organic component by using “Positive Matrix Factorization (PMF)”as Receptor model, for identifying the main organic aerosol sources in Kigali city. The PMF results revealed the Oxygenated Organic Aerosol (OOA) which was the dominant source with an average 49.48% of the OA mass fraction, plus the Hydrocarbon-like Organic Aerosol (HOA) and Biomass-Burning Organic Aerosol (BBOA) represented 29.58% and 20.94% respectively.

1.2. PROBLEM STATEMENT AND RESEARCH RELEVANCE

To date, air pollution – both ambient (outdoor) and household (indoor) – is considered as the world’s biggest environmental risk to health, carrying responsibility for about one in every nine deaths annually. Ambient air pollution alone kills around 3 million people each year, mainly from non-communicable diseases. Only one person in ten lives in a city that complies with the WHO Air quality guidelines. Air pollution continues to rise at an alarming rate, and affects economies and people’s quality of life. Thus, it is a public health emergency.

A huge gap in monitoring and reporting air pollutants is an issue settled down in low and middle-income regions such as Africa, South East Asia and Eastern Mediterranean. The figure.1.1 shows the ACSMs distribution all over the world. Only two ACSM stations are located on the entire Africa continent: one in South Africa and another in Rwanda (has operated since January, 2018). Strengthening capacities of cities to monitor their air quality with standardized methods, reliable and good quality instrumentation, and sustainable structures is the key to be taken by public authorities, both at the national and city levels, to tackle the multisectoral challenge of addressing air pollution **[12].**

In addition to the air pollution and corresponding health effects aerosol particles are most important with respect to global climate change, as discussed in section 1.1. A clear understanding of the formation, chemical composition and transformation of aerosols in the atmosphere is of critical importance in order to better quantify these effects **[13].**

Kigali as a fast growing city in urbanization with increasing population and motorization, the air quality of its atmosphere is poor **[11].**

The studies by Nsengimana et al. (2011) and REMA, 2018 have showed that the aerosols (particulate matter) have a great contribution in Kigali city air pollution.

They have found that the PM_{10} and $PM_{2.5}$ concentrations in Kigali city greatly exceeded WHO guidelines, with their emissions attributed to both vehicles and the burning of biomass. In 2012, the heavy trucks, which make 3.4% of national vehicle fleet, were estimated to contribute to 83.4% of all total suspended particulate (TSP) emissions **[14].** Although all studies on air quality in Rwanda in this recent decade revealed the main sources of the particulate matter as well as their mass concentrations, their chemical compositions have not yet been studied. Furthermore, the types of sources contributing to the organic aerosols in Rwanda, especially in urban area (Kigali city) have not yet been identified.

Since the focus of this study is to quantify the mass concentration of chemical components of non-refractory aerosol particles of diameter less than 1 micrometer (PM_1) in Kigali city, the successful completion of this study is a foundation:

- in understanding the chemical composition of Kigali city atmosphere
- in sustaining the Kigali as cleanest city on the planet", not only in clearing land for community gardens and picking up rubbish from the streets, but also reducing the particles emitted into atmosphere.

Figure 1. 1. ACSMs distribution all over the world

1.3.RESEARCH OBJECTIVES

1.3.1. General Objective:

This study aims at measuring aerosol mass and chemical composition of non-refractory submicron aerosol particles in Kigali city. To achieve this main research objective, the following specific objectives were taken into account:

1.3.2. Specific Objectives:

- To analyze the diurnal variation of PM_1 components mass concentration in Kigali City.
- To correlate the PM_1 components with meteorological parameters such as temperature, RH and wind speed in Kigali City.
- To identify and apportion the organic aerosol sources in the study area.

1.4. RESEARCH METHODOLOGY

The data for this study are time series data. Since the main objective was to measure aerosol mass and chemical composition of non-refractory submicron aerosol particles, time series analysis was used in diurnal variation analysis. To achieve this, the ACSM data analysis software package (ACSM Local), written in Wavemetrics Igor™ (Igor Pro 7.05 32 bit) was used as data analysis tool.

1.5. THESIS STRUCTURE

The present study has been organized in five chapters and the outline of each chapter is detailed as follows: Chapter one presents an overview of the research. It includes also the problem statement and research relevance, main objectives and specific objectives. Chapter two is the literature review of the aerosol particles. The research methodology of this study is detailed in chapter three. Chapter four contains the results and their interpretation. Conclusion and recommendation for further work are presented in chapter five.

CHAPTER 2: LITERATURE REVIEW

2.1. INTRODUCTION

This chapter provides a general concept to the aerosols by offering a definition and discussing various ways of categorizing and characterizing aerosols. The sources and sinks of aerosols as well as their environmental, human health and climate effects are discussed. Reviews and discussions on the urban aerosol particles are also particularly introduced in this chapter.

2.2. GENERAL CONCEPT OF THE AEROSOLS

The suspended complex and dynamic mixture of solid and liquid particles in the atmosphere are known as (atmospheric) aerosols**[15].** They are generally considered to be the particles that range in size from a few nanometers (nm) to tens of micrometers (μm) in diameter. The aerosols are produced from natural sources, such as windborne dust, sea spray and volcanoes, and from anthropogenic activities, such as industrial and urban aerosols from fuel combustion and vehicular traffic **[16, 17]**. Despite of being natural or anthropogenic, the aerosols can be also classified into two ways:

Firstly, two classes of aerosols are distinguished base on the origin of their formation. The aerosols emitted directly from their sources into atmosphere are called Primary aerosols, while those are formed in atmosphere by gas-to-particles conversion processes are called Secondary aerosols **[16, 18]**.

Secondly, particles can be also classified on the basis of their size. The aerosol particles less than 2.5 μm in diameter are generally referred to as "fine" and those greater than 2.5 μm diameter as "coarse." The fine aerosols can be further subdivided into three modes as follows: The nucleation (or nuclei) mode comprises particles with diameters up to about 0.01 μm. The particles of size ranging from about 0.01 μm to 0.1 μm diameter are in Aitken mode. The coagulation of particles in the nuclei mode and the condensation of hot vapors onto existing particles from combustion processes form the mode called accumulation mode. Accumulation mode is extending from 0.1 μm to about 2.5 μm in diameter, and is so named because particle removal mechanisms are least efficient in this regime, causing particles to accumulate there.

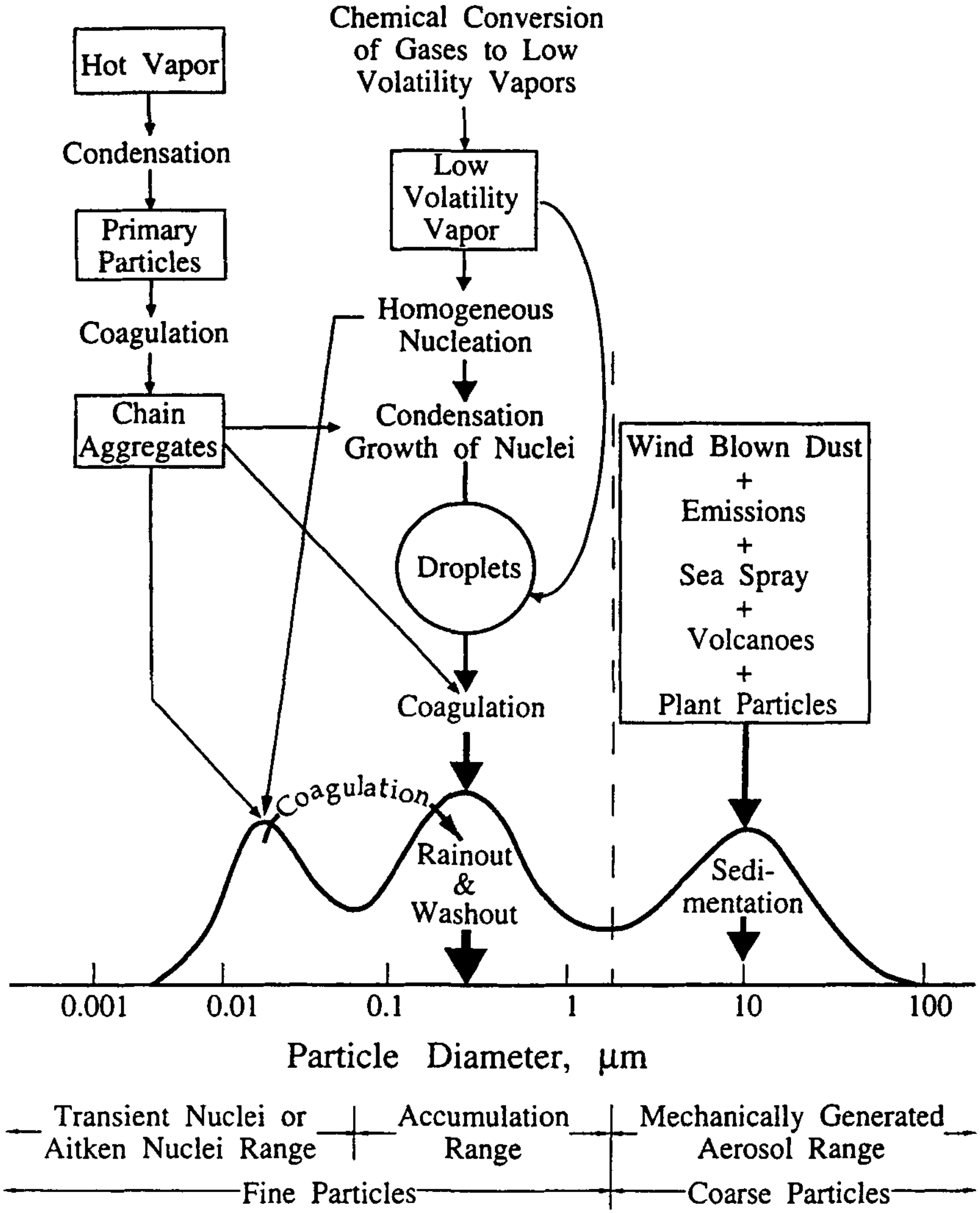


Figure 2. 1. Idealized schematic of the distribution of particle surface area of an atmospheric aerosol as function of particle diameter, showing the principal modes, sources, and particle formation processes, and removal mechanisms [16].

Aerosols are always present in the atmosphere but in extremely variable concentrations due to the very large heterogeneity in aerosol sources and their relatively short residence time in the atmosphere (of the order of hours to weeks)**.**

Due to their microscopic size, the vast majority of aerosols are not visible to the naked eye. They can be only seen in the atmosphere through their collection as soon as their concentrations are large enough. For example, a haze that reduces the atmospheric visibility and whitens the sky is nothing else than a collection of aerosol particles that interact with solar radiation. A smoke plume is, as another example, composed of microscopic particles that stem from incomplete combustion of carbonated fuels; these particles collectively darken the sky. Aerosols can also be visible when they get deposited in great quantity on the Earth's surface, as it is occasionally the case for Saharan dust particles. Furthermore, one can "see" aerosol particles one by one with the help of an electron microscope **[13].**

Once particles, both primary and secondary, are formed, their properties can be modulated in space and time by atmospheric physical and chemical processes such as condensation, evaporation and coagulation. The particles undergoing activation in the presence of water supersaturation become fog and cloud droplets **[16, 10]**. The particles smaller than 1 μm diameter generally have atmospheric concentrations in the range from around ten to several thousand per cm^3, while those exceeding 1 μm diameter are usually found at concentrations less than 1 cm^{-3} **[16]**.

Eventually, the particles are removed from the atmosphere by wet or dry deposition, with such removal occurring minutes to weeks after their release or formation, and after travelling metres to thousands of kilometres **[10]**.

2.3. PHYSICAL AND CHEMICAL PROPERTIES OF AEROSOLS

2.3.1. Physical properties of aerosols

Physical properties such as number concentrations, size, surface area, mass, morphology, shape and mixing states are fundamental parameters of aerosol particles, but usually not directly measured or readily available. These physical properties combined with the chemical, aerodynamic and optical properties are important to the aerosols role in atmospheric processes **[18, 19]**.

The most important physical property is size of particle. Particle size reflects the nature of source of the particles **[19, 20].** For example different types of dusts from construction, road and soil are predominantly in PM_{10} size range, while combustion particles are dominated by the $PM_{2.5}$ size range **[21].** Particle size also relates to their health effects including to their aesthetic and climatic effects via their light scattering properties. Size of particulate matter covers a wide range between approximately 0.002 µm to 100 µm, however the most important particles with respect to atmospheric chemistry and physics are in the 0.001 – 10 µm. Size is often expressed in terms of effective diameter, which depends on a physical rather than a geometric property. The most commonly used effective diameter is the aerodynamic diameter, D_p, which is defined as the diameter of the unit density (ρ_p = 1 g cm^{-3}) sphere that has the same settling velocity as the particle being measured **[19].**

Terms often used to describe the aerosol mass concentration include total suspended particulate matter (TSP) and PM_x. PM_x stands for Particulate Matter with diameter smaller than x µm, and the most known PM_x are PM_1, $PM_{2.5}$ and PM_{10}. TSP refers to the mass concentration of atmospheric particles smaller than 40-50 µm, while $PM_{2.5}$ and PM_{10} are routinely monitored **[16]**.

The aerosol particles can have various shapes and morphologies. The shape of particles determines their optical properties, and it affects also the area in contact with the surface they are deposited upon, including cell membranes. The morphology and composition of these particles may change through several processes, including vapour condensation, evaporation and coagulation; whereas the structure of particles is usually a result of the chemical interactions and reactions during the transportation from their sources to the receptor sites **[20]**.

2.3.2. Chemical properties of aerosols

Based on their size (as discussed in section 2.2), the aerosol particles are generally classified into two modes: namely fine particles, those are with diameter less than 2.5 μm and coarse particles, those are with diameter greater than 2.5 μm. Particles from specific sources can fall into characteristic size ranges and, therefore, particle composition can vary with particle size, reflecting this effect. For example, sulphate arising from the oxidation of SO_2 is typically present in fine particles, whereas silicon from the re-suspension of soils and surface dusts is normally found in coarse particles.

In general, the predominant chemical components of PM are sulphate, nitrate, ammonium, sea salt, mineral dust, organic compounds and black or elemental carbon, each of which typically contributes about 10–30% of the overall mass load. The predominance of these chemical components in PM_{10} and $PM_{2.5}$ and their size distribution are closely linked to the emitting source and the formation mechanisms of the particles. Below are the major components of PM and the details on how they are formed:

1. **Sulphate**: it arises primarily as a secondary component from atmospheric oxidation of SO_2;
2. **Nitrate**: typically present as NH_4NO_3, resulting from the neutralization of HNO_3 vapour by NH_3, or as sodium nitrate ($NaNO_3$), due to displacement of hydrogen chloride from NaCl by HNO_3 vapour;
3. **Ammonium**: usually present in the form of ammonium sulphate ($(NH_4)_2SO_4$) or NH_4NO_3;
4. **Sodium** and **chloride** formed from sea salt;
5. **Elemental carbon**: formed during the high-temperature combustion of fossil and biomass fuels;
6. **Organic carbon** (carbon in the form of organic compounds): could be either primary, resulting from automotive or industrial sources, or secondary, resulting from the oxidation of volatile organic compounds;
7. **Mineral components**: mainly present in the coarse fraction and rich in elements such as aluminium, silicon, iron and calcium;

(8) **Water** may also be present within, for example $(NH_4)_2SO_4$, NH_4NO_3 and NaCl. The water soluble components can take up water from the atmosphere at high relative humidity, thereby turning from crystalline solids into liquid droplets.

In addition to these above major components, there are many minor chemical components present in airborne particles depending on the detection limit, sensitivity of the analytical procedure to determine their concentrations. Minor components comprise the trace metals (lead, cadmium, mercury, nickel, chromium, zinc and manganese) which are used in metallurgical processes or in industrial products, and the trace organic compounds. Although the total mass of organic compounds can comprise a significant part of the overall mass of particles, it is made up of a very large number of individual organic compounds, each of which is present at a very low concentration **[10, 19, 20]**.

2.4. SOURCES, LIFETIME AND SINKS OF AEROSOLS

2.4.1. Sources of aerosols:

Aerosols originate from a wide variety of natural and anthropogenic sources. Within both natural and anthropogenic sources, we find primary and secondary sources. This classification is only based on the aerosols formation processes (as discussed in General concept on aerosols). Oceans and dry continental regions are the two main natural sources of atmospheric aerosol. A large amount of water droplets and sea salts are released to the atmosphere through sea spray and air bubbles at the surface of the seas. As a water droplet evaporates, the salt is left suspended into the atmosphere forming a maritime aerosol particle (e.g. sodium-chloride (NaCl), magnesium sulphate ($MgSO_4$)). Other major source of primary particles is the windblown mineral dust from dry continental area, like deserts and semi-arid regions. Further natural sources are volcanic ash, clay particles from soil erosion and biological materials (plant debris, pollen etc.). Additionally, different particles are formed by anthropogenic activities, like biomass burning, combustion of fossil fuel, industrial activities, nonindustrial fugitive sources (roadway dust from paved and unpaved roads, wind erosion of cropland, construction), and transportation sources such as automobiles **[22, 16].**

2.4.2. Lifetime of aerosols:

The aerosol lifetime or residence time is, by definition an averaging time of how long the aerosol particle will stay in the atmosphere before it is removed **[16]**. Once emitted, aerosols and aerosol precursors undergo a number of atmospheric processes such as to grow by vapor condensation or by coagulation with other particles. After undergoing these atmospheric processes, the particles are removed by dry or wet deposition processes. Small particles have lifetimes of days in the troposphere while large particles (D_p> 20 µm) are removed in a matter of hours (i.e the bigger the particles are, the shorter lifetime they have). The particles lifetimes in the stratosphere are 1-2 years, compared with 1-2 weeks in the lower troposphere. Thus, the lifetime of aerosol particles in the atmosphere depends on the altitude and the sizes **[12, 13, 15, 20].**

2.4.3. Sinks of aerosols:

Once particles are in the atmosphere, their size, number, and chemical composition are changed by several mechanisms until ultimately they are removed by natural processes **[16, 15]**. The process by which aerosols collect or deposit themselves on solid surfaces, with causing a decrease in their atmospheric concentration is called Deposition. Two main types of deposition are distinguished: wet deposition and dry deposition.

Wet deposition: The aerosols are incorporated into cloud droplets and transported to the ground by precipitation. Wet deposition is the main sink of atmospheric aerosol particles. In an annual global mean, about 80–90% of aerosol particles are removed from the atmosphere by wet deposition. Remaining part of particles is removed by dry deposition.

Dry deposition: The aerosols are directly transferred from atmosphere to the Earth's surface and proceeds without the aid of precipitation. Dry deposition may be caused by different ways such as gravitational settling (sedimentation), turbulent diffusion, impaction, interception and diffusion or Brownian motion **[16, 17, 22].**

In addition, the type of aerosols removal mechanism from atmosphere depends on their size and altitude at which they are.

For example, very close to the ground, the main mechanism for particle removal is gravitational settling on surfaces; whereas at altitudes above about 100 m, precipitation scavenging is the predominant removal mechanism **[16]**.

Small particles may diffuse to surfaces or serve as nucleation sites for raindrops (rainout) whereas larger particles may be swept out by falling rain or snow (washout) **[15].**

2.5. URBAN AEROSOLS

As said in section 2.2, the aerosols sources are classified into types based on their origin: natural and anthropogenic sources. On global scale the natural sources exceed the anthropogenic sources by a wide margin, although the urban aerosol is dominated by the anthropogenic sources. The anthropogenic sources are globally smaller (less than 10 to 50%) in amount than the natural sources, but are concentrated in a small portion of globe such as industrialized regions, with some of them are located in cities. In these areas, the human contribution exceeds that from natural sources. The urban aerosol that found in the lowest kilometer of the atmosphere over large cities has mass concentrations ranging from a few tens of μgm^{-3} to 1 mgm^{-3}during air pollution episodes in heavily polluted cities in developing countries **[15]**; while in urban areas of developed countries, the fine (PM_1 and $PM_{2.5}$) and coarse (PM_{10}) particles concentrations vary respectively in the range of 10-40 μgm^{-3} and 30-50 μgm^{-3}, with higher values during the cold season. These higher concentrations observed during the cold season are generally due to the higher emissions also affected by residential heating and accumulation of pollutants in the shallow boundary layer and consequent lack of dispersion **[17]**.

The horizontal distribution of aerosol concentration in urban areas varies greatly, depending on the proximity to natural and anthropogenic sources. Atmospheric stability and the thickness of the mixing layer (usually 0-2km) also affect local concentrations.

The particle size distribution of urban aerosol is complex (mixture of aerosols from various sources) and is commonly presented in terms of three modes: the nuclei, accumulation and coarse particle modes. Each mode has different sources, size range, formation mechanisms, and chemical compositions. The nuclei and accumulation modes together constitute fine particles.

The later contains from 1/3 to 2/3 of the total mass, with the remainder in the coarse particle mode. The ratio varies according to the region of the country. Fine and coarse-particles have different chemical compositions, sources, and lifetimes in the atmosphere (as discussed in 2.3.2).

Because there is little mass transfer between the fine and coarse particles, they exist together in the atmosphere as two chemically distinct aerosols. As group, the fine particles are acidic and contain most of the sulfates, ammonium compounds, hydrocarbons, elemental carbon (soot), toxic metals, and water in the atmosphere. Whereas the coarse particles are basic and contain most of the crustal materials and their oxides, such as silicon, iron, calcium, and aluminum, as well as large sea salt particles and vegetation debris **[15]**.

Furthermore, the highest values of fine particle concentration in the urban area are found at curbside locations, where $PM_{2.5}$ levels can be as high as twice the urban background. Curbsides are characterized by higher concentrations of BC, OA, and mineral dust. BC and OA are emitted by vehicle as engine exhaust, while mineral dust is produced by re-suspension of soil dust from road pavement abrasion.

Coarse particle concentration in urban background and curbside locations are about 5–20 μgm^{-3}, and are mainly composed by mineral dust, produced by nonexhaust vehicle emissions, that is, particulate matter from the abrasion of tire wear, break wear, road wear, and road dust suspension **[17]**.

Kigali, case study of this thesis, is fast growing city in urbanization with increasing population and motorization. Prior studies have showed that the particulate matter have a great contribution in Kigali city air pollution. They have found that the PM_{10} and $PM_{2.5}$ concentrations in Kigali city greatly exceeded WHO guidelines, with their emissions attributed to both vehicles and the burning of biomass. In 2017, the $PM_{2.5}$ and PM_{10} concentrations in Kigali city were respectively 133 μgm^{-3} and 156 μgm^{-3}. The mean 24 hour concentrations of $PM_{2.5}$ were therefore more than five times greater than the WHO guideline value of 25µg/m3 **[23].**

2.6. EFFECTS OF AEROSOLS

2.6.1. Climate effect:

Atmospheric aerosol particles play important role in radiation budget of the Earth's as they scatter and absorb both shortwave solar radiation and longwave terrestrial radiation. They are also highly involved in the formation of clouds and precipitation since they operate as cloud condensation and ice nuclei (CCN and IN). The measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system is called a radiative forcing; and it is measured in Wm^{-2}. The climate forcing by aerosols can be realized in two ways, basically: in direct and indirect radiative forcing.

2.6.1.1. Direct radiative forcing

This radiative forcing is due the scattering of radiation. Aerosol particles that reflect/and scatter a part of shortwave solar radiation back into the space, reducing the amount of energy that the planet Earth absorbs and therefore cooling it **[2, 22]**. This cooling effect of aerosols, especially by sulphate components may be compensated by the absorption of longwave terrestrial radiation primarily by elemental (black) carbon aerosols and dust particles. This combination of scattering and absorption of solar and terrestrial radiations is known as the "direct" effect of aerosols on the global climate. Depending on the proportion of light scattered to that absorbed, the direct effect of aerosols on global climate can lead to either cooling or warming of the atmosphere **[2].**

The global, annual mean radiative forcing still less certain and is estimated -0.4 ± 0.2 W m^{-2} for sulphate, -0.05 ± 0.05 W m^{-2} for fossil fuel organic carbon, $+0.2 \pm 0.15$ W m^{-2} for fossil fuel black carbon, $+0.03 \pm 0.12$ W m^{-2} for biomass burning, -0.1 ± 0.1 W m^{-2} for nitrate and -0.1 ± 0.2 W m^{-2} for mineral dust **[24]**. A large volcanic eruption can greatly increase the concentration of stratospheric sulphate aerosols, thereby increasing the negative radiative forcing. However, a single, large eruption can cool our atmosphere only for a few years **[22]**.

2.6.1.2. Indirect radiative forcing

Aerosol particles can also affect the radiation balance by formation of cloud droplets. Cloud droplets are formed in the troposphere by condensation of water vapour onto aerosol particles when the relative humidity exceeds the saturation level. Without these particles, a very large supersaturation (about 400%) would be necessary for the homogeneous condensation of water vapour **[22**].

As aerosol concentration increases within a cloud, the water in the cloud gets spread over many more droplets, each of which is correspondingly smaller. This has two consequences: clouds with smaller droplets reflect more sunlight, and such clouds last longer, because it takes more time for small droplets to coalesce into droplets that are large enough to fall to the ground. The latter effect has been supported by certain observations indicating that aerosols from forest fires and urban pollution can suppress rain and snow fall **[25**]. In this way, changing aerosol in the atmosphere can change the frequency of cloud occurrence, cloud thickness, and rainfall amounts. These changes in cloud droplets number concentration and size, and their longevity are respectively known as the "first" and "second" indirect effects of aerosol on climate and they are both believed to increase the amount of sunlight that is reflected into space without reaching the Earth's surface, resulting in a cooling effect **[2]**.

It was shown (IPCC, 2007) that the anthropogenic aerosols effects on water clouds through the cloud albedo effect cause a negative radiative forcing of –0.3 to –1.8 W m^{-2}.

2.6.2. Human health effect

Air pollution represents the biggest environmental risk to health. In 2012, one out of every nine deaths was the result of air pollution-related conditions. Since the aerosol particles are the main contributors to air pollution, they have an adverse effect on human health. The numerous epidemiological studies have shown that there exists an association between ambient aerosol levels and adverse health outcomes, including premature death, respiratory and cardiovascular disease, and neurodegenerative disorders **[4]**. Short-term epidemiological studies showed that the people with asthma, COPD (Chronic Obstructive Pulmonary Diseases), pneumonia, and other respiratory diseases as well as patients with cardio-vascular diseases and diabetes are affected by mortality shortly after days with high ambient particle concentrations.

To investigate the health effects of aerosol particles, it is significant to take particle size, chemical composition and number-concentrations into account, since these metrics reflect the biological mechanism through which particle pollution is thought to cause health effects. The particles size governs the site of particle deposition along the respiratory tract. Smaller particles, such as UFPs, that can penetrate deeply into the pulmonary system have serious adverse effects on human health, leading to pulmonary and cardiovascular diseases **[3, 5, 6, 7, 8].** UFPs have even been observed in the brain and central nervous system of rats. Toxicity of particles also relates to their chemical composition **[26]** and there is a significant amount of evidence showing an association between the chemical composition of aerosol particles and their health outcomes **[26, 27].**

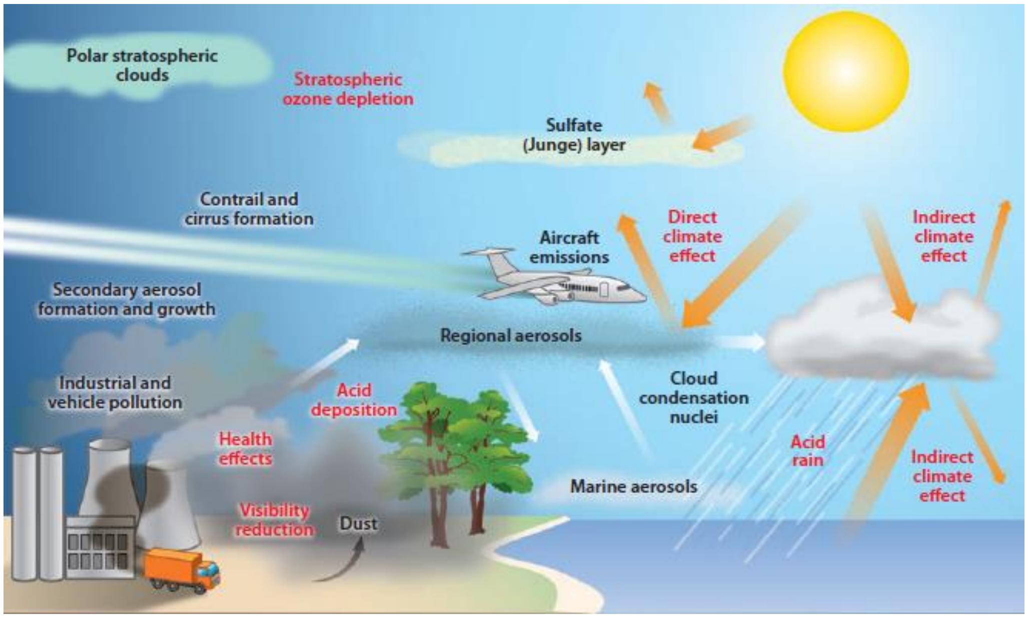


Figure 2. 2. Main sources and effects of atmospheric aerosol particles [28]

2.6.3. Environment effect

Particles of particulate matter, especially fine particles, can be carried over long distances by wind and then settle on ground or water. The effects of this settling may include: acidification, eutrophication, affecting the diversity of ecosystems and smog.

Acidification is the process whereby air pollution, mainly ammonia, sulphur dioxide and nitrogen oxides, are converted into acid substances.

These substances cause acidification of lakes and streams, and contribute to the damages of trees at high elevations and many sensitive forest soils. Moreover, acidification contributes to visibility degradation and possibly harms public health. Eutrophication is the process in which an ecosystem is disturbed by an increase of chemical nutrients.

Eutrophication occurs in soil or water and results in excessive plants growth/decay of other plants, lack of oxygen and severe reduction of water quality and animal populations. The mixture of smoke and fog or smog is the cause of a restricted visibility due to particle pollution in the air. Photochemical smog is formed when the sunlight interacts with different kinds of pollutants in the atmosphere and form harmful substances such as ozone (O_3), aldehydes and peroxyacetylnitrate (PAN) [**3**].

CHAPTER 3: MATERIALS AND METHODS

3.1. STUDY AREA DESCRIPTION:

As the largest and fastest growing city in the country, Kigali was chosen as location where the sampling study was undertaken. It is situated almost in the centre of the country, with covering a total area of about 730 km^2. Its population was estimated to be 1,318,000 in 2015, with 4.2% as an annual population change **[15].** Its geographical position is on latitude 1º 57'S and on longitude 30º 04' E **[3].**

Kigali City is built in hilly landscape sprawling across about 4 ridges and the valleys in between. The tops of the ridges have an average elevation of 1,600 meters while the valleys are around 1,300 meters. The city is almost ringed by higher hills, the highest of which is Mount Kigali, with an elevation of 1,850 meters above sea level. Because of the high altitude, Kigali has a pleasant tropical highland climate. The temperatures range from 20°C to 21.6°C year round. There are four seasons: Long rains from mid-March to mid-May, short rains from mid-September to mid-December; a long dry period from mid-May to mid-September; and a short dry season from mid-December to mid-March. Average annual precipitation is 900 mm **[20].**

Prior studies on air pollution in Kigali indicated that a fast growing population and the coherent rising rate of motorization were a reason for a sustainable degradation of the urban air quality. Poorly maintained, old mopeds, motorcycles and vehicles cause an increasing concentration of different air pollutants. Apart from the traffic emissions, the usage of simple stoves and open fireplaces are the other sources of air pollution which are representative for the developing world. Burning wood for domestic energy, cooking and household chores produce a lot of emission, indoor and outdoor. Kigali with its distinctive relief, as described above, is a good example of topographical and meteorological influences on spatial climatic modifications and the spatial distribution of air quality [**16**]**.**

Figure 3. 1. Map of study area, designed by using Arc GIS

3.2. DATA MEASUREMENT

The data for this study were the ACSM data recorded from 29th April to 20th May, 2018. The ACSM has been deployed since 25th January, 2018 by the Rwanda Climate Observatory Project, to monitor long-term records of the non-refractory submicron aerosol species (organics, nitrate, sulfate, ammonium and chloride) in real time emitted in Rwanda.

3.2.1. Instrument operational description

The ACSM is designed and built around the same technology as the larger research grade Aerosol Mass Spectrometer (AMS) but uses lower performance components and thus operates with reduced sensitivity and time resolution. However, the ACSM has sufficient sensitivity to operate as a monitoring instrument providing chemically speciated mass loadings and aerosol mass spectra at data rates up to 15 min for typical urban aerosol loadings (several $\mu g m^{-3}$ loadings). The instrument operates by sampling air into a high vacuum system through a particle aerodynamic lens.

The particle lens focuses submicron aerosol (~40-1000 nm aerodynamic diameter) into a narrow beam which is directed to a resistively heated particle vaporizer, typically operated at 600°C, mounted inside the ionization chamber of a mass spectrometer where non-refractory components in/on the particle flash vaporize on impact. The vaporized constituents are ionized by electron impact then analyzed with a quadrupole mass spectrometer which reports aerosol mass spectra (<200 amu). These spectra are used to extract the chemically speciated aerosol mass loadings.

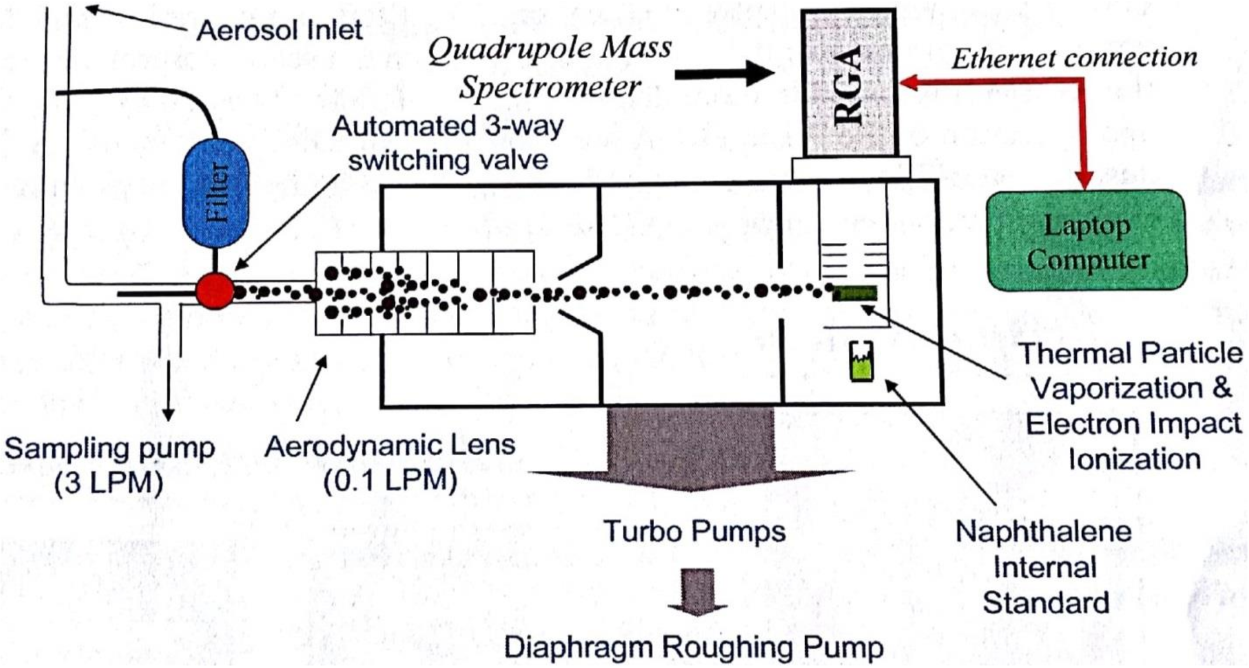


Figure 3. 2. Schematic of the ACSM operation during the sampling data (adopted from ACSM Data Acquisition Software Manual, ARI Website)

Three turbo molecular pumps provide differential pumping to efficiently separate the gas from the particle beam. A small oil free diaphragm pump is used to back the turbo pumps. An aerosol inlet system couples the particle lens flow to a larger sample flow. The flow into the ACSM through the particle lens is ~ 0.1LPM fixed by a 100µm diameter critical aperture. This rather small flow is sub-sampled from the main aerosol inlet system flow that is designed to be 3 PLM for near iso-kinetic sampling conditions. The user must supply an appropriate pump for this flow. ARI offers an optional sampling line flow controller system for this.

Since the ion source operates continuously, there is always a background mass spectra (present in the absence of any particles) which must be measured and subtracted from the particle mass spectra. This is done routinely during data acquisition by drawing the sample thru an aerosol inlet system that combines a 3-way valve and a particle filter. The position of the 3-way valve is alternately switched between filter position and sample position at the completion of each full mass scan. This results in a particle mass spectrum and a particle free mass spectrum. The difference between these two spectra contains the particle composition information. The frequent zero measurement adds to the term stability on the ACSM data sets.

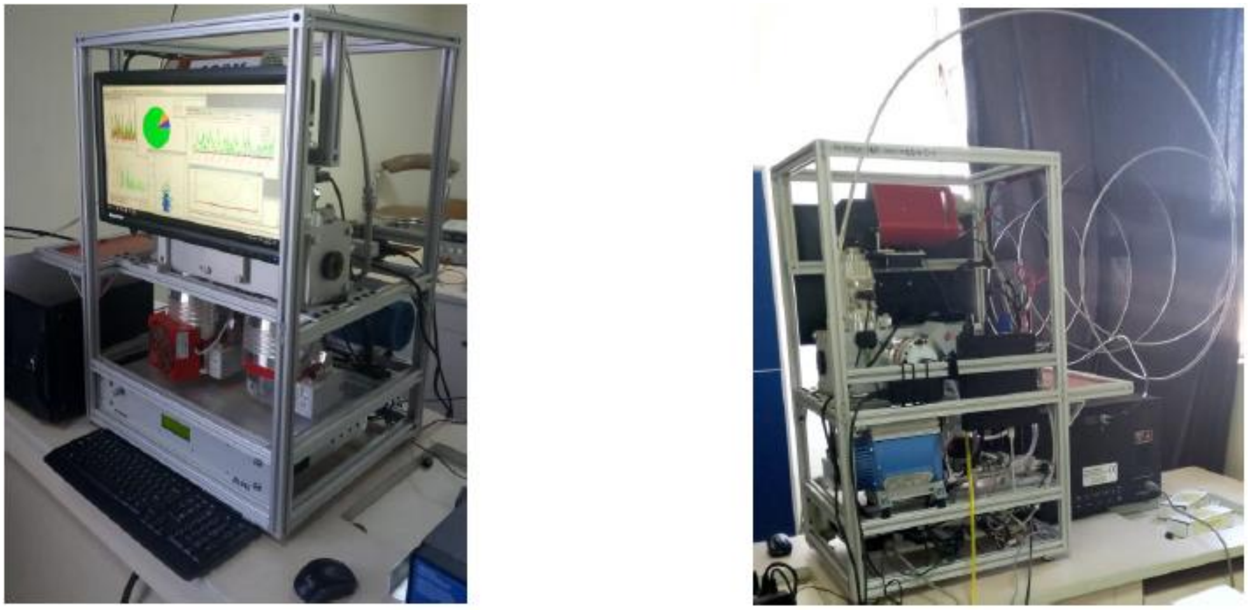
The ACSM also incorporates a small effusive source of naphthalene that is mounted in the detection region. This source provides a reference for calibration such as mass-to- charge for the amu scale, instrument stability and ion transmission through the quandrupole mass filter.

3.2.2. Instrument physical description and conditions for its operation

The ACSM stands for Aerosol Chemical Speciation Monitor. It measures aerosol mass and chemical composition of non-refractory submicron aerosol particles in real-time. It provides composition information for particulate ammonium, nitrate, sulfate, chloride, and organic species. It is designed for continuous monitoring of aerosol composition with long term (weeks) unattended operation.

The ACSM in its single bench-top frame measures 19.5"D x 28.5"W x 32.5"H (49.5 cm x72.4 cm x 82.6 cm) and weights 140 lbs (64kg). Typically a 14" laptop computer is provided with the ACSM for instrument control and data acquisition.

The ACSM requires approximately 300 Watts of power, not including a sampling pump and instrument computer, and operates on 85-260 VAC, 50/60 Hz using an auto sensing/auto-switching supply. A 65 Watts power supply delivered with the laptop operates on 100-240 VAC, 50-60Hz. An uninterruptible battery backed up supply (UPS) is recommended to protect the system against short duration power outages. The ACSM maximum ambient operating temperature is approximately 33^0C. It operates at a time resolution of about 15 min with sampling the ambient air at a total flow rate of 3 L min^{-1} [**13**].



(a) (b)

Figure 3. 3. ACSM photo taken in Air Quality and Climate Lab at CST Campus: (a) Back view, (b) front view

3.2.3. Instrument calibrations

The ACSM reports integrated aerosol mass loading in units of $\mu g m^{-3}$ at ambient pressure conditions over a user defined sampling interval (typically 30 min). To assure data quality, proper calibration and operating protocals should be followed.

The ACSM requires three fundamental calibrations which allow the measured mass spectra ion signals to be converted to aerosol mass loadings. These include:

- Ionization efficiency of the mass spectrometer necessary to convert measured ion signals to aerosols mass.
- Instrument volumetric sampling flow rate so measured mass can be normalized to the volume of air sampled during the integration period
- Mass-to-charge (m/z) calibration of the mass analyzer.

Ionization Efficiency

Calibration of the ACSM is based on determining an instrument response factor (RF) using NH_4NO_3 aerosol. Ammonium nitrate is used as the primary mass calibration species for the following reasons: (1) there is minimal fragmentation (NO^+, NO_2^+, NH^+, NH_2^+, NH_3^+), (2) it does not leave residual background levels in the vacuum system which can interfere with subsequent measurements, (3) it vaporizes with 100% efficiency, so the NO_3 ions can be quantitatively measured, (4) it is well-focused by the aerodynamic lens so that all the particles can be detected.

The calibration procedure requires generating a known mass loading using a combination of a differential mobility analyzer (DMA) and condensation particle counter (CPC). The calibration aerosol mass is calculated based on an assumed spherical particle shape of a given mobility diameter at a concentration reported by the CPC. RF_{NO3} is measured in units of amps of NO_3 signal (sum of NO^+ and NO_2^+) per $\mu g m^{-3}$ of sampled aerosol. When normalized to the volumetric sample flow rate Q_{cal} (in units of $cm^3\ s^{-1}$) and multiplier gain G_{cal} (~20,000), RF_{NO3} is proportional to the ionization efficiency of NO_3 (in units of ions/molecule) as follows:

$$IE_{NO3} * \frac{N_A}{MW_{NO3}} = \frac{RF_{NO3}}{Q_{Cal} G_{Cal}}$$

With the ACSM direct determination of the multiplier gain by measuring single ion signals is not possible owing to the slow detection electronics. The gain can be estimated based on the measured ratio of the electron multiplier signal to the Faraday cup signal (raw ion current) for a particular ion, typically m/z 28. During RF calibration (and operation), the multiplier voltage in the ACSM is set so that the gain is ~20,000.

The equation relating mass concentrations of species s from measured ion current, IC (in amps), at fragments i is as follows:

$$C_S = \frac{CE}{T_{m/z}} * \frac{10^{12}}{RIE_S} \frac{Q_{Cal} G_{Cal}}{RF_{NO3}} \frac{1}{QG} \sum_{alli} IC_{S,i}$$

In general, operating values for Q and G are similar to their respective values during calibration (Q_{cal} and G_{cal}) and so these parameters effectively cancel each other out. This equation also includes correction for m/z dependent ion transmission efficiency of the quadrupole ($T_{m/z}$) and the non-unit particle collection efficiency (CE) of the ACSM.

A typical calibration setup is shown in Figure. 3.4 and requires an atomizer, DMA, aerosol diluter and a CPC. The NH_4NO_3 aerosol generation system (DMA) should be set up so that 250-300nm mobility size particles are produced and delivered to the ACSM sampling inlet.

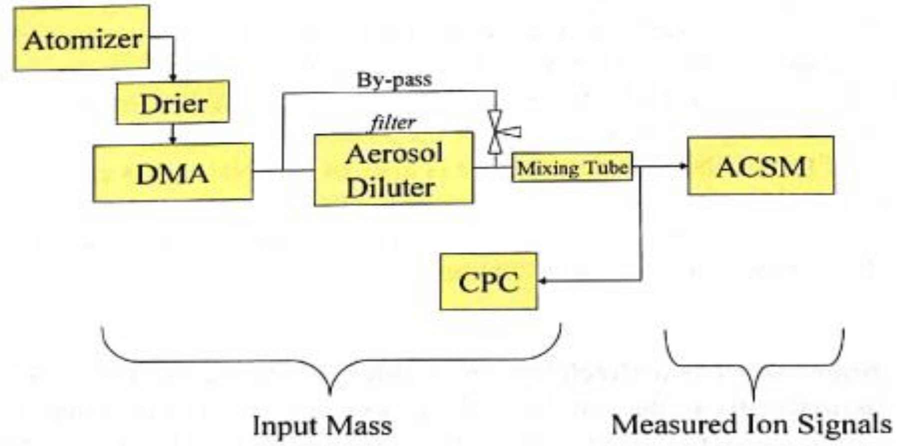
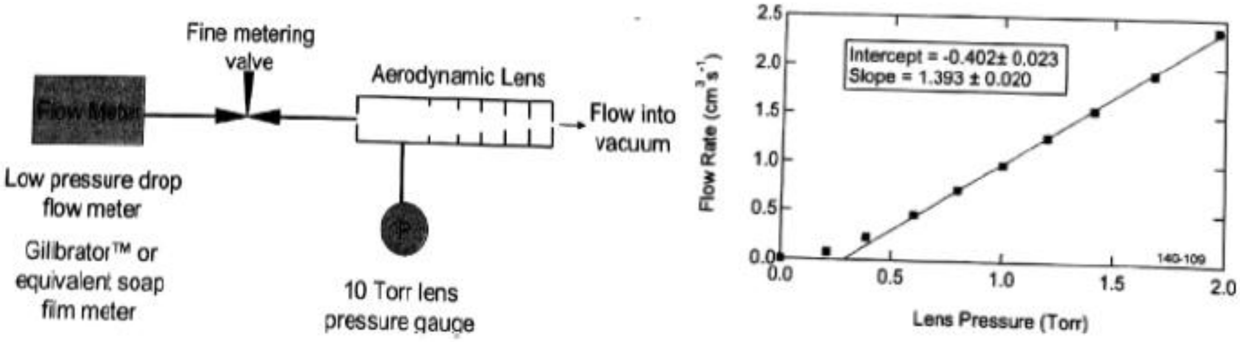


Figure 3. 4. ACSM calibration setup based on mono-disperse ammonium nitrate particle aerosol (NH_4NO_3) generation

The accuracy of this calibration depends on the accuracy of the CPC and the assumption that the aerosol is mono-disperse and that all particles counted by the CPC also reach the ACSM detector. For this reason 300 nm diameter particles are chosen and the atomizer solution concentration should not be greater than 5 mM so that the number (mass) of multiple charged larger diameter particles (of equivalent mobility diameter) is minimized. In practice, the full procedure of ACSM calibration based on ammonium nitrate is available on ARI website (www.aerodyne.com).

Flow rate calibration

The instrument volumetric sample flow rate is calibrated using a low pressure drop flow measuring device such as a Gilibrator^{TM} or soap film meter. For this procedure, the 100µm diameter sampling aperture is removed from the sampling valve on the lens tube and replaced with a fine metering valve. The particle lens pressure is recorded for different leak rates (needle valve settings). The result of a linear regression is the flow calibration. Note that the negative intercept is caused by a change in the flow regime from viscous to kinetic, the poiseuille equation no longer describes the linear flow-pressure drop relationship in the lens tube. Data points below ~0.5 torr should not be included in the regression. The flow rate into the instrument is calculated using this calibration. The particle lens pressure is a measure of the instrument flow and this signal is recorded by the data acquisition system for a continuous measure of instrument flow rate.



(a) (b)

Figure 3. 5. (a) ACSM flow rate calibration using a Gilibrator^{TM} or soap film meter. (b) Flow rate-Lens pressure linear regression

Mass-to-charge calibration

The mass-to-charge calibration of the quadrupole can be performed using the mzCal scanning mode. In practice this is a two point calibration using the N_2 (m28) and naphthalene (m128) peaks. Detail of this procedure that electronically calibrates the mass analyzer is available in ARI website.

3.3. DATA ANALYSIS

At sampling site, the ACSM has been deployed with a laptop computer which was provided for ACSM control and data acquisition. Once the ACSM data is acquired by the ACSM data acquisition software (ACSM DAQ) installed into this computer, ACSM data analysis software package (ACSM Local), written in Wavemetrics Igor™ (Igor Pro 7.05 32 bit) was used in visualizing, analyzing and presenting the ACSM data in time series approach.

Further investigation was applied to the organic components of PM_1 by using “Positive Matrix Factorization (PMF)”as Receptor model, for identifying the main organic aerosol sources in Kigali city.

Briefly PMF is expressed mathematically in the form of X = GF + E, and is called a bilinear factor analytic model because it decomposes a matrix of speciated sample data (X) into two matrices: factor contributions (G) and factor profiles (F).

In component form, we have $X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + \varepsilon_{ij}$, where:

X_{ij} represents the concentration of measured ambient species j in sample i;

p is the number of factors contributing to the measured sample and is provided to the model by the user;

f_{kj} is the concentration of species j in factor profile k;

g_{ik} is the relative contribution of factor k to sample i; and

ε_{ij} is the residual for the species j in sample i.

The elements of G and F are constrained to non-negative values only, since neither a source contribution (G) nor its composition (F) can be negative. In PMF, G and F are fit using a least squares algorithm that minimizes the $Q_m = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{\varepsilon_{ij}}{\sigma_{ij}} \right]^2$ (Q_m: the residuals squared and weighted by measurement and model uncertainty) **[29].**

CHAPTER 4: RESULTS AND DISCUSSION

4.1. PM_1 MASS CONCENTRATION AND THEIR COMPONENTS

4.1.1. Time series of PM_1 components and Pie chart

The time series of the mass concentration of the NR-PM_1 components measured by the ACSM in Kigali City are shown in Figure 1 from Addendum 1. During the study period, the average cumulative mass concentration of PM_1 components was $0.99 \pm 0.69 \mu g m^{-3}$ with an hourly average ranging from 0.39 to 1.87 $\mu g m^{-3}$. The highest PM_1 concentration was $4.01 \mu g m^{-3}$, whereas its lowest concentration was $0.01 \mu g m^{-3}$. The PM_1 components, with their average mass concentration, was organic species $0.85 \mu g m^{-3}$, nitrate $0.05 \mu g m^{-3}$, sulfate $0.02 \mu g m^{-3}$, ammonium $0.06 \mu g m^{-3}$ and chloride $0.01 \mu g m^{-3}$ (as shown in Table 1 from Addendum 2). On partitional basis, the most abundant component of PM_1 was organic aerosol with 85.57%, followed by ammonium (6.2%), nitrate (5.41%), sulfate (1.59%) and chloride (1.21%) (Figure 2 from Addendum 1).

As shown in Figure 1 from Addendum 1, all aerosol species exhibited very dynamic variations in mass concentrations. This may be resulted from the changes of source emissions, meteorological factors (such as WS, RH, T , and planetary boundary layer height), photochemical reactions, and regional transport (e.g., the BB plumes). For example, a significant diurnal variation in OA mass concentrations (Figure 3 from Addendum 1) is due to the changes of source emissions such as traffic, demostic cooking and BB emissions.

4.1.2. Diurnal variation of PM_1 components

Figure 4 (from Addendum 1) shows that OA exhibits two peaks occurring between 04:00–08:30 LT (UTC+2) and 18:00–22:00 LT. The peak in early morning hours was mainly attributed to the primary emissions during the morning traffic rush–hour. While evening peak was attributed to both traffic and demotic cooking.

These observations are in accordance with the prior studies which showed that traffic and demotic cooking contribute significantly in air pollution of Kigali city [**23**].

The average hourly mass concentration was ranging in $0.31-1.66\mu gm^{-3}$ for organic species, $0.02-0.11\mu gm^{-3}$ for nitrate, $0.01-0.02\mu gm^{-3}$ for sulfate, $0.04-0.10\mu gm^{-3}$ for ammonium and $0.00-0.03\mu gm^{-3}$ for chloride. On average total mass loading, PM_1 was between $0.39\mu gm^{-3}$ as minimum emission to $1.87\mu gm^{-3}$ as maximum emission. Furthermore, it is clearly deduced that maxima PM_1 mass concentrations are recorded during night-time and mostly during meteorological conditions favoring pollutants emission and accumulation, such as low wind speed and low temperature (as shown in Figure 4 from Addendum 1) **[30]**.

4.2. IMPACTS OF METEOROLOGICAL PARAMETERS ON PM_1 COMPONENTS

Figure 4 from Addendum 1, shows the diurnal variation of PM_1 components in the presence of different meteorological parameters (i.e WS, RH, T) during the study period. The diurnal average values were $75.29\pm11.76\%$, $2.25\pm0.80m/s$ and $22.11\pm3.90^{0}C$ for the ambient RH, WS, and T, respectively.

As depicted in Figures 4 & 8, the concentrations of organic, NO_3 and Chloride were generally negatively correlated with the temperature and wind speed; and positively correlated with the relative humidity. The concentrations of NO_3 were strongly negatively correlated with temperature and wind speed, with the **r** of -0.90 and -0.84 respectively. Strong negative correlations of the concentrations of organic species with the temperature and wind speed were observed in this study. Their coefficients of correlation are respectively equal to -0.50 and -0.65. The concentrations of Chloride was highly negatively (r=-0.62) correlated with the temperature and moderately negatively (r=-0.45) correlated with the wind speed. The correlations of these PM_1 species (Organic, NO_3 and Chloride) with relative humidity were strong positive with the **r** of 0.54, 0.87 and 0.50 respectively.

Exception was observed to the correlation of sulfate (SO_4) and ammonium (NH_4) with the meteorological parameters. SO_4 mass concentrations were moderately positively (r=0.43) correlated with the wind speed and negatively (r=-0.45) correlated with the relative humidity.

High positive correlation between the SO_4 mass concentrations and the temperature was observed in this study with r=0.56. This increase of SO_4 mass concentrations with temperature may reflect the high oxidation of SO_2 [**30**]. Through this study, the observation showed that in Kigali city there were a weak positive (r=0.09) and negative (r=-0.11) correlations of NH_4 with the wind speed and the relative humidity respectively, and no relationship with the temperature.

4.3. ORGANIC AEROSOL SOURCE APPORTIONMENT

The Figure 5 from Addendum 1, shows the time series of the main sources of OA species obtained by sources apportionment through applying the PMF techniques to the organic aerosols mass spectra obtained with ACSM. In this study three PMF factors were identified which are namely: Hydrocarbon-like Organic Aerosol (HOA), Oxygenated Organic Aerosol (OOA) and Biomass-Burning Organic Aerosol (BBOA). Results revealed that OOA was the dominant source with an average 49.48% of the OA mass fraction, while the two remaining factors HOA and BBOA represented 29.58% and 20.94% respectively.

The HOA related to the traffic sources and BBOA related to the biomass burning such as demostic heating/cooking, are both primary organic aerosl sources, while the OOA formed by oxidation of organic vapour precursors is a secondary organic aerosol source **[31-35]**. Furthermore, the evolution processes of atmospheric OA such as aging and oxidation are the sources of secondary organic aerosols. The secondary formation, atmospheric transport, and diffusion, as well as the mass loadings and oxidation state of ambient OA, can be affected by the aging processes of OA **[35]**.

From this PMF results, it may be concluded that the organic aerosols in kigali city are mainly emitted from the traffic, demostic cooking acitivities (i.e food cooking, meat charboiling and frying) and the oxidation of gaseous precursors that have already been emitted from these two first organic aerosols sources.

4.3.1 HOA+OOA and total OA Correlation

As stated earlier, the OOA was secondary organic aerosols and was formed by the oxidation of gaseous precursors that have already been emitted from the HOA and BBOA (primary organic aerosols sources). However, influence of HOA and BBOA in formation of OOA is different from one another. OOA measurements showed a high correlation with BBOA (R= 0.82) compared to that was between OOA and HOA (R= 0.70). This difference in correlation indicates that the influence in variability of OOA formation was highly caused by the emission from biomass burning sources rather than that was from traffic sources. Similar way the correlation between OA and HOA+OOA has high value (R= 0.98, R^2=96.04%) compared to those calculated between any PMF factor or combination of the two among the known PMF factors (HOA, OOA, BBOA) and OA. This high value of coefficient of determination (R^2) indicates that the variability of the OA is likely explained by HOA+OOA sources.

4.3.2. Diurnal variation of PMF Factors

Figure 7 from Addendum 1, shows the diurnal variation of PMF factors, which in turn indicate the diurnal variation of organic aerosol particles emitted from their sources, during the study period in Kigali city.

This diurnal cycle that exhibits the typical rush-hour peaks around from 04:00 to 08:00, and from 17:00 to 21:00 LT indicates an influence from vehicle emissions.

The early evening rush-hour peak show a significant high concentrations of all PFM factors compared with the early morning rush-hour peak. This observation indicates that there was an additional source (the other is traffic) contributing in the evening organic aerosols emission and which was not in the morning time. This is due to that the organic aerosols emission in the morning was only mainly attributed to the traffic sources, while evening emission was attributed to both traffic and domestic cooking sources. This observation is in accordance with the one denoted in section 4.1.2. The lower concentrations of PMF Factors observed during the daytime (around 9:00-15:00 LT) can be associated with the dilution effects of higher planetary boundary layer and reduced traffic emissions.

Furthermore, the mass concentration of organic aerosols emission from the traffic sources during the whole day was generally always higher than those from the biomass burning such as domestic cooking. Whereas, the emission from oxidation of organic vapour precursors (OOA) indicates to have a very high mass concentration compared with those from both traffic and domestic cooking, except the time from 17:30 to 20:30 the organic aerosols concentrations from traffic surpassed those from OOA.

CHAPTER: 5. CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

This study presents the first investigation in quantifying the chemical composition of non-refractory submicron aerosol particles (NR-PM_1) emitted in Kigali city. ACSM was used in recording the data from 29th April to 20th May, 2018, and the effect of meteorological parameters on diurnal variation of NR-PM_1 mass concentrations was highlighted in this study. The OA source apportionment was also studied.

The average cumulative mass concentration of NR-PM_1 during the study period was $0.99 \pm 0.69 \mu gm^{-3}$,with an hourly average ranging from 0.39 to 1.87 μgm^{-3}. The highest NR-PM_1 concentration during the study period was $4.01 \mu gm^{-3}$, whereas its lowest concentration was $0.01 \mu gm^{-3}$. On partitional basis, the most abundant component of NR-PM_1 was organic aerosol with 85.57%, followed by ammonium (6.2%), nitrate (5.41%), sulfate (1.59%) and chloride (1.21%).

Strong correlation found between the total NR-PM_1 mass concentrations and the meteorological parameters showed that the mass concentrations of NR-PM_1 were significantly affected by the changes in meteorological conditions (such as Temperature, Wind Speed and Relative Humidity). Individual NR-PM_1 components show similar correlations as total NR-PM_1 for all meteorological parameters except that the ammonium was weakly correlated with all of these parameters, chloride moderately correlated with wind speed, and sulfate moderately correlated with both wind speed and relative humidity.

PMF analysis was conducted to the ACSM organic aerosol mass spectra and resulted in the OOA as mojor source OA in kigali city with average 49.48% of the OA mass spectra, followed by HOA (29.58%) and BBOA (20.94%). These PMF results showed that the OA sources in kigali city are traffic, biomass burning like demostic cooking, and oxidation of organic gaseous procursors.

5.2. RECOMMENDATIONS FOR FURTHER STUDY

The results from this study showed that the all study objectives have been achieved. However the goodness of these results is, the study was conducted on small area of country with a small study period. Therefore, it is recommended that the study extended for a long period is needed for studying a seasonal variation of mass concentrations of NR-PM_1 components not only in Kigali city, but also in rural area of our country.

As the one of specific objectives of this study, the relationship between NR-PM_1 components mass concentrations and the three meteorological parameters (Temperature, Wind Speed and Relative Humidity) were found, and it was shown that apart from these meteorological parameters, there exist other parameters which may influence the strong variability of mass concentrations of some NR-PM_1 components such as SO_4 and NH_4. It is therefore recommended to conduct a further study on other parameters influencing the variability of NR-PM_1 mass concentrations such as wind direction and planetary boundary layer (PBL).

Addendum 1: Figures

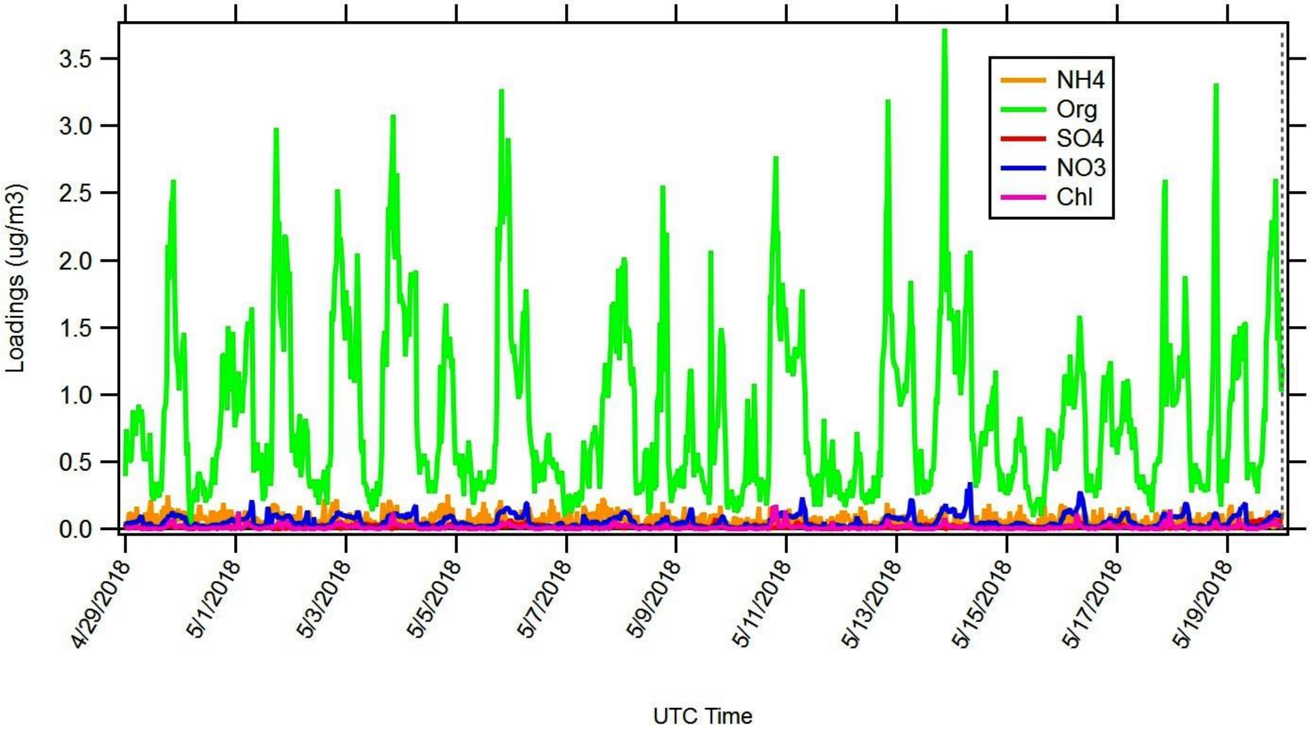


Figure 1.Time series of submicron aerosol species (i.e., organic aerosol (OA), ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), chloride (Chl)) mass concentrations measured by the ACSM

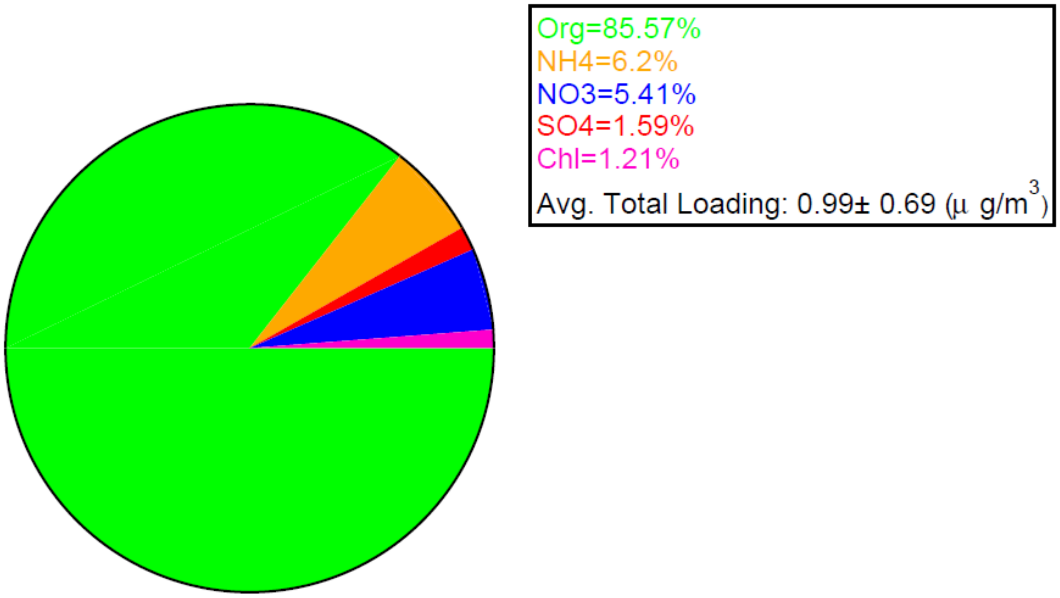


Figure 2. Percentage of PM_1 components emissions by the study period

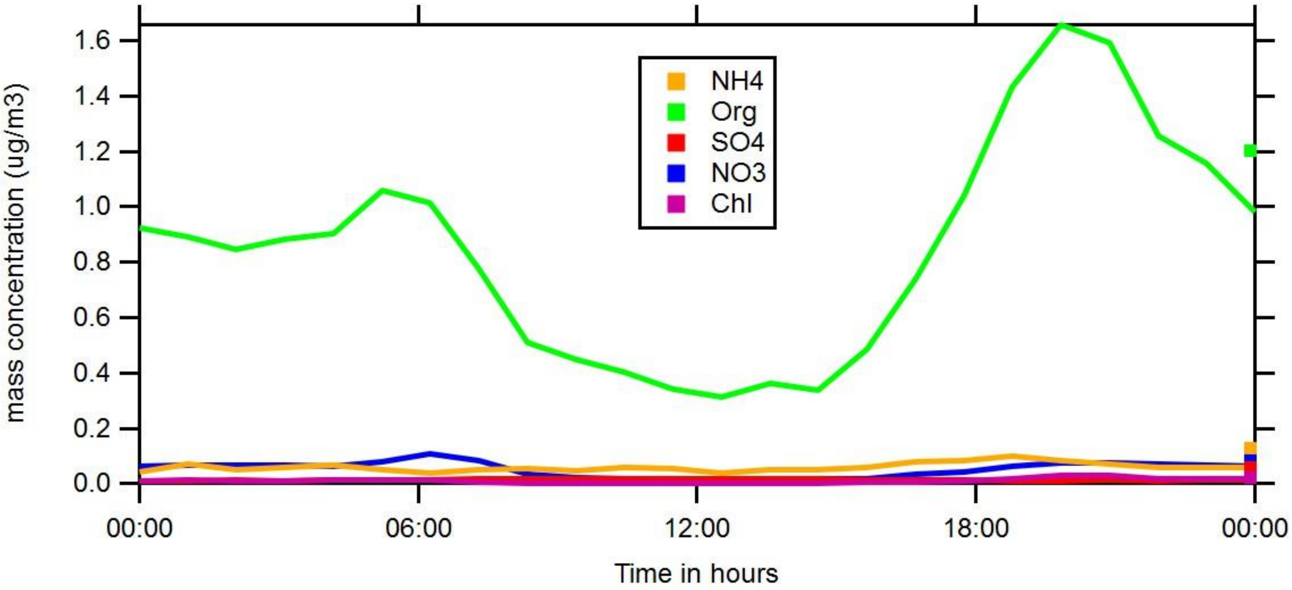
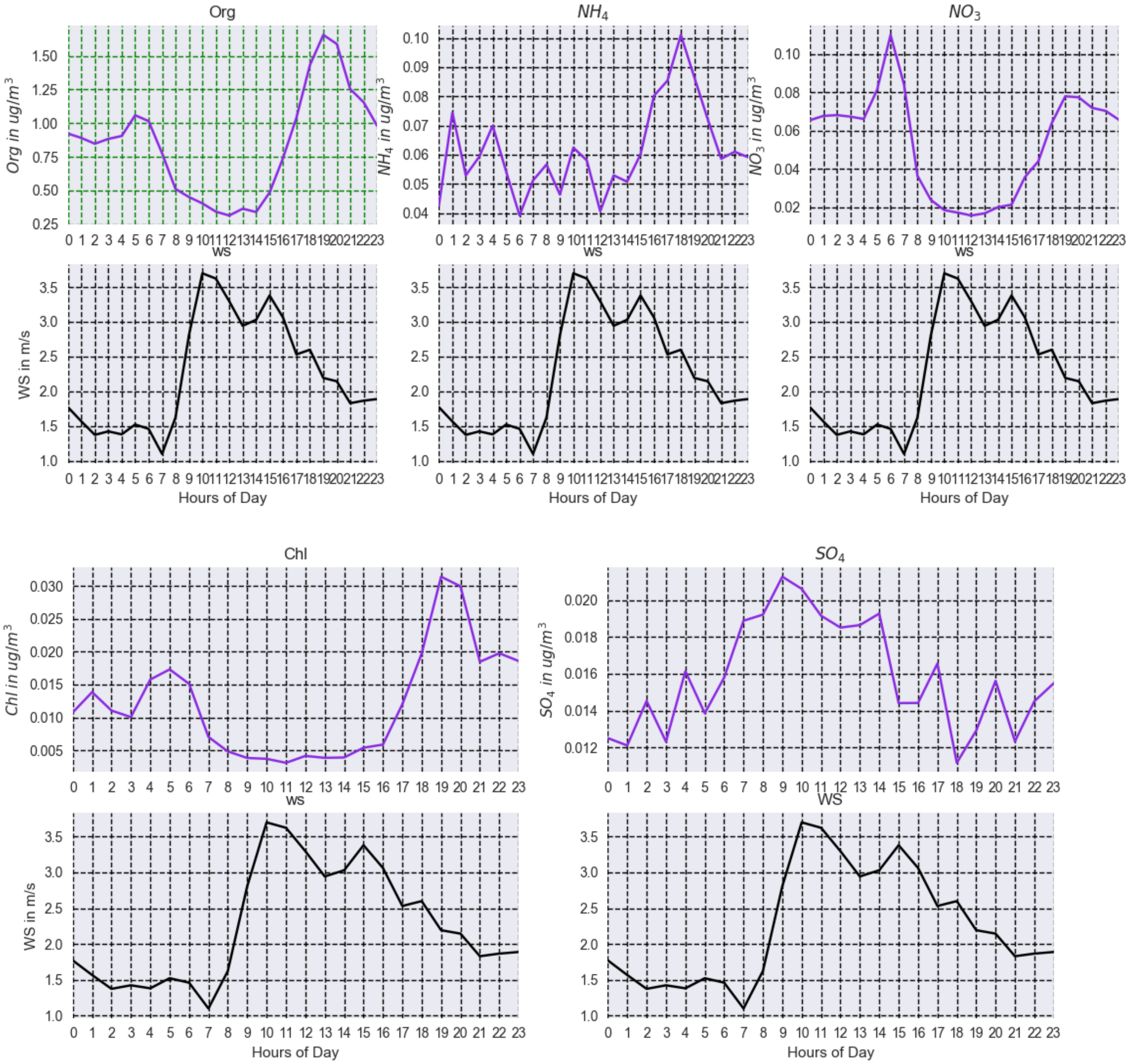
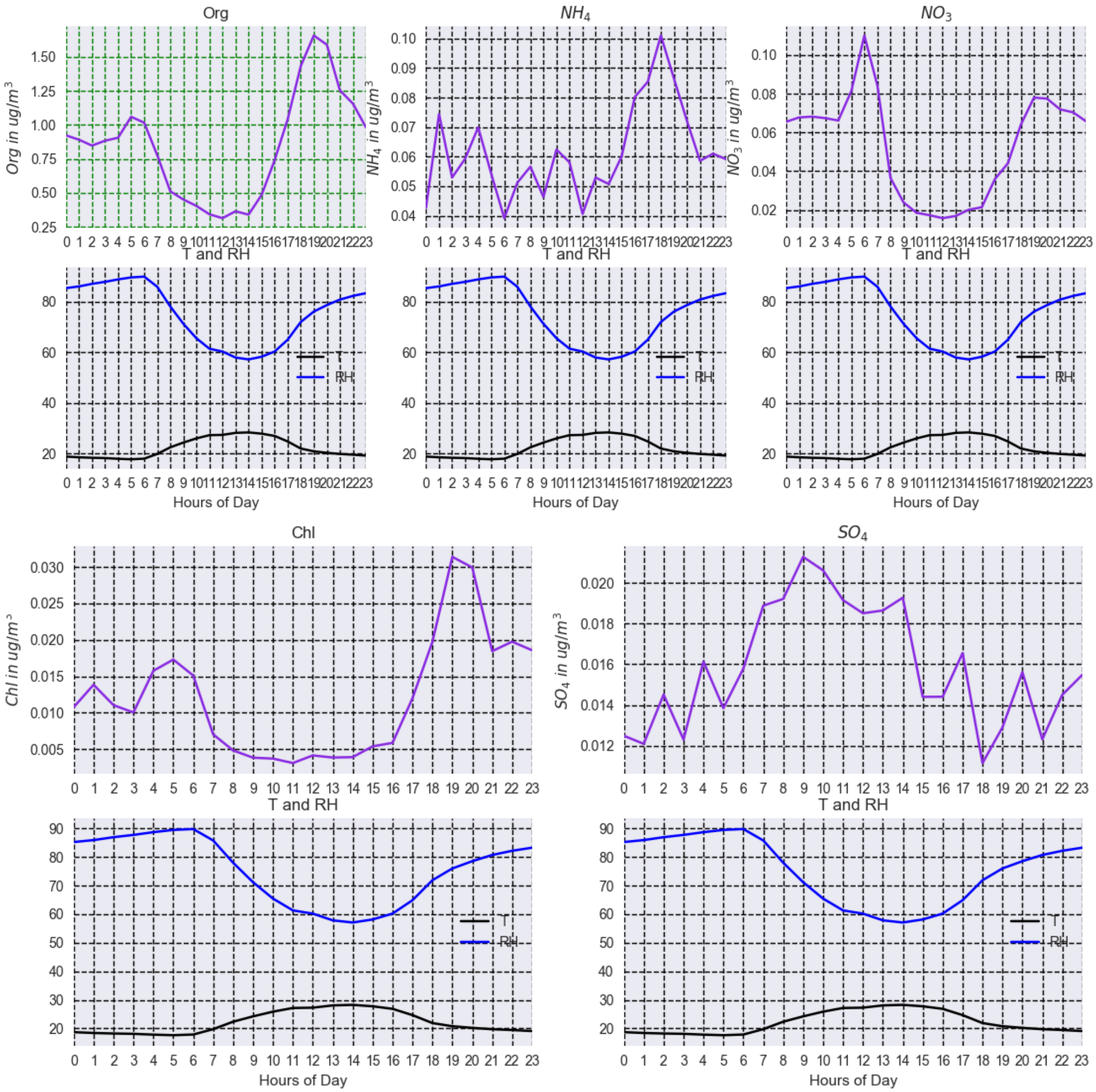


Figure 3. Diurnal variation patterns of PM_1 species (OA, NO_3, SO_4, NH_4 and Chl)


Org
Org in ug/m^3
1.50
1.25
1.00
0.75
0.50
0.25
NH_4
NH_4 in ug/m^3
0.10
0.09
0.08
0.07
0.06
0.05
0.04
NO_3
NO_3 in ug/m^3
0.10
0.08
0.06
0.04
0.02
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
ws
WS in m/s
3.5
3.0
2.5
2.0
1.5
1.0
Hours of Day
Chl
Chl in ug/m^3
0.030
0.025
0.020
0.015
0.010
0.005
SO_4
SO_4 in ug/m^3
0.020
0.018
0.016
0.014
0.012
WS

(a)



(b)

Figure 4. Diurnal variation patterns of meteorological parameters (WS, T and RH) and PM_1 components during the study period: (a) WS and PM1 components, and (b) T, RH and PM_1 components

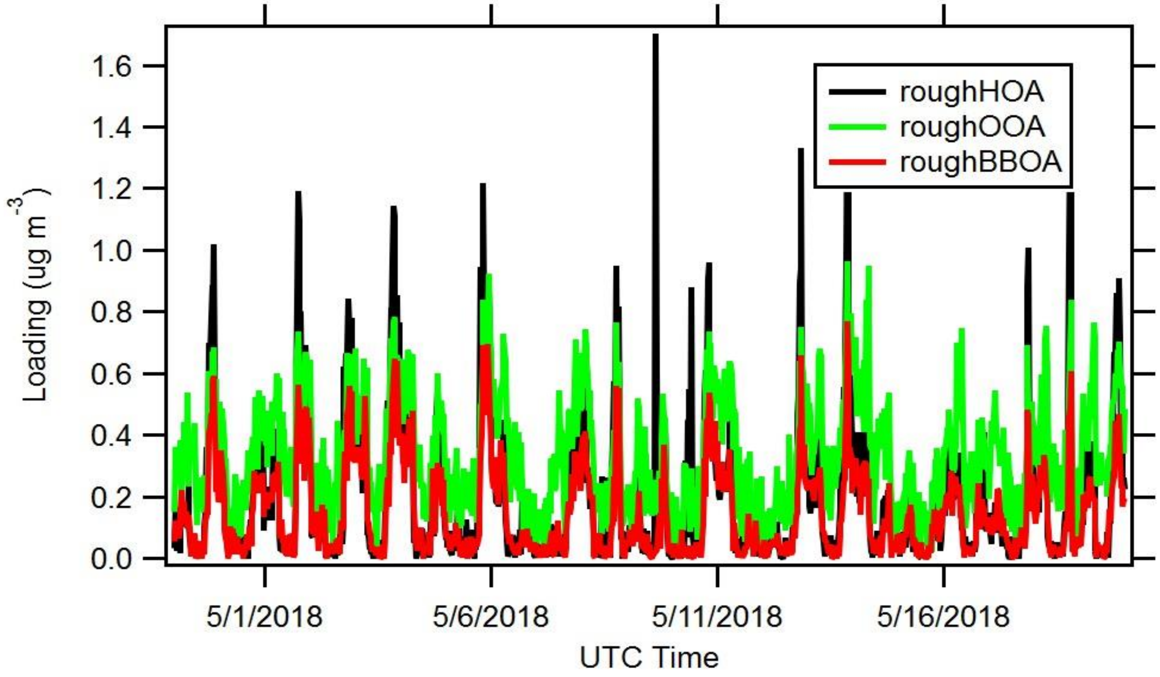


Figure 5.Time series of the contribution of different factors identified by PMF, to the organic species emitted in Kigali city

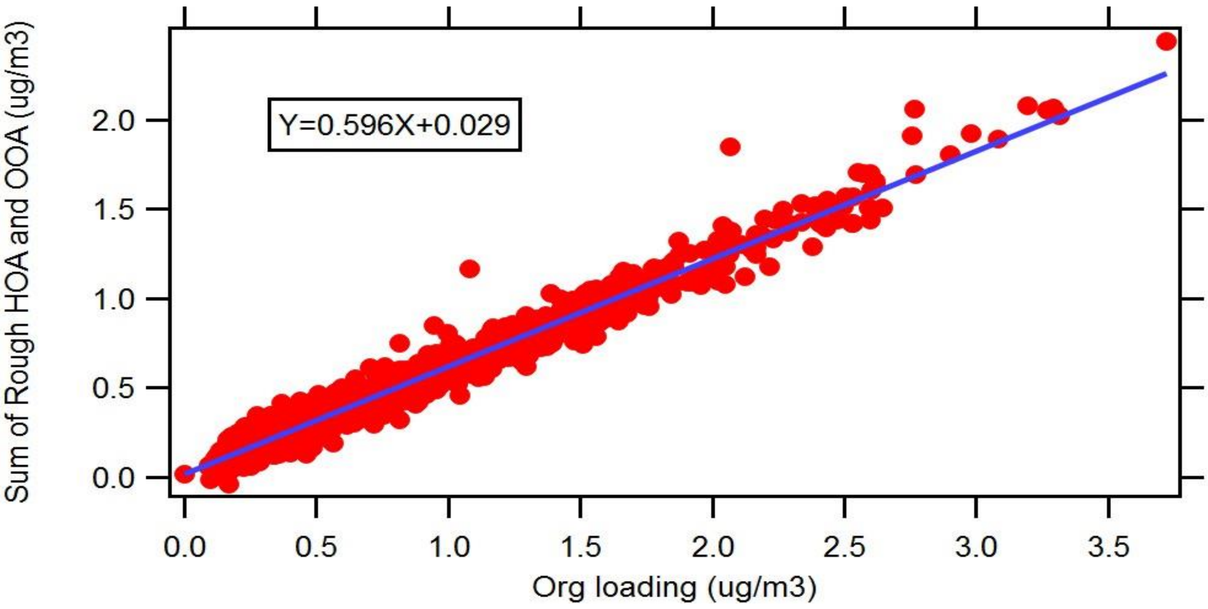


Figure 6. Scatter plot for HOA+OOA and total OA correlation

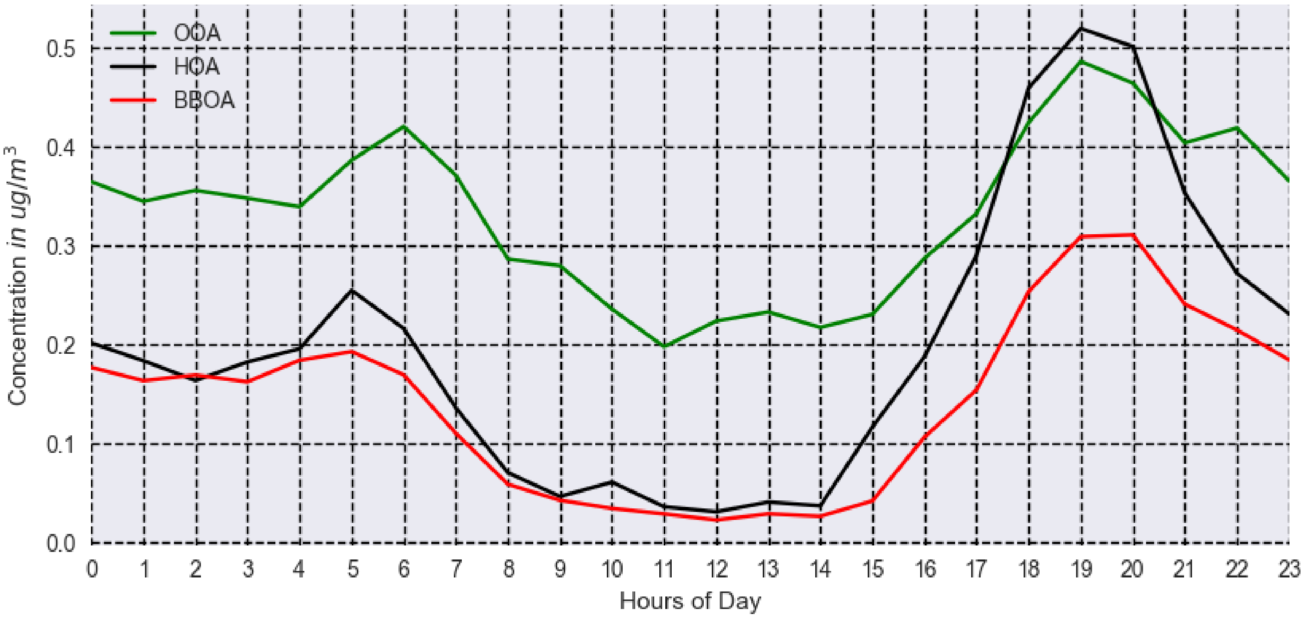
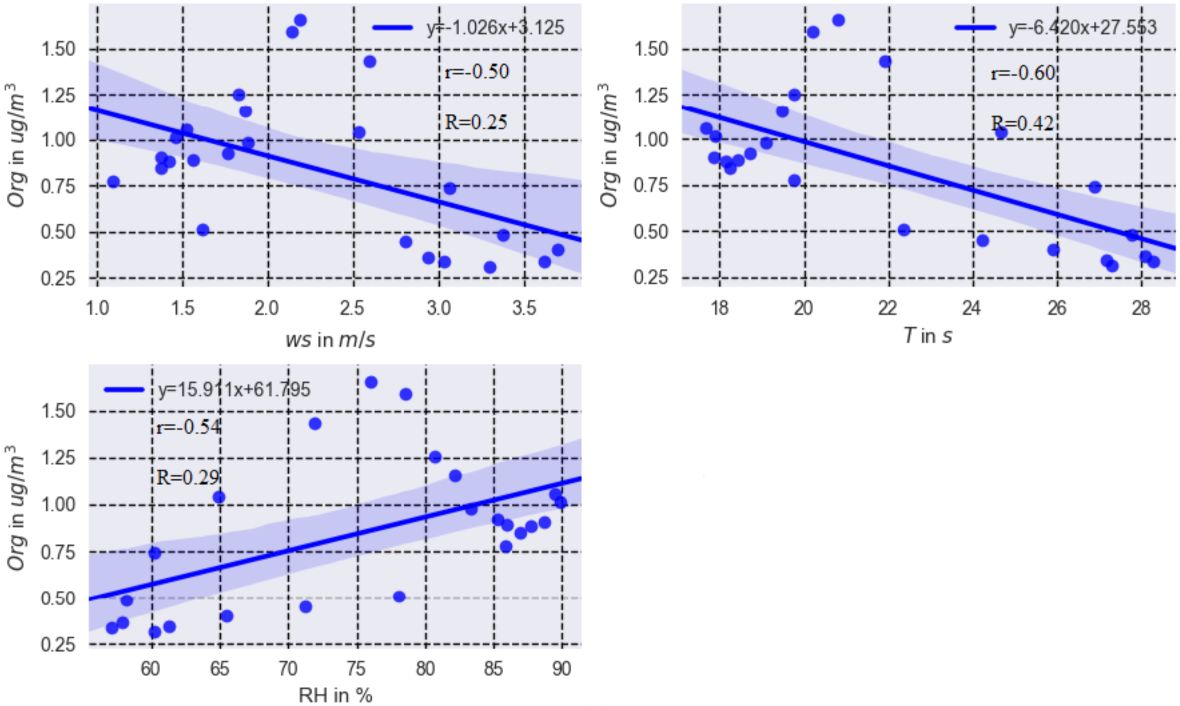
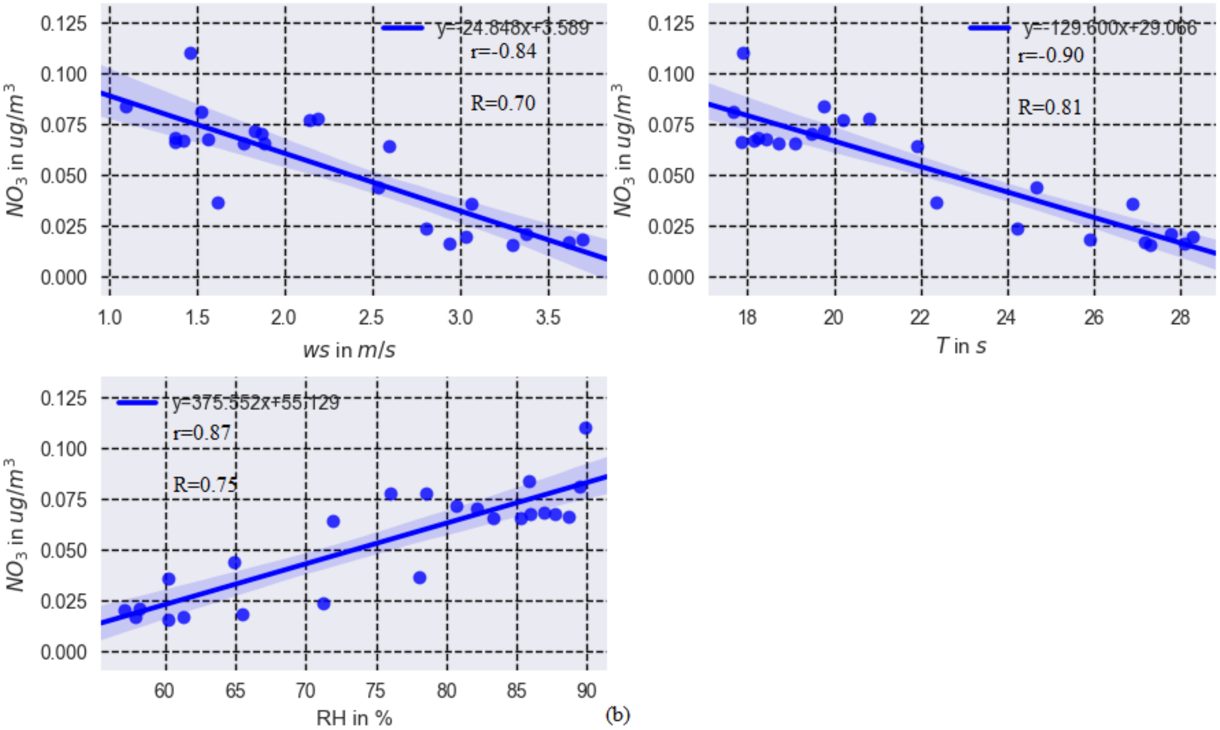


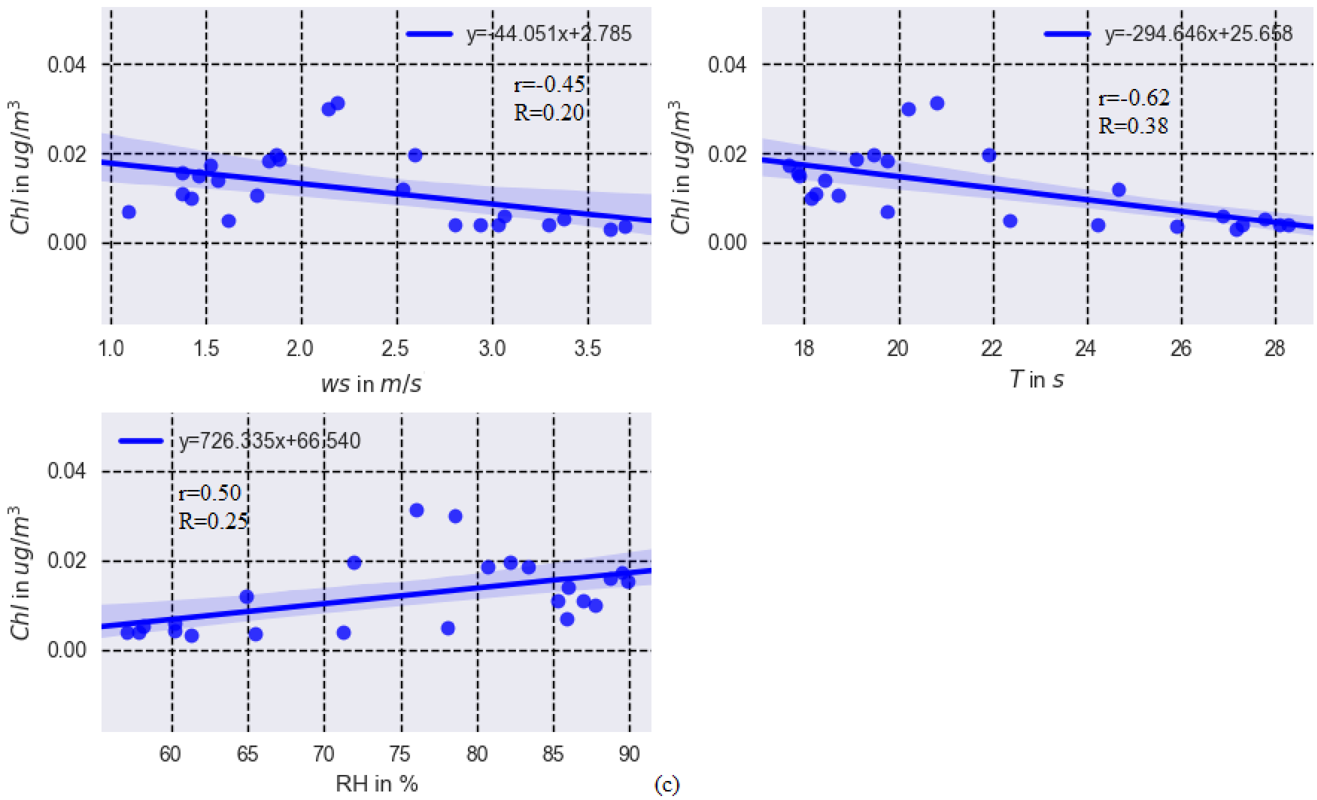
Figure 7. Average diurnal cycles of PMF Factors


y=-1.026x+3.125
r=-0.50
R=0.25
Org in ug/m^3
ws in m/s
y=-6.420x+27.553
r=-0.60
R=0.42
T in s
y=15.911x+61.795
r=-0.54
R=0.29
RH in %

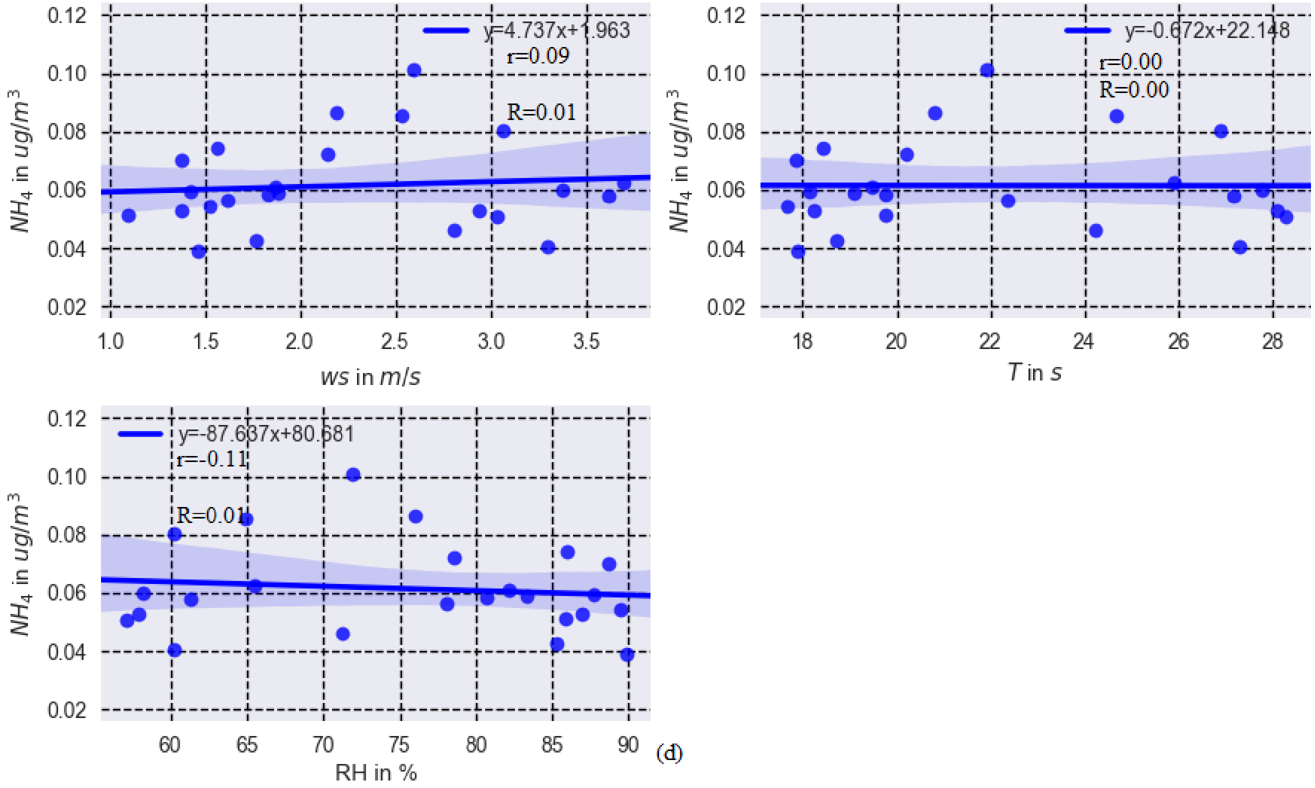
(a)


y=-24.848x+3.589
r=-0.84
R=0.70
NO_3 in ug/m^3
ws in m/s
y=-129.600x+29.066
r=-0.90
R=0.81
T in s
y=375.552x+55.129
r=0.87
R=0.75
RH in %

(b)


y=-44.051x+2.785
r=-0.45
R=0.20
Chl in ug/m³
ws in m/s
0.04
0.02
0.00
1.0
1.5
2.0
2.5
3.0
3.5
y=-294.646x+25.658
r=-0.62
R=0.38
Chl in ug/m³
T in s
18
20
22
24
26
28
y=726.335x+66.540
r=0.50
R=0.25
Chl in ug/m³
RH in %
60
65
70
75
80
85
90

(c)


y=4.737x+1.963
r=0.09
R=0.01
NH₄ in ug/m³
ws in m/s
0.12
0.10
0.08
0.06
0.04
0.02
1.0
1.5
2.0
2.5
3.0
3.5
y=-0.672x+22.148
r=0.00
R=0.00
NH₄ in ug/m³
T in s
18
20
22
24
26
28
y=-87.637x+80.681
r=-0.11
R=0.01
NH₄ in ug/m³
RH in %
60
65
70
75
80
85
90

(d)

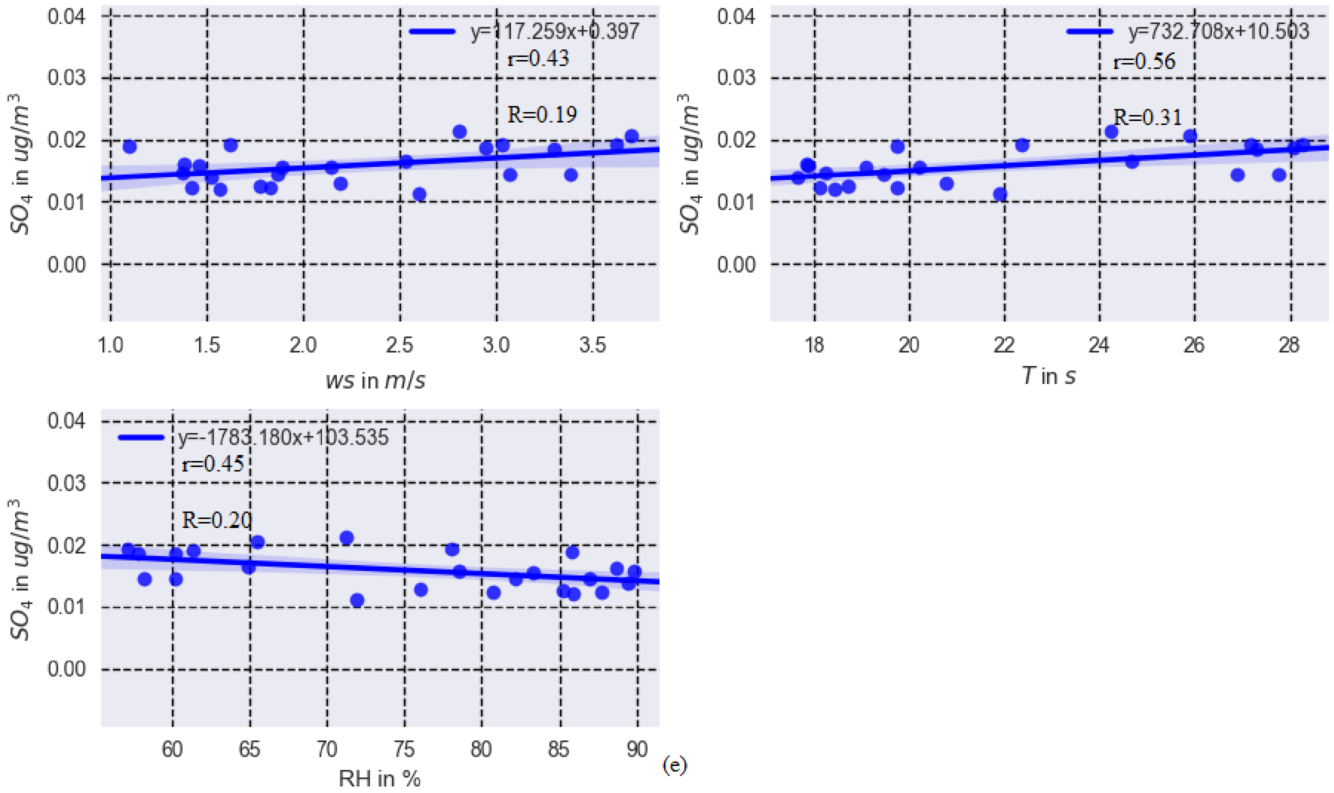


Figure 8. Scatter plots for the meteorological parameters (WS, T and RH) correlating with the PM_1 components: (a) meteorological parameters with organic; (b) meteorological parameters with nitrate; (c) meteorological parameters with Chloride; (d) meteorological parameters with ammonium; (e) meteorological parameters with sulfate

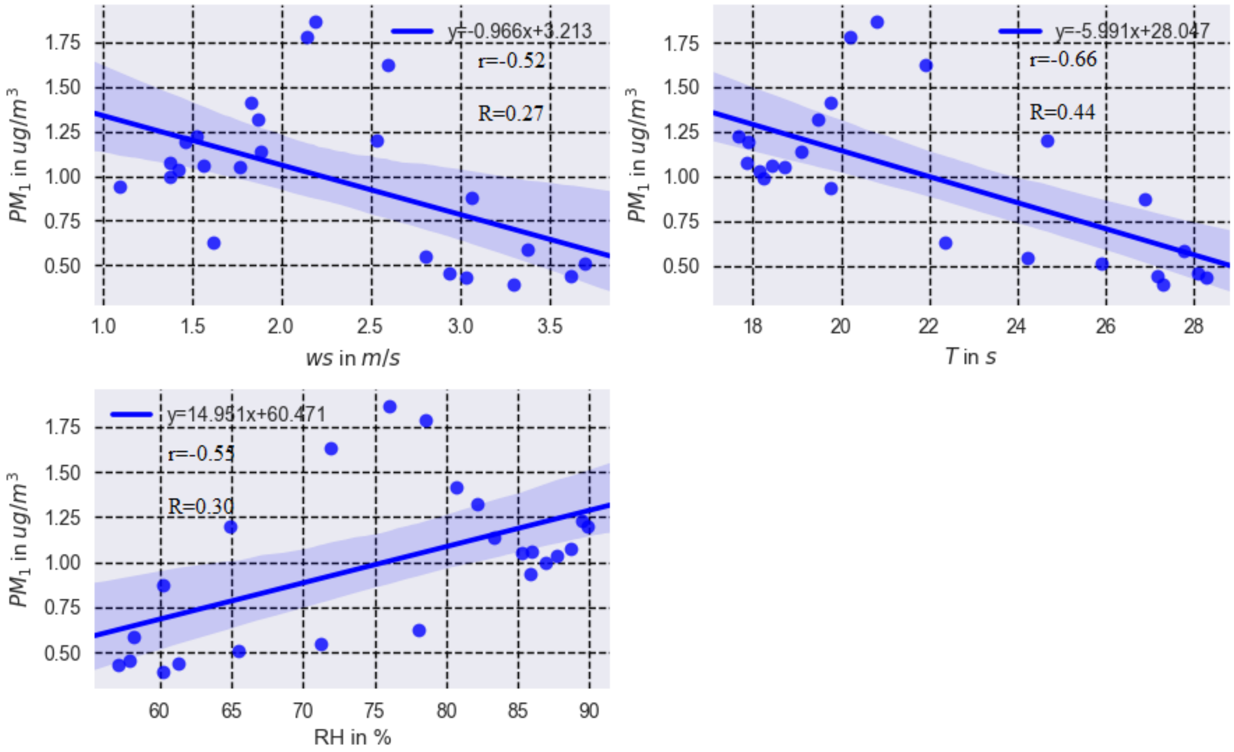


Figure 9. Scatter plot for meteorological parameters correlating with PM_1

Addendum 2: Tables

Table 1. Average mass concentrations (µgm^{-3}) of PM_1 and their components for the campaign of sampling data

Statistical measures	Org	NO_3	SO_4	NH_4	Chl	PM_1
Average	0.85	0.05	0.02	0.06	0.01	0.99
Maximum	3.72	0.35	0.08	0.25	0.17	4.01
Minimum	0.00	0.00	0.00	0.00	0.00	0.01
S.D	0.63	0.05	0.01	0.05	0.02	0.69

Table 2. Average hourly mass concentrations (µgm^{-3}) of PM_1 and their components for the study period

Statistical measures	Org	NO_3	SO_4	NH_4	Chl	PM_1
Average	0.85	0.05	0.02	0.06	0.01	0.99
Maximum	1.66	0.11	0.02	0.10	0.03	1.87
Minimum	0.31	0.02	0.01	0.04	0.00	0.39
S.D	0.40	0.03	0.00	0.02	0.01	0.43

Table 3. PMF Factors for Organic Aerosols

Statistical measures	HOA	OOA	BBOA
Average	0.20	0.33	0.14
Maximum	1.70	0.96	0.77
Minimum	0.00	0.01	0.00
S.D	0.24	0.18	0.14

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