Chemical analysis and statistical study on the composition of airborne particulate matter (PM_{2.5} and PM₁₀), aerosols (PM_{2.5}) inorganic trace gases and precipitation in Singapore between 2009 – 2012

Bahareh Khezri

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School of Physical and Mathematical Science

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**A thesis submitted to the Nanyang Technological University
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For any errors or inadequacies that may remain in this work, of course, the responsibility is entirely my own.

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Abstract

At a Nanyang Technological University (NTU) rooftop sampling site, airborne particulates were sampled in two different sizes of 10 and 2.5 μm between October 2009 to December 2011. Airborne particulate matter samples were acid digested using a microwave system in closed vessels. The amount of acids, power setting and digestion times were optimized in order to achieve an efficient digestion. An inductively coupled plasma mass spectrometry (ICP-MS) method was developed for the determination of the elemental composition of airborne particulate matter. The developed microwave procedure and ICP-MS method were tested with NIST Standard Reference Material 2783 Urban Particulate Matter based on the recovery test.

It was found that major elements were present in the airborne particulate matter with high concentrations ($\mu\text{g m}^{-3}$) in the order of $\text{Na} > \text{Ca} > \text{Al} > \text{K} > \text{Mg} > \text{Zn} > \text{Fe}$.

The enrichment factor (EF) was used as a means to determine whether the elements originated from natural or anthropogenic sources. Their main sources were likely to be anthropogenic, for instance vehicular and industrial emissions.

PMF applied to the 54-variable model apportioned the airborne particulate matter into several sources including sea salt, crustal and windblown dust, road dust, vehicular emissions, refineries and chemical industries, electronics and semiconductors, high temperature operations and construction.

Rainwater samples (wet and dry sampling) were collected from a rooftop site in NTU between August 2009 to December 2011. The elemental composition of rainwater samples were determined using ICP-OES and ICP-MS. Ion chromatography was employed to measure common ions present in rainwater samples, in addition to pH and conductivity measurements. Over 400 samples were collected for all major rainwater events covering the traditional dry and monsoon seasons, as well as during “haze” events caused by deforestation by “slash-and-

burn” practices in Indonesian. The average pH value over the sampling period was found to be 4.33, with the acidity mainly originating from sulfuric acid levels, and with a smaller contribution from nitric acid. There was a positive correlation between the PSI (for PM₁₀ particles) and the electrical conductivity of the precipitation samples, due to an increase in dissolved ions during high haze events. The average concentration of ions (in $\mu\text{eq L}^{-1}$) in rainwater samples occurred in the following order: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$ for anions, and $\text{H}_3\text{O}^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{2+}$ for cations. The ICP measurements indicated that several elements (including As, Cd, Pb, Hg, Sb, Mo and Zn) were substantially enriched from anthropogenic sources compared their expected non-anthropogenic background readings.

The automatic MARGA (Monitor for AeRosols and Gases) sampling system was used to measure the inorganic components Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} in the PM_{2.5} aerosol phase and the corresponding inorganic molecules HCl, HNO₂, SO₂, HNO₃ and NH₃ present in the gas phase. Samples were collected and analysed hourly for 3 months between 2nd April and 25th June, 2011 to determine how the concentration of species in gas and aerosols contribute to the levels found in precipitation.

SO₂ was the most abundant gas that appeared in an order of magnitude higher concentration than the other trace gases, and correspondingly SO_4^{2-} was also found to be at least 3 to 10 times higher than other anionic aerosol species. The concentration of major ions in aerosol samples and the related gaseous compounds followed the order of: $\text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{K}^+ > \text{Na}^+ > \text{Cl}^- > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{SO}_2 > \text{NH}_3 > \text{HNO}_2 > \text{HNO}_3$, respectively. The maximum value for most of the target analytes was observed during the hazy period in May when there was significant contamination from regional fires. The results from the automatic aerosol and gas analysis were compared with the results from the analysis of rain water samples that were collected at the same sampling site, as a means of correlating aerosol and gas phase concentrations (measured in units of $\mu\text{g m}^{-3}$) with the liquid precipitation concentrations of ions (measured in $\mu\text{eq L}^{-1}$).

Chapter 1: Introduction

In recent years, as countries worldwide have developed and industrialized, an increase in air pollution is often observed or at least presumed to occur. For instance, fossil fuel combustion can lead to an increase in the amount of sulfur and nitrogen oxides being emitted into the atmosphere. These gases are in turn converted to sulfuric and nitric acids under atmospheric conditions, leading to an increase in the acidity of precipitation. The problems of increased acidity in precipitation have resulted in intense research of precipitation chemistry in both rural and urban areas in the last two decades.

Anthropogenic emission is commonly the main cause of air pollution, which has been under close surveillance by environmental regulatory agencies and scientific communities worldwide. Anthropogenic emissions have significant impacts on the local environment, visibility reduction, acid deposition and in altering the earth's radiation balance [1]. Thus, there has been an increase in awareness of the fine particles suspended in these emissions in lieu of their influence on the environment and health effects.

1.1 Particulate Matter

Airborne particulate matter (PM) is a general term for solid material and liquid droplets suspended in the atmosphere with different size and chemical composition. Airborne particulate matter may be a complex mixture of organic and inorganic substances. Particles are emitted directly from the sources (primary) or formed in the atmosphere from gaseous precursors (secondary). Airborne particulate matter ranges in size from 0.01 up to 100 μm in diameter. Particles which are mechanically generated from natural sources such as agriculture, mining, volcanoes and sea salt are generally larger than 2.5 μm and these particles are usually called "coarse particles". The particles which are generated from combustion processes or through gas to particle conversion

processes usually have diameter between 0.1 and 2.5 μm and are categorized as "fine particles" [2].

Figure 1-1 compares sizes of particulate matter smaller than 2.5 microns in diameter ($\text{PM}_{2.5}$) and smaller than 10 microns in diameter (PM_{10}) against the average diameter of a human hair, which is approximately 70 microns in diameter to understand how big particle pollution is.

Figure 1-1. Sizes of particulate matter smaller than 2.5 microns in diameter ($\text{PM}_{2.5}$) and smaller than 10 microns in diameter (PM_{10}) are compared against the average diameter of a human hair, which is approximately 70 microns in diameter.*

* Graphic based on US Environmental Protection Agency image.

1.2 Effects of Particulate Matter

1.2.1 Health Effects of Particulate Matter

From a health perspective, particulate matter has been connected to a range of serious respiratory and cardiovascular problems. Figure 1-2 explains how particulate matter enters your body.

Most effects related to exposure to ambient particulate matter include: premature mortality, aggravation of respiratory and cardiovascular disease, aggravated asthma, acute

respiratory symptoms, chronic bronchitis, decreased lung function, and increased risk of myocardial infarction [3-11].

Figure 1-2. How particulate matter enters your body: 1. Particulate matter enters our respiratory (lung) system through the nose and throat. 2|3. The larger particulate matter is eliminated through coughing, sneezing and swallowing. 4. Smaller particulate matter can penetrate deep into the lungs. It can travel all the way to the alveoli, causing lung and heart problems and delivering harmful chemicals to the blood system.*

* (<http://www.desso-airmaster.com>)

Figure 1-3. Particles lodge deep in lung's air sacs and damage lungs.*

* (<http://www.mde.maryland.gov>)

Recent epidemiologic studies show that exposure to particulate matter may cause tens of thousands of excess deaths per year, and many more cases of illness among populations.

Figure 1-3 shows how particles damage lungs.

It is interesting to note that particle size distribution, wind-speed range, airborne concentration, particle morphology, and chemical mineralogy composition influence the nature and magnitude of these health effects [12].

1.2.2 Visibility Effects of Particulate Matter

Visibility decreases due to the scattering and absorption of light by particles and gases in the atmosphere [13-17]. More than half of 95% visibility reduction might be related to scattering of light by particulate matter. Fine particles are responsible for the majority of the light scattering. The rest (5-50 %) of the reduction in visibility is due to absorption of light by particulate matter (EPA, Visibility Intro).

1.3 Sources of Particulate Matter

Particulate matter can be emitted to the atmosphere from a wide range of sources, both natural and anthropogenic or it may form in the atmosphere through reactions of gaseous precursors.

The size and chemical composition of particles can be used as an indicator of formation processes. Although the composition of particles emitted from certain sources may be different from region to region, the main sources of particulate matter include road dust, construction, fossil fuels (combustion and motor vehicles), biomass burning, sea salt spray, cooking, and industrial activity. It is interesting to note that the size and chemical composition of primary particles can change during long range transportation [18-33].

1.4 Literature Review

In sites that report particle data, the monitored particle size fractions include total suspended particulate (TSP, mass of particles with aerodynamic diameter $< 30\ \mu\text{m}$), PM_{10} (aerodynamic diameter $< 10\ \mu\text{m}$), and $\text{PM}_{2.5}$ (aerodynamic diameter $< 2.5\ \mu\text{m}$). Among these sizes, $\text{PM}_{2.5}$ is becoming more frequently measured because this fraction can penetrate deep into human lungs and is able to more efficiently penetrate between outdoor and indoor environments.

$\text{PM}_{2.5}$ contains most of the carbon, sulfate, nitrate, and heavy metal components, while the larger particles are dominated by suspended dust, with some contributions from sea salt, pollen and plant debris. Trace elements on particles in the atmosphere or in any other environmental sample are becoming recognized as being extremely important because of their toxic effects or as catalysts for many biological reactions. Therefore, information on the sources of emission of these particles is needed for the development of effective control strategies [34].

Knowledge of the concentrations of trace metals in fine particles is fundamental for assessing their anthropogenic levels in urban areas and evaluating possible implications for public health [35]. In addition, data on elemental composition of an atmospheric aerosol at a given location are widely used for the characterization of local air conditions [36, 37].

The accurate determination of total concentrations of trace metals in environmental matrices such as urban residential particles, dust, airborne particulate matter, soils and sediments presents a significant challenge. This has led to the development and continuous improvement of various analytical methods for sample digestion, and development of instrumental techniques to obtain exhaustive chemical information.

Different digestion procedures (ashing, acid leaching, and microwave digestion) and analysis schemes for the determination of trace elements in environmental samples were

reported [38-40]. Microwave digestion is a rapid and efficient method of sample preparation prior to determination of trace metals [41]. The elemental compositions of environmental samples have been determined by various methods.

Direct methods include X-ray fluorescence (XRF), proton-induced X-ray emission (PIXE) and instrumental neutron activation analysis (INAA). The techniques used by most studies include atomic absorption spectroscopy (AAS), both flame and electrothermal, and inductively coupled plasma (ICP) techniques. The application of inductively coupled plasma-based techniques to air quality monitoring is now widespread. These techniques can be used for all possible matrices and analytes and are characterized by extended dynamic concentration ranges (several orders of magnitude), are multi elemental in nature and have high sensitivity and appropriate detection power [42-47].

This work has attempted to study additional elements such as Ce, La, Rh, Pt and Pd that have recently found more application in industrial processes. There is currently no data that shows the relationship between health effects and exposure to airborne particulate matter containing Pt, Pd and Rh. However some Pt and Pd salts are allergenic and their tendency to form methylation compounds and their ability to bind proteins make it important to know their concentration in airborne particulate matter [48]. Since other studies have reported difficulties [49-57] for detecting these elements with polyatomic interference using ICP – MS analysis, the Agilent 7700 with helium collision cell was selected for this work to reduce spectral interferences. Helium (He) mode has been established as one of the most reliable cell method for complex and variable samples, because it filters out all polyatomics, even unidentified ones [57a].

1.5 Particulate Matter Regulation

Concerns about atmospheric particulate matter have notably grown as researchers have found a significant association between rising particle levels in the air and an increase in

the number of respiratory symptoms, hospital admissions and people that die prematurely from heart and respiratory problems. Studies have not found a level that is completely safe for people and at which no health effects are seen. Elderly people, people with heart disease, and people with respiratory problems, such as asthma, are at greatest risk from short-term exposure to particles [58, 59].

1.5.1 Particulate Matter in the US

Early efforts to control particulate matter focused on reducing large particles. As a result, early National Ambient Air Quality Standards (NAAQS) were established for total suspended particulate and later for PM_{10} (EPA Web Ref 1-3). Recent focus has been given to $PM_{2.5}$ (Table 1-1). There is an on-going discussion in the United States to lower the annual mean averaged over 3 years for $PM_{2.5}$ to in the range $12\text{--}13\ \mu\text{g m}^{-3}$.

Table 1-1. History of the national ambient air quality standards for particulate matter during the period 1971-2006.*

Final Rule	Primary/ Secondary	Indicator	Averaging Time	Level
Apr 30 1971	Primary	TSP	24 Hours	$260\ \mu\text{g m}^{-3}$
			Annual	$75\ \mu\text{g m}^{-3}$
	Secondary	TSP	24 Hours	$150\ \mu\text{g m}^{-3}$
Jul 1, 1987	Primary and Secondary	PM_{10}	Annual	$150\ \mu\text{g m}^{-3}$
			24 Hours	$50\ \mu\text{g m}^{-3}$
Jul 18, 1997	Primary and Secondary	$PM_{2.5}$	Annual	$15\ \mu\text{g m}^{-3}$
			24 Hours	$65\ \mu\text{g m}^{-3}$
		PM_{10}	Annual	$50\ \mu\text{g m}^{-3}$
			24 Hours	$150\ \mu\text{g m}^{-3}$
Oct 17, 2006	Primary and Secondary	$PM_{2.5}$	Annual	$35\ \mu\text{g m}^{-3}$
			24 Hours	$15\ \mu\text{g m}^{-3}$
		PM_{10}	24 Hours	$150\ \mu\text{g m}^{-3}$

* http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_history.html

1.5.2 Particulate Matter in the EU

The concern about health effects of PM pollution in Europe started with the London Smoke episode in 1952 (from coal burning). Due to severe particle pollution in the most

industrialised areas during the 1970s and 1980s, development of legislation emission became stricter. The first EU Directive 80/779/EEC on air quality for sulfur dioxide and suspended particulates set limit values for PM in terms of TSP. Other existing PM₁₀ regulations can be found in document EU Directive 199/30/EC. The numerical Limit Values for PM₁₀ are:

- Annual average of $40 \mu\text{g m}^{-3}$
- Daily limit value of $60 \mu\text{g m}^{-3}$ not to be exceeded more than 35 days of the year.

The Limit Values became legally binding on January 1, 2005 with $50 \mu\text{g m}^{-3}$ daily. Furthermore, second stage PM₁₀ limits, took effect from 2010, which permitted only seven daily average concentrations in excess of $50 \mu\text{g m}^{-3}$ while the annual mean limit reduced to $20 \mu\text{g m}^{-3}$ [60].

1.6 Rain

Rain plays a role in the removal of gases and aerosols from the atmosphere, therefore, the study of the chemical composition of rainwater can aid in understanding the contribution of the different sources of atmospheric pollutants [61-66].

The rainwater composition is often influenced by anthropogenic activities releasing acidic (such as SO_x, NO_x) or basic (such as NH₃) gases into the atmosphere. Acidic rainwater aids the dissolution of many trace metals, which enhances their bioavailability, thus, the study of trace metals in rainwater has increased because of their adverse environmental and human health effects. Some metals such as Cd, Hg, and Pb are dangerous to biological systems and can accumulate in the biosphere [67, 68]. If the concentrations are too high, many of the trace metals can potentially be harmful to human health through the direct consumption of rainwater or aquatic organisms. Toxic trace metals from precipitation can also accumulate in surface waters and soils where they may be harmful to aquatic life and forest ecosystems [69].

Although there has been extensive research carried out on acid rain chemistry and processes, there is no single reaction cycle that can be proposed for the event because the exact chemical composition of the rain varies from each site and region due to the influences of local actions [70-73]. Furthermore, individual rainwater events are highly variable, dependent on local anthropogenic conditions, land topology and microclimates. Both anionic and cationic indexes [72-77] and the study of trace metals [71, 78-83] are necessary to evaluate the overall characteristics of rainwater. NO_x and SO_x (or H₂S) emissions into the atmosphere in East Asia, Europe and Northern United States are known to have had a number of adverse consequences, such as acidification of soils and waters, harm to vegetation, damage to buildings and monuments through increased corrosion affects, and decreased visibility in the atmosphere [76, 84, 85].

Singapore is a small island country with a land area of approximately 700 km², with a population close to 5 million and is one of the few countries in South East Asia which provides safe piped potable water nationwide [86]. Due to its high urban population density and lack of land available for water reservoirs, Singapore traditionally relied on imported water from Malaysia, subject to water treatment regimes. More recently Singapore has introduced processes for reclaimed water (locally termed NEWater), desalination (reverse osmosis) of seawater and introduced new water reservoirs to boost and secure the water supplies into the future [87]. Currently it is estimated that rainfall collected in local catchment areas (which comprise two thirds of Singapore's total land area) make up approximately 20% of Singapore's water needs [86, 87].

Presently, all of the potable water in Singapore undergoes a centralized purification regime managed through the Public Utilities Board (PUB), whose holistic approach to water management has been considered a model for urban water management [87, 88]. Nevertheless, it has been suggested that improvements to water sustainability can be achieved through harvesting some rainwater in a decentralized fashion for non-potable

uses [88]. Therefore, it is important to have knowledge of the quality of the source rainwater, in order to design decentralized treatment strategies. Due to the heavy local industry within Singapore and nearby Malaysia, particularly in petrochemical refining, the rain water can suffer from contamination through atmospheric pollutants. Furthermore, parts of South East Asia suffer severe air quality problems due to annual biomass burning carried out in Indonesia, which can affect rainwater compositions.

Considering the importance and consequences of acid rain, the present study has been carried out on the rooftop of School of Physical and Mathematical Science in Nanyang Technological University, Singapore.

The aim of this study is to investigate an initial understanding of the rain water chemistry, to identify possible sources that contribute to its chemical composition. The results obtained in this study are compared with those other studies conducted at various places in the world.

1.6.1 What is Acid Rain and How is it Formed?

Water initially evaporates from the land and sea into the atmosphere. Since this vapour is rich with warm air, it subsequently cools and then condenses to form clouds. Clouds are transported *via* wind action until they release the water back to the earth as rain, snow or fog. Water droplets can trap particles, gases and chemicals that are present in the atmosphere while they form, and fall to the earth.

Rain can become acidic because of pollutants that are released into the atmosphere due to anthropogenic activities (and some natural processes). Two major pollutants that make rain acidic are sulfur dioxide (SO_2) and oxides of nitrogen (NO_x). In the atmosphere, and in the presence of water vapour, SO_2 chemically changes into sulfuric acid and NO_x changes into nitric acid. Sunlight can increase the speed of these reactions. Figure 1-4 explains how acid rain is formed.

Figure 1-4. How acid rain is formed (<http://env-ngo.wikispaces.com>).

1.6.2 Sources of Acid Rain

1.6.2.1 Natural Phenomena

Volcanoes are one of the natural phenomena that release gases into the atmosphere (SO_x) [89]. In addition, natural biological processes that occur on the land, in wetlands, and in the oceans can form and release acidic gases. Nitrogen from plant material, and electrical activity in the atmosphere such as lightning, can also be major sources of nitric acid in rainwater [90].

1.6.2.2 Human Activity

Human activities are one of the main sources that release sulfur and nitrogen compounds. These sources include electricity generation, factories, and motor vehicles. Coal power plants are one of the most polluting. Released gases can be transferred hundreds of kilometres in the atmosphere before they are converted to acids and deposited [90]. Globally, burning of fossil fuels, such as coal, oil and gas are responsible for half of all SO_2 and most NO_x emissions.

In Singapore, the major sources of SO_2 are burning of fossil fuels for heat generation in industries, electricity generation and transportation, industrial emissions (e.g., chemical

and petroleum), and oil and gas refining. In the past, factories had short chimneys to vent smoke and toxic emissions but this caused many problems locally; thus, factories now have taller smoke chimneys. However, dispersal from these taller stacks causes pollutants to be carried farther, causing widespread ecological damage. Also, livestock production plays a major role and is responsible for almost two-thirds of all anthropogenic sources of ammonia produced through human activities, which contributes significantly to acid rain [91].

1.6.3 The Effects of Acid Rain

Natural clean rainwater has a pH of 5.6 because of the carbonic acid that occurs through reactions of dissolved CO₂ [70, 92]. Therefore, if the measured pH is less than 5.6, it can be called “acid rain”. Nature can balance this acidity by offsetting it with other alkaline minerals, such as ones that contain calcium, magnesium and potassium that are present in air, soil and lakes. It has been found that each natural ecosystem has an upper limit in its ability to endure the effects of acid rain. "Critical load" is referred to the highest level of acid rain that an ecosystem can receive over the long-term without any harmful effects to the environment. It is vital to know the critical load for a region since it can measure how much SO₂ and NO_x can be put into the environment without causing damage to lakes, fish and plants.

When the environment fails to neutralize the acid rain — that is, when the critical load is exceeded — severe damage to an area can occur. Acid rain has negative impacts on lakes and aquatic ecosystems, forests and soils, human-made structures and materials, human health and visibility (<http://www.epa.gov/acidrain/effects/>).

1.6.3.1 Lakes and Aquatic Ecosystems

Research has shown that, in general, lakes with a pH of 6.0 or more support a wide variety of wildlife. Conversely, lakes with a pH of less than 6.0 have fewer species of fish

and other aquatic organisms. Acid rain causes a range of effects that harm or kill individual fish and reduce fish populations. Acidic compounds can get into the water in a number of ways. They can fall directly into lakes as dry deposits from the atmosphere in the form of gases and particles, or they can enter the water as wet deposits in the form of rain, snow or fog (http://www.epa.gov/acidrain/effects/surface_water.html, Figure 1-5).

Figure 1-5. Effects of Acid Rain - Surface Waters and Aquatic Animals.*

*(<http://www.epa.gov/acidrain/effects/>)

Figure 1-6. Effects of Acid Rain - Forest and soils. *

* (<http://news.sciencemag.org/sciencenow/2012/06/is-acid-rain-a-thing-of-the-past.html>)

1.6.3.2 Forests and Soils

Forests and soils are also affected by acid rain. Since acid rain falls onto the earth, it can dissolve and wash out minerals and nutrients that are necessary for plant growth.

Acid rain can also releases metals that may be very harmful to trees and plants. Aluminium, for example, once freed up in the soil, can be absorbed by the roots of trees. When this happens, it becomes difficult for the trees to absorb other needed nutrients, such as calcium and magnesium.

Figure 1-7. Effects of Acid Rain - Structures and Materials. (a) Sculptures

(<http://gardenofeaden.blogspot.sg/2012/07/effects-of-acid-rain.html>), (b) Colosseum in Rome

(<http://www.nachi.org/acid-rain.htm>). Acid rain significantly increases the rate of corrosion on limestone, sandstone, and marble.

Sulfur dioxide present in the atmosphere may also combine with other chemicals. One of the results is ammonium sulfate, which can be absorbed into the soil and react to form sulfuric acid. Nitrogen compounds, the other major component of acid rain, affect trees as well although act differently to sulfuric acid. Nitrogen encourages the growth of plants, and trees are no exception. In the presence of acid rain, the weak nitric acid solution may force the trees to grow, although there are not enough other nutrients accessible in the soil (<http://www.epa.gov/acidrain/effects/forests.html>, Figure 1-6).

1.6.3.3 Human-Made Structures and Materials

Natural environments are not the only things affected by acidic rain. Almost anything that is exposed to acid rainwater over a long period of time will be damaged or changed in some way, due to corrosion processes. This includes buildings, sculptures, paint, metal, glass, paper, leather and fabrics (<http://www.epa.gov/acidrain/effects/materials.html>, Figure 1-7).

1.6.3.4 Human Health

Very importantly, acid rain can indirectly affect the health of humans. SO_2 or NO_x interact in the atmosphere to form fine sulfate and nitrate particles, which can cause harmful effects to the cardiac and respiratory systems. Many scientific studies have been done to identify a relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis (<http://www.epa.gov/acidrain/effects/health.html>).

1.6.3.5 Visibility

In many areas of Singapore, magnificent vistas are obscured by an acidic haze. The chemical reactions that sulfur dioxide and oxides of nitrogen undergo in the atmosphere lead to the formation of particles that can reduce the clarity of what can be seen in the distance (<http://www.epa.gov/acidrain/effects/visibility.html>).

1.7 Source apportionment

In order to decrease PM levels in the atmosphere a deep knowledge of the contributing sources, of the influence of the meteorological conditions and formation and transport processes of PM are required. The purpose of the work described here is the characterization PM_{10} and $\text{PM}_{2.5}$ composition over a long temporal period to achieve a statistically significant data-set, and to distinguish and estimate the impact of various anthropogenic and natural sources on the city air quality through the use of receptor

modelling. Receptor models derive contributions from different source types by multivariate measurements taken at one or more receptor locations. Various receptor modelling techniques including the chemical mass balance method (CMB), principal component analysis (PCA), and positive matrix factorization (PMF), multiple linear regression and individual particle analysis have been applied to source distribution of urban aerosols [93]. In this work, the results of PM sampling are discussed using PMF to characterize accurately major sources in $PM_{2.5}$ and PM_{10} in the atmosphere.

Factor Analysis is used to investigate relationships between concentrations of different ions and elements in rainwater samples, which allows the identification of a small number of factors that could explain most of the original data variability [93].

Chapter 2: Experimental

2.1 Sampling Site

All airborne particulate matter and rainwater sampling was conducted from August 2009 to December 2011 at the roof top of School of Physical and Mathematical Sciences (SPMS) approximately 15 meters above the ground and 67 meters above sea level. This sampling site is situated in the western part of Singapore and is influenced by emissions from major power plants, incinerators, chemical industries and petroleum refineries located on Jurong Island, Tuas and Jurong Industrial Estate and urban vehicular traffic [Pan Island Expressway (PIE)] (Figure 2-1).

Singapore is located in Southeast Asia, south of West Malaysia, south of Java in Indonesia and east of Sumatra in Indonesia with a latitude of 1°18' N and a longitude of 103°48' E. Singapore includes the main island of Singapore and 63 islets within its territorial waters. The main island is approximately 42 km from west to east and 23 km from north to south. Because of its geographical location and maritime coverage, its climate is characterized by uniform temperature and pressure, high humidity and abundant rainfall. The climate of Singapore can be divided into two main seasons, the Northeast Monsoon and the Southwest Monsoon season, Figure 2-2, separated by two relatively short inter-monsoon periods.

2.1.1 Climatology of South East Asia

The word "monsoon" is derived from the Arabic word "Mausim" which means season. The monsoon, having stable, seasonal winds with a changeable precipitation regime, has a major influence on the climates of the southern and south-eastern coasts of Asia, as well as far into inland areas (Figure 2-2).

Table 2-1 has summarized detailed information about the Singapore climate.

Figure 2-1. Sampling location: Singapore Map (A), sampling site location towards main road (B) and Industrial areas (C).

Figure 2-2. Northeast Monsoon (Left) and Southwest Monsoon (Right)

Table 2-1. Detailed information about the Singapore climate.

Classification	Duration	Wind Direction	Rainfall
Northeast Monsoon	December - March	from the land towards the sea (Northeast winds)	Continuous heavy rain
Southwest Monsoon	June - September	from the sea towards land (Southeast/Southwest Winds)	Isolated to scattered late morning and early afternoon showers
Pre South-West Monsoon	late March - May	Light and variable winds	Afternoon and early evening showers often with thunder
Pre North-East Monsoon	October - November	Light and variable winds	Scattered showers with thunder in the late afternoon and early evening.

2.1.2 Sumatra Squalls

Squalls refer to a sudden increase in the wind speed over a short time period, with higher gusts and rain showers expected during a squall event. "Sumatra" squall is a term used in Singapore and Peninsular Malaysia for squall lines and named as such because the storm develops overnight in Sumatra. Following their passage, Singapore experiences strong gusts, heavy rain, spectacular lightning and thunder and it sometimes persists till

the early afternoon. Sumatra squalls usually occur during the Southwest Monsoon, but it can reach to Singapore any time the steering level winds change to a south-westerly direction (Figure 2-3).

Figure 2-3. A Sumatra Squall approaching eastern Singapore on 4 July 2005.*

* (Source: NEA's WEATHERWise Singapore).

2.1.3 Thunderstorm and Lightning

Singapore has one of the highest rates of lightning activity in the world (capital of lightning). Singapore experiences hot and humid weather all year round due to being located very near the equator. This condition is favourable for the development of lightning producing thunderstorm clouds (Figure 2-4).

Over a 30 year period, the monthly distribution of mean thunder days has been recorded in the National Environmental agency database. It can be seen from Figure 2-5-a that thunder peaks in April/May and October/November, with at least 18 thunder days each. January and February are the months with the least number of thunder days (4 to 6 days). Figure 2-5-b shows that thunderstorms mostly occur between 2 PM and 6 PM in the afternoon for all months of the year, as diurnal heating and convection play an important role in thunderstorm development in Singapore (<http://app2.nea.gov.sg/tsl.aspx>).

Figure 2-4 Lightning in Singapore.

Figure 2-5 Average NO. Of Thunder (a) * NO. Of hourly Thunderstorm occurrences (b) **

*, ** (Source: NEA's WEATHERWise Singapore)

2.1.4 Mist and Fog

Mist and fog are similar phenomenon and take place due to tiny droplets of water suspended in the air affecting visibility at ground level (Figure 2-6). The only difference between these two terms is the sight distance. The phenomenon is called mist if visibility is greater than 1 km through the cloud of water droplets. However, if visibility is less than 1 km it is termed fog. Fog and mist are most likely to occur during the Inter-monsoon periods.

Figure 2-6. Mist is commonly observed over grass patches in the early morning.*

* 50 Nanyang Crescent, Nanyang Technological University, Singapore.

2.1.5 El Niño / La Niña

El Niño is an ocean-atmosphere climate phenomenon that is associated with the cyclic warming of waters across the central and eastern tropical Pacific Ocean. The El Niño event occurs every 2 to 7 years and typically lasts about 9 to 18 months. Figure 2-7 describes the difference in a normal year and in an EL Nino year. Generally El Niño perturbs normal weather patterns. The effect of the El Niño on the weather in Singapore depends on its intensity. Normally, a moderate or strong El Niño leads to drier and

warmer than normal weather, while a weak El Niño has less impact on the weather (<http://www.nationalgeographic.com/elnino/mainpage.html>).

Figure 2-7. Ocean-Atmospheric conditions in a normal year (a) * Ocean-Atmospheric conditions in an EL Niño year (b) **.

*, ** (Source: NEA's WEATHERWise Singapore)

A very strong El Niño in 1997/98 led to a long dry season which resulted in the worst haze episode to affect Singapore and the region. Singapore was last affected by a major haze episode in 2006 and 2010 when there was an El Niño of moderate intensity.

La Niña is a coupled ocean – atmospheric phenomena which is the opposite of El Niño. During La Niña the sea surface temperature in the central and eastern tropical Pacific Ocean is lower than normal and it causes the region to experience stronger than usual trade winds. La Niña occurs at irregular intervals every 2-7 years and can last from approximately 6 to 18 months and it affects the normal weather patterns.

2.1.6 Haze

Haze is another common phenomenon that Singapore experiences each year. Under certain conditions of weather, when pollutants and smoke are not able to disperse, they stick together to form a hazy cloud at a low level.

Over the past few decades, transboundary smoke haze from land and forest fires during the traditional dry season between June and October have been a periodic trait in the southern Association of South East Asian Nations (ASEAN) region. Land clearing and “slash and burn” agricultural practices in Indonesia are responsible for these annual fires, particularly from Sumatra and Kalimantan (Figure 2–8–a). Furthermore, agricultural burning activities are common during the other traditional dry season between December and March. Thus, Singapore often experiences haze two times each year. The smoke haze situation is usually worsened when it coincides with the El Niño.

Table 2-2. Review of Haze event during this study.

Year	Date	PSI
2009	5 - 9 Aug 2009	57
	15 - 16 Sep 2009	64
	26 – 27 Sep 2009	55
	30 Sep – 3 Oct 2009	55
	23 – 25 Oct 2009	52
2010	20-23 Oct 2010	96
	11 - 14 May 2010	58
2011	11 – 13 Sep 2011	62
	13 - 14 May 2011	60

Figure 2-8-b shows Singapore's financial district skyline on a clear day (left) on May 7, 2012 and shrouded in haze (right) on October 19, 2010. Figure 2-8-c shows Marina Bay Sands Hotel view on a clear day (left) on May 7, 2012 and shrouded in haze (right)

on September 11, 2011. The impact of the transboundary smoke haze in Singapore depends on factors such as the proximity and extent of the fires, the strength and direction of the prevailing winds and the incidence and amount of rain.

Figure 2-8. Indonesia forest fire and land cleaning 2010 (a) Haze in Singapore October 2010 (b) Haze return to Singapore September 2011 (c).

2.2 Review of Singapore Weather during this Study

Table 2-3 presents a summary of the monthly Singapore weather conditions at the NTU sampling site based partly on information published by the National Environmental

Agency. Singapore weather conditions have been affected by El Nino and La Nina phenomena in years 2010 and 2011.

January and February were unusually dry in 2010, while June and July were mainly wet. Overall, meteorological data recorded a total annual rainfall of 2153.1 mm which was 8% below the long term average of 2341.1mm. The moderate El-Niño at the start of the year weakened by April and a moderate to strong La Niña was established by August 2010.

Weak to moderate La Niña conditions prevailed for most of 2011 although there were around five months of neutral conditions between May and September.

The moderate to strong La Niña conditions at the start of the year weakened gradually towards May and strengthened again after September. In general, the annual rainfall was above average in 2011. A monsoon surge coinciding with peak La Niña conditions contributed to a particularly wet January.

As the Northeast monsoon switched into the dry phase and La Niña conditions began to weaken, February 2011 turned out to be an exceptionally dry month. Overall, metrological data recorded a total annual rainfall of 2524.2 mm which was 8% above the long term average of 2341.1mm. Table 2-4 to Table 2-6 compare air quality and climate data over Singapore in years 2010 and 2011.

Table 2-3 . Review of Singapore weather during this study.

12	Year	Weather Conditions	Significant Events	Rainfall Outlook
Jan	2010	Mild Northeast Monsoon condition. Singapore experienced mainly dry and windy conditions.	Sumatra Squalls: 4, 6 and 7 Jan Two monsoon Surge 6-12 th Oct 2010 26-30 th Oct 2010	Below average
	2011	Northeast Monsoon	Strong La Nina condition	60% Above average (due to the prevailing La Nina)
Feb	2010	Mild Northeast Monsoon condition. Dry condition in Singapore due to coincident passage of a dry phase of the Madden Julian Oscillation (MJO) and a moderate El-Nino over the maritime.	Moderate El-Nino Recorded as driest February (data collected from 1986, rainfall: 6.3 mm) Hottest day recorded in Feb 2010 (data collected from 1929, 26 Feb 2010: 35.2 C)	Below average (5 rainy days)
	2011	Start of dry phase of Northeast Monsoon	---	Below average (9 rainy days)
Mar	2010	Mild Northeast Monsoon condition. Warm and dry condition till first week of March. Singapore experienced increasing shower activities in March 2010 with the transition to Inter-Monsoon conditions.	The highest temperature of year 2010 was recorded on 6 March 2010 as one of the 5 hottest days since 1983.	Above average (due to tropical storm “Omais” formed in the north-western Pacific Ocean)
	2011	Northeast Monsoon	Sumatra squalls Thunderstorm (due to sea breeze)	Above average
Apr	2010	Weak Inter-Monsoon condition Singapore experienced moderate to heavy shower and thunderstorm activities in the afternoon and early evening for about 10 days in April	Hotspot activities were mostly subdued in the southern ASEAN region due to shower activities.	Above average
	2011	Inter-Monsoon condition	Sumatra squalls	Above average (Due to the passage of a Madden-Julian Oscillation (MJO)2 wet phase over the Maritime continent)

Continue Table 2-3. Review of Singapore weather during this study.

Month	Year	Weather Conditions	Significant Events	Rainfall Outlook
May	2010	Weak to moderate Inter-Monsoon (First) Singapore experienced moderate to heavy shower and thunderstorm activities in the afternoon and early evening for about 7 days in April.	In the southern ASEAN region, hotspot activities were mostly subdued.	Above average (highest amount of rainfall was recorded in western part of the island).
	2011	Inter Monsoon	Sumatra squalls Heavy rain 4 th May 2011 led to flash floods in parts of northern Singapore. Hot Weather due to the passage of the MJO dry phase (6-8 th May 2011, Temp (8 th May 2011) = 35.3 C). The air quality in Singapore dipped into the moderate range on a few days in May and the highest PSI level of 60 was recorded on 13th May 2011 due to slight smoke haze.	Below average
Jun	2010	Southwest monsoon	Intense thunderstorm events on 16 (Sumatra squall) and 25 (strong convergence of wind over the region) June 2010 which resulted in flash floods over many parts of Singapore. La Nina condition	Above average (80%)
	2011	Southwest monsoon	Flash flood on 5 th June 2011 due to intense rainfall	Above average (90-150 %)
Jul	2010	Southwest monsoon	Intense thunderstorm event on 17 July 2010 (heaviest daily rainfall recorded in last 3 years - Sumatra Squall) which resulted in flash flood over many parts of Singapore. La Nina condition	Above average (50%)
	2011	Southwest monsoon Drier than normal weather conditions	---	Below average (50 - 60 %) (7 rainy days, the lowest recorded rainy days for July from 1942)

Continue Table 2-3 . Review of Singapore weather during this study.

Month	Year	Weather Conditions	Significant Events	Rainfall Outlook
Aug	2009	Southwest Monsoon conditions (dry weather conditions during the first half of August 2009). The second half of the month was wet due to the incursion of moist easterly winds and a surge in the Southwest Monsoon winds.	Transboundary smoke haze from the fires in Sumatra was transported by prevailing winds (5-9th August 2009 moderate PSI has been recorded).	Above average
	2010	Southwest monsoon	Moderate to strong La Nina condition	Above average
	2011	Southwest monsoon Drier than normal weather conditions	5 days affected by Sumatra squalls at end of August	Below average (50 - 60 %)
Sep	2009	Weak Southwest Monsoon conditions Dry weather, interspersed with occasional shower activities.	The smoke haze from South Sumatra was transported northwards by the prevailing southerly to south-westerly winds (16-18th August 2009 moderate PSI has been recorded)	Below average
	2010	Weak Southwest monsoon Inter monsoon (last week of Sep 2010)	---	Above average
	2011	Southwest monsoon	Haze returned to Singapore (11-13 th Sep 2011, The highest 24hr PSI was recorded on 12 September at 62, which turned out to be the highest in 2011)	below average (20%)
Oct	2009	Southwest Monsoon season (first half of October 2009) Inter-Monsoon season around the middle of the month.	----	normal rainfall
	2010	Southwest monsoon Inter-Monsoon (last week of October)	The hotspot count in Sumatra reached a maximum of 358 on the 18 th of October. The prevailing southwest to westerly surface winds brought smoke haze from the fires in Sumatra to Singapore for several days. PSI (moderate to unhealthy, 24hr PSI 22 ^{ed} Oct 2010: 96) low level winds over the region were generally light and variable.	Above average
	2011	Southwest monsoon Inter-Monsoon (mid of October)	Sumatra squalls for first half of October 2011, highest daily rainfall (134 mm) and maximum wind gusts (80.6 km/ h) was recorded in 4 th October 2011) Re-developing La Nina condition. Heaviest rainfall in 21 st and 27 th October 2011, reported flash flood in many areas.	Above average

Continue Table 2-3. Review of Singapore weather during this study.

Month	Year	Weather Conditions	Significant Events	Rainfall Outlook
Nov	2009	Inter-Monsoon conditions (during the first half of November 2010, the low level winds over the region were generally light and variable). Northeast Monsoon conditions (in the second half of the month, winds over the region became progressively from the northeast).	---	Above average
	2010	Inter-Monsoon conditions (first half of November 2010) Northeast Monsoon (second half of November 2010) During the first week of November, Singapore experienced mostly localized morning showers with thunder. Towards the middle of the month, scattered showers occurred mostly in the afternoon.	---	Above average
	2011	Inter-Monsoon conditions (first half of November 2011) Northeast Monsoon (second half of November 2011) The second half of November turned out to be wetter than normal.	2011 experienced the wettest November since 1934, with 24 rain days recorded for the whole month.	Above average (50 %, due to the passage of an intense wet phase of MJO)
Dec	2009	Northeast Monsoon The surges (a steady strengthening of moisture-laden winds over the South China Sea) brought strong winds and spells of moderate to heavy rain to Singapore.	---	Above average
	2010	Weak to moderate Northeast Monsoon	---	Below average
	2011	Northeast Monsoon	Monsoon Surge: 11 th , 17 th , 23 rd Dec 2011	Normal (close to long term average)

Table 2-4. Comparison of air quality in year 2010 and 2011*

Parameters	2010	2011
Sulfur Dioxide ($\mu\text{g} / \text{m}^3$) (mean)	11	10
Nitrogen Dioxide ($\mu\text{g} / \text{m}^3$) (mean)	23	25
PM 10 ($\mu\text{g} / \text{m}^3$) ¹		
(2nd Maximum 24-hourly mean)	127	76
(mean)	26	27
Carbon Monoxide (mg / m^3)		
(2nd Maximum 8-hourly mean)	2.2	2.0
Ozone ($\mu\text{g} / \text{m}^3$)		
(4th Maximum 8-hourly mean)	129	110

Table 2-5. Comparison of Temperature and Sunshine *

Parameters	2010	2011
Air Temperature in Degree Celsius		
Means		
Daily Maximum	31.9	31.3
Daily Minimum	24.9	24.7
Absolute Extremes		
Maximum	35.5	35.3
Minimum	21.7	21.4
Bright Sunshine		
Daily Mean Hours	5.7	5.6

Table 2-6. Comparison of Relative Humidity and Rainfall *

	2010	2011
Mean Relative Humidity ¹		
at 2.00 pm (Per Cent)	71	73
Rainfall		
Total (mm)	2,075	2,525
Maximum in a Day (mm)	121	216
Number of Rainy Days	178	188

* Source: National Environmental Agency, Singapore.

Long term weather records from the NEA station are presented in Table I to Table V in Appendix A for the purpose of determining climatic trends.

2.3 Local Events during this Study

2.3.1 Hungry Ghost Festival

The Hungry Ghost Festival is a traditional Chinese festival and holiday celebrated by the Chinese in the seventh month of the lunar calendar. The fifteenth day of the seventh month in the lunar calendar is called Ghost Day and at the beginning of this day people burn bank notes, joss paper and incense all over Singapore.

Activities during the month include preparing ceremonial food offerings, burning incense, joss paper, and burning crumpled forms of material items such as clothes, gold and other fine goods for visiting spirits of the ancestors. At the beginning of ghost day people commence to burn bank notes, joss paper and incense all over Singapore so that the burning odour is quite noticeable. Figure 2-9 shows pictures that were taken at the beginning of Ghost Day in Singapore. Table 2-7 presents dates of the Hungry Ghost Festival and Ghost day that occurred during this study.

Table 2-7. Ghost Festival and Ghost day from 2009 to 2011.

Year	Ghost Festival	Ghost Day
2009	August 19 to September 15	2 Sep
2010	August 10 to September 7	24 Aug
2011	July 31 to August 28	14 Aug

2.3.2 Large Fire at a Factory in Benoi Crescent

On 3rd September at approximately 4 am a large fire happened in a factory in Benoi Crescent. The fire ravaged the storage and production areas of the factory, devouring a huge volume of paper products (Figure 2-10). This event happened only 4 kilometers away from the NTU sampling site.

Figure 2-9. Hungry Ghost Day in Singapore.

Figure 2-10. Fire breaks out in Benoi Crescent factory.

2.3.3 Fire at Shell Refinery

A major fire occurred at the 500,000 barrel per day (bpd) plant, Shell's biggest worldwide refinery located in Pulau Bukom Island burning between September 28 to October 2 2011. Shell announced that damage was contained to the vicinity of the pump house with other facilities and units unaffected. NEA Singapore said it had not detected the presence of any toxic gases on the mainland as a result of the fire at the Shell Refinery in Pulau Bukom, although the gases it was monitoring were not publicized.

Figure 2-11 (a) Shell Refinery Fire from Pulau Bukom Island and (b) from Singapore.

2.4 Meteorological Conditions at NTU Monitoring Site

Monthly meteorological data for the months of NTU sampling are presented in Table 2-8 and Table 2-9 which showed good agreement with data taken from the National Environmental Agency for year 2010 and 2011 and long term data. This data shows that prevailing winds mostly were of north east and east directions

Table 2-8. Wind direction in NTU sampling site during study.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2010	NNE	NNE	NNE	NNE	SSW	S	S	S	SSW	SSW	NNE	NNE
2011	NNE	NNE	NNE	NNE	S	S	S	SSE	SSE	NW	N	N

2.5 Airborne Particulate Matter

Airborne particulate matter samples (PM₁₀ and PM_{2.5}) were collected on Emfab filters (Borosilicate glass microfibers reinforced with woven glass cloth and bonded with PTFE, Size: 8×10 inch, Pallflex, Emfab TX40HI20-WW, Pall, USA, Figure 2 -12) with high-volume air samplers (HiVol-3000, Ecotech, Australia) equipped with one PM₁₀ and one PM_{2.5} sampling head, both operating at the high flow rate of 67.0 m³h⁻¹ and the average total sampling time was 24-48 h to achieve a concentration of trace metals sufficient for their quantification.

2.5.1 Filter Handling

Filters were heated in an oven at 100 °C for 24 hour prior to use and after sampling, then they were weighed to determine the net particulate mass gain. Each filter was kept in a clean polyethylene bag during transport and storage in the refrigerator. Filters were used in ways to minimize possible contamination. For the majority of the study period, samples were collected continuously for 48-hours, with a replacement filter installed immediately after the used filter was removed.

Table 2-9 Metrological data collected in NTU sampling site during study.

	Mean (Temp)		Min (Temp)		Max (Temp)		Mean Humidity (%)		Min Humidity (%)		Max Humidity (%)		Mean wind speed (m s^{-1})		Rainfall (mm)	
Month/year	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011
Jan.	27.6	26.6	22.5	24.5	35.8	29.9	76.2	85.8	67.2	70.7	85.1	95.3	4.6	6.6	185.9	513.2
Feb.	28.3	27.3	23.6	24.1	36.8	31.7	75.1	81.1	68.1	61.6	81.3	94.1	4.9	7.2	9.8	23.0
Mar.	32.6	27.0	23.8	23.9	38.4	31.3	75.4	85.5	69.8	64.9	85.1	96.9	4.0	3.85	70.0	256.6
Apr.	31.9	27.9	24.8	24.6	38.2	31.9	76.7	83.9	71.3	65.6	90.7	95.6	2.6	2.52	90.8	217.8
May	29.4	28.5	23.7	25.2	38.1	32.4	75.3	85.3	67.7	66.3	87.4	96.9	2.2	2.27	210.1	127.0
Jun.	28.4	28.4	23.1	25.2	35.1	31.3	76.6	83.7	66.8	69.5	87.6	95.1	2.1	3.08	351.0	213.0
Jul.	27.9	28.7	22.2	25.5	35.0	31.9	76.9	81.3	66.9	65.5	91.2	93.1	2.0	4.36	423.2	76.6
Aug.	28.1	27.9	22.7	25.6	35.2	31.0	75.9	82.6	65.4	65.7	84.5	94.2	2.3	4.34	147.3	81.4
Sep.	30.0	27.8	23.3	25.1	35.0	30.9	73.4	82.7	63.2	65.4	84.2	95.1	2.1	4.65	104.9	136.4
Oct.	28.8	27.3	23.8	24.7	35.6	31.0	73.0	87.4	56.6	87.4	87.2	98.3	1.9	3.43	93.2	216.8
Nov.	27.7	27.1	22.9	24.6	35.8	31.1	78.9	87.8	60.4	67.7	91.3	98.9	2.1	2.65	311.7	377.8
Dec.	27.2	26.6	22.7	24.5	35.4	29.9	77.8	88.4	69.3	73.1	90.2	97.8	2.6	4.67	155.2	284.6
Two Years	28.9	27.6	22.2	23.9	38.4	32.4	75.9	84.6	56.6	61.6	91.3	98.9	2.8	4.1	2153.1	2524.2

Figure 2-12. (a) High-volume air samplers (HiVol-3000, Ecotech), (b) filter placed inside instrument to start sampling, (c) collected sample after 24 hours.

After collection of the particulates on the filter, the filter frames were transferred to the laboratory in clean, sealed bags. Filters were stored in a freezer to minimize biological activity until digestion and analysis (Figure 2-13).

Figure 2-13. Filter handling: collected sample after 24 hour (a), clean filter before sampling (b), clean filters and collected samples storage (c).

2.5.2 Microwave Digestion

A programmable 1600W microwave (MARS 5, CEM Corp., Matthews, NC, USA, Figure 2-14) with a rotor and 12 Easy Prep Teflon-lined vessels were used as the closed vessel digestion system. Pressure and temperature were monitored by external ESP-1500Plus and RTP-300 Plus sensors respectively. Microwave digestion was equipped by Duo Temp to better monitor and control the temperature. Easy Prep vessels were cleaned before each digestion using 4 mL ultra-pure HNO_3 heated at 160°C for 15 min at 800 W.

Effective digestions were achieved by setting the microwave program and power settings and optimizing the nature and amount of acids. To evaluate the amount of acids, a multi-elemental standard was prepared and sprayed on a clean filter. The spiked filter was placed inside the air sampler for 2 minutes and removed.

Figure 2-14. Microwave digestion systems (MARS 5, CEM Corp., Matthews, NC, USA).

2.5.3 Sample Preparation and Microwave Digestion Procedure

Collected samples were placed in the oven for 24 hours prior to digestion, then the dried filter was cut into small pieces using a disposable stainless steel knife blade. Filter strips were transferred into digestion vessels followed by addition of 3 mL HNO_3 + 1 ml

HCl to each vessel (Figure 2-15). In a one-step digestion program, the temperature was increased to 185 °C, applying a ramp time of 15 min and a subsequent hold time of 15 min. At the end of the program, the vessels were cooled to room temperature in a fume hood and the pressure inside the vessels slowly released. After cooling the digested samples were diluted with ultra-pure water, filtered, transferred to polyethylene bottles and then stored in the fridge for ICP analysis.

All these steps were repeated for 2783 standard reference material (SRM 2783) of Urban Particulate Matter samples to evaluate different parameters. Prior to digestion, each sample vessel was filled with 5 ml ultrapure nitric acid and placed in the microwave digester. The temperature was ramped to 185°C in 10 minutes and then held i for 10 minutes. After cooling down, all vessels were rinsed with ultrapure water and dried in a clean environment. All utensils for sample handling were soaked in 5% HNO₃ solution over night and rinsed several times with ultra-pure water prior to use. Blank filters were prepared identically to the samples.

Figure 2-15. Different steps of sample preparation

2.5.4 Reagents and Chemicals

Ultra-pure 65% HNO_3 was purchased from J. T. Baker, Canada and 30% HCl was purchased from Merck, Germany. ICP-MS single element calibration standards (1000 ppm) were obtained from High Purity Standards (Charleston, SC, USA), Inorganic Venture (Christiansburg, VA, USA) and Environmental Express (Charleston, SC, USA). For all solution preparation and dilutions, high purity water with 18.2, $\text{M}\Omega\text{ cm}$ resistivity was used (ELGA, PURLAB Option – Q, UK). HNO_3 – HCl 2% solutions were used as the background matrix of reagent blanks, calibrations standards and digested samples to avoid errors related to matrix inconsistencies. Multi-element ICP-MS and ICP-OES calibration solutions were prepared using single element standards (Figure 2-16).

Figure 2-16. ICP - MS and ICP - OES Standard preparation.

2.5.5 ICP

2.5.5.1 ICP-OES

A Thermo Scientific iCAP 6000 Series Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Scientific, UK) was used in the first year of this study for the determination of major and trace elements in rainwater samples. Figure 2-17 presents major components and layout of a typical ICP-OES instrument.

Figure 2-17. Major components and layout of a typical ICP-OES instrument.

ICP-OES works on the principle that atoms/ions are electronically thermally excited into higher energy levels, and energy is emitted when the atoms/ions return to their ground state. The energy is emitted as radiation with characteristic wavelengths for a particular element.

An element can have a number of emission lines that can be used for determination by ICP-OES. The emission lines to be selected depend on its sensitivity and whether there is any interference with emission lines of another element [94].

Figure 2-18. Scientific iCAP 6000 Series ICP-OES.

An ultrasonic nebulizer (USN 5000AT+) was employed in ICP-OES instead of a conventional nebulizer. By using an ultrasonic nebulizer, the analyte concentration needed to produce enough of a signal is reduced, resulting in better detection limits.

The inductively coupled plasma optical emission spectroscopy parameters were optimized by altering the instrument settings when examining the 2783 standard reference material (SRM 2783) for Urban Particulate Matter. The signal intensity is partly dependent on the plasma temperature as the amount of species in excited states increases with higher temperature according to the Boltzmann distribution. The plasma power, also termed the radiofrequency (RF) power, can be optimized as it has an influence on the plasma temperature. A higher plasma power results in higher signal intensity.

Using high RF power for Na resulted in poor accuracy when it was calibrated in the presence of other elements. Improved results were obtained by analysing Na with a

reduced RF power (1200W). Another instrumental setting was the nebulizer flow rate, where maximum intensity was observed at 0.7 L min^{-1} for almost all analytes. A low flow rate results in lower transport of excitable molecules to the plasma while too high a flow rate leads to a decrease in plasma temperature due to the large amount of molecules being injected into the plasma, which eventually lead to a decrease in the signal intensity.

The plasma “view” is also important as different views result in different detection limits. The axial view results in a longer path length, where the detection limits can be greatly improved. The axial view, being more sensitive, was preferred for elements of a lower concentration, while the less sensitive radial view was used for major elements such as Al, Ca, Fe, Mg, K, Na.

Wavelength selection is another important factor which can be used to avoid situations where certain elements emit radiation at similar wavelengths.

In general, optimization of the instrument settings was directed to increase robustness of plasma source and signal to background ratios. Thus, the instrument settings were adjusted to suit the sample matrix in this study.

2.5.5.2 ICP-MS

In this study the concentration of 60 elements were measured using an Agilent 7700 series Inductively Coupled Plasma-Mass Spectrometer (Japan, Figure 2-19) equipped with a 3rd generation He reaction / collision cell (ORS³) to minimize interferences. An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts a percentage of elements in the sample into ions. These ions are then separated and detected by the mass spectrometer. Figure 2 -20 shows a schematic representation of an ICP-MS. Figure 2 -21 explains interference mode using He mode and kinetic energy discrimination. Final optimized instrumental operating parameters for this application are summarized in Table 2-10. The method used for

microwave digestion of particulate matter and ICP - MS analysis were evaluated using SRM 2783.

Figure 2-19. Agilent 7700 series Inductively Coupled Plasma-Mass Spectrometer.

All other parameters, such as torch position, sample depth, extraction, and ion focusing lenses voltages, omega lenses voltages, quadrupole settings, and carrier and blend gas flow rates was optimized daily by aspirating a $1.0 \mu\text{g L}^{-1}$ solution of Ce, Co, Li, Mg, Tl and Y in 2 wt % HNO_3 . Oxides and doubly charged ion ratios were kept below 2%.

Figure 2-20. Major components and layout of a typical ICP-MS instrument coupled with He reaction cell (from Agilent software).

The morphology of the particulate matter on some filters was examined using transmission electron microscopy field-emission scanning electron microscopy (FESEM) (JEOL, Model JSM-7600F).

Table 2-10. Operating condition and instrumental setup for ICP

Parameter	ICP-MS	ICP-OES
Instrument	Agilent 7700 Series (Japan), MicroMist nebulizer, Quartz spray chamber, 3 channel peristaltic pump	Thermo Scientific iCAP 6000 Series, standard nebulizer (Concentric glass nebulizer) and ultrasonic nebulizer (USN 5000AT+), Duo quartz torch, Glass spray chamber, 4 channel peristaltic pump
Torch View	Not Applicable	Duo view System, Auto view used for this application
Tuning Solution	Li, Mg, Y, Ce, Tl, Co; 1 µg/L; 2% HNO ₃	Not Applicable
RF Power	1550 W	1200 W
Nebulizer gas flow	0.7 L min ⁻¹	0.7 L min ⁻¹
Auxiliary gas flow	0.35 L min ⁻¹	0.5-0.7 L min ⁻¹
Lens voltage	Extract 1: 0 V, Extract 2: -200 V, Omega Bias: -90 V, Omega Lens: 10.8 V	Not Applicable
Octopole Parameter	Octp RF: 200 V, Octp Bias: -18 V	Not Applicable
Cone	Ni Sampling cone, Ni Skimmer cone	Not Applicable
Collision Cell	3 rd generation Octopole Reaction System (ORS ³), He mode	Not Applicable
Sample Parameter	Agilent Integrated. Autosampler (I-AS), sample uptake rate 0.3 mL min ⁻¹ , rinsing time 190 s (Ultra pure water and 2% HNO ₃)	ASX-529 Cetac autosampler, sample uptake rate 0.3 mL min ⁻¹ , rinsing time 60 s (Ultra pure water)
Data Acquisition	3 readings per replicate	3 readings per replicate
Time	3-4 min	2-3 min

ICP-MS calibration graphs, QC graph and tuning report are presented in Appendix B.

Interference removal using He mode and Kinetic Energy Discrimination (KED)

Figure 2-21. Interference mode using He mode and kinetic energy discrimination. *

* (<http://www.chem.agilent.com>).

2.6 Rain Samples

Rainwater samples were monitored according to the following criteria:

a) Monitoring site and interval: The rainwater samples were collected within the campus of Nanyang Technological University, SPMS building roof top, in Singapore, from Aug 2009 to Dec 2011 (Figure 2 -22). Rain samples were immediately collected after each rain event.

b) Monitoring parameters: pH, electric conductivity (EC), concentration of ions (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) with ion chromatography and concentration of trace element: (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Gd, Ge, Hf, Hg, In, Ir, K, La, Li, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Zn, and Zr) with ICP-OES and ICP-MS.

c) Meteorological measurement: wind direction/speed, temperature, humidity, rainfall amount (WatchDog 2800 Weather Station, Figure 2 -23).

d) Other information: potential contamination sources, geographical description, climate, sampling methods and sample handling, analytical methods and QA/QC activities.

Figure 2-22. Rainwater sampler (a), collected rainwater samples from NTU sampling site

Figure 2-23. WatchDog weather station.

Rainwater monitoring was carried out by common methodologies specified in most technical documents (GAW Precipitation Chemistry Program, Acid Deposition Monitoring Network in East Asia (EANET) and National Atmospheric Deposition Program (NADP)). An example of the flow chart that was carried out is given in Figure 2 -24.

Figure 2-24. Flow chart of sampling and chemical analysis of wet deposition

2.6.1 Rainwater Sampling

A manual rainwater collector (a large diameter PVC funnel (diameter 50 cm) fitted to a 5 L high density polyethylene container, Figure 2-22) used on the roof of the School of Physical and Mathematical Sciences building (around 12 m height). Since each surface that comes in contact with a sample is a potential source or sinks for the dissolved compositions

in rainwater, every effort was made to minimize sample handling and transfers between containers.

2.6.2 Handling and Transferring Rainwater Samples:

Because of the potential for chemical changes, samples were transferred to their sample container immediately after the rain event or in the early morning following night events. Samples were only transferred by pouring directly from sample collector to sample container to avoid another contact surface (pipettes, syringes, funnels, etc.). Polyethylene (PE) containers were used to store rainwater during the period of the sampling (Figure 2-22).

Ultrapure water was used to clean rainwater sample containers instead of a detergent or acid solution to prevent any residues. Rainwater sample containers were soaked in ultrapure water for 24 to 48 hours. A clean sponge used to remove visible residues from the rainwater sample container surfaces. Wearing nitrile gloves was necessary to clean and handle rainwater sample containers. Cleaned rainwater sample containers that were not used immediately were dried inside an oven in a clean environment, sealed in plastic and stored in a clean area.

2.6.3 Rainwater Sample Preparation

After collection, the samples were separated into two aliquots and transferred into polyethylene containers for different analytical determinations. An unfiltered aliquot was used for pH (Metrohm 826 pH meter, Figure 2-25) and electrical conductivity (EC, IONcheck 30 Conductivity Meter, Figure 2-25) measurements immediately on arrival of the samples in the laboratory, while for chromatographic and inductively coupled plasma determination, the remaining aliquot was filtered through a 0.25 μm Pall Acrodisc syringe filter with Supor membrane (hydrophilic polyethersulfone).

Once the sample preparation was completed, samples were covered quickly and then sealed tightly to minimize the potential for contaminating materials to fall into the sample prior to the instrumental analysis. Sealed sample containers were placed in clean plastic bags.

Figure 2-25. Metrohm 826 pH meter (a), IONcheck 30 Conductivity Meter (b).

2.6.4 Sample Storage

Water samples were sent for analysis as soon after collection as practical. The best practice is to keep storage times short. Samples were stored in fridge (4°C) prior to analysis.

2.6.5 Laboratory Operation:

Analyzed parameters for collected rain samples have been listed in Table 2 -11.

Table 2-11. List of laboratory parameters.

Analyte	Preferred Methods
pH	Glass electrode
Conductivity	Conductivity Cell
F ⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ and SO ₄ ²⁻	IC *
Na ⁺ , K ⁺ , NH ₄ ⁺ , Ca ²⁺ and Mg ²⁺	IC *
Li, Be, B, Al, Ca, Na, K, Mg, Mn, Sc, Ti, La, Zr, Hf, Ge, Ga, Rh, Ru, Re, Th, Te, Tl, Ti, Pd, Sr, Os, Hg, Pt, Au, Gd, Ce, Sb, U, Zn	ICP-OES ** and ICP-MS ***

*IC = ion chromatography; ** ICP-OES = inductively coupled plasma optical emission spectroscopy; *** ICP-MS = inductively coupled plasma mass spectrometry

2.6.5.1 pH Measurements

Initial studies showed that the pH of rain at the sampling site varied between approximately 3.0 and 6.5 pH unit (with the concentration of hydrogen ions normally from 1000 $\mu\text{eq L}^{-1}$ to $< 0.5 \mu\text{eq L}^{-1}$). The pH is related to the free acid activity as the negative logarithm of the hydronium ion concentration by the equation:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad (\text{Eq. 2-1})$$

Where $[\text{H}_3\text{O}^+]$ is the activity or concentration of free hydronium ions. pH measurements were performed using a Metrohm pH meter (Model: 826 pH mobile) with a glass (H_3O^+) electrode in combination with a reference electrode. The glass electrode potential varies with the activity of H_3O^+ ions in solution. Since the temperature has an effect on the pH measurements, it must be controlled by using instruments that have temperature compensation. A temperature setting of 25°C is recommended for pH measurement.

The pH meter was calibrated every week using commercially prepared pH 4.0, 7.0 and 10.0 buffer solutions. After each rain sample pH measurement, ultrapure water was used to thoroughly rinse the glass semipermeable membrane. The pH electrode was stored in 3 M KCl solution when it was not in use and immediately prior to use, the pH electrode was thoroughly rinsed with ultrapure water.

2.6.5.2 Conductivity

The conductivity of a solution is the inverse value of its specific resistance and can be directly measured using a conductivity bridge with a measuring cell. A NaCl solution of known concentration and conductivity (1000 $\mu\text{S / cm}$) was used for calibration (Radiometer analytical, France). Conductivity is measured and expressed in units of microsiemens per centimetre ($\mu\text{S cm}^{-1}$), corrected to 25°C.

2.6.5.3 Cation and Anion Determination by Ion Chromatography

Ion chromatography (IC) has been widely used in recent years to analyse major anions in rainwater samples, mainly in combination with electrochemical detection. [95-97].

Ion chromatography is a quantitative analytical method based on ion exchange which is used to separate anions or cations. Dionex ion chromatography conditions that were used in this project are listed in Table 2 -12.

Table 2-12. Ion Chromatography Conditions

Parameters	Cation Instrumentation Setting	Anion Instrumentation Setting
System	Dionex ICS-900	Dionex ICS-1000
Column	IonPac® CS12A 4×250 mm Analytical	IonPac® AS22 4×250mm Analytical
Mode of detection	Conductivity	Conductivity
Eluent composition	1.8 M MethaneSulfonic Acid (MSA)	0.1 M Sodium Carbonate and 0.1 M Sodium Bicarbonate
Regenerant composition	100 mM TetraButylAmmonium Hydroxide (TBAOH)	Nil (electrochemical suppressor)
Eluent flow rate	1.0 mL/min	1.2 mL/min
Conductivity	< 2 μ S $\pm$ 10%	< 20 μ S $\pm$ 10%
Pressure	1280 psi $\pm$ 100 psi	1880 psi $\pm$ 100 psi
Analysis Time	16 mins	14 mins
Loop	10 μ L	25 μ L

2.6.6 Ion Chromatography Instrumentation

In this study major cations and anions were determined by two Dionex ion chromatography systems (ISC-900 and ISC-1100 respectively) with conductivity detection (Figure 2-26).

Figure 2-27 shows a simple sketch of general arrangements of IC components. IC calibration graphs have been attached in Appendix C.

Figure 2-26. IC-1100 used for cation (left) and IC-900 used for anion measurements.

2.6.7 Reagents and Solutions

All reagents were purchased from Dionex and Thermo Fischer. Since the purity of water used for dilution is highly important, ultra-pure water with conductivity of $<1.8 \mu\text{S cm}^{-1}$ was used.

2.6.7.1 Cation Analysis

Eluent (20 mM Methanesulfonic acid) was prepared by diluting 1.8 M methanesulfonic acid as a stock solution with ultrapure water to achieve the desired eluent properties. Regenerate (100 mM tetrabutylammonium hydroxide) was prepared by mixing tetrabutylammonium hydroxide (40%) with ultrapure water. The prepared regenerate and eluent were stable for two weeks.

2.6.7.2 Anion Analysis

Anion analysis with the Dionex ICS-1000 required only the preparation of the eluent (since it utilized an electrochemical rather than chemical suppressor) Anion eluent (4.5 mM sodium carbonate/4mM sodium bicarbonate) was prepared by mixing and diluting of 0.5 M sodium carbonate and 0.5 M sodium bicarbonate as stock solutions.

2.6.8 Calibration Solutions

Several calibration solutions and one zero standard (blank, normally ultrapure water) were used to generate a suitable calibration curve. Standards were purchased from the supplier (Dionex). Calibrations of standards were done before analyses of rainwater samples. The standards were prepared with three five-fold serial dilutions for the anions and four five-fold serial dilutions for the cations. The calibration standards, stored in cleaned polyethylene containers in a refrigerator, were stable up to one month but a weekly fresh preparation was preferred.

Table 2-13 and Table 2-14 illustrate the serial dilutions.

Table 2-13. Serial dilution of cation standards.

Cations (mg/mL)	Original Concentration	Dilution 1	Dilution 2	Dilution 3	Dilution 4
Li ⁺	50	10	2	0.4	0.08
Na ⁺	200	40	8	1.8	0.32
NH ₄ ⁺	400	80	16	3.2	0.64
K ⁺	200	40	8	1.8	0.32
Mg ²⁺	200	40	8	1.8	0.32
Ca ²⁺	1000	200	40	8	1.6

Table 2-14. Serial dilution of anion standards.

Anion (mg/mL)	Original Concentration	Dilution 1	Dilution 2	Dilution 3
F ⁻	20	4	0.8	0.16
Cl ⁻	30	6	1.2	0.24
NO ₂ ⁻	100	20	4	0.8
Br ⁻	100	20	4	0.8
NO ₃ ⁻	100	20	4	0.8
PO ₄ ³⁻	150	30	6	1.2
SO ₄ ²⁻	150	30	6	1.2

Figure 2-27. General arrangements of components in an IC instrument

2.6.9 Ion Chromatography Analytical Procedure

Samples for injection into the ion chromatograph must be free from particles to avoid blockage of the capillary connectors and of the inlet on the head of the separator column. Typically, one-way filters were used (0.2 to 0.45 μm) for filtration of rainwater samples. One example of a measurement procedure is as follows:

- 1- Prepare new eluent, regenerate and standards solution.
- 2- Set up the chromatograph for most sensitive range.
- 3- Purge system for 10 minutes
- 4- Begin to pump the eluent and regenerate through the columns. If necessary, allow the IC to warm up (~2 hours).
- 5- Inject ultrapure water followed by standard solutions through the loop injector and start analysis.

Calibration curves should be made using the working standard solutions prior to each measurement set of rainwater samples. The injection was started with the lowest concentration standard followed by increasing concentrations.

2.7 Data Processing

Particulate Matter data were processed by using a home designed Windows based application written in C# programming language in .Net platform. Particulate Matter Data Processor (PMDP) application facilitates the user to deliver highly accurate results in a short time through a user friendly user interface. The details of this application are explained in Appendix D.

The graphs presented in this study were drawn using Excel (2007 and 2010), Origin 8.1 and Statistica 10.

Chapter 3: Study of Airborne Particulate Matter

3.1 Parameter Optimization

Several parameters such as the concentration, volume and acid composition, and microwave oven settings including ramping time, temperature and holding time were optimized in order to achieve complete dissolution of particulate matter prior to ICP-MS analysis [98].

3.1.1 Microwave Digestion Setting

The microwave digester parameters were optimized by examining different power values and temperature using spiked filters and SRM 2783 (a standard PM reference material). Table 3 -1 summarizes all the examined programs. The differences between the microwave digestion programs used in this work were; the number of steps, the power applied, and the temperature applied. Recovery tests from first few methods showed that low power values and low temperatures were not able to digest particulate matter completely. Digestion times were studied by increasing the holding time; the result indicated that the difference was only around 5 % in the recovery tests. In another study it was suggested that changes in microwave digestion times should not significantly affect the results [99]. This does not mean that the decomposition time has no effect on the acid digestion, but it specifies that 10 to 15 minutes time is adequate to complete the digestion of most samples.

On the other hand, after setting the power to 1600 W the number of stages were investigated in order to achieve the shortest time with highest recovery. The results of the recovery tests of spiked samples showed there was not any significant difference between the one stage and two stages programs.

Table 3-1. Microwave digestion programs to study the effect of temperature and power on acid digestion.

Program		Parameter				Recovery test*
		Power (W)	Ramping Time min	Temp (°C)	Holding Time min	
I ¹	Stage 1	400	10	85	10	40-50 %
	Stage 2	800	10	145	10	
II ¹	Stage 1	800	10	80	10	50-65 %
	Stage 2	1600	10	145	10	
III ¹	Stage 1	800	10	80	10	55-75 %
	Stage 2	800	10	145	10	
	Stage 3	1600	10	185	10	
IV ¹	Stage 1	800	15	80	20	65-83 %
	Stage 2	800	10	145	20	
	Stage 3	1600	10	185	15	
V ¹	Stage 1	800	15	80	10	70-88 %
	Stage 2	1600	10	145	10	
	Stage 3	1600	10	185	10	
VI ¹	Stage 1	1600	10	125	10	75-95 %
	Stage 2	1600	10	185	10	
VII ¹	Stage 1	1600	15	125	10	80-117 %
	Stage 2	1600	15	185	10	
VII ^{1,2}	Stage 1	1600	15	125	15	80-116 %
	Stage 2	1600	15	185	15	
VIII ^{1,2}	Stage 1	1600	15	185	15	80-121 %
IX ^{1,2}	Stage 1	1600	10	185	15	80 - 112 %

* All digestion were performed with 4 ml nitric acid and replicated 7 times. ¹ Spiked filters used for digestion. ² SRM 2783 used for digestion.

Finally, the last three methods in Table 3-1 were examined with SRM 2783 to optimize method development, and Program IX was selected as the most suitable procedure to use for microwave assisted acid digestions.

3.1.2 Acid Optimization

A large number of different acid and acid mixtures have been used for microwave digestions [100]. The effects of HNO₃ volume and HCl addition on elemental recoveries were evaluated using spiked filters (Table 3 -2 and Table 3 -3).

Table 3-3 show elemental recoveries (%) of spiked filters ($n = 7$) by ICP–MS after microwave digestion. Most studies have selected nitric acid as reagent for acid digestion due to the solubility of the nitrates as well as its oxidizing ability while avoiding chemical and spectral interferences compared to using acids containing Cl, S, F, or P [101-103].

Recovery tests for different amounts of nitric acid were performed and the results showed that increasing amount of nitric acid helped to improve acid digestion but had an effect on the ICP–MS sensitivity. Higher amounts of HNO₃ would decrease ICP–MS signal intensity and when above 5%, it speeds up corrosion of the cones used in the ICP-MS instrument [104]. In this work, ~ 4.0 % HNO₃ was employed for all standards, blanks and samples.

As it can be seen from Table 3-2, that Ti, Zr, Hf, Ta, W, Ge, Sn, Sb, Os, Ru, Rh, Ir, Pt and Au did not meet acceptable recovery (100 ± 20 %) which can be related to their poor solubility in HNO₃. Therefore, recovery tests were also performed with a mixture of 3 ml of HNO₃ and different amounts of HCl to examine how HCl affected the acid digestion. It is apparent from Table 3-3 that recovery of Ru, Rh, Ir, Pt and Au improved with adding HCl, however the higher amount of HCl showed an inverse effect on the successful acid digestion for other elements due to dilution of HNO₃ and consequently reduction of its oxidizing stability.

From the data in Table 3-2 it can be seen that Ti, Zr, Hf, Ta, W, Ge, Sn, Sb, Mo and Os did not have significant differences in recovery values when using HCl. Os in the presence of HNO_3 forms OsO_4 which is volatile. Other cases might relate to the silicon components of the particulate matter that cannot be dissolved easily in HNO_3 and HCl. The addition of low amounts of HF might improve the acid digestion, but because of the difficulty of working with HF due to the safety, instrumentation compatibility and the need to add H_3BO_3 to remove excess HF, using HF was avoided in this work. It is inevitable that when testing for the presence of a large number of elements that the digestion procedure will not be perfect for every element, thus the concentrations that are observed represent the minimum amount of each element present in the sample.

Table 3-2 and Table 3-3 show elemental recoveries (%) of spiked filters ($n = 7$) by ICP-MS after microwave digestion. Most studies have selected nitric acid as reagent for acid digestion due to the solubility of the nitrates as well as its oxidizing ability while avoiding chemical and spectral interferences compared to using acids containing Cl, S, F, or P [101-103].

Table 3-2. Elemental recoveries (%) of spiked filters ($n = 7$) by ICP–MS after microwave digestion to study the effect of HNO_3 amount on acid digestion.

[1]: no gas mode, [2] He mode.

Elements	2 ml	3 ml	4 ml	5 ml	Elements	2 ml	3 ml	4 ml	5 ml
7 Li [1]	51	77	74	61	103 Rh [2]	25	14	12	66
9 Be [1]	10	22	25	10	105 Pd [2]	48	89	82	65
11 B [1]	52	70	67	37	107 Ag [2]	37	80	76	40
23 Na [2]	67	71	74	150	111 Cd [2]	25	64	56	50
24 Mg [2]	65	84	71	58	115 In [2]	44	73	72	61
27 Al [2]	48	79	64	50	118 Sn [2]	12	34	33	33
39 K [2]	66	87	77	65	121 Sb [2]	43	46	43	44
44 Ca [2]	48	78	76	56	125 Te [2]	29	79	61	54
45 Sc [2]	39	70	68	54	133 Cs [2]	41	80	77	51
48 Ti [2]	36	65	68	53	138 Ba [2]	58	90	84	66
51 V [2]	51	61	59	26	139 La [2]	29	79	64	43
52 Cr [2]	31	57	53	34	140 Ce [2]	24	72	67	46
55 Mn [2]	29	55	49	33	178 Hf [2]	39	46	46	45
56 Fe [2]	21	40	37	14	181 Ta [2]	37	56	53	54
58 Ni [1]	18	31	27	13	182 W [2]	34	59	57	53
59 Co [2]	35	42	39	10	185 Re [2]	40	66	68	54
63 Cu [2]	54	80	75	52	189 Os [2]	36	42	46	39
64 Zn [1]	57	72	63	59	193 Ir [2]	11	17	23	20
69 Ga [2]	38	65	57	46	195 Pt [2]	33	32	33	36
72 Ge [2]	37	54	53	47	197 Au [2]	25	28	30	17
75 As [2]	39	55	43	21	202 Hg [2]	10	16	13	16
78 Se [2]	25	56	53	31	205 Tl [2]	45	86	40	25
85 Rb [2]	32	75	64	27	208 Pb [2]	42	31	18	14
88 Sr [2]	41	98	84	54	209 Bi [2]	36	81	75	30
90 Zr [2]	33	58	52	56	232 Th [2]	43	79	68	64
95 Mo [2]	9	19	20	11	238 U [2]	47	74	70	58
101 Ru [2]	20	33	35	14					

Table 3-3. Elemental recoveries (%) of spiked filters ($n = 7$) by ICP–MS after microwave digestion to study the effect of HCl on acid digestion.

Elements	3 ml HNO ₃ + 0.5 ml HCl	3 ml HNO ₃ + 1 ml HCl	3 ml HNO ₃ + 2 ml HCl	Elements	3 ml HNO ₃ + 0.5 ml HCl	3 ml HNO ₃ + 1 ml HCl	3 ml HNO ₃ + 2 ml HCl
7 Li [1]	82	82	67	103 Rh [2]	45	85	32
9 Be [1]	68	78	60	105 Pd [2]	88	90	62
11 B [1]	72	84	66	107 Ag [2]	78	77	65
23 Na [2]	97	101	142	111 Cd [2]	67	81	58
24 Mg [2]	76	97	67	115 In [2]	71	77	65
27 Al [2]	79	99	71	118 Sn [2]	54	62	61
39 K [2]	83	98	71	121 Sb [2]	65	67	71
44 Ca [2]	90	105	83	125 Te [2]	62	79	74
45 Sc [2]	62	81	60	133 Cs [2]	73	82	75
48 Ti [2]	74	77	76	138 Ba [2]	71	92	88
51 V [2]	71	97	70	139 La [2]	81	105	90
52 Cr [2]	59	89	66	140 Ce [2]	54	76	49
55 Mn [2]	71	96	62	178 Hf [2]	50	52	45
56 Fe [2]	35	88	47	181 Ta [2]	53	57	60
58 Ni [1]	35	84	60	182 W [2]	54	57	53
59 Co [2]	59	111	62	185 Re [2]	70	72	66
63 Cu [2]	82	95	79	189 Os [2]	69	75	81
64 Zn [1]	78	93	62	193 Ir [2]	66	79	79
69 Ga [2]	57	94	59	195 Pt [2]	80	92	91
72 Ge [2]	54	584	59	197 Au [2]	54	77	80
75 As [2]	78	92	62	202 Hg [2]	43	79	81
78 Se [2]	70	92	63	205 Tl [2]	92	104	59
85 Rb [2]	67	88	33	208 Pb [2]	53	112	42
88 Sr [2]	65	105	68	209 Bi [2]	80	85	75
90 Zr [2]	57	60	52	232 Th [2]	76	87	84
95 Mo [2]	60	67	55	238 U [2]	76	89	70
101 Ru [2]	64	82	67				

3.2 Blanks, Detection Limits and Precision

The Emfab filters used to collect PM samples were tested to check for the presence of any impurities. The concentrations of target elements were measured by ICP-MS in solutions of the filter that were digested the same way as the samples. It was found that the filter materials contributed negligible interference to the analysis.

Using optimized conditions, the detection limits and precision of replicate measurements were established. Detection limits were calculated following the IUPAC rules on the basis of 3σ criterion for ten replicated measurements of the blank signal.

3.3 Validation of Measurements of Trace Elements

Several ICP-MS methods for PM have been developed using Standard Reference Material (SRM) 2783 as a surrogate.

Table 3-4 illustrates the results of the determination of analytes evaluated in the standard reference material NIST 2783 (urban particulate matter 2.5) as measured by ICP-MS. Briefly, the average analytical results are in good agreement with the related certified values with the difference between the two values being less than 20% for most of the elements.

3.4 Elemental Composition of Airborne Particulate Matter

A total of 54 elements were determined by ICP-MS in airborne particulate matter ($PM_{2.5}$ and PM_{10}). Annual and two years arithmetic mean, concentration range (maximum to minimum), median and percentile 95% are given in Table 3-5 to Table 3-7 for both $PM_{2.5}$ and PM_{10} , with the corresponding box plots for all measured elements and particulate matter concentrations given in Figure 3-1.

Table 3-4. Analysis of the Standard Reference Material NIST 2783 (SRM 2783 - urban particulate matter 2.5) by ICP-MS*

Elements	Certified	Found	Recovery %
Al	23210	21100	91
As	11.8	11.9	101
Ba	335	319	95
Ca	13200	12623	96
Co	7.7	7.4	96
Cr	135	116	86
Cu	404	396	98
Fe	26500	25830	97
K	5280	4827	91
Mg	8620	8394	97
Mn	320	336	105
Na	1860	1840	99
Ni	68	65	95
Pb	317	316	100
Sb	71.8	64.4	90
Ti	1490	1462	98
V	48.5	47.1	97
Zn	1790	1582	88
Ce	23.4	22.6	96
Rb	24	26	108
Sc	3.54	3.13	88
Th	3.23	2.98	92
U	1.234	1.07	87
W	5	3.9	78

*Two sets of replicates, each set consisting of 10 measurements.

A total of 279 PM₁₀ samples and 276 PM_{2.5} samples were collected from October 2009 to December 2011. For each data set, the data below detection limits and backgrounds were examined using Particulate Matter Data Processing software (PMDP).

In both PM sizes, the major elements (Na, Ca, Zn, K, Al, and Mg) and B were in greater concentrations, ranging from 5 ng/m³ to a maximum of approximately 50000 ng/m³ (50 µg/m³). Elemental concentrations for elements expected to be present in much lower amounts (trace elements) were found to vary from values less than the detection limit to a maximum of 1000 ng/m³ (1 µg/m³).

The maximum concentrations of crustal elements such as Al, Sc, Fe, Mn etc., were measured in PM₁₀ as was expected.

(a)

(b)

Figure 3-1. Box and whisker plots for average concentrations of measured elements in particulate matter (a) PM_{10} and (b) $PM_{2.5}$, for the period between Oct 2009 and 31st December 2011. Horizontal box lines: 25, 50 and 75th percentile values; error bars, 5 and 95th percentile values; $\top$ and $\perp$ are maximum and minimum valid values, respectively. The arithmetic mean corresponds to cross inside the box ($\square$).

Continue Figure 3-1. Box and whisker plots for average concentrations of measured elements in particulate matter (a) PM_{10} and (b) $\text{PM}_{2.5}$, for period between Oct 2009 and 31st December 2011.

(a)

(b)

Continue Figure 3-1. Box and whisker plots for average concentrations of measured elements in particulate matter (a, PM_{10} and b $PM_{2.5}$) for the period between Oct 2009 and 31st December 2011.

(a)

(b)

Continue Figure 3-1. Box and whisker plots for average concentrations of measured elements in particulate matter (a) PM_{10} and (b) $PM_{2.5}$, for the period between Oct 2009 and 31st December 2011.

(a)

(b)

Continue Figure 3-1. Box and whisker plots for average concentrations of measured elements in particulate matter (a) PM_{10} and (b) $\text{PM}_{2.5}$, for the period between Oct 2009 and 31st December 2011.

Table 3-5. Annual arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ in year 2010 (ng m⁻³).

Elements	2010 - PM _{2.5}			2010 - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
7 Li (1)	5.45 37.69 - 0.30	4.51	3.11 - 6.94	5.60 ± 3.52 24.12 - 0.56	4.78	3.27 - 6.80
9 Be (1)	0.03 0.14 - < DL	0.03	0.02 - 0.04	0.04 ± 0.02 0.141 - < DL	0.03	0.02 - 0.05
11 B (1)	29.52 × 10 ² 10.91 × 10 ³ - 2.54 × 10 ²	23.63 × 10 ²	16.05 × 10 ² - 38.39 × 10 ²	32.07 × 10 ² ± 31.96 × 10 ² 24.20 × 10 ³ - 1.93 × 10 ²	25.51 × 10 ²	15.14 × 10 ² - 37.92 × 10 ²
23 Na (2)	86.94 × 10 ² 38.76 × 10 ³ - 10.02 × 10 ²	76.03 × 10 ²	43.76 × 10 ² - 11.29 × 10 ³	89.37 × 10 ² ± 53.14 × 10 ² 42.92 × 10 ³ - 11.44 × 10 ²	82.91 × 10 ²	52.83 × 10 ² - 10.96 × 10 ³
24 Mg (2)	10.56 × 10 ² 68.78 × 10 ² - 16.71	8.93 × 10 ²	4.26 × 10 ² - 15.34 × 10 ²	13.68 × 10 ² ± 28.55 × 10 ² 33.42 × 10 ³ - 20.95	9.70 × 10 ²	4.31 × 10 ² - 14.51 × 10 ²
27 Al (2)	27.21 × 10 ² 54.57 × 10 ³ - 21.45	19.55 × 10 ²	7.88 × 10 ² - 35.00 × 10 ²	23.61 × 10 ² ± 22.99 × 10 ² 15.78 × 10 ³ - 33.31	19.31 × 10 ²	7.80 × 10 ² - 30.97 × 10 ²
39 K (2)	26.25 × 10 ² 19.38 × 10 ³ - 21.49	20.54 × 10 ²	11.09 × 10 ² - 35.47 × 10 ²	24.92 × 10 ² ± 20.01 × 10 ² 14.88 × 10 ³ - 27.35	21.26 × 10 ²	12.41 × 10 ² - 34.00 × 10 ²
44 Ca (2)	46.31 × 10 ² 33.23 × 10 ³ - 67.74	38.00 × 10 ²	20.85 × 10 ² - 64.69 × 10 ²	50.06 × 10 ² ± 37.20 × 10 ² 24.41 × 10 ³ - 1.62 × 10 ²	42.19 × 10 ²	25.58 × 10 ² - 62.83 × 10 ²
45 Sc (2)	0.30 1.98 - 0.68 × 10 ⁻²	0.23	0.15 - 0.37	0.29 ± 0.22 1.52 - 0.02	0.24	0.16 - 0.39
48 Ti (2)	17.67 1.32 × 10 ² - 1.04	14.49	9.01 - 21.17	22.18 ± 28.25 2.24 × 10 ² - 2.16	15.93	9.55 - 23.59
51 V (2)	9.9 74.78 - 0.56	7.04	2.69 - 12.61	11.04 ± 9.01 42.16 - 0.28	9.58	3.46 - 15.48
52 Cr (2)	4.96 86.65 - 0.28	4.01	2.38 - 5.76	4.81 ± 3.08 19.74 - 0.63	4.31	2.89 - 6.09
55 Mn (2)	11.40 43.75 - 0.79	8.99	4.68 - 15.57	15.31 ± 11.65 61.09 - 1.12	12.13	5.40 - 22.02
56 Fe (2)	1.84 × 10 ² 7.52 × 10 ² - 8.29	1.59 × 10 ²	93.28 - 2.37 × 10 ²	3.11 × 10 ² ± 2.48 × 10 ² 18.81 × 10 ² - 6.58	2.63 × 10 ²	1.33 × 10 ² - 4.26 × 10 ²
58 Ni (1)	6.08 97.31 - 0.27	4.74	2.32 - 7.93	7.68 ± 5.91 33.10 - 0.31	6.34	2.61 - 11.01
59 Co (2)	0.23 1.34 - 0.02	0.21	0.12 - 0.31	0.36 ± 0.3035 2.06 - 0.03	0.29	0.14 - 0.50
63 Cu (2)	11.49 35.18 - 1.48	10.33	6.57 - 15.60	18.74 ± 12.08 99.05 - 2.00	17.07	11.28 - 23.52
64 Zn (1)	16.74 × 10 ² 75.90 × 10 ² - 90.03	13.67 × 10 ²	5.55 × 10 ² - 23.53 × 10 ²	18.27 × 10 ² ± 15.78 × 10 ² 11.30 × 10 ³ - 83.32	15.01 × 10 ²	6.57 × 10 ² - 23.67 × 10 ²
69 Ga (2)	1.01 × 10 ² 4.97 × 10 ² - 3.77	66.70	37.15 - 1.37 × 10 ²	1.17 × 10 ² ± 1.07 × 10 ² 7.66 × 10 ² - 3.77	83.73	38.51 - 1.72 × 10 ²

Continue Table 3–5. Annual arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ in year 2010 (ng m⁻³).

Elements	2010 - PM _{2.5}			2010 - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
72 Ge (2)	0.03 0.22 - < DL	0.02	0.01 - 0.03	0.04 ± 0.04 0.40 - < DL	0.03	0.02 - 0.04
75 As (2)	1.0877 3.63 - 0.16	0.99	0.75 - 1.34	1.47 ± 0.89 4.96 - 0.22	1.28	0.85 - 1.83
78 Se (2)	0.52 2.83 - 0.06	0.39	0.23 - 0.63	0.59 ± 0.46 3.11 - 0.07	0.44	0.28 - 0.77
85 Rb (2)	2.08 6.01 - 0.31	1.91	1.40 - 2.48	2.34 ± 1.16 7.60 - 0.45	2.20	1.55 - 2.82
88 Sr (2)	57.08 3.29 × 10 ² - 3.75	47.59	31.41 - 76.33	59.12 ± 39.45 2.76 × 10 ² - 7.64	53.05	36.64 - 78.72
90 Zr (2)	2.24 13.68 - 0.08	1.89	1.18 - 2.89	2.72 ± 2.72 20.79 - 0.09	2.10	1.41 - 3.16
95 Mo (2)	0.26 4.86 - 0.01	0.16	0.08 - 0.31	0.42 ± 0.34 1.55 - 0.02	0.32	0.13 - 0.58
101 Ru (2)	0.14 × 10 ⁻² 0.9 × 10 ⁻² - < DL	0.00	0.04 × 10 ⁻² - 0.18 × 10 ⁻²	0.22 × 10 ⁻² ± 0.46 × 10 ⁻² 0.04 - < DL	0.00	0.05 × 10 ⁻² - 0.21 × 10 ⁻²
103 Rh (2)	0.05 0.24 - < DL	0.04	0.03 - 0.07	0.05 ± 0.04 0.17 - < DL	0.05	0.03 - 0.07
105 Pd (2)	0.01 0.08 - < DL	0.01	0.43 × 10 ⁻² - 0.02	0.01 ± 0.91 × 10 ⁻² 0.05 - < DL	0.01	0.32 × 10 ⁻² - 0.01
107 Ag (2)	0.08 2.39 - < DL	0.04	0.03 - 0.07	0.20 ± 1.28 15.16 - < DL	0.05	0.03 - 0.10
111 Cd (2)	0.69 26.89 - 0.06	0.37	0.25 - 0.56	0.77 ± 2.48 29.86 - 0.08	0.46	0.29 - 0.67
115 In (2)	0.01 0.10 - < DL	0.01	0.72 × 10 ⁻² - 0.01	0.02 ± 0.01 0.13 - < DL	0.01	0.87 × 10 ⁻² - 0.02
118 Sn (2)	0.95 3.79 - 0.03	0.77	0.39 - 1.20	1.31 ± 0.99 4.96 - 0.16	0.99	0.63 - 1.72
121 Sb (2)	0.03 0.7249 - < DL	0.02	0.01 - 0.03	0.10 ± 0.43 3.45 - < DL	0.03	0.02 - 0.05
125 Te (2)	0.89 × 10 ⁻² 0.05 - < DL	0.01	0.44 × 10 ⁻² - 0.01	0.01 ± 0.95 × 10 ⁻² 0.06 - < DL	0.01	0.58 × 10 ⁻² - 0.01
133 Cs (2)	0.09 0.48 - 0.01	0.08	0.05 - 0.12	0.11 ± 0.08 0.49 - < DL	0.09	0.06 - 0.13
138 Ba (2)	4.86 × 10 ² 23.54 × 10 ² - 24.78	3.19 × 10 ²	1.74 × 10 ² - 6.72 × 10 ²	5.63 × 10 ² ± 5.16 × 10 ² 37.76 × 10 ² - 22.75	4.02 × 10 ²	1.95 × 10 ² - 8.20 × 10 ²
139 La (2)	0.65 2.77 - 0.02	0.53	0.34 - 0.90	0.75 ± 0.50 2.63 - 0.05	0.66	0.39 - 1.03

Continue Table 3–5. Annual arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ in year 2010 (ng m⁻³).

Elements	2010 - PM _{2.5}			2010 - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
140 Ce (2)	1.46 7.15 - 0.06	1.15	0.75 - 2.0	1.6 ± 1.21 7.85 - 0.16	1.35	0.81 - 2.11
157 Gd (2)	0.09 0.37 - < DL	0.07	0.05 - 0.12	0.09 ± 0.06 0.45 - < DL	0.08	0.06 - 0.12
178 Hf (2)	0.05 0.33 - < DL	0.04	2.68 × 10 ⁻² - 6.32 × 10 ⁻²	0.07 ± 0.07 0.59 - < DL	0.04	0.03 - 0.07
181 Ta (2)	0.15 × 10 ⁻² 0.05 - < DL	0.12 × 10 ⁻²	0.01 × 10 ⁻² - 0.18 × 10 ⁻²	0.01 ± 0.04 0.32 - < DL	0.87 × 10 ⁻²	0.04 × 10 ⁻² - 0.01
182 W (2)	0.12 0.78 - < DL	0.08	3.84 × 10 ⁻² - 0.15	0.17 ± 0.19 1.51 - < DL	0.10	0.05 - 0.21
185 Re (2)	0.16 × 10 ⁻² 0.83 × 10 ⁻² - < DL	0.14 × 10 ⁻²	0.09 × 10 ⁻² - 0.2 × 10 ⁻²	0.2 × 10 ⁻² ± 0.18 × 10 ⁻² 0.02 - < DL	0.18 × 10 ⁻²	0.11 × 10 ⁻² - 0.24 × 10 ⁻²
189 Os (2)	0.01 0.06 - < DL	0.95 × 10 ⁻²	0.63 × 10 ⁻² - 0.02	1.25 × 10 ⁻² ± 1.16 × 10 ⁻² 0.10 - < DL	0.97 × 10 ⁻²	0.6 × 10 ⁻² - 1.56 × 10 ⁻²
193 Ir (2)	.022 × 10 ⁻² 0.03 - < DL	0.18 × 10 ⁻²	0.05 × 10 ⁻² - 0.27 × 10 ⁻²	0.38 × 10 ⁻² ± 0.66 × 10 ⁻² 0.050 - < DL	0.22 × 10 ⁻²	0.04 × 10 ⁻² - 0.43 × 10 ⁻²
195 Pt (2)	0.01 0.08 - < DL	0.99 × 10 ⁻²	0.7 × 10 ⁻² - 0.02	0.01 ± 0.84 × 10 ⁻² 0.06 - < DL	0.96 × 10 ⁻²	0.66 × 10 ⁻² - 1.48 × 10 ⁻²
197 Au (2)	0.78 × 10 ⁻² 0.03 - < DL	0.68 × 10 ⁻²	0.51 × 10 ⁻² - 0.98 × 10 ⁻²	0.89 × 10 ⁻² ± 0.67 × 10 ⁻² 0.05 - < DL	0.73 × 10 ⁻²	0.55 × 10 ⁻² - 1.08 × 10 ⁻²
202 Hg (2)	0.02 0.06 - < DL	0.01	0.73 × 10 ⁻² - 0.02	0.02 ± 0.018 0.15 - < DL	1.67 × 10 ⁻²	0.82 × 10 ⁻² - 2.42 × 10 ⁻²
205 Tl (2)	0.04 0.13 - < DL	0.04	0.03 - 0.05	0.05 ± 0.02 0.13 - 0.01	4.23 × 10 ⁻²	2.95 × 10 ⁻² - 5.91 × 10 ⁻²
208 Pb (2)	7.09 25.85 - 0.88	6.13	3.83 - 9.38	9.20 ± 5.01 23.66 - 1.27	8.46	5.24 - 12.47
209 Bi (2)	0.23 0.89 - < DL	0.19	0.13 - 0.31	0.29 ± 0.21 1.31 - 0.03	0.24	0.14 - 0.39
232 Th (2)	0.19 0.75 - < DL	0.16	0.10 - 0.26	0.22 ± 0.15 1.02 - 0.27 × 10 ⁻²	0.19	0.13 - 0.28
238 U (2)	0.10 0.36 - < DL	0.09	0.06 - 0.15	0.12 ± 0.07 0.38 - 0.01	0.11	0.07 - 0.15

Table 3-6. Annual arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ in year 2011 (ng m⁻³).

Elements	2011 - PM _{2.5}			2011 - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
7 Li (1)	4.37 32.58 - 0.16	3.65	1.81 - 5.36	6.02 ± 7.75 89.31 - .37	4.68	3.77 - 6.66
9 Be (1)	0.04 0.68 - 0.22 × 10 ⁻²	2.72 × 10 ²	0.02 - 0.04	0.03 ± 0.05 0.51 - 0.31 × 10 ⁻²	0.03	0.02 - 0.04
11 B (1)	27.45 × 10 ² 46.79 × 10 ⁻² - 6.24	21.45 × 10 ²	11.12 × 10 ² - 31.95 × 10 ²	23.34 × 10 ² ± 32.47 × 10 ² 32.14 × 10 ³ - 1.85	17.34 × 10 ²	9.30 × 10 ² - 29.76 × 10 ²
23 Na (2)	88.39 38.51 × 10 ³ - 1.62 × 10 ²	72.83 × 10 ²	50.78 × 10 ² - 11.14 × 10 ³	10.21 × 10 ³ ± 71.27 × 10 ² 34.39 × 10 ³ - 5.66 × 10 ²	82.31 × 10 ²	55.92 × 10 ² - 13.02 × 10 ³
24 Mg (2)	11.62 × 10 ² 75.59 × 10 ² - 18.23	10.79 × 10 ²	6.49 × 10 ² - 14.39 × 10 ²	14.19 × 10 ² ± 21.09 × 10 ² 24.11 × 10 ³ - 84.80	11.45 × 10 ²	6.91 × 10 ² - 16.99 × 10 ²
27 Al (2)	25.93 × 10 ² 17.23 × 10 ³ - 26.92	25.42 × 10 ²	11.08 × 10 ² - 33.35 × 10 ²	32.47 × 10 ² ± 59.32 × 10 ² 67.79 × 10 ³ - 10.15 × 10 ²	25.20 × 10 ²	13.12 × 10 ² - 39.29 × 10 ²
39 K (2)	24.78 × 10 ² 11.47 × 10 ³ - 3.61 × 10 ²	19.64 × 10 ²	13.70 × 10 ² - 30.34 × 10 ²	31.52 × 10 ² ± 39.84 × 10 ² 42.91 × 10 ³ - 1.69 × 10 ²	22.12 × 10 ²	14.28 × 10 ² - 37.37 × 10 ²
44 Ca (2)	51.97 × 10 ² 36.21 × 10 ³ - 1.02 × 10 ²	47.94 × 10 ²	26.63 × 10 ² - 66.63 × 10 ²	46.03 × 10 ² ± 66.76 × 10 ² 74.86 × 10 ³ - 2.57 × 10 ²	35.65 × 10 ²	22.48 × 10 ² - 53.27 × 10 ²
45 Sc (2)	0.32 1.97 - 0.02	0.28	0.14 - 0.42	0.38 ± 0.68 7.80 - 0.01	0.31	0.15 - 0.47
48 Ti (2)	20.76 5.11 × 10 ² - 0.71	14.06	8.30 - 22.23	23.44 ± 50.49 5.18 × 10 ² - 1.86	16.04	8.75 - 24.6
51 V (2)	13.15 2.06 × 10 ² - 0.16	6.48	2.47 - 18.59	14.99 ± 15.08 92.02 - 0.27	8.67	3.32 - 24.54
52 Cr (2)	25.47 6.04 × 10 ⁻² - 0.29	6.19	3.16 - 12.26	63.21 ± 1.68 × 10 ² 11.48 × 10 ² - 0.79	7.97	3.81 - 32.33
55 Mn (2)	14.14 59.21 - 0.46	11.51	5.3 - 18.98	20.34 ± 15.97 76.71 - 0.98	17.52	7.81 - 27.13
56 Fe (2)	3.33 × 10 ² 46.79 × 10 ² - 5.92	1.93 × 10 ²	1.17 × 10 ² - 2.95 × 10 ²	7.49 × 10 ² ± 12.51 83.22 × 10 ² - 18.07	3.94 × 10 ²	239.15 - 597.52
58 Ni (1)	8.30 37.33 - 0.23	7.20	3.43 - 11.95	13.18 ± 14.41 92.26 - 0.73	9.58	5.10 - 15.89
59 Co (2)	0.34 1.48 - 0.01	0.29	0.19 - 0.44	0.62 ± 0.60 4.12 - 0.03	0.42	0.25 - 0.78
63 Cu (2)	11.77 31.75 - 1.15	9.99	6.23 - 16.28	19.59 ± 11.21 77.77 - 1.38	18.23	11.90 - 26.18
64 Zn (1)	12.04 × 10 ² 84.99 × 10 ² - 92.57	8.65 × 10 ²	4.50 × 10 ² - 13.80 × 10 ²	12.06 × 10 ² ± 13.66 × 10 ² 11.754 × 10 ² - 70.42	7.43 × 10 ²	3.83 × 10 ² - 17.11 × 10 ²

Continue Table 3-6. Annual arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ in year 2011 (ng m⁻³).

Elements	2011 - PM _{2.5}			2011 - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
69 Ga (2)	94.37 5.46 × 10 ² - 5.81	59.92	38.22 - 1.29 × 10 ⁻²	1.01 × 10 ² ± 97.69 4.63 × 10 ² - 1.08	73.27	28.98 - 1.44 × 10 ²
72 Ge (2)	0.05 0.71 - 0.14 × 10 ⁻²	0.04	0.02 - 0.06	0.06 ± 0.09 0.95 - 0.19 × 10 ⁻²	0.04	2.32 × 10 ⁻² - 6.46 × 10 ⁻²
75 As (2)	1.15 6.88 - 0.22	1.03	0.72 - 1.45	1.65 ± 0.93 6.72 - 0.13	1.53	1.02 - 2.09
78 Se (2)	0.65 2.67 - 0.09	0.52	0.31 - 0.78	0.83 ± 0.51 2.74 - 0.10	0.73	0.45 - 1.01
85 Rb (2)	1.90 6.19 - 0.32	1.73	1.32 - 2.29	2.42 ± 1.25 10.10 - 0.29	2.26	1.65 - 2.95
88 Sr (2)	56.83 3.17 × 10 ² - 0.41	54.76	28.50 - 79.16	73.97 ± 1.20 × 10 ⁻² 13.62 × 10 ² - 1.26	57.97	29.15 - 91.25
90 Zr (2)	1.99 34.05 - 0.04	1.52	0.75 - 2.20	2.51 ± 5.92 61.78 - 0.11	1.71	0.91 - 2.49
95 Mo (2)	0.36 2.24 - 0.01	0.24	0.12 - 0.43	0.95 ± 1.52 12.52 - 0.05	0.52	0.27 - 1.01
101 Ru (2)	0.01 0.49 - < DL	0.26 × 10 ⁻²	0.05 × 10 ⁻² - 0.79 × 10 ⁻²	0.38 × 10 ⁻² ± 0.93 × 10 ⁻² 0.08 - < DL	0.15	0.06 × 10 ⁻² - 0.33 × 10 ⁻²
103 Rh (2)	0.05 0.49 - < DL	3.59 × 10 ⁻²	0.02 - 0.07	0.05 ± 0.08 0.79 - 0.04 × 10 ⁻²	0.03	0.01 - 0.08
105 Pd (2)	0.02 0.40 - < DL	0.98 × 10 ⁻²	0.49 × 10 ⁻² - 0.02	0.96 × 10 ⁻² ± 0.01 0.15 - 0.02 × 10 ⁻²	0.68 × 10 ⁻²	0.37 × 10 ⁻² - 0.01
107 Ag (2)	0.05 0.30 - < DL	3.89 × 10 ⁻²	0.02 - 0.06	0.11 ± 0.23 2.48 - 0.37 × 10 ⁻²	6.19 × 10 ⁻²	0.03 - 0.12
111 Cd (2)	0.48 16.43 - 0.05	0.30	0.19 - 0.47	0.58 ± 1.10 12.67 - 0.07	0.43	0.27 - 0.63
115 In (2)	0.03 0.50 - < DL	0.02	0.01 - 0.03	0.03 ± 0.05 0.45 - 0.1 × 10 ⁻²	0.03	0.01 - 0.05
118 Sn (2)	3.74 13.40 - 0.03	1.55	0.72 - 6.87	5.24 ± 4.79 16.16 - 0.08	2.59	1.16 - 8.87
121 Sb (2)	0.30 14.91 - 0.2 × 10 ⁻²	0.07	0.03 - 0.32	0.37 ± 0.62 5.93 - 0.91	0.13	0.05 - 0.57
125 Te (2)	0.02 0.53 - < DL	0.01	0.01 - 0.02	0.02 ± 0.04 0.46 - 0.08 × 10 ⁻²	0.98 × 10 ⁻²	0.6 × 10 ⁻² - 1.65 × 10 ⁻²
133 Cs (2)	0.09 0.75 - 0.01	0.07	0.05 - 0.11	0.10 ± 0.07 0.44 - 0.02	0.09	0.06 - 0.13

Continue Table 3-6. Annual arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ in year 2011 (ng m⁻³).

Elements	2011 - PM _{2.5}			2011 - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
138 Ba (2)	3.85×10^2 22.99 $\times 10^2$ - 2.63	2.46×10^2	1.47×10^2 - 4.88×10^2	$4.26 \times 10^2 \pm 4.34 \times 10^2$ 22.72 $\times 10^2$ - 6.26	2.99×10^2	1.32×10^2 - 5.57×10^2
139 La (2)	0.88 5.17 - 0.03	0.77	0.35 - 1.17	1.29 ± 2.39 27.41 - 0.05	0.89	0.53 - 1.48
140 Ce (2)	2.46 15.32 - 0.07	2.16	1.06 - 2.94	2.51 ± 4.70 53.84 - 0.15	1.74	1.04 - 2.87
157 Gd (2)	0.13 0.84 - < DL	0.10	0.06 - 0.17	0.15 ± 0.33 3.81 - 0.01	9.94×10^{-2}	0.06 - 0.16
178 Hf (2)	0.05 0.92 - 0.2×10^2	0.03	0.02 - 0.05	0.04 ± 0.12 1.35 - < DL	2.45×10^{-2}	0.01 - 0.04
181 Ta (2)	0.03 1.21 - < DL	0.01	0.06×10^{-2} - 0.03	0.01 ± 0.03 0.21 - < DL	0.61×10^{-2}	0.12×10^{-2} - 0.93×10^{-2}
182 W (2)	0.25 5.46 - < DL	0.16	0.08 - 0.27	0.36 ± 0.62 6.46 - < DL	0.24	0.11 - 0.46
185 Re (2)	0.68×10^{-2} 0.46 - < DL	0.21×10^{-2}	0.09×10^{-2} - 0.35×10^{-2}	$0.4 \times 10^{-2} \pm 0.73 \times 10^{-2}$ 0.08 - < DL	0.32×10^{-2}	0.19×10^{-2} - 0.43×10^{-2}
189 Os (2)	0.02 0.52 - 0.16×10^{-2}	0.01	0.58×10^{-2} - 0.02	0.03 ± 0.09 1.07 - < DL	0.01	0.93×10^{-2} - 0.02
193 Ir (2)	0.01 0.44 - < DL	0.65×10^{-2}	0.13×10^{-2} - 0.01	$0.33 \times 10^{-2} \pm 0.52 \times 10^{-2}$ 0.03 - < DL	0.18×10^{-2}	0.03×10^{-2} - 0.35×10^{-2}
195 Pt (2)	0.02 0.64 - < DL	0.98×10^{-2}	0.45×10^{-2} - 0.01	0.01 ± 0.03 0.27 - < DL	0.95×10^{-2}	0.4×10^{-2} - 0.01
197 Au (2)	0.03 0.32 - < DL	0.02	0.01 - 0.03	0.02 ± 0.04 0.29 - < DL	0.01	0.55×10^{-2} - 0.02
202 Hg (2)	0.03 0.46 - < DL	0.02	0.64×10^{-2} - 0.04	0.08 ± 0.43 5.02 - < DL	0.02	0.96×10^{-2} - 0.05
205 Tl (2)	0.05 0.49 - 0.42×10^{-2}	0.04	0.03 - 0.05	0.06 ± 0.06 0.50 - < DL	0.04	0.03 - 0.07
208 Pb (2)	8.42 27.76 - 0.79	7.54	5.12 - 10.61	10.39 ± 5.86 32.38 - 1.62	9.68	6.04 - 13.48
209 Bi (2)	0.27 1.58 - 0.02	0.22	0.14 - 0.34	0.34 ± 0.29 2.39 - 0.02	0.28	0.17 - 0.41
232 Th (2)	0.26 1.40 - < DL	0.22	0.09 - 0.34	0.29 ± 0.64 7.39 - < DL	0.21	0.09 - 0.34
238 U (2)	0.10 0.50 - < DL	0.09	0.04 - 0.13	0.11 ± 0.17 2.01 - 0.01	0.08	0.05 - 0.13

Table 3-7. Two years arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ (ng m⁻³).

Elements	Two Years - PM _{2.5}			Two Years - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
7 Li (1)	4.92 (0.16 - 37.68)	4.17	2.26 - 6.10	5.81 ± 5.96 (89.31 - 0.37)	4.72	3.43 - 6.76
9 Be (1)	0.03 (0.67- < DL)	0.03	0.02 - 0.04	0.04 ± 0.04 (0.5107 - < DL)	0.03	0.02 - 0.04
11 B (1)	28.51 × 10 ² (46.79 × 10 ³ - 6.24)	22.61 × 10 ²	14.61 × 10 ² – 34.75 × 10 ²	27.82 10 ² ± 32.44 × 10 ² (32.14 × 10 ³ - 1.85)	22.02 × 10 ²	12.11 × 10 ² – 32.88 × 10 ²
23 Na (2)	87.65 × 10 ² (38.77 × 10 ³ – 1.62 × 10 ²)	74.34 × 10 ²	46.91 × 10 ² – 11.23 × 10 ³	95.56 × 10 ² ± 62.85 × 10 ² (42.92 × 10 ³ – 5.66 × 10 ²)	82.73 × 10 ²	54.17 × 10 ² – 11.99 × 10 ²
24 Mg (2)	11.07 × 10 ² (75.59 × 10 ² - 16.70)	10.01 × 10 ²	5.39 × 10 ² – 14.63 × 10 ²	13.93 × 10 ² ± 25.15 × 10 ² (33.42 × 10 ³ - 20.95 × 10 ²)	10.61 × 10 ²	5.76 × 10 ² – 15.88
27 Al (2)	2658.594 (54567.6965 - 21.4493)	20.63 × 10 ²	10.32 × 10 ² – 34.08 × 10 ²	27.93 × 10 ² ± 44.70 × 10 ² (67.79 × 10 ³ - 33.31 × 10 ²)	21.21 × 10 ²	9.45 × 10 ² - 35.77 × 10 ²
39 K (2)	25.54 × 10 ² (19.38 × 10 ³ - 21.48)	20.01 × 10 ²	12.31 × 10 ² – 32.13 × 10 ²	28.14 × 10 ² ± 31.40 × 10 ² (42.91 × 10 ² - 27.36 × 10 ²)	21.71 × 10 ²	13.25 × 10 ² – 35.99 × 10 ²
44 Ca (2)	49.05 × 10 ² (36.21 × 10 ³ - 67.73)	42.36 × 10 ²	23.33 × 10 ² – 65.57 × 10 ²	48.09 × 10 ² ± 53.62 × 10 ² (74.86 × 10 ³ – 1.61 × 10 ²)	40.56 × 10 ²	23.74 × 10 ² – 58.84 × 10 ²
45 Sc (2)	0.31 (1.98 - 0.68 × 10 ⁻²)	0.24	0.15 - 0.39	0.34 ± 0.504 (7.81 - 0.014)	0.27	0.15 - 0.43
48 Ti (2)	19.16 (5.11 × 10 ² - 0.71)	14.35	8.82 - 21.80	22.79 ± 40.58 (5.18 × 10 ² - 1.87)	15.95	9.42 - 24.42
51 V (2)	11.47 (2.05 × 10 ² - 0.16)	6.77	2.48 - 15.59	12.97 ± 12.48 (92.02 - 0.27)	9.26	3.40 - 17.56
52 Cr (2)	14.91 (6.04 × 10 ² - 0.27)	4.64	2.65 - 7.63	33.27 ± 12.11 × 10 ² (11.48 × 10 ² - 0.63)	5.23	3.06 - 10.25
55 Mn (2)	12.73 (59.21 - 0.46)	9.74	5.12 - 17.74	17.76 ± 14.13 (76.71 - 0.98)	14.92	6.51 - 24.31
56 Fe (2)	2.56 × 10 ² (46.79 - 5.92)	173.09	1.01 × 10 ² – 2.67 × 10 ²	5.25 × 10 ² ± 9.16 × 10 ² (83.22 × 10 ² - 6.58 × 10 ²)	3.28 × 10 ²	1.58 × 10 ² – 5.13 × 10 ²
58 Ni (1)	7.16 (97.31 - 0.23)	5.47	2.81 - 9.29	10.36 ± 11.24 (92.27 - 0.31)	8.05	3.46 - 13.26
59 Co (2)	0.28 (1.47 - 0.01)	0.25	0.15 - 0.34	0.49 ± 0.49 (4.12 - 0.03)	0.34	0.19 - 0.62
63 Cu (2)	11.63 (35.18 - 1.15)	10.13	6.29 - 15.72	19.10 ± 11.74 (99.06 - 1.39)	17.28	11.28 - 24.49
64 Zn (1)	14.45 × 10 ² (84.99 × 10 ² - 90.03)	9.81 × 10 ²	4.82 × 10 ² – 18.76 × 10 ²	15.22 × 10 ² ± 15.07 × 10 ² (11.75 × 10 ² - 70.43)	10.32 × 10 ²	4.88 × 10 ² – 21.37 × 10 ²
69 Ga (2)	97.94 (5.46 × 10 ² - 3.76 × 10 ²)	62.39	37.89 – 1.32 × 10 ²	1.09 × 10 ² ± 1.03 × 10 ² (7.66 × 10 ² - 1.08)	77.28	35.67 – 1.54 × 10 ²

Continue Table 3-7. Two years arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ (ng m⁻³).

Elements	Two Years - PM _{2.5}			Two Years - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
72 Ge (2)	0.04 (0.72 - 0.13 × 10 ⁻²)	0.03	0.02 - 0.05	0.05 ± 0.07 0.95 - < DL	0.03	0.02 - 0.05
75 As (2)	1.12 (6.88 - 0.16)	1.02	0.73 - 1.36	1.56 ± 0.92 6.72 - 0.13	1.36	0.92 - 1.95
78 Se (2)	0.59 (2.83 - 0.06)	0.46	0.26 - 0.71	0.70 ± 0.49 3.11 - 0.07	0.58	0.34 - 0.92
85 Rb (2)	1.99 (6.19 - 0.31)	1.80	1.36 - 2.42	2.38 ± 1.20 10.10 - 0.29	2.20	1.59 - 2.88
88 Sr (2)	56.96 (3.29 × 10 ² - 0.41)	49.56	30.36 - 77.52	66.36 ± 89.04 13.62 × 10 ² - 1.26	54.53	34.64 - 83.98
90 Zr (2)	2.1217 (34.05 - 0.04)	1.72	1.01 - 2.48	2.62 ± 4.56 61.78 - 0.09	1.92	1.13 - 2.82
95 Mo (2)	0.31 (4.87 - 0.01)	0.19	0.09 - 0.37	0.68 ± 1.12 12.53 - < DL	0.42	0.19 - 0.81
101 Ru (2)	0.55 × 10 ² (0.49 - <DL)	0.11 × 10 ²	0.04 × 10 ² - 0.39 × 10 ²	0.3 × 10 ⁻² ± 0.73 × 10 ⁻² 0.09 - < DL	0.12 × 10 ⁻²	0.05 × 10 ⁻² - 0.25 × 10 ⁻²
103 Rh (2)	0.05 (0.49 - < DL)	0.04	0.02 - 0.07	0.05 ± 0.06 0.79 - < DL	0.04	0.02 - 0.07
105 Pd (2)	0.013 (0.40 - < DL)	0.95 × 10 ²	0.47 × 10 ⁻² - 0.02	0.01 ± 0.01 0.15 - < DL	0.01	0.37 × 10 ⁻² - 0.01
107 Ag (2)	0.07 (2.39 - < DL)	0.04	0.02 - 0.07	0.15 ± 0.93 15.16 - < DL	0.06	0.03 - 0.11
111 Cd (2)	0.59 (26.89 - 0.05)	0.35	0.22 - 0.53	0.68 ± 1.76 29.19 - 0.08	0.51	0.32 - 0.69
115 In (2)	0.02 (0.50 - < DL)	0.01	0.74 × 10 ⁻² - 0.02	0.03 ± 0.03 0.45 - < DL	0.02	0.96 × 10 ⁻² - 0.03
118 Sn (2)	2.31 (13.40 - 0.03)	1.02	0.51 - 2.19	3.22 ± 3.94 16.16 - 0.08	1.47	0.75 - 3.43
121 Sb (2)	0.16 (14.91 - < DL)	0.03	0.02 - 0.08	0.23 ± 0.54 5.93 - < DL	0.05	0.03 - 0.16
125 Te (2)	0.01 (0.53 - < DL)	0.84 × 10 ⁻²	0.48 × 10 ⁻² - 0.01	0.01 ± 0.03 0.46 - < DL	0.01	0.59 × 10 ⁻² - 0.016
133 Cs (2)	0.09 (0.75 - 0.01)	0.07	0.05 - 0.11	0.11 ± 0.08 0.49 - < DL	0.09	0.06 - 0.13
138 Ba (2)	4.36 × 10 ² (23.54 × 10 ² - 2.63)	2.73 × 10 ²	1.57 × 10 ² - 5.81 × 10 ²	4.96 × 10 ² ± 4.82 × 10 ² 37.76 × 10 ² - 6.26	3.49 × 10 ²	1.59 × 10 ² - 6.81 × 10 ²
139 La (2)	0.76 (5.17 - 0.02)	0.67	0.35 - 1.02	1.02 ± 1.73 27.41 - 0.05	0.75	0.47 - 1.26

Continue Table 3-7. Two years arithmetic mean, concentration range (maximum to minimum), median and percentile 95% for both PM_{2.5} and PM₁₀ (ng m⁻³).

Elements	Two Years - PM _{2.5}			Two Years - PM ₁₀		
	Ave	Median	Percentile 95%	Ave	Median	Percentile 95%
140 Ce (2)	1.95 (15.32 - 0.06)	1.61	0.81 - 2.59	2.05 ± 3.42 53.842 - 0.152	1.56	0.90 - 2.416
157 Gd (2)	0.11 (0.84 - 0.47 × 10 ⁻²)	0.09	0.05 - 0.13	0.13 ± 0.24 3.81 - 0.01	0.09	0.06 - 0.14
178 Hf (2)	0.05 (0.92 - 0.18 × 10 ⁻²)	0.04	0.02 - 0.06	0.05 ± 0.09 1.35 - < DL	0.04	0.02 - 0.06
181 Ta (2)	0.01 (1.21 - <DL)	0.14 × 10 ⁻²	0.03 × 10 ⁻² - 0.02	0.01 ± 0.04 0.33 - < DL	0.66 × 10 ⁻²	0.06 × 10 ⁻² - 0.01
182 W (2)	0.18 (5.46 - 0.12 × 10 ⁻²)	0.11	0.05 - 0.23	0.26 ± 0.46 6.47 - < DL	0.14	0.07 - 0.32
185 Re (2)	0.42 × 10 ⁻² (0.46 - <DL)	0.15 × 10 ⁻²	0.09 × 10 ⁻² - 0.27 × 10 ⁻²	0.3 × 10 ⁻² ± 0.53 × 10 ⁻² 0.08 - < DL	0.23 × 10 ⁻²	0.15 × 10 ⁻² - 0.37 × 10 ⁻²
189 Os (2)	0.02 (0.53 - < DL)	0.01	0.61 × 10 ⁻² - 0.02	0.02 ± 0.06 1.08 - < DL	0.01	0.71 × 10 ⁻² - 0.02
193 Ir (2)	0.65 × 10 ⁻² (0.44 - <DL)	0.25 × 10 ⁻²	0.08 × 10 ⁻² - 0.7 × 10 ⁻²	0.36 × 10 ⁻² ± 0.6 × 10 ⁻² 0.05 - < DL	0.19 × 10 ⁻²	0.04 × 10 ⁻² - 0.37 × 10 ⁻²
195 Pt (2)	0.02 (0.65 - < DL)	0.01	0.61 × 10 ⁻² - 1.52 × 10 ⁻²	0.01 ± 0.02 0.27 - < DL	0.01	0.52 × 10 ⁻² - 0.01
197 Au (2)	0.02 (0.32 - < DL)	0.01	0.6 × 10 ⁻² - 0.02	0.01 ± 0.03 0.29 - < DL	0.01	0.55 × 10 ⁻² - 0.01
202 Hg (2)	0.03 (0.46 < DL)	0.02	0.72 × 10 ⁻² - 0.03	0.05 ± 0.30 5.02 - < DL	0.02	0.0087 - 0.03
205 Tl (2)	0.05 (0.49 - < DL)	0.04	0.03 - 0.05	0.05 ± 0.04 0.50 - < DL	0.04	0.03 - 0.06
208 Pb (2)	7.74 (27.76 - 0.79)	6.80	4.33 - 10.16	9.78 ± 5.46 32.38 - 1.27	8.91	5.69 - 12.74
209 Bi (2)	0.25 (1.59 - < DL)	0.21	0.14 - 0.32	0.326 ± 0.26 2.40 - 0.02	0.26	0.16 - 0.41
232 Th (2)	0.23 (1.405 - < DL)	0.19	0.10 0.30	0.26 ± 0.46 7.396 - < DL	0.206	0.12 - 0.31
238 U (2)	0.10 (0.50 - < DL)	0.09	0.06 0.14	0.12 ± 0.13 2.01 - < DL	0.106	0.07 - 0.14

Figure 3-2. Percent PM₁₀ and PM_{2.5} fractions of element.

For pollution derived elements, such as V, Ni, As, Ru, Pd, In, Te, Ta, Re, Ir, Pt and Au, higher relative concentrations were present in PM_{2.5} (based on the mass of material that was collected).

Percent PM₁₀ and PM_{2.5} fractions of elements are depicted in Figure 3-2. 40 % - 60 % of the masses of pollution (anthropogenic) derived elements are associated with PM₁₀ in the Singapore atmosphere. This unexpectedly high PM₁₀ fraction of pollution derived elements might be related to high humidity at the sampling site affecting the particle size or trapping of combustion particles by surface dust. Since higher concentrations of pollution derived elements were detected in PM₁₀ during haze periods when atmospheric loading of dust were high, it suggests that pollution derived elements and particles bearing these elements have been enriched in the surface dust.

The Pearson's correlation coefficients between Al as a crustal index and Ca, Sc, Ti, Sr, La, Ce and Hg are high in PM₁₀, while correlations of these elements with Al are moderate to low in PM_{2.5}.

3.5 Temporal Variations in the Concentration of Elements

Among the measured elements, some are categorized as toxic or carcinogenic such as Fe, Zn, Cu, As, Ni, Cd, Cr, Hg, V, Mn and Pb. Trace metals with density greater than 6 g/cm³ are also termed as heavy metals (Cd, Cu, Pb, Cr, Hg, Ni and Zn). Although certain metals such as Zn, Cu and Fe are essential for body functions, the sorption of excessive amounts can lead to undesirable outcomes. For instance, the accumulation of metals might occur in the lungs or internal organs resulting in an increased risk of respiratory and cardiovascular disease.

11 potentially toxic elements are first discussed. Zn and Fe present higher concentrations compared to other elements in this group, which might be due to the enrichment from various possible sources such as earth crust, combustion, industries and road dust. Zn is often used

for corrosion protection, thus its presence in high amounts in Singapore may be due to its use in the marine environment (such as protecting steel structures from corrosion).

For As, Cr, Pb, and Ni, they are usually anthropogenically enriched by industrial emissions. Metal smelters, oil refinery and industries manufacturing batteries, paints and alloys are some examples that contribute to these elements [105-107].

Both natural and anthropogenic activities contribute to emission of Hg and Cd. Most of the Hg comes from power plants (located in Indonesia and Malaysia), incineration and volcanic activities. On the other hand, much of the Cd concentration comes from industrial emission related to the manufacturing of batteries [1].

Metals such as Cr, Ni, V and Mn are also common catalysts used in chemical plant reactions. Most of the trace metals mainly originate from anthropogenic sources such as industrial processes, incineration and vehicular emissions. Only a small percentage comes from natural events such as volcanic activities [1].

The concentration of platinum group elements (PGE) in the environment has increased significantly in the last 25 years mainly due to their use as catalysts in different industrial, chemical, and pharmaceutical applications. In regards to increasing demand to reduce the emission of carbon monoxide, nitrogen oxides, and hydrocarbons by vehicles, recently these rare noble metals, especially platinum (Pt), rhodium (Rh), and palladium (Pd), are also used as catalysts in automobile catalytic converters and this application, accounts for the largest consumption of the global supply of these metals on a per weight basis [108-113].

By using PGE the deleterious by-products of fossil fuel combustion have been significantly reduced in automotive exhausts, but several studies have shown PGE have been released in the atmosphere and the concentrations are increasing [108-113]. Recent evidence

suggests that the environmental and health risks of exposure to these metals should be of concern [110, 114-118].

Figure 3-3 presents Pt, Pd and Rh daily trends in PM₁₀ and PM_{2.5}. The time series graph showed exactly the same trend for PM₁₀, while the Pt, Pd and Rh time series graph for PM_{2.5} suggest that other sources might contribute to emission of Pt and Rh.

The rare earth elements (REEs) La and Ce (Figure 3-4) have been reported as a tracer for vehicle PM_{2.5} emissions [119-121] and occasionally in ambient PM [122, 123]. REEs are also excellent tracers to track fluidized-bed catalytic cracking (FCC) emissions from petroleum refining operations and it is important to monitor REEs in PM, especially in industrial areas [124-126].

In order to estimate the contribution of other sources to emission of La and Ce, their trends were examined with respect to index elements of vehicle emissions (Zn, Mn, Cr and Fe). There was a significant difference between La - Ce daily trends and vehicle emissions indicators for both PM₁₀ and PM_{2.5} indicating the contribution of chemical and oil refinery industries located nearby the NTU sampling site.

As it can be seen in be seen in Figure 3-5, La and Ce followed the same daily trends with catalyst indicator elements (Ru, Pt, Rh, Re) in most sampling dates confirming other emission sources, most likely petrochemical refineries.

Figure 3-3. Time Series of Pt, Pd and Rh during sampling period (a) PM_{10} , (b) $PM_{2.5}$

Figure 3-4. Time Series of La and Ce during sampling period (a) PM_{10} , (b) $\text{PM}_{2.5}$

Figure 3-5. Time Series of Ru, Rh, Pt, Re, La and Ce during sampling period (a) PM₁₀, (b) PM_{2.5}.

3.5.1 Daily Trends during Haze Periods

As was discussed in Chapter 2, during the last two years Singapore experienced two haze periods between 16th to 23rd October 2010 and between 8th to 13th of September 2011, with maximum pollution standard index (PSI) values of 96 and 62 respectively.

Figure 3-6 to Figure 3-9 present daily trends of measured elements in year 2010 and year 2011 for both PM_{2.5} and PM₁₀. It is interesting to note that significant increases were observed not only for crustal elements (Mg, Al, Fe, Zn, Ba, Ga, Ce, La, Mn, Sc, Ti and Ba) but also for trace elements (V, Cu, Ge, As, Se, Rb, Sr, Zr, Mo, Rh, Pd, Ag, Sn, Te, Cs, Gd, Hf, Os, Pt, Tl, Pb, Bi, Th, U) during the haze periods.

The examination of daily trends on measured elements for individual months suggest that although the average concentration on hazy days is higher compared to clear days, for some of these elements (V, Co, Zn, Se, Cu, Ga, Ge, As, Zr, Cd, Mo, Rh, In, Sn, Te, Cs, Hf, Os and Tl), the significantly higher concentration ranges in clear days suggest that it can mainly be due to variances in their local industrial emissions.

Since measured trace elements during haze period could be affected by background particles, source apportionment is more difficult. These elements may have two different sources: the combustion of vegetation or the remobilisation of particles that were previously deposited on the vegetation.

3.5.2 Hungry Ghost Festival Results

An interesting feature in this data is a local event (common in all counties with a Chinese population), called the Hungry Ghost Festival, that has surprisingly increased concentrations of a large number of elements (B, Na, Mg, Al, K, K, V, Mn, Fe, Ni, Co, Zn, Cu, Ga, Sb, Ba, Hf, W, As, Rb, Zr, Rh, Tl, Pb, Bi) during August 2010 and 14th August 2011, due to burning large amount of bank notes, joss paper and incense all over Singapore (a strong smoke smell pervades everywhere during this month). The highest

concentration is related to Ghost Day 24th and 14th August in 2010 and 2011, respectively (Figure 3-10 to Figure 3-13). These results are consistent with findings during haze periods that suggest the burning of vegetation and papers release similar elements.

Monthly statistical data (Appendix E) in Year 2010 and 2011 for both PM₁₀ and PM_{2.5} showed a high range of concentrations for most of the elements, especially K and Ca, during August confirming strong contribution of biomass burning to release particulate matter during this event.

3.5.3 Fire at a Factory in Benoi Crescent

As it can be seen in from Figure 3-7 and Figure 3-9, no significant increases were observed in measured elements due to the fire in Benoi Crescent close to NTU on 3rd September 2011.

3.5.4 Fire at Shell refinery

Another important finding was related to the Shell Refinery fires on 28th Sep to 2nd Oct 2011 in Pulau Bukom Island, Singapore. Although the National Environmental Agency (NEA) reported it did not detect the presence of any toxic gases on the mainland as a result of the fire at the Shell Refinery in Pulau Bukom, a significantly high concentration of trace metals were observed for V, Mn, Fe, Ni, Co, Cu, Ag, Rh, Mo, Sr, Ti, Pt and Os during these days (Figure 3 -14 and Figure 3 -15).

Figure 3-6. Daily Trends of measured elements in $PM_{2.5}$ during Haze period year 2010.

Continue Figure 3-6. Daily Trends of measured elements in PM_{2.5} during Haze period year 2010.

Figure 3-7. Daily Trends of measured elements in $PM_{2.5}$ during Haze period year 2011.

Continue Figure 3-7. Daily Trends of measured elements in $\text{PM}_{2.5}$ during Haze period year 2011.

Figure 3-8. Daily Trends of measured elements in PM_{10} during Haze period year 2010.

Continue Figure 3-8. Daily Trends of measured elements in PM_{10} during Haze period year 2010.

Figure 3-9. Daily Trends of measured elements in PM_{10} during Haze period year 2011.

Continue Figure 3-9. Daily Trends of measured elements in PM_{10} during Haze period year 2011.

Figure 3-10. Daily Trends of measured elements in PM_{10} during Hungry Ghost Festival (August 2010).

Continue Figure 3-10. Daily Trends of measured elements in PM₁₀ during Hungry Ghost Festival (August 2010).

Figure 3-11. Daily Trends of measured elements in PM_{10} during Hungry Ghost Festival (August 2011).

Continue Figure 3-11. Daily Trends of measured elements in PM₁₀ during Hungry Ghost Festival (August 2011).

Figure 3-12. Daily Trends of measured elements in $\text{PM}_{2.5}$ during Hungry Ghost Festival (August 2010).

Continue Figure 3-12. Daily Trends of measured elements in $\text{PM}_{2.5}$ during Hungry Ghost Festival (August 2010).

Figure 3-13. Daily Trends of measured elements in $\text{PM}_{2.5}$ during Hungry Ghost Festival (August 2011).

Continue Figure 3-13. Daily Trends of measured elements in $PM_{2.5}$ during Hungry Ghost Festival (August 2011).

Figure 3-14. Daily trend of measured elements present in PM_{10} during fire in Shell refinery, Singapore ($[X] / \text{ng m}^{-3}$).

Continue Figure 3-14. Daily trend of measured elements present in PM_{10} during fire in Shell refinery, Singapore ($[X] / ng\ m^{-3}$).

Continue Figure 3-14. Daily trend of measured elements present in PM_{10} during fire in Shell refinery, Singapore ($[\text{X}] / \text{ng m}^{-3}$).

Continue Figure 3-14. Daily trend of measured elements present in PM_{10} during fire in Shell refinery, Singapore ($[\text{X}] / \text{ng m}^{-3}$).

Table 3-8 shows a general decreasing trend of air pollution by heavy metals in Singapore from the year 2001. The emissions of Pb, Cd, Co, and Ni have significantly decreased with Pb reduction perhaps reflecting the shift from leaded to unleaded petrol in Singapore. It is possible that the emissions of heavy metals have reduced because of more strict requirements in the environmental legislation and replacing with new technologies. However, the

comparison can be made based on only one other study in 2001, there is insufficient data available to be sure of this decrease.

Table 3-8. Comparison on statistical summary of trace elements in PM_{2.5} in Singapore in Year 2000 and this study (ng/m⁻³).

Elements	NUS	NTU, this study		
	(2000, March - May)	Oct 2009 -Dec 2010	Jan 2011- Dec 2011	NTU (Oct 2009 - Dec 2011)
Al	$2.33 \times 10^2 \pm 1.38 \times 10^2$ 37.9-741.6	27.20×10^2 $54.57 \times 10^3 - 21.45$	25.93×10^2 $17.23 \times 10^3 - 26.92$	26.58×10^2 $54.57 \times 10^3 - 21.45$
Ag	0.4 ± 0.7 0.1-6.0	0.09 2.38 - 0. < DL	0.05 0.30 - < DL	0.07 2.39 - < DL
Ba	9.0 ± 5.3 0.9-28.3	4.86×10^2 $23.54 \times 10^2 - 24.77$	385.29 $22.99 \times 10^2 - 2.63$	4.37×10^2 $23.54 \times 10^2 - 2.63$
Cd	2.5 ± 2.4 0.3-17.9	0.68 26.89 - 0.06	0.48 16.43 - 0.05	0.59 26.89 - 0.05
Cr	18.3 ± 11.5 1.7-217.3	4.95 $86.64 - 0.27$	25.47 $6.04 \times 10^2 - 0.29$	14.91 $6.04 \times 10^2 - 0.27$
Co	3.5 ± 1.6 0.4-53.3	0.23 1.34 - 0.02	0.34 1.48 - 0.01	0.28 1.48 - 0.01
Cu	25.8 ± 21.3 2.3-233.3	11.49 35.18 - 1.48	11.77 31.74 - 1.15	11.62 35.18 - 1.15
Fe	$2.13 \times 10^2 \pm 1.22 \times 10^2$ $29.7-6.19 \times 10^2$	1.84×10^2 $7.52 \times 10^2 - 8.29$	3.33×10^2 $46.79 \times 10^2 - 5.91$	2.56×10^2 $46.79 \times 10^2 - 5.91$
Ga	0.5 ± 0.5 0.1-6.1	46.31×10^2 $33.23 \times 10^3 - 67.73$	94.37 $5.47 \times 10^2 - 5.82$	97.9459 $5.47 \times 10^2 - 3.76$
Li	0.3 ± 0.3 0.1-1.0	5.44 37.68 - 0.30	4.37 32.59 - 0.16	4.93 0.16 - 37.69
Mn	16.4 ± 14.1 2.1-98.0	11.39 43.75 - 0.79	14.14 59.21 - 0.46	12.73 59.21 - 0.46
Ni	39.0 ± 15.2 1.4-183.4	6.08 97.30 - 0.27	8.30 37.33 - 0.23	7.16 97.31 - 0.23
Pb	74.3 ± 76.8 7.6-509.2	7.09 25.85 - 0.88	8.43 27.76 - 0.79	7.74 27.76 - 0.79
Sr	1.7 ± 1.4 0.5-11.5	57.08 $3.29 \times 10^2 - 3.75$	56.83 $3.17 \times 10^2 - 0.41$	56.96 $3.29 \times 10^2 - 0.41$
Zn	$4.38 \times 10^2 \pm 4.05 \times 10^2$ $45.4-11.67 \times 10^2$	16.74×10^2 $75.89 \times 10^2 - 90.03$	12.04×10^2 $84.99 \times 10^2 - 92.56$	14.45×10^2 $84.99 \times 10^2 - 90.03$
V	11.1 ± 10.1 0.7-129.4	9.88 74.77 - 0.56	13.15 $2.06 \times 10^2 - 0.16$	11.47 $2.06 \times 10^2 - 0.16$
Ti	7.9 ± 5.6 1.0-27.2	17.67 $1.32 \times 10^2 - 1.04$	20.7634 $5.11 \times 10^2 - 0.71$	19.16 $5.11 \times 10^2 - 0.71$
PM _{2.5}	23.0 ± 11.0 12.2-48.1	18.80 ± 11.88 $1.06 \times 10^2 - 5.25$	19.46 ± 8.85 63.57 - 5.35	19.12 ± 10.51 $1.06 \times 10^2 - 5.25$

3.6 Comparison with Other Countries

As was mentioned in Chapter 2, the sampling site for the present research is located near several major industrial complexes in Singapore such that it there is exposure to the inflow of pollutants from various types of man-made sources. As a simple means to evaluate the pollution levels in the study area, the concentration data measured from the present work were compared to those derived previously from other comparable studies (Table 3 -9 and

Table 3 -10). For this purpose, data sets collected from different urban areas around the world have been selected along with one comparable to the background environment. Comparison of metal concentrations among different studies indicates not only the difference in the diversity of metal species analyzed but also the magnitude of variability in the observed concentration levels of metals. The extent of pollution in our study area is most significant for several metals, simply based on comparison of absolute metal concentrations among different sites. For example, the concentrations of the crustal metals are among the highest values given in the table (except Taiwan). The crustal elements in airborne particles in Singapore are mainly derived from local construction and land reclamation activities and are enhanced sporadically during extensive uncontrolled forest fires in the region due to soil remobilization. As for Zn, it can originate from automobiles (wearing of car tyres), municipal solid waste incinerators, or corrosion protection activities. In addition to these elements, the concentrations of V and Ni in the present study area are higher than those determined in most of the urban cities given in the table, possibly due to the presence of oil-fired power plants and oil-refineries in Singapore.

Table 3-9. Selected elements mean levels of PM_{2.5} compared with other urban site (or location) around world (ng m⁻³).

Elements (ng/m ³)	Australia	Turkey	Japan	Austria	Mexico	UK	Switzerland	Tiwan	USA	Spain			Singapore					
	Brisbane	Tasmania	Ankara	Kyoto	Vienna	Strehofen	Mexico city	Birmingham	Chaumont	Taiwan	California ^a	Sterling Forest	Mt Cimone	Villar Arzobispo	Villar Arzobispo	Montsery	Singapore	This Study
Al	29.2	15	110							97.2							196.8	2658.6
As			1.5			0.5		4.2	0.2					0.3	0.3	0.3		1.1
Ba												0		5	5		7.6	436.9
Cd			0.1			0.3			0.2			0.3	0.1	0.1			1.6	0.6
Cr		0.1	3.2	2.9	2.3	0.3	6			250				1	2	0.9	11.2	14.9
Co			3.3			0.003								0.2	0.1	0.1	1.9	0.3
Cu		1.4		7.2	8.4	2	99		6	31		1		9	1		16.8	11.6
Fe	51.1	4	100	100	150		24	114		1560	194						182	256.2
Ga									0.02					0.1	0.07	0.1	0.3	97.9
Li						0.3			0.1			0.1		0.1	0.2		0.2	4.9
Mn	4.1	0.7	4.9	8.4	6.7	2	4	9.9	1	25	27.7	1		3	3	3	12.2	12.7
Ni		0.4	3.1	3.3	4.5	0	3		1			4		4	4	2	14.3	7.2
Pb		1.1	71	33	60	12	292		5	86		2	2	7	6	5	45.7	7.7
Sr												1	1	1	5		1.4	57
Zn	26.3	1.2	16	53	33	17	144	297		210	112	9	6	17	12		279.1	1445
V		1	3.9	3.9	5.4	1	19	4.9	1			3		4	3	3	5.6	11.5

^a City not given in report.

Table 3-10. Selected elements mean levels of PM₁₀ compared with other urban site around world (ng m⁻³)

Elements (ng/m ³)	Turky	Austria	Switzerland	Italy	Spain			Singapore		
	Ankara	Strehofen	Payeme	Chaumont	Mt Cimone	Benantes	Villar Arzobispo	Magrega	Montsery	This Study
Al										2793.3
As		0.7	0.5	0.2		0.4	0.2		0.3	1.6
Ba						6	4	6	4	496.4
Cd		0.2	0.3	0.1	0.2	0.1	0.1			0.7
Cr	5.7	0.5				1	2.1	1	1	33.3
Co		0.004	1.2			0.1	0.1		0.1	0.5
Cu		4	6	7	3	8	2	3	5	19.1
Fe										524.7
Ga			0.03	0.04		0.2	0.07		0.1	109.3
Li		0.1	0.2	0.2		0.1	0.3	0.2	0.1	5.8
Mn	8	4	2.8	2	6	5	4	5	5	17.8
Ni	4	1	1	1	1	3	3		2	10.4
Pb		17	10	5	4	8	5	10	4	9.8
Sr					3	1	1	2	1	66.4
Zn	10	27			10	16	11	30	12	1522.4
V	9	1	0.7	0.8	3.1	5	3	2	4	13

3.7 Microscopic Analysis

Several studies have applied Electron Microscopy techniques to characterize particulate matter. The SEM uses a focused electron beam across the sample and scans it under vacuum. The electron beam interacts with the sample and produces secondary electrons that can be monitored using secondary electron and EDX detectors. Figure 3-15 and Figure 3-16 compare SEM micrographs of $PM_{2.5}$ and PM_{10} in the same sampling date in “normal” periods and during a high haze event respectively.

The microscopic observation of the biomass burning for $PM_{2.5}$ and PM_{10} samples confirmed the presence of most major components (microsoot particles, salt condensate, vegetation relicts, and soil-dust derived particles) mentioned in other literature reports [127, 128].

Figure 3-17 presents Energy Dispersive X-ray (EDX) images and spectra for a selected $PM_{2.5}$ sample collected few days after haze in October 2011.

The morphology of different type of particles is shown in Figure 3-18. According to the EDX elemental analysis (Table 3-11) and SEM images (Figure 3-18), the presence of Ca ($CaSO_4$ and Ca - Aluminosilicate), K (K - Aluminosilicate, KCl), Na, Al (Aluminosilicate), Fe (Iron oxides and Fe - Aluminosilicate), Si, Ti, S, C (Soot) and surprisingly Pt compounds can be confirmed. The morphological differences between soot aggregates and other particles are mainly related to differences in their formation and size.

Figure 3-15. Compares PM_{10} and $PM_{2.5}$ SEM image in normal days.

Figure 3-16. Compares PM_{10} and $PM_{2.5}$ SEM image during Haze period.

Table 3-11. Energy Dispersive X-ray (EDX) elemental analysis.

(a)

Element	Weight%	Atomic%
C	27.53	40.54
O	18.26	20.19
F	32.14	29.92
Na	1.98	1.52
Al K	1.13	0.74
Si K	7.81	4.92
S K	0.87	0.48
K K	0.88	0.40
Ca K	0.44	0.19
Ti K	0.42	0.15
Zn K	0.97	0.26
Pt M	7.58	0.69
Totals	100.00	

(b)

Element	Weight%	Atomic%
C K	29.30	42.19
O K	22.18	23.98
F K	28.66	26.09
Na K	1.82	1.37
Al K	1.49	0.96
Si K	5.24	3.23
S K	1.42	0.77
K K	0.60	0.27
Ca K	0.30	0.13
Ti K	0.35	0.13
Fe K	0.55	0.17
Pt M	8.09	0.72
Totals	100.00

Figure 3-17. Energy Dispersive X-ray (EDX) images (a) EDS spectra (b)

Figure 3-18. Surface characterization of PM_{2.5}.

(Numbers refers to enlargement of area in red circles in original image.)

Continue Figure 3-18. Surface characterization of PM_{2.5} (Numbers refers to enlargement of area in red circles in original image).

Continue Figure 3-18. Surface characterization of $PM_{2.5}$.
 (Numbers refers to enlargement of area in red circles in
 original image.)

3.8 Crustal Enrichment Factors

Rahn [129] introduced the concept of Enrichment Factor (EF) to detect contributions of non-crustal sources on observed concentrations of elements. EF compares the ratio of the concentration of element to a selected reference element in a sample, and the corresponding ratio in the average composition of the earth's crust (Figure 3-19).

$$EF_X = \frac{\left(\frac{[X]_{\text{sample}}}{[Al]_{\text{sample}}} \right)}{\left(\frac{[X]_{\text{crust}}}{[Al]_{\text{crust}}} \right)} \quad \text{Eq. 3-1}$$

The enrichment factor can show natural volatilization, marine sources and anthropogenic activities. Elements with EF less than 10 are assumed to originate from crustal erosion. Some potentially toxic elements such as Fe, Mn, V, Cr and Ni are found in this category. Elements with EF values ranging from 10 to 100 are likely to be moderately enriched by anthropogenic sources. Elements such as Pb, Hg and Sn fit into this category and are commonly enriched by industries and incinerators in Tuas and Jurong Island areas. However, Na is not enriched by anthropogenic sources as most of it usually comes from seawater instead of crustal erosion. Highly enriched elements with EF values greater than 100 are most probably related to industrial, incineration and automobile emissions. The presence of Pt, Rh, Re, Ru and Pd in the enriched group suggests the contribution of oil refineries and chemical production in emission of particles, as discussed in sections 3.5 and 3.6. On the other hand Zn and Cd are common materials used in industries and automobiles. Likewise, B is used as a raw material in the manufacturing of glass, detergents and bleaching agents. An exception is seen for Os as it usually comes from volcanic ashes instead of industrial emissions.

Figure 3-19. PM_{2.5} and PM₁₀ Enrichment Factors.

3.9 Source Apportionment

3.9.1 Positive Matrix Factorization Overview

Positive Matrix Factorization (PMF) is an advanced multivariate factor analysis algorithm developed by Paatero and Tapper [130-132]. Among the different type of available receptor models (Principal Component Analysis (PCA), Unmix and Target Transformation Factor Analysis (TTFA)), attention is mainly on the PMF model [133]. The reason that most researchers are interested in PMF is because of its property to be a technique that can manage and resolve inhomogeneous data-sets without any previous univariate analysis. Another important aspect of PMF is the introduction of error estimates (or weight) associated to the data. Problematic data such as outliers or below-detection-limit values can be entered into the model with appropriated weight, avoiding rejection of such data. By applying and fine-tuning this bootstrapping feature (which provides uncertainty estimates for the factor profiles based on re-sampling the initial factor solutions in a user-specified number of random runs), one can determine in quantitative terms the percentage of bootstrapped factors assigned (mapped) to their corresponding base factors and thus the uniqueness of a given factor profile. PMF treats factor analysis as a true least squares problem [131] i.e., for a data set denoted by matrix X ($i \times j$), X can be solved for as:

$$X_{i,j} = \sum_{k=1}^p f_{ik} \cdot g_{kj} + e_{ij} = FG + E \quad \text{Eq. 3-2}$$

where F , G and E are the factor profile, contribution and residual matrices, respectively and f_{ik} is the mass fraction (%) of the i^{th} parameter in particulate matter sample emitted by the k^{th} source, g_{kj} is the particulate matter concentration parameter from the k^{th} source contributing to the j^{th} sample, e_{ij} is the residual associated with the i^{th} parameter concentration measured in the j^{th} sample, and p is the total number of independent sources.

PMF provides a solution that minimises a weighted sum of the squared residual function Q [131, 132, 134] taking into account non-negativity constraints on the mass fraction (F) and the mass concentration matrix (G):

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{e_{ij}}{S_{ij}} \right)^2 \quad (\text{Eq. 3-3})$$

$$\text{With } e_{ij} = x_{ij} - \sum_{k=1}^p f_{ik} \cdot g_{kj} \quad (\text{Eq. 3-4})$$

with S_{ij} corresponding to the uncertainty of the concentration x_{ij} .

3.9.1.1 Uncertainty Estimation

Appropriate uncertainty estimates S_{ij} are imperative for PMF analyses. PMF programs allow the user to generate the S matrix based on the method detection limit and the uncertainty in the chemical measurements. PMF treats missing data values differently from values below the detection limit for an optimized model fit to the data. For example, EPA PMF Version 3.0, based on the multilinear engine (ME) program [135, 136], can replace missing data values with the median or geometric value of the species prior to analysis. The robust mode is the default mode with EPA PMF Version 3.0. This reduces the effect of very large variables by treating them as outliers so that they do not distort the model's fitting process [137].

3.9.1.2 Number of factors

The numbers of factors identified in the PMF solution were selected by examining both mathematical PMF diagnostics and interpretability of the identified factors. The two criteria used to diagnose PMF mathematically were Q values and the explained variation (EV) by the identified factors. Testing various numbers of factors allowed a better adjustment of the PMF and to choose the appropriate number of factors to finally retain the most physically meaningful results [138]. Although there are also other mathematical criteria for selecting the

final number of factors, most authors use the minimisation of the Q factor and of the residuals, associated with a good knowledge of the source profiles expected on sites [134, 139].

3.9.2 NTU Particulate Matter Data Sets

The following sections detail a complete PMF analysis of PM₁₀ and PM_{2.5} data sets from the NTU sampling site, Singapore.

3.9.2.1 Pre-PMF Processing / Data set Development / Uncertainty Development

Concentration input file prior to use in EPA PMF v3.0, needs to be formatted in MS Excel; each row corresponds to one sample and each column one species.

In this study, data were checked with PMDP application prior to use in EPA PMF v3.0. Data below the detection limit were substituted with one-half of the detection limit and missing data were substituted with the geometric mean [133].

In addition, the percentage below detection limit was calculated as a guideline to categorize the individual elements.

Uncertainties for the PM₁₀ and PM_{2.5} data set were calculated using PMDP application. Data were checked and individual uncertainty was applied for error estimation in this study:

$$\left\{ \begin{array}{ll} x_{ij}, & x_{ij} > DL \\ x_{ij} = DL/2, & x_{ij} < DL \\ \bar{x}_{ij}, & \text{missing} \end{array} \right. \quad (\text{Eq. 3-5})$$

And

$$\left\{ \begin{array}{ll} DL/3 + 0.15x_{ij}, & x_{ij} > DL \\ s_{ij} = 5DL/6, & x_{ij} < DL \\ 4\bar{x}_{ij}, & \text{missing} \end{array} \right. \quad (\text{Eq. 3-6})$$

where x_{ij} is the geometric mean of the samples greater than analytical detection limit (DL) of the j_{th} species.

3.9.2.2 Analysis of Input Data

Input data were examined to determine if there was a need to increase uncertainties or exclude any elements, by categorizing an element as “weak” or “bad”. Paatero and Hopke [135, 136] have presented some guidelines by using signal-to-noise ratios (S/N) to categorize an element as “bad” or “weak”. If $\frac{S}{N} \leq 0.2$, the element is “bad” and if $0.2 < \frac{S}{N} \leq 2$, the element is “weak”.

For the NTU particulate matter (PM₁₀ and PM_{2.5}) data set, no elements had a signal-to-noise ratio less than 0.64 (Figure 3-20). Estimated source apportionment were done using concentration time series plots. Figure 3-21-(a) shows a good agreement between Al and Mg suggesting crustal origin; in contrast, other two crustal elements (Mn and Sc, Figure 3-21-(b)) do not show the same trend. This suggests the possibility of distribution of other origins.

Scatter graphs were examined to further confirm the common sources of emission between elements (i.e. Al and Mg or Sc and Mn for crustal sources). In the NTU PM₁₀ data set, Al and Mg are strongly related while Sc and Mn are weakly related indicating a soil source and a potential secondary source of Mn (Figure 3-22).

The model was first run with all elements characterized as “strong”. Model results were used to guide further categorization of elements.

Species	Cat	S/N	Min	25th	50th	75th	Max
103 Rh (2)	Strong	5.30597	0.00044	0.01867	0.04159	0.07483	0.79746
105 Pd (2)	Strong	2.01100	0.00014	0.00365	0.00758	0.01281	0.15257
107 Ag (2)	Strong	2.22371	0.00374	0.02595	0.05543	0.11450	15.16477
111 Cd (2)	Strong	0.95624	0.07251	0.27602	0.45417	0.64383	29.85951
115 In (2)	Strong	5.41817	0.00101	0.00961	0.01581	0.03244	0.45708
118 Sn (2)	Strong	4.83969	0.08338	0.74272	1.46943	3.49865	16.16436
121 Sb (2)	Strong	5.57981	0.00333	0.02504	0.04929	0.15979	5.93735
125 Te (2)	Strong	3.30989	0.00061	0.00592	0.00949	0.01575	0.46451
133 Cs (2)	Strong	5.56506	0.00792	0.05870	0.09003	0.13191	0.48871
138 Ba (2)	Strong	5.55855	6.26041	159.20387	349.64023	681.21697	3776.30714
139 La (2)	Strong	5.59480	0.04854	0.46305	0.74857	1.25823	27.41349
140 Ce (2)	Strong	5.60740	0.15145	0.90184	1.56038	2.43590	53.84348
157 Gd (2)	Strong	5.62115	0.01033	0.05614	0.08933	0.14022	3.81492
178 Hf (2)	Strong	5.04424	0.00120	0.01990	0.03497	0.05515	1.35031
182 W (2)	Strong	3.13915	0.00091	0.06720	0.13752	0.32491	6.46811
185 Re (2)	Strong	0.64811	0.00005	0.00149	0.00231	0.00370	0.08542
189 Os (2)	Strong	4.59325	0.00022	0.00705	0.01169	0.01738	1.07894
193 Ir (2)	Strong	2.27063	0.00002	0.00038	0.00187	0.00372	0.05332
195 Pt (2)	Strong	4.30134	0.00040	0.00519	0.00952	0.01494	0.26869
197 Au (2)	Strong	1.34485	0.00006	0.00545	0.00915	0.01465	0.28997
202 Hg (2)	Strong	4.53252	0.00018	0.00847	0.01880	0.03334	5.01927
205 Tl (2)	Strong	4.37549	0.00154	0.03116	0.04416	0.06293	0.50246
208 Pb (2)	Strong	5.52201	1.26632	5.69288	8.91193	12.75052	32.37644
209 Bi (2)	Strong	5.58388	0.01994	0.15456	0.26314	0.40801	2.39601

Species	Cat	S/N	Min	25th	50th	75th	Max
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195 Pt (2)	Strong	4.30134	0.00040	0.00519	0.00952	0.01494	0.26869
197 Au (2)	Weak	1.34485	0.00006	0.00545	0.00915	0.01465	0.28997
202 Hg (2)	Strong	4.53252	0.00018	0.00847	0.01880	0.03334	5.01927
205 Tl (2)	Strong	4.37549	0.00154	0.03116	0.04416	0.06293	0.50246
208 Pb (2)	Strong	5.52201	1.26632	5.69288	8.91193	12.75052	32.37644
209 Bi (2)	Strong	5.58388	0.01994	0.15456	0.26314	0.40801	2.39601

Figure 3-20. Input Data Statistics table for the NTU PM_{2.5} data set within initial categorizations (a) and final analysis (b).

Figure 3-21. Concentration time series of crustal elements (in PM_{10}).

Figure 3-22. Concentration scatter plots for crustal elements in PM_{10} .

3.9.2.3 Excluding Samples (Concentration Time Series)

Concentration time series plots (Figure 3-23) were examined to verify if the elements selected for PMF have any seasonal patterns as well as unusual events. Often, these events are easily identified such as haze in October 2010 and September 2011 which contribute to high levels of K, Sr, and other trace elements. These unusual events should be excluded since the overall profiles may be distorted and not reflect the actual composition of the sampling site. Hence, all excluded data were justified and documented.

3.9.2.4 Base Run

➤ *Initial Model Parameters (Model Execution)*

The model was initially run 20 times with 5 factors and random seed. After the run, the fluctuations of Q-values between different runs were checked to be stable. All runs were converged and the Q-values were stable, with a range of only ± 2 . The Q robustness was within 1% of the Q true value, indicating outliers are not heavily impacting the Q value.

➤ *Base Run Results*

After each run, the predicted scatter and concentration time series were overlaid with the experimental plots to check the modelling results of all elements. In Figure 3 -24 two graphs have been presented to show a well modelled (a) and a poorly modelled (b) element.

Contributing factors to a poorly modelled element could be due to incorrect calculated uncertainties and categorization, too few factors considered or this element was not reliably quantified.

Figure 3-23. Concentration time series illustrating extreme events for potassium (top) and metals (bottom).

➤ *Rotations (G-Space Plots)*

G-Space Plots of the solution were examined to determine presence of edges. Figure 3-25 (a) show a G-Space Plot with no edges. Figure 3-25 (b) have an edge that is indicated by a red line. So Fpeak was used to explore the rotational ambiguity of the data set.

Figure 3-24. Example output graphs for a well modeled element (Na, top) and a poorly modeled element (Ir, bottom) – PM_{10} . (red line: predicted concentration, blue line: observed concentration).

Figure 3-25. Example of G-space plots for independent (top) and weakly dependent factors (bottom)

3.9.2.5 Base Model Runs with Updated Species Categorization

To determine the minimum number of factors required to obtain a good fit of the model parameters to the observed data numerous repetitions were performed. The Q-values were used to decide the optimal number of entries.

The optimum numbers of factors were found by trial and error while performing the best fit. Another consideration in the determination of number of factors is to examine the scaled – residual matrix which is also calculated by the model. Juntto and Paatero have reported a value between -2 and 2 for a good fit (Juntto and Paatero, 1994). In this work the scaled residual varied between -3 to 3.

For PM₁₀ and PM_{2.5}, it was found that an 8-factor model and 7- factor model respectively, gave the most satisfactory source profile and agreement between theoretical and calculated values of Q.

➤ *Bootstrap Runs*

After selecting a solution, bootstrapping of the solution was performed to observe the stability and ensure consistency of results. NTU particulate matter data sets were bootstrapped 100 times with random seed. Table 3-12 summarizes bootstrap parameters for both PM₁₀ and PM_{2.5}. The suggested block size and minimum R² value were used as shown in Table 3-12.

Table 3-12. Bootstrap parameter.

	Run	Selected base run	Seed	Block size	R ²
PM ₁₀	100	12	random	16	0.6
PM _{2.5}	100	9	random	21	0.6

➤ *Bootstrap Run Results*

All factors were mapped to a base factor in every single 100 runs, and no factors were unmapped, indicating a stable result. In examining bootstrapping results, the inter-quartile

value of elements within each run was checked in terms of mass and percentage. For this data set, more variability was seen in the industrial factors, which is not unusual.

➤ *Fpeak Runs*

A range of Fpeak values were examined using Fpeak to rotate the solution. Several attributions had been noted in determining which solutions are reasonable, including the change in Q values (from the original solution), changes in the profiles of the original solution, and the G-Space Plots between factors. A range of Fpeak values, positive and negative, were used. Fpeak values of -1.0 to +1.0 (by 0.1) were used with the selected base run.

➤ *Final Results*

We ran PMF with 3 to 10 factors and examined how the factors changed. The optimum factor number for the PMF appeared at 8 for PM₁₀ and 7 for PM_{2.5}.

The best PMF solutions were therefore determined by testing different numbers of sources, different Fpeak values and random seeds. To check the effect of the number of factors on the data set, we used the optimal subset of 7 and 8 factors respectively on 276 PM_{2.5} and 279 PM₁₀ samples. Figure 3-26 and Figure 3-27 present the contributed factors and suggested sources for each factor in PM_{2.5} and PM₁₀ respectively. In this study, the selected index elements were used to determine different sources.

3.9.3 PM_{2.5} Source Profiles

The first factor was identified as a combined factor include sea salt and crustal sources, since from one side the crustal index elements such as Al, Sc, Mg, Ca, K, Mn, Fe and REE elements (La and Ce) and in other side sea spray index elements (Na, Ca, Mg) showed high contributions [140].

The second factor characterized using Mg, Al, Mn, Ba and Ce as index elements for road dust and vehicle emissions [120, 125, 141, 142].

In recent studies, Zn was thought to be emitted by motor vehicles from the combustion of motor oil [143-146]. However, in Singapore Zn is also widely used for corrosion protection, which can be counted as another origin for Zn..

Factor 3 presents high contribution of La, Ce and Al. As it is mentioned in section 3-5, all these elements can be categorized as crustal and from petrochemical industries based on the sampling site situation, background and nearby industries. Factor 3 also includes the elements (Pt, Ru, Rh, Re, Pd, Ag, V, Ni, Cr, Co, Cd and Sn that are mostly used in refineries, petrochemicals and chemicals as catalysts. La and Ce occur with other index elements that originate from petrochemical and refinery industries, thus this factor can also be related to chemical and petrochemical industries.

In factor 4, Ni and V showed the highest contribution. These two elements have been introduced as an index for oil burning [1, 122, 125, 147].

Factor 5 is attributed to the electronics (with W, Au, Cr and Cd used as indexes) and semiconductor industries, which are growing rapidly and are distributed all over Singapore [1].

Since the NTU sampling site was located in a highly industrialized area, it seems that elements present in factor 6 were most likely emitted from local industrial high-temperature combustion sources such as incineration (Pb, As and K), oil combustion (V, Ni), coal combustion (As), and smelters/metal works (Ni, Fe) [122, 147-150].

The last factor showed high contribution of Fe, Al, Ba, Mg, W and Mn. These elements are most likely introduced into the ambient air by widespread construction activities in Singapore.

3.9.4 PM₁₀ Source profiles

PMF results for PM₁₀ is represented by 8 sources including (i) sea salts, (ii) crustal and windblown dust, (iii) road dust and vehicular emission, (iv) refineries, petrochemicals and chemicals, (v) oil combustion, (vi) electronics and semiconductors industries, (vii) high temperature industries, (viii) construction.

Figure 3-26. Source profiles resolved from PM_{2.5} samples.

Continue Figure 3-26—. Source profiles resolved from PM_{2.5} samples.

Figure 3-27. Source profiles resolved from PM₁₀ samples.

Continue Figure 3 -27. Source profiles resolved from PM₁₀ samples.

Chapter 4: Study of Chemical Composition of Rainwater Samples in Singapore

4.1 Chapter 4: Rainwater Chemistry

Rainwater can absorb a number of chemical species (either in the gas or aerosol phase), which are released from both natural and anthropogenic sources. Sea salt, eroded earth crystalline materials and biogenic activities are the major wide-spread natural sources, and fossil fuel combustion and agricultural activities are the major anthropogenic sources. The chemical species that dissolve in rainwater include both acids and bases, and it is these that determine the acidity of water. H_2SO_4 and HNO_3 are regarded as the major acids, whereas calcium carbonate and ammonia are regarded as the major contributing bases [73].

Once the acids in rain droplets were identified as a potential cause of acidification of lakes and soils, it was widely recommended that regular monitoring of the pH and chemical composition of rainwater should commence in order to accurately estimate the amount of acid deposition. In August 2009, a sampling site in Nanyang Technological University, School of Physical and Mathematical Sciences was established to monitor rainwater and dust daily.

The results of monitoring the rainwater at the NTU site (2009–2011) are analyzed here to identify the chemical properties of rainwater samples. First, the chemical composition of rainwater samples was overviewed to investigate the characteristics of rainwater. Second, the acid concentrations observed were analyzed to identify their roles in determining the acidity of rainwater. Third, rainwater data were compared with collected data in different sampling sites in Singapore and reported data from sites around the world.

As this is NTU's first periodic report, daily or event-wise values were analyzed to find any anomalies or spurious monitoring of data, and then to check the representation of monthly and yearly averaged values in addressing the properties of rainwater. Monthly or yearly averaged values were also utilized to reveal any general trends whenever possible.

4.2 Variations of pH and Conductivity

The natural acidity of rainwater is often taken to be *pH* 5.6, which is that of pure water in equilibrium with the global atmospheric concentration of CO_2 (390 ppm) (<http://co2now.org/>, <http://www.esrl.noaa.gov/gmd/ccgg/trends/>). Values of *pH* below 5.6 indicate the presence of strong acids in rainwater while neutral or alkaline *pH* values indicates neutralization of acids by windblown soil, dust and ammonia. In the absence of common basic compounds such as NH_3 and $CaCO_3$, rainwater *pH* values may be expected to range from 4.5 to 5.6 due to the presence of natural acidic gases such as SO_x and NO_x [92, 151-153].

The *pH* values from the collected rain samples indicate that most samples have acidic components (Figure 4-1). 98.40% of the analyzed samples were characterized as acid rainwater ($pH < 5.6$), while the largest fraction (81%) had *pH* values between 3.6 – 4.8. The average *pH* of the rainwater and standard deviation were found to be 4.33 ± 0.55 . The *pH* of individual rainwater events ranged from 3.22 to 6.24 for the NTU sampling site.

Conductivity measurements on the individual collected samples fell within the range 2.5 to $278 \mu S cm^{-1}$, with an average value of $35.5 \mu S cm^{-1}$. The National Environmental Agency (NEA) in Singapore (<http://app.nea.gov.sg/psi/>) uses a Pollutant Standards Index (PSI) to report the air quality based on 5 major contaminants (SO_2 , PM_{10} , O_3 , CO and NO_2). An overall number (0 – 500) is assigned based on the highest value obtained for any individual reading, and usually it is determined by the PM_{10} reading (although the SO_2 reading can sometimes be dominant).

Figure 4-1. *pH* distribution.

Figure 4-2. Correlation between PSI and Conductivity.

It was found that the sample linear correlation coefficient (r_{XY}) between the conductivity and PSI (West Singapore) was moderately strong ($r_{XY} = 0.5$). Figure 4-2 shows the plot of PSI and conductivity on days that there was rainfall, which demonstrates that there was a correlation between the PSI readings (and therefore, PM_{10} readings) and the conductivity. An interesting observation is that higher conductivity was detected after periods of dryness and haze, while lower readings occurred when rain continued for several days. This correlation was also observed for the total ionic content. The correlation between the PSI and conductivity can be rationalized by the increased pollution (mainly in the form of particles) increasing the number of dissolved salts in the rain water. The distribution of PSI value during rainwater sampling is presented in Appendix E.

4.3 Data Screening

Ion balance is an important parameter for data quality assessment. It gives an indication of the quality of analysis as well as the possibility of any missing parameters. Data quality of each rainwater sample was checked by ion balance. The data was rejected if it did not meet the quality criteria, which allowed for 15% deviation of ion balance ratio (sum of cations / sum of anions). Consequently, 25 samples were rejected.

Figure 4-3. . Plot of sum of cations against sum of anions

The average equivalent sum of cations to that of anions $\left(\frac{\Sigma cations}{\Sigma anions}\right)$ was 0.92 (Figure 4-3).

The less than unity ratio suggests that a small amount of cations was not measured, although the ion chromatograms (anion and cation) did not contain any additional unidentified peaks.

4.4 Overview of chemical compositions

Rainwater contains various dissolved anions and cations after incorporating gaseous and aerosol species from the ambient air. Rainwater quality is partly a function of the contents of both acid and alkaline compounds. The major ions present in rainwater are presented in Table 4-1 with the corresponding box plots for all of the data over the sampling period given in Figure 4-4. A plot that gives the percentage of each major charged species on a monthly basis is given in

Figure 4-5.

The ionic concentration of rainwater samples showed a trend of $SO_4^{2-} > Cl^- > NO_3^- > F^-$ for anions and $Ca^{2+} > Na^+ > K^+ > NH_4^+ > Mg^{2+}$ for cations. Among the ionic constituents determined, the average (of total ions measured) percentage sulfate levels were the highest (19.10%) followed by chloride (17.43%), calcium (14.40%), nitrate (7.95%), sodium (7.45%), potassium (6.59%), ammonium (5.25%), and magnesium (2.56%). The low concentration of F^- in rainwater could be due to occurrence of the fluoride elution very close to the acetate ion, making it complicated to achieve a more accurate quantification.

Table 4-1. Major ions composition of rainwater ($\mu\text{eq L}^{-1}$).

	2010			2011			Two Year Data		
	Average	Median	Percentile 95%	Average	Median	Percentile 95%	Average	Median	Percentile 95%
F^-	4.93±0.05 (0.32-31.37)	3.66	1.55-5.87	3.57±0.12 (0.33-73.80)	2.24	1.42-4.07	4.17±0.10 (0.32-73.80)	2.64	1.42-4.95
Cl^-	64.06±4.15 (7.57-644.09)	33.09	19.23-63.23	83.86±4.09 (0.74-933.20)	55.12	25.14-95.18	75.38±3.78 (0.74-933.20)	40.72	22.36-86.94
NO_3^-	39.54±1.76 (2.82-323.86)	29.22	16.15-47.92	30.14±1.99 (0.33-208.81)	20.65	9.02-41.18	34.37±2.25 (0.33-323.86)	23.83	11.51-44.40
SO_4^{2-}	84.36±1.79 (8.31-413.16)	72.93	39.25-112.13	81.02±3.54 (1.88-388.04)	55.83	32.20-102.91	82.60±3.32 (1.88-413.16)	64.1	36.80-104.50
Na^+	31.18±0.77 (3.59-229.93)	21.81	13.17-41.16	32.57±1.08 (1.70-486.82)	17.43	11.07-33.88	32.2 (1.70-486.82)	20.35	12.03-37.31
NH_4^+	30.19±0.36 (1.02-345.42)	21.31	10.90-38.57	18.67±0.40 (0.45-145.68)	12.88	3.40-22.34	23.89 (0.45-345.42)	15.55	6.32-30.59
K^+	34.89±3.97 (0.66-533.80)	12.65	5.69-27.08	23.23±2.96 (0.38-839.90)	7.642	3.42-15.53	28.51 (0.38-839.90)	9.5	4.32-20.41
Mg^{2+}	11.16±0.15 (1.61-76.28)	7.15	4.46-12.82	10.91±0.17 (1.0-123.53)	5.81	3.94-11.96	11.08 (1.0-123.53)	6.58	4.16-12.41
Ca^{2+}	61.043±0.89 (6.00-340.22)	41.61	22.35-87.58	63.31±1.69 (3.18-495.63)	33.56	16.39-72.07	62.28 (3.18-495.63)	36.27	18.52-79.30
pH	4.29±0.53 (3.22-6.24)	4.2	3.93-4.53	4.4±0.53 (3.39-6.22)	4.27	4.02-7.76	4.35 (3.22-6.24)	4.24	3.99-4.66

Figure 4-4. Box and whisker plots for average concentrations of cations (H_3O^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) and anions (Cl^- , F^- , NO_3^- and SO_4^{2-}) in rainwater samples for the period between Aug 2009 and 31st December 2011. Horizontal box lines: 25, 50 and 75th percentile values; error bars, 5 and 95th percentile values; $\top$ and $\perp$ are maximum and minimum valid values, respectively. The arithmetic mean corresponds to cross inside the box ($\square$).

Figure 4-5. Anion and cation percentile concentration of rainwater at *NTU* monitoring site.

Figure 4-6. Distribution of major ions in rainwater.

Because Singapore is located in a coastal area, it is likely that some of the Cl^- is present as sea salt-driven ions and appears in higher concentration compared to Ca^{2+} which is a soil-driven ion. Also, the SO_4^{2-} is present in higher concentration than NO_3^- for most samples, making it the most important anionic species. Figure 4-6 shows a plot of the average percentage distribution of major ions in the rainwater samples.

4.4.1 Major anions

Some quantitative parameters were proposed to analyse the rain sample measurements in terms of acid-base chemistry. The acidity, or pH , is a fundamental measure of rainwater properties, and it is determined by the nature and proportions of acids and bases in aqueous solutions. In this sense, pH is a secondary parameter, whereas the concentration of acids and bases are the primary parameters. If any two of these three quantities are properly determined, then the other can be obtained theoretically.

The acid-base balance is assumed to involve only four compounds: H_2SO_4 , HNO_3 , NH_4^+ , and $CaCO_3$. Particulate NH_4^+ species are involved in the formation of ammonium salts such as $(NH_4)_2SO_4$. SO_4^{2-} is produced from SO_2 both in the gas phase and in the liquid phase by photochemical reactions, whereas NO_3^- is produced from NO_x by photochemical reactions only in the gas phase [154]. The following sequence of chemical processes suffices for the quantification of acidity or pH [155]:

SO_4^{2-} and NO_3^- ions are released from the strong acids, H_2SO_4 and HNO_3 , and they are not involved in any neutralization reaction once dissociated. Because the concentrations of SO_4^{2-} and NO_3^- remain unchanged throughout the neutralization reactions, the SO_4^{2-} and NO_3^- concentrations are numerically identical to those of H_2SO_4 and HNO_3 , respectively.

If it is assumed that the concentration of H_3O^+ ions is equal to the concentration sum of SO_4^{2-} and NO_3^- , the input acidity (A_i) in Eq. 4-7 can be used to determine the maximum expected acidity, where the concentrations are in units of $eq\ L^{-1}$ [156, 157]. The parameter pA_i is defined in a similar manner to pH (Eq. 4-8). Therefore, the pH and pA_i will be equivalent if no neutralization of the SO_4^{2-} and NO_3^- occurs. Since seawater contains sulfate anions (in a neutral form), the non-sea salt sulfate ($nss - SO_4^{2-}$) concentration is used in the calculation by subtracting the expected atmospheric sulfate contribution from seawater.

$$A_i = [nss - SO_4^{2-}] + [NO_3^-] \quad \text{Eq. 4-8}$$

$$pA_i = -\log 10([nss - SO_4^{2-}] + NO_3^-) \quad \text{Eq. 4-9}$$

$$ssSO_4^{2-} = Na^+ \times (SO_4^{2-}/Na^+)_{Seawater} \quad \text{Eq. 4-10}$$

$$nssSO_4^{2-} = SO_4^{2-} - ssSO_4^{2-} \quad \text{Eq. 4-11}$$

Figure 4 -7 shows the relation between the pH and pA_i for the *NTU* site. All the measured data are situated above the theoretical $pH - pA_i$ diagonal line (the theoretical line is the pH if all the SO_4^{2-} and NO_3^- are derived from their fully dissociated acidic forms), indicating that measured pH values were larger (higher pH) than the corresponding theoretical $pH - pA_i$ values, and therefore; the anions do not exist in their fully acidic forms. It was found that the pH data collected in rainy months exhibited lesser degrees of overshooting the theoretical $pH - pA_i$ values than those in dry months, presumably because the aerosols contained less neutralizing ions in rainy months, limiting their role in increasing the pH values.

Figure 4-7. Measured pH versus pA_i at *NTU* monitoring site in Singapore (Aug 2009–Dec2010).

The relative contribution of each detected anion (after subtraction of the sea salt contribution) to the potential free acidity, *PFA*, of a rainwater sample was determined by using Eq. 4-12, where $[X]$ is the individual concentration of the anion multiplied by the number of hydrogen atoms that are produced in the ionization process [157, 158].

$$PFA = \frac{[X]}{\sum Anions} \quad \text{Eq. 4-12}$$

$$\sum Anions = [Cl^-] + [NO_3^-] + [SO_4^{2-}] \quad \text{Eq. 4-13}$$

The results of the relative contribution of each acid to the potential free acidity in rainwater at the *NTU* sampling site are presented in Table 4-2. If all the major acidic anions (Cl^- , NO_3^-) and SO_4^{2-} in rainwater are assumed to exist in the form of free acids (completely ionized), the sum of the concentrations of these chemical species should produce a precipitation with a *pH* of 3.73, which is lower than the average *pH* measured of 4.33. The significant difference is an indication that other alkaline forming species (such NH_3) are present, or that the anions occur naturally paired with other cations [157, 158]. As can be seen from Table 4-2, H_2SO_4 has the most significant contribution (0.23-0.65), followed by HCl (0.20-0.63) and HNO_3 (0.07-0.35), respectively. What is interesting in this data is that HCl showed the highest contribution in December for both 2010 and 2011, while correspondingly H_2SO_4 had the lowest contribution. The difference in distribution could be related to wind direction and speed, change in monsoon season, haze events and industrial activities.

4.4.2 Major Cations

A main reason for the *pH* values being larger than pA_i values is the effect of cations, mainly non-sea salt Ca^{2+} and NH_4^+ . The amount of $nss - Ca^{2+}$ that appears in rainwater from dust blown up from the soil and its effect on the aquatic environment is small. On the

other hand, NH_4^+ is produced in rainwater from the NH_3 that is emitted by various agricultural and industrial sources. Furthermore, NH_4^+ in rainwater may play a role as a nutrient in aquatic environments or it may cause nitrification in soils.

The relative importance of Ca^{2+} and NH_4^+ can be identified by calculating the ratios of these two ions. Through data analysis, the ratios of $nss - Ca^{2+}$ versus NH_4^+ were found to vary significantly, and are represented by the frequently used corresponding scatter diagram. The ratios (D_{mc}) of Ca^{2+} versus NH_4^+ were plotted against the corresponding pH values to fully visualize their variability in rainwater (Figure 4-8).

Figure 4-8. $D_{mc} = ([NH_4^+]/[nss - Ca^{2+}])$ versus pH at NTU monitoring site.

Table 4-2. Acids contribution to the potential free-acidity (*PFA*) of the rainwater for NTU sampling site during sampling month.

	<i>PFA</i>		
	<i>H₂SO₄</i>	<i>HNO₃</i>	<i>HCl</i>
Aug-09	0.55	0.19	0.26
Sep-09	0.56	0.13	0.31
Oct-09	0.46	0.18	0.36
Nov-09	0.44	0.25	0.31
Dec-09	0.52	0.20	0.28
Jan-10	0.43	0.22	0.35
Feb-10	0.44	0.24	0.32
Mar-10	0.42	0.27	0.31
Apr-10	0.51	0.35	0.15
May-10	0.32	0.23	0.45
Jun-10	0.50	0.20	0.30
Jul-10	0.52	0.18	0.30
Aug-10	0.65	0.12	0.22
Sep-10	0.56	0.16	0.28
Oct-10	0.60	0.15	0.25
Nov-10	0.42	0.20	0.38
Dec-10	0.27	0.18	0.55
Jan-11	0.28	0.14	0.58
Feb-11	0.42	0.21	0.37
Mar-11	0.42	0.22	0.36
Apr-11	0.47	0.18	0.35
May-11	0.61	0.19	0.20
Jun-11	0.66	0.07	0.27
Jul-11	0.46	0.11	0.42
Aug-11	0.59	0.18	0.22
Sep-11	0.39	0.12	0.49
Oct-11	0.28	0.24	0.48
Nov-11	0.34	0.18	0.48
Dec-11	0.23	0.14	0.63
Total	0.44	0.18	0.38

$$D_{mc} = \frac{[NH_4^+]}{nss - Ca^{2+}} \quad \text{Eq. 4-14}$$

The values of D_{mc} at the NTU site were mostly less than 1.0, indicating that $nss - Ca^{2+}$ is the major cation (Figure 4-8). As NH_4^+ is a weak base, its apparent solubility is therefore dependent on pH, as follows [159] :

$$S_{ap,NH_3} = \frac{NH_3(aq) + NH_4^+}{NH_3(g)} = \frac{NH_3(aq)}{NH_3(g)} \left(1 + \frac{K_{eq} \cdot NH_3 [H^+]}{K_w} \right) \quad \text{Eq. 4-15}$$

where S_{ap,NH_3} is the apparent solubility of NH_3 , and K_{eq} , NH_3 and K_w denote the equilibrium constant for NH_3 and water, respectively. In particular, the pH affects the equilibrium between NH_4^+ and NH_3 .

4.4.3 Neutralization Factors (NF)

The presence of cations, mainly non-sea salt Ca^{2+} (nss- Ca^{2+}), nss- Mg^{2+} and NH_4^+ are the main reason that experimental pH values are larger than theoretical pH (pA_i), since they form ion-pairs with the anions. The nss- Ca^{2+} and Mg^{2+} that appear in rainwater are likely to originate from dust blown up from the soil. In contrast, NH_4^+ is converted in rainwater from the NH_3 that is emitted by agricultural activities and industrial sources. NH_4^+ in rainwater may play a role as a nutrient in aquatic environments or it may cause nitrification in soil environments.

Since acidity originates primarily from sulfuric and nitric acid coupled to neutralization by crustal components and ammonia, the ratios of anions/cations can be considered as an indicator for acidity. If the ratio of anions/cations is < 1 (excluding H_3O^+), it indicates an alkaline nature of rainwater, whereas ratios > 1 indicates the presence of free anions which may be responsible for increasing rainwater acidity [160]. The role of NH_4^+ , nss- Ca^{2+} and nss- Mg^{2+} has been validated by calculating neutralization factors as follows [72]:

$$NF_{Ca} = \frac{Ca^{2+}}{NO_3^- + SO_4^{2-}} \quad \text{Eq. 4-16}$$

$$NF_{NH_4^+} = \frac{NH_4^+}{NO_3^- + SO_4^{2-}} \quad \text{Eq. 4-17}$$

$$NF_{Mg^{2+}} = \frac{Mg^{2+}}{NO_3^- + SO_4^{2-}} \quad \text{Eq. 4-18}$$

For the calculations in Eq. 4-15 to Eq. 4-17, the average equivalent concentrations of the ions were used. The values of the neutralization factors for Ca^{2+} , NH_4^+ and Mg^{2+} were 0.60, 0.26 and 0.13, respectively, suggesting that the major neutralization of acidity has occurred due to Ca^{2+} salts. Therefore, in Singapore, aerosols containing Ca^{2+} salts (such as carbonates) followed by NH_4^+ help to increase the pH of the rain water and lower the acidity that is due to relatively high concentrations of the acidic gases SO_2 and NO_2 [161]. To be exact, neutralization by NH_4^+ is likely attributed to escaped NH_3 converted from fertilizers consisting of NH_4NO_3 and $(NH_4)_2SO_4$ that participate in the neutralization process in rain [162].

Though NF calculations provide an insight into the neutralization effects of different cations, they tend to over-estimate because these values assume that 100 % of the alkaline species contribute to acidity neutralization in precipitation, which might not be the case.

Figure 4-9. Triangular diagram relating neutralization factor (NF) of Ca^{2+} , NH_4^+ and Mg^{2+} .

It has been reported that neutralization occurs when Ca^{2+} and NH_4^+ exist in their alkaline forms ($CaCO_3$ and NH_3) in precipitation and subsequently neutralize the available H_3O^+ [163]. However, a portion of Ca^{2+} may already exist as neutral $CaSO_4$ and/or $Ca(NO_3)_2$ salts from previous reactions with H_2SO_4 and HNO_3 during transport processes [164]. Similarly, not all NH_4NO_3 and $(NH_4)_2SO_4$ from fertilizers are converted to NH_3 ; much of these compounds become air-borne and are subsequently introduced into precipitation droplets as *pH* neutral NH_4NO_3 and $(NH_4)_2SO_4$ aerosols which in the absence of further conversion processes into NH_3 , do not contribute to precipitation neutralization.

4.4.4 Ratio of Different Species

The ratio of $\frac{(Ca^{2+}+NH_4^+)}{(NO_3^-+SO_4^{2-})}$ has been calculated in order to determine the relative significance of these ions to the acidity and alkalinity of the rainwater in the study area. The ratio of $\frac{(Ca^{2+}+NH_4^+)}{(NO_3^-+SO_4^{2-})}$ varies between 0.1 to 7.67 in the analysed rainwater samples and the bivariate plot between $(Ca^{2+} + NH_4^+)$ and $(NO_3^- + SO_4^{2-})$ shows that most of the plotted points fall below the equiline, indicating that that Ca^{2+} and NH_4^+ alone do not neutralize the acidic ions $(NO_3^- + SO_4^{2-})$, with possibly some other cations also likely contributing in this process (Figure 4 -10).

According to some reports [165-167] the ratio of $\frac{[H^+]}{[NO_3^-+SO_4^{2-}]}$ is an indication of whether the acidity is neutralized or not. Specifically, this ratio would be unity if the acidity in rainwater that is caused by strong acids (H_2SO_4 and HNO_3) is not neutralized at all, while deviations from unity represent the percentage of the neutralized acidic components.

The average calculated $\frac{SO_4^{2-}}{NO_3^-}$ ratio (4.17) was compared to values obtained from other studies from urban areas. As can be seen from Table 4 -3 this ratio was lower than the ratios

found in other studies such as Guaiba [163], Figueira [164], Galilee [168], Erzurum [162]. It was, however, higher than the ratio found in Mexico [161] and Spain but it is near to the finding in last study for Singapore [165].

Figure 4-10. Relation between alkaline and acidic species

The ratio of $\frac{(NO_3^- + SO_4^{2-})}{(Ca^{2+} + Mg^{2+})}$ was observed to be 2.24 indicating the acidic nature of the rainwater. The ratio of $\frac{NH_4^+}{NO_3^-}$ and $\frac{NH_4^+}{SO_4^{2-}}$ was observed as 0.93 and 0.42 indicating that the likely compounds which predominate in the atmosphere are NH_4NO_3 and $(NH_4)_2SO_4$ [169]. In some studies ammonium nitrate dominates over ammonium sulfates [170] whereas in other studies ammonium sulfate dominates over ammonium nitrate [75].

It becomes clear that neutralization of acidity took place in collected rainwater samples because the mean fractional acidity is only 0.66. Such neutralization is frequently reported and attributed to NH_3 and/or $CaCO_3$. It has been reported that the abundance of SO_4^{2-} and NO_3^- is relatively constant with altitude, while ammonia and ammonium ions diminish in concentration rapidly with height [78].

Table 4-3. $\frac{SO_4^{2-}}{NO_3^-}$ comparison ratio at various locations in the world.

Locations	$\frac{SO_4^{2-}}{NO_3^-}$	Ref
Erzurum	11.60	[162]
Guaiba	8.70	[163]
Galilee	5.37	[168]
Figueira	5.30	[164]
Present Study	4.17	-
Singapore	3.50	[165]
Spain	2.22	[171]
Jordan	1.20	[172]
Mexico	0.75	[161]

The observation implies that at cloud level acidic species such as H_2SO_4 , HNO_3 , NH_4HSO_4 are likely to predominate over the pH neutral species such as $(NH_4)_2SO_4$ and NH_4NO_3 . Therefore, it appears that at cloud level neutralization is due to a reaction of cloud condensation nuclei containing *Ca* and *Mg* with H_2SO_4 and HNO_3 , while below cloud level neutralization is brought about by both ammonia and adsorption of SO_2 suspended particulate matter containing *Ca* and *Mg* [78].

In Figure 4 -11 and Figure 4 -12 are shown the linear regression of $(NO_3^- + SO_4^{2-})$ with NH_4^+ and Ca^{2+} . The correlation co-efficient between these variables was 0.26 and 0.51, respectively, indicating that these ions are neutralizing rainwater acidity.

If H_2SO_4 , HNO_3 , NH_4^+ and $CaCO_3$ are the only species involved in acidity precipitation, a linear relation it is expected between the concentrations of $(H^+ + Ca^{2+} + NH_4^+)$ and $(SO_4^{2-} + NO_3^-)$ [78]. This relation is shown in Figure 4-13; the correlation coefficient between the variables is 0.60 indicating that the acidity is caused by H_2SO_4 and HNO_3 which could not be neutralized by NH_4^+ and $CaCO_3$ [78, 173]. The contribution of other anions and cations on the neutralization process and hence, on the acidity of the rainwater is significant.

4.4.5 Sea Salt Contribution

In order to estimate the marine and non-marine contribution to the ion composition of the rain water, the ratio of the ions were compared with their expected ratios in sea water using Na^+ as the reference element [72]. Table 4-4 gives the ratios of Cl^- , K^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} with respect to Na^+ . All ratios of ions in rainwater were found to be higher than compared to the ratios in seawater, although the observed rainwater ratio of $\left(\frac{Cl^-}{Na^+}\right) = 2.94$ is significantly higher than that of the seawater ratio (1.17), indicating that part (40 %) of the rain chemistry is influenced by the marine sprays coming from sea (when winds are favorable) but around 60% might be emitted from other industrial or natural sources.

The enrichment factors (EF) of different ions with respect to Na^+ are given in Table 4-4 and were calculated according to Eq. 4-18, where X is the ion of interest. The enrichment factors of SO_4^{2-} , Ca^{2+} , and especially NO_3^- were $\gg 1$, indicating a large contribution from anthropogenic and crustal sources.

The sea salt fraction (ssF) was calculated by assuming that all the Na^+ originated from sea water, thus the sea salt fraction is the percentage of the seawater ratio/rainwater ratio (Table 4-4).

The non-sea salt fractions ($nssF$) were the remaining difference between the sea salt contribution and 100% of the ionic constituents, and in most cases were calculated to be very high (Table 4-4).

$$EF = \frac{(X/Na)_{Rainwater}}{(X/Na)_{Seawater}} \quad \text{Eq. 4-19}$$

The elevated $\frac{K^+}{Na^+}$, $\frac{Mg^{2+}}{Na^+}$, $\frac{Ca^{2+}}{Na^+}$ and $\frac{SO_4^{2-}}{Na^+}$ ratios indicate the possible contribution of other components, probably from the soil.

Figure 4-11. Relationship between neutralizing factor NH_4^+ and acidic species.

Figure 4-12. Relationship between neutralizing factor Ca^{2+} and acidic species.

Figure 4-13. Relationship between neutralizing factors and acidic species.

The observation of high relative ratios among the ionic species suggests that the possible combinations are $NaCl$, KCl , $CaSO_4$, $MgSO_4$, $MgCl_2$, HNO_3 , NH_4NO_3 , NH_4HSO_4 and $(NH_4)_2SO_4$. The $nss - Ca^{2+}$ contribution was observed as 99.00% suggesting its crustal

origin. $nss - Mg^{2+}$ and $nss - K^+$ contributions were 89.02% and 82.13%, respectively, indicating the influence of crustal dust. For the anions, the $nss SO_4^{2-}$ and $nss - NO_3^{2-}$ contributions were 96.61% and 99.99%, respectively, also showing a crustal (non-marine) and anthropogenic origin.

Table 4-4. Equivalent ratios of various species to Na and estimated non sea salt (nss) fraction in rain water samples and the corresponding values for sea water

	Cl^-/Na^+	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+	SO_4^{2-}/Na^+	NO_3^-/Na^+
Ratio in rainwater	2.94	1.27	2.39	0.40	3.69	1.55
Sea Water ratio	1.17	0.227	0.0218	0.0439	0.125	0.00021
EF	2.51	5.59	109.63	9.11	29.52	7380.95
SSF	39.80	17.87	1.00	10.98	3.39	0.01
NSSF	60.20	82.13	99.00	89.02	96.61	99.99
EF: Enrichment factor, SSF= Sea Salt Fraction, NSSF=Non-Sea Salt Fraction						

4.4.6 Ionic Correlation of Rainwater

The correlation between ions present in rainwater is given in Table 4-5 with K^+ and Cl^- displaying a particular high value (0.80). A strong correlation was seen between Ca^{2+} and Mg^{2+} ($r = 0.62$); suggesting their occurrence was from crustal origin. Na^+ has a relatively significant correlation with Cl^- ($r = 0.50$), Mg^{2+} ($r = 0.75$), SO_4^{2-} ($r = 0.57$) and Ca^{2+} ($r = 0.59$). The acidic ions SO_4^{2-} and NO_3^- correlated strongly ($r = 0.62$) indicating their origin was from similar sources, because of the similarity in their behaviour in rainwater and the co-emissions of their precursors SO_2 and NO_x . Other significant correlations were observed between, Ca^{2+} and SO_4^{2-} ($r = 0.69$), Mg^{2+} and SO_4^{2-} ($r = 0.58$), Ca^{2+} and NO_3^- ($r = 0.61$). Most of these well-correlated pairs have common sources or occur in rainwater as a result of atmospheric chemical reactions probably from the reaction of acids H_2SO_4 , HNO_3 and HCl with alkaline compounds rich in Ca^{2+} and Mg^{2+} carried into the atmosphere by windblown dust. This suggests that wind carried dust and soil

play an important role in rainwater chemistry [75]. Ammonium compounds generally occur in the atmosphere as $(NH_4)_2SO_4$ and NH_4NO_3 [169], which is supported by the moderate correlation between NH_4^+ and NO_3^- ($r = 0.47$) followed by NH_4^+ and SO_4^{2-} ($r = 0.47$).

4.4.7 Trace Elemental Analysis of Rainwater Samples

The average, median, and concentration range (in terms of minimum and maximum) of dissolved trace elements in rainwater samples are listed in Table 4-6. This variability can be explained either by industrial activities and natural events or by atmospheric cleansing mechanisms. Based on data reported in the table the trace elements can be divided to four groups: *Zn, Fe, Al* and *Cu* with average concentrations of larger than $10 \mu g L^{-1}$, *V, Ba, Mn, Pb, Ni, Sr, Ga* and *As* with concentrations between $1-10 \mu g L^{-1}$, *Mo, Co, Rb, Cr, Hg, W, Sb, Os, La, Cd, Ce, Sn* and *Se* with concentrations between $0.1-1 \mu g L^{-1}$ and finally *Cs, Te, Bi, Gd, Ir* and *U* with concentrations lower than $0.1 \mu g L^{-1}$.

These results are in agreement with our study on atmospheric particulate matter ($PM_{2.5}$ and PM_{10}) that was conducted at the *NTU* sampling site (Chapter 3), where high concentrations of *Al, Zn* and *Fe* were detected, with the other elements also detected in the same relative order during the same sampling period (August 2009–December 2011). This can be explained by the presence of particulate matter partly or fully dissolving in the rainwater sample, thus causing a higher solubilisation of certain elements, such as *Al, Zn* and *Fe* [79].

The high concentrations of *Al* present in rainwater may be attributed to two sources; (a) the relative abundance in crustal or geological material [79, 174], and (b) currently, many vehicle motors are made out of aluminium, thus the wear of such motors may emit substantial amounts of this metal into the atmosphere.

Table 4-5. Ionic correlation of rainwater

	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	H^+
F^-	1.00									
Cl^-	0.30	1.00								
NO_3^-	0.31	0.24	1.00							
SO_4^{2-}	0.43	0.25	0.62	1.00						
Na^+	0.36	0.50	0.36	0.57	1.00					
NH_4^+	0.44	0.27	0.47	0.47	0.35	1.00				
K^+	0.15	0.80	0.10	0.04	0.14	0.10	1.00			
Mg^{2+}	0.31	0.42	0.41	0.58	0.75	0.38	0.13	1.00		
Ca^{2+}	0.43	0.44	0.61	0.69	0.59	0.42	0.12	0.62	1.00	
H^+	0.03	-0.17	0.37	0.29	-0.11	0.07	-0.11	-0.04	0.05	1.00

However, the solubility of elements is a complicated process which depends on the pH of rainwater. It has been observed that when the pH increases from 4 to 5, the solubility of certain metals (Cd, Cu, V, Zn, Ni, Pb) decreases 5 to 10 times.

4.4.8 Enrichment of Elements

The enrichment factors (EF) of the elements compared with the relative abundances of that element in crustal material were calculated using Al and Fe as the reference elements (Eq. 4-9), where $(X/R)_{Rainwater}$ and $(X/R)_{Crust}$ refer to the ratio of concentration of element X to that of Al in the rainwater and in the average crustal material, respectively [166, 175]. If it is assumed that the main source of Al is crustal material, EF values close to 1 for element X indicates that the element mainly arises from crustal sources.

$$EF = \frac{X/R_{rainwater}}{X/R_{Crust}} \quad \text{Eq. 4-20}$$

EF values that fall in the range of 1–10 are not considered to be enriched, since there are natural variations in local soil compositions. EF values between 10 – 100 are considered to be moderately enriched, indicating that the element in rainwater is present at a higher level

than expected. *EF* values greater than 100 indicate highly enriched conditions, suggesting an anthropogenic source [176].

Table 4-7 presents the calculated enrichment factors of elements in rainwater samples. *Al, Ba, Ce, Cr, Cs, Fe, Gd, La, Mn, Rb, Sr, Ti and U* are not enriched >10 indicating that they have mainly originated from airborne dust. The elements *Bi, Co, Ga, Ni, Sn, Tl, V and W* are moderately enriched compared to the mean crustal composition indicating the presence of other sources contributing to these elements. The elements *As, Cd, Cu, Hg, Ir, Mo, Os, Pb, Sb, Se, Te and Zn* are highly enriched compared to mean crustal composition and are likely to be of anthropogenic origin in rainwater.

Table 4-6. Summary statistics for rainwater samples in NTU sampling Site ($\mu\text{eq L}^{-1}$).

Elements	Al ¹	As ¹	Ba ¹	Bi ²	Cd ¹	Ce ²	Co ²	Cr ¹
Average (Min-Max)	126.09±136.51 (1.85-863) n=	1.06±0.97 (0.04-9.7)	7.47±4.80 (0.30-85.00)	0.01±0.02 (<DL-0.08)	0.15±0.21 (<DL-1.63)	0.14±0.24 (<DL-1.83)	0.57±0.72 (0.02-3.03)	0.49±1.68 (<DL-29.61)
Median	75.55	0.93	4.80	0.01	0.10	0.06	0.23	0.20
Q ₁ -Q ₃	29.22-179.75	0.40-1.40	2.32-9.38	0.00-0.02	0.03-0.20	0.02-0.16	0.13-0.77	0.08-0.43
Elements	Cu ¹	Cs ²	Fe ¹	Gd ²	Ga ²	Hg ²	Ir ²	La ²
Average (Min-Max)	14.93±17.58 (0.09-156.00)	0.08±0.13 (<DL-0.98)	126.19±229.80 (<DL-3214.24)	0.01±0.01 (<DL-0.06)	1.65±1.48 (0.10-8.24)	0.28±0.318 (<DL-1.76)	0.01±0.01 (<DL-0.04)	0.16±0.24 (<DL-1.27)
Median	8.41	0.04	60.96	0.004	1.21	0.18	0.003	0.10
Q ₁ -Q ₃	3.52-20.70	0.02-0.08	20.05-151.73	0.00-0.01	0.52-2.42	0.09-0.38	0.00-0.01	0.03-0.27
Elements	Mo ²	Mn ¹	Ni ²	Os ²	Pb ¹	Rb ²	Sb ²	Se ²
Average (Min-Max)	0.58±0.65 (<DL-4.80)	7.14±13.35 (0.15-200.00)	3.42±4.49 (0.02-22.19)	0.17±0.15 (0.02-0.73)	4.15±5.24 (0.02-68.1)	0.51±0.65 (0.047-5.14)	0.23±0.19 (<DL-0.93)	0.12±0.10 (<DL-0.65)
Median	0.34	3.75	1.57	0.13	2.90	0.32	0.16	0.09
Q ₁ -Q ₃	0.21-0.71	1.89-8.69	0.81-4.14	0.08-0.23	1.40-5.10	0.21-0.56	0.09-0.31	0.05-0.16
Elements	Sn ²	Sr ¹	Te ²	Ti ²	Tl ²	U ²	V ¹	W ²
Average (Min-Max)	0.14±0.16 (0.01-0.99)	2.49±3.22 (0.10-28.57)	0.03±0.04 (<DL-0.35)	2.43±3.43 (0.11-27.64)	0.03±0.04 (<DL-0.24)	0.01±0.01 (<DL-0.04)	7.68±9.76 (0.10-55.90)	0.27±0.31 (<DL-1.75)
Median	0.08	1.40	0.02	1.30	0.02	0.01	3.99	0.16
Q ₁ -Q ₃	0.05-0.15	0.75-2.70	0.01-0.04	0.73-2.72	0.01-0.03	0.00-0.01	2.13-8.60	0.05-0.40
Elements	Zn ¹	1- Rainwater samples collected from August 2009 to December 2011. Elemental analysis were done with ICP-OES and ICP-MS from August 2009 to March 2011 and April 2011 to December 2011, respectively.						
Average (Min-Max)	143.02±162.98 (1.10-1293.00)							
Median	92.00	2- Rainwater collected from April 2011 to December 2011. All measurements were done by ICP-MS.						
Q ₁ -Q ₃	48.08-176.73

Figure 4-14 Box and whisker plots for average concentrations of trace elements in rainwater samples for the period of August 2009 up to December 2011.

Table 4-7. Enrichment Factors.

Elements	<i>Al</i>	<i>As</i>	<i>Ba</i>	<i>Bi</i>	<i>Cd</i>	<i>Ce</i>	<i>Co</i>	<i>Cr</i>
<i>EF (Al)</i>	1.00	144.23	7.74	51.92	1083.3	1.49	21.31	3.43
<i>EF (Fe)</i>	0.48	68.54	3.68	24.67	514.82	0.71	10.13	1.63
Elements	<i>Cu</i>	<i>Cs</i>	<i>Fe</i>	<i>Gd</i>	<i>Ga</i>	<i>Hg</i>	<i>Ir</i>	<i>La</i>
<i>EF (Al)</i>	346.85	10.75	2.1	1.14	61.14	3706.28	171116.7	3.89
<i>EF (Fe)</i>	164.83	5.11	1.00	0.54	29.06	1761.35	81320.28	1.85
Elements	<i>Mo</i>	<i>Mn</i>	<i>Ni</i>	<i>Os</i>	<i>Pb</i>	<i>Rb</i>	<i>Sb</i>	<i>Se</i>
<i>EF (Al)</i>	340.58	6.03	47.32	3650688.11	158.63	3.95	374.26	885.68
<i>EF (Fe)</i>	161.85	2.87	22.49	1734926.94	75.39	1.88	177.86	420.90
Elements	<i>Sn</i>	<i>Sr</i>	<i>Te</i>	<i>Ti</i>	<i>Tl</i>	<i>U</i>	<i>V</i>	<i>W</i>
<i>EF (Al)</i>	42.96	5.06	20891.49	0.42	24.68	1.64	51.46	91.97
<i>EF (Fe)</i>	20.41	2.41	9928.32	0.20	11.73	0.78	24.46	43.71
Elements	<i>Zn</i>							
<i>EF (Al)</i>	1388.25							
<i>EF (Fe)</i>	659.74

Figure 4-15. Crustal enrichment factors of measured elements in rainwater.

4.5 Effect of Meteorological Conditions on Elemental and Ionic Concentrations

The ionic (IC) and elemental analysis (ICP) results were compared with the amount of rainfall during the sampling period as a function of the sampling date. The value of the maximum and minimum temperatures, during the sampling period and the mean wind speed were plotted separately and provided additional information. Typical graphs of elemental concentration chosen from a great number of graphs are shown in (Figures 4-16, 4-17 and 4-18). It was found that the concentrations of elements detected in the rainwater were often negatively correlated with the rainfall amount. The variation of concentration of these metals in rainwater samples can be explained by the scavenging of pollutants [177]. For high volumes of rainfall, the concentration of the measured ions and elements were significantly lower than the average values. Furthermore, the highest concentrations of elements and ions were detected immediately after long periods of dryness, while low values were observed when rain occurred over several days. Rainfall that occurred during periods of high haze, usually showed relatively high elemental and ionic concentrations. The variation in the values of trace metals between different rainfall events could be related to the source of pollutant emissions.

To analyze the influence of wind speed and wind direction over the content of ions and metals in the collected rainwater samples, the distribution of elements according to wind direction were investigated. As a result, south and southeast directions were determined to be responsible for approximately 60–70% of trace elements and north / northeast for the remainder. The concentrations of most chemical species in the rainwater samples were higher when the air masses moved towards south and southeast, probably due to the

presence of industrial activity nearby. Additionally, it noted that the ion concentrations were higher at lower wind speeds. This can be explained by the fact that when the wind speed decreases, the removal of particles and gases from the immediate vicinity are lower; this allows a higher wash out during the rain events.

The results of this study indicate that the maximum concentrations appeared in the beginning of the rainy month, because there is a large amount of pollutants soluble in less solvent. As can be seen in Figures 4-16, 4-17 and 4-18, relatively high concentrations for most species were measured in January 2010 to March 2010 and July 2011 to September 2011, as Singapore experienced mainly dry and windy conditions during these periods.

From the graph below (Figures 4-16 and 4-17 and 4-18) it can be seen that from August to December for each year there are significant increases observed for most elements. Their increased presence could be attributed to the prevailing S/SE winds which transport air mass from forest fires in Indonesia and every year Singapore experiences haze periods during these months.

The effect of the origin of the air mass on the chemical composition of rainwater has been investigated by several studies [171, 178-180]. To analyze the influence of wind speed and wind direction over the content of ions and metals in the collected rainwater samples, the distribution of elements according to wind direction were calculated and presented in

Table 4-8.

As a result, south and southeast directions were responsible for approximately 50–60% of trace elements and north / northeast for the rest. The concentrations of most chemical

species in the rainwater samples were higher when the air masses moved towards the south and southeast, probably due to the presence of industrial activity nearby.

Table 4-8. Relation of Elemental concentration with wind direction and speed.

	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Pb	Sr
%N	13.59	14.8	11.88	22.19	30.7	21.9	24.69	7.39	10.33	9.63
%N/NE	35.79	32.06	14.11	23.09	11.33	17.47	13.95	10.58	36.35	15.11
%S/SE	27.09	18.47	27.64	20.46	21.5	19.57	25.23	14.87	21.38	24.38
%S	15.14	18.59	24.81	12.19	7.89	19.89	20.44	16.9	18.86	24.44
%NW	8.39	16.07	21.56	22.07	28.58	21.17	15.7	50.26	13.08	26.45
	V	Zn	Ti	Ni	Co	Ga	As	Se	Rb	Mo
%N	21.57	13.39	11.09	10.22	6.03	10.38	13.79	19	11.04	20.41
%N/NE	9.07	11.99	13.75	16.74	19.65	14.45	22.36	13.9	16.39	11.07
%S/SE	25.64	26.81	38.38	25.62	22.14	29.85	17.96	29.42	33.53	27.24
%S	15.12	16.39	26.18	38.95	40.01	29.78	31.86	27.3	27.47	28.42
%NW	28.61	31.42	10.6	8.47	12.17	15.54	14.03	10.38	11.57	12.86
	Sn	Sb	Te	Cs	La	Ce	Gd	W	Os	Ir
%N	9.12	14.32	31.67	5.67	6.58	9.98	12.85	17.43	14.61	10.55
%N/NE	22.04	19.54	14.26	11.66	14.21	8.64	16.77	7.82	19.32	20.88
%S/SE	23.82	23.9	28.96	38.5	38.89	27.9	39.42	43.44	18.72	20.68
%S	37.22	27.76	13.12	35.15	27.59	21.03	15.21	14.93	22.1	15.58
%NW	7.8	14.49	11.99	9.02	12.74	32.45	15.75	16.39	25.25	32.32
	Hg	Tl	Bi	U						
%N	11.17	12.7	12.62	11.49						
%N/NE	20.76	8.67	50.97	22.65						
%S/SE	32.54	47.55	13.54	31.75						
%S	18.96	21.75	16.19	21.4						
%NW	16.58	9.32	6.68	12.71

Figure 4-16. The monthly trend (mean concentrations) of some selected elements present in rainwater samples and their correlation with rainfall from August 2009 to December 2011.

Figure 4-18. The monthly trend (mean concentrations) of anions (a) and cations (b) present in rainwater samples and their correlation with rainfall from August 2009 to December 2011.

The monthly variations in the mean concentrations ($\mu\text{eq L}^{-1}$) of the measured ions were studied to investigate the effect of different wind masses on the concentrations of ions spatially, the general wind direction and the mean wind speeds (m/s) in both monsoon and inter-monsoon seasons.

While the early part of the Southwest monsoon (June to August) was characterized by above average, heavy and intense rainfall, interspersing wet and dry weather conditions soon took over from late August to mid-October. It may be considered that rain events during August to October 2009, October 2010 and September 2011 had relatively higher concentrations of all ions as compared to other months notably, Ca^{2+} , K^+ and Cl^- peaks were most evident. This was because during the late dry season from August to October, dominant *S/SE* winds brought air masses from biomass burning activities in Sumatra, Indonesia, resulting in slight and periodical haze in certain parts of Singapore. This was supported by *PSI* readings that increased to moderate levels ($50 < \text{PSI} < 100$).

The high concentrations of NO_3^- , SO_4^{2-} and NH_4^+ observed could be attributed either to emissions of their precursors, NO_x , SO_2 and NH_3 , or compounds containing these ions. Biomass burning directly results in the volatilisation of N-containing compounds from tissues of plants in the form of NH_3 , NO and HCN , which are then released in the burning plumes. Emissions of NO and NH_3 are likely to originate from fertilizers and soil moisture respectively (<http://www.fao.org>). The source of SO_4^{2-} has been attributed to the burning of peat bog [181]. SO_2 gas is first produced, and is then converted to SO_4^{2-} during the long transportation (usually around 3 days) from the fires to the sampling site at *NTU*. Similar gas to particle conversion processes (e.g. oxidation by O_3 and neutralization by alkaline species) also likely exist for NO_x and NH_3 . At the *NTU* sampling site,

subsequent scavenging of NO_3^- , SO_4^{2-} and NH_4^+ then resulted in peaks in the observed ions. Additionally, biomass burning also releases large quantities of K^+ and its associated compounds, the most common being KCl . K_2SO_4 and KNO_3 may also be present due to reactions with S and N-containing species. Peaks in concentrations for the rest of the ions are presumed to result from the direct emissions from forest fires.

The inter-monsoon season from late October to mid-November was characterized by light, variable winds and heavy precipitation. Thus, the lower and more consistent concentrations of ions observed were possibly due to the dilution effect of ions brought about by heavy rainfall. This wet season continued into December, thus ion concentrations remained low. At this point, the Northeast monsoon was characterized by *NW* winds due to a tropical disturbance occurring between Borneo and Malaysia. Thus, the regional sources of ions probably came from Malaysia. From January onwards, strong *N/NE* winds brought air masses from Malaysia and South China Sea to Singapore.

Table 4-9. Statistical data of major ions in different sampling site around Singapore ($\mu\text{eq L}^{-1}$).

Sampling Period	Location/ Number of Sampling	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	H ⁺
Aug 11- Feb 12	Woodlands (North, n=50)	8.93	91.2	66.23	134.89	37.14	33.3	20.85	13.23	251.71	0.71
	Toa Payoh (Central , n=50)	5.17	57.45	32.1	73.17	25.5	30.01	10.87	13.05	101.19	8.71
	NTU (West, n=78)	4.27	97.87	33.17	70.76	23.33	28.82	10.35	9.33	75.59	53.7
Jun 11 – Oct 11	Queenstown (QT) (Central Western, n=34)	9.53	255.84	83.35	275.15	143.55	40.68	51.93	38.77	343.25	18.15
	NTU (West, n= 47)	4.54	85.22	34.91	121.14	42.6	22.16	25.76	13.61	68.75	86.64
Sep 10 - Apr 11	Bukit Panjang (North–West, n=93)	4.69	65.69	32.55	63.95	40.28	25.61	29.73	9.37	57.03	2.02
	NTU (West, n= 103)	2.94	86.76	26.76	75.69	15.55	7.58	68.23	4.32	16.11	60.75
Dec 09 – Mar 10	Holand Road (Central, n=25)	5.58	89.97	78.8	75.46	74.85	20.14	65.66	15.95	262.66	0.23
	NTU (West, n= 41)	4.79	40	29.17	25.48	35.35	30.07	14.06	6.4	24.76	69.67
Sep 09-Nov 09	Yishun (Y) (North, n=53)	3.52	28.95	23.22	52.83	20.35	23.69	17.21	9.3	74.2	21.38
	NTU (West, n= 67)	3.92	58.26	30.53	86.7	31.88	25.6	28.07	8.7	38.26	69.95

4.6 Comparison of Different Sampling Sites in Singapore

The chemical composition of rainwater samples were studied at different sampling sites around Singapore for short periods in order to investigate and compare with the *NTU* sampling site. Table 4-9 compares data obtained at different sampling sites with *NTU* during the same sampling periods. It is interesting to note that in all the Singapore locations the lowest *pH* value was recorded at the *NTU* sampling site with 60 to 90% of *pH* values in the range of 3.60 to 4.60. These findings confirm that *NTU* is most prone to the effects of manufacturing emissions rich in NO_2 and SO_2 originating from a concentrated mix of oil refining and steelworks industries located in Tuas (heavy industries) and Jurong Island (oil refineries). Other possible emission sources include plastic and paper incineration from Tuas, Tuas South and Ulu Pandan and automobiles from Pan Island Expressway.

Although at first glance it appears that the acidic SO_4^{2-} concentration is present in higher value for Woodlands, Queenstown and Holland Road sampling sites, the Ca^{2+} concentration data does not support this belief. Table 4-10 presents different parameters for each sampling site for a better understanding. $\frac{SO_4^{2-}}{NO_3^-}$, $\frac{Cl^-}{Na^+}$ and $\frac{Mg^{2+}}{K^+}$ ratios were calculated as indexes for anthropogenic (automobile, industries), marine (sea-salt) and crustal (minerals, soil) origins, respectively. *NF* was calculated for NH_4^+ , Ca^{2+} and Mg^{2+} to support the *pH* findings and to rationalize the data. Similar ionic concentration trends across the different sampling sites could suggest that the sources of these ions were similar. It is apparent from Table 4-10 there is not a significant difference between the different sampling sites. Major neutralization appears to have occurred due to Ca^{2+} salts. It appears that coarse *Ca* aerosols have contributed to the ambient air in Singapore.

Therefore, Ca^{2+} salt aerosols seem to be a major component for neutralization of rainwater acidity, followed by NH_4^+ neutralization.

Table 4-10. Comparison ion ratios at different sampling sites around Singapore.

	SO_4^{2-}/NO_3^-	Cl^-/Na^+	Mg^{2+}/K^+	NF_{Ca}	NF_{NH_4}	NF_{Mg}
Woodlands	2.04	2.46	0.63	1.25	0.17	0.07
Toa Payoh	2.28	2.25	1.2	0.96	0.29	0.12
NTU	2.13	4.2	0.9	0.73	0.28	0.28
Queenstown	3.3	1.78	0.75	0.96	0.11	0.11
NTU	3.47	2	0.52	0.44	0.14	0.09
Bukit Panjang	1.96	1.63	0.32	0.59	0.27	0.1
NTU	2.83	5.58	0.06	0.16	0.07	0.04
Holland Road	0.95	1.64	0.58	1.70	0.13	0.1
NTU	2.9	1.57	0.24	0.20	0.26	0.05
Yishun	2.28	1.42	0.45	0.98	0.31	0.12
NTU	2.84	1.83	0.31	0.33	0.22	0.07

Inorganic ions in rainwater commonly originate from the sea, crust or man-made activities. Thus, ionic compositions of rainwater tend to reflect the extent of contribution from these sources. To understand this quantitatively, the Sea Factor (SF), Crustal Factor (CF) and Anthropogenic Factor (AF) were computed as follows [182]:

$$\% SF = \left(\frac{[X]}{[Na^+]} \right)_{\text{sea}} \div \left(\frac{[X]}{[Na^+]} \right)_{\text{sample}} \times 100 \quad \text{Eq. 4-21}$$

$$\% CF = \left(\frac{[X]}{[Mg^{2+}]} \right)_{\text{crust}} \div \left(\frac{[X]}{[Mg^{2+}]} \right)_{\text{sample}} \times 100 \quad \text{Eq. 4-22}$$

$$\% AF = 100 - \% SF - \% CF \quad \text{Eq. 4-23}$$

where $\left(\frac{[X]}{[Na^+]}\right)_{sea}$ is the standard ratio of the concentrations of X , the desired ion and Na^+ from marine composition, while $\left(\frac{[X]}{[Mg^{2+}]}\right)_{crust}$ is obtained from the crustal composition and $\left(\frac{[X]}{[Na^+]}\right)_{sample}$ and $\left(\frac{[X]}{[Mg^{2+}]}\right)_{sample}$ refer to concentration ratios from the experimental data [183, 184]. These equations assume firstly, that the sea and soil are the only natural sources in question, and that other natural sources e.g. volcanic eruption, make negligible contributions. Secondly, all total Na^+ and Mg^{2+} in the precipitation samples originate entirely from sea-salt spray and earth's crust respectively, and are hence, employed as the reference ions to calculate SF and CF . Thirdly, all remaining ions, after calculation of SF and CF , are derived from man-made origins, and AF is obtained by subtracting SF and CF from the total ion concentrations.

It is apparent from Table 4-11 that the relative contributions of sea-salt, crust and anthropogenic factors were close for F^- , SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ and Mg^{2+} .

Typically, natural sources of NH_4^+ are mainly crustal, and are derived from NH_4^+ containing compounds in vegetation or soil. However, in this study, CF (%) for NH_4^+ was negligible, and thus 100 % of sampled NH_4^+ in precipitation at all sampling sites was likened to anthropogenic origins. The most commonly employed fertilizers are NH_4NO_3 , $(NH_4)_3PO_3$, $(NH_4)_2SO_4$, compounds which when applied, are likely to enter the atmosphere from adsorbed particulate matter or in the form of gaseous NH_3 [185]. Other anthropogenic sources include NH_3 released from biomass burning, agriculture, and animal excretions from livestock breeding [186].

SO_4^{2-} was generally derived from marine and anthropogenic origins since its CF (%) was (0.1-0.3 %) at all sites and the AF (%) was fairly consistent (20 %—80 %). Other

than sea-salt, other natural sources include hot springs and volcanic eruptions, which if accounted for in the calculations, would decrease the computed AF (%) values.

Table 4-11. Contribution of different sources to ions (%)

		Woodlands	Toa Payoh	NTU	Queenstown	NTU	Bukit Panjang	NTU	Holand Road	NTU	Yishun	NTU
F^-	CF	3.97	6.77	5.86	10.91	8.04	5.36	3.94	7.67	3.58	7.09	5.95
	SF	0	0	0	0	0	0	0	0	0	0	0
	AF	96.03	93.23	94.14	89.09	91.96	94.64	96.06	92.33	96.42	92.91	94.05
Na^+	CF	-	-	-	-	-	-	-	-	-	-	-
	SF	100	100	100	100	100	100	100	100	100	100	100
	AF	-	-	-	-	-	-	-	-	-	-	-
Ca^{2+}	CF	9.36	22.97	21.98	20.12	35.26	29.26	47.76	10.82	46.04	22.32	40.5
	SF	0.64	1.1	1.35	1.83	2.71	3.09	4.22	2.91	6.24	1.2	3.64
	AF	89.99	75.93	76.67	78.05	62.03	67.65	48.02	86.28	47.72	76.48	55.86
Cl^-	CF	0.08	0.13	0.05	0.08	0.09	0.08	0.03	0.1	0.09	0.18	0.08
	SF	47.65	51.93	27.89	65.65	58.49	71.74	20.97	71.33	74.15	82.24	64.02
	AF	52.27	47.94	72.06	34.27	41.42	28.18	79	28.57	25.76	17.58	35.89
SO_4^{2-}	CF	0.11	0.2	0.15	0.16	0.13	0.16	0.06	0.24	0.28	0.2	0.11
	SF	30.87	39.07	36.96	58.48	39.42	70.61	23.03	81.48	33.24	43.18	41.22
	AF	69.03	60.73	62.89	41.36	60.45	29.23	76.91	18.28	66.48	56.62	58.67
NO_3^-	CF	0.02	0.03	0.02	0.04	0.03	0.02	0.01	0.02	0.02	0.03	0.02
	SF	0.01	0.02	0.01	0.04	0.03	0.03	0.01	0.05	0.03	0.02	0.02
	AF	99.97	99.95	99.96	99.92	99.94	99.95	99.97	99.94	99.96	99.95	99.95
NH_4^+	CF	-	-	-	-	-	-	-	-	-	-	-
	SF	-	-	-	-	-	-	-	-	-	-	-
	AF	100	100	100	100	100	100	100	100	100	100	100
K^+	CF	56.92	70	80.86	66.97	47.39	28.27	5.68	21.79	40.83	48.47	27.8
	SF	3.79	3.55	4.8	5.89	3.52	2.89	0.49	5.67	5.36	2.52	2.42
	AF	39.29	26.6	14.34	27.14	49.09	68.84	93.84	72.54	53.81	49.01	69.78

^a NO_3^- containing compounds were taken for entire crustal N³⁰

^b SO_4^{2-} containing compounds were taken for entire crustal S³⁰

^c NH_4^+ containing compounds were completely from man-made sources

Nonetheless, SO_4^{2-} is mainly derived from the oxidation of SO_2 produced by fossil fuel combustion in factories, traffic, and coal-powered power stations (from neighbouring countries) [187]. As previously noted, SO_4^{2-} from $(NH_4)_2SO_4$ in fertilizers may also be

adsorbed onto particulate aerosols before being incorporated into rain. Based on the calculations, NO_3^- was entirely from anthropogenic origins; main sources include NO_x emissions from high temperature combustion of fossil fuels in engines of automobiles. At all three sampling sites, F^- was shown to predominantly originate from man-made sources ($> 99.99\%$) and to a smaller extent ($< 0.01\%$) from crustal sources. Anthropogenic sources of F^- include the emissions of HF from the production of fluorochemicals such as fluoropolymers (e.g. Teflon) and fluorinated surfactants, toothpaste and bricks from clay rich in F^- . Crustally, F^- is present in minerals such as fluorapatite, $Ca_5(PO_4)_3F$ and fluorspar, CaF_2 .

In contrast, crustal and anthropogenic sources of K^+ were comparatively high (30%—80.0 %) while contributions from sea spray ($< 6\%$) was limited. Local man-made sources of K^+ are diverse, and range from production of fertilizers (KCl , KNO_3 and K_2SO_4), inks and dyes, toughened glass (KNO_3), glass coatings (Rochelle salt) to potassium soaps, textiles, alkaline batteries and detergents (<http://www.chemicool.com/>). More notable is the long-range transport of K^+ containing anthropogenic aerosols (e.g. adsorbed KCl) from biomass burning in Indonesia, which may be significant during the Southeast Monsoon [188]. Naturally, K^+ is present in Earth's crust as minerals, such as feldspars and clays, and is also a key constituent of plants.

Typically, terrestrial sources of Ca^{2+} are usually significant and are mainly derived from the dissolution of Ca containing minerals such as $CaCO_3$, $CaCO_3 \cdot MgCO_3$ and $CaSO_4 \cdot 2H_2O$ [77].

Although Cl^- is a typical sea-salt ion, the SF (%) ranged from 21.0 % to 83 %; correspondingly, highest AF (%) was (79.0 %) and lowest (18.0 %) while CF (%) was

negligible at all three sampling sites ($\leq 0.5\%$). In nature, Cl^- is mostly in the form of $NaCl$ (from sea-spray) or in the minerals sylvite and carnallite. Differences in AF (%) could be due to varying extents of exposure to aerosol particulates (KCl) from biomass burning in Indonesia and/or different proximities to various Cl^- producing industries/activities locally. These anthropogenic activities/uses include wood pulp bleaching in paper production, in antiseptics and insecticides, paints, plastics, textiles, and in organic industries as solvents and to produce for instance, chloroform, chlorates and carbon tetrachloride (<http://www.chemicool.com/>).

Because Na^+ and Mg^{2+} were utilized as the reference ions for SF and CF calculations respectively, it was assumed that human sources of these ions were negligible. However, in the actual case, contributions from human activities are inevitable, and hence analyses for their sources are given though the AF (%) for both ions were assumed to be 0%. Anthropogenically, Na^+ is commonly employed in chemical and petroleum industries as a desiccant and reducing agent; in the metal industries Na^+ is used to refine and descale metals (<http://www.chemicool.com/>). Mg^{2+} is a useful metal in the aircraft, automobile and electronics industries and is commonly utilized in alloys in component parts. Other sources include paper manufacturing, textiles, and fireworks (as sparklers) (<http://www.chemicool.com/>).

Table 4-12. Chemical composition of rainwater at various sampling sites

City /Country	pH	[Ion] / $\mu\text{eq L}^{-1}$								
		F^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
Al-Hashimya / Jordan [172]	6.9	n.a.	142.36	67.31	112.36	165.32	93.12	130.56	85.21	75.36
Tibet [189]	6.6	n.a.	19.17	10.37	15.50	65.58	7.43	15.44	14.49	18.13
Shanghai, China [190]	6.62	n.a.	142.64	39.55	241.78	295.40	31.69	23.01	12.06	193.18
Tirupati / India [75] ^b	6.5	4.72	33.91	40.84	127.96	150.66	55.51	33.08	33.89	20.37
Nagpur / India [191]	6.3	n.a.	13.30	10.30	20.70	29.10	3.30	12.10	2.30	7.00
Galilee / Israel [168]	6.0	n.a.	308	27.6	117	244	99.1	253.00	15.1	n.a.
Delhi / India [192]	5.7	n.a.	140.1	66.8	89.7	133.7	69.6	81.70	44.3	25.8
Guaiba / Brazil [164]	5.7	4.96	9.18	2.74	15.90	28.6	4.60	10.90	3.15	30.50
NanJing, China [193]	5.51	n.a.	22.11	16.70	58.71	21.73	7.46	31.08	3.96	17.27
Mexico City / Mexico [161] ^b	5.1	n.a.	9.56	42.62	61.94	26.44	2.46	7.00	2.16	92.35
Longone / Italy [194] ^l	4.8	n.a.	12.00	45.00	51.00	46.00	7.00	11.00	2.00	64.00
Seoul / South Korea [73] ^b	4.7	n.a.	18.2	29.9	70.9	34.9	6.9	10.5	3.5	66.40
Ankara / Turkey [166] ^a	4.7	n.a.	41.18	35.48	52.05	115.0	7.16	15.22	2.56	66.52
Hong Kong [83] ^b	4.6	1.8	37.6	18.9	48.6	15.3	7.8	31.8	2.2	n.a.
Newark / USA [195] ^a	4.6	1.58	30.46	22.26	55.00	10.47	4.11	26.09	1.54	35.56
NUS / Singapore [165]	4.5	n.a.	22.11	16.79	58.71	21.73	7.46	31.08	3.96	17.27
Tokyo / Japan [84]	4.4	n.a.	34.00	34.00	51.00	13.00	5.00	16.00	1.00	24.00
Present study (NTU) / Singapore	4.3	4.17	75.38	34.35	82.60	62.28	11.08	32.20	28.51	23.89

n.a. = data not available. ^aIon concentrations have been converted from $\mu\text{g L}^{-1}$ to $\mu\text{eq L}^{-1}$. ^bpH values converted from $\mu\text{g L}^{-1}$.

4.7 Comparison of Singapore Rainwater with Data from other Countries

A summary of the average rainwater composition from a number of urban sites is given in Table 4-12 in units of $\mu\text{eq L}^{-1}$ and in Table 7 in units of ppb, for ionic and elemental compositions, respectively. The sulfate concentration ($82.60 \mu\text{eqL}^{-1}$) was found to be relatively high when compared with those in the literature for similar sampling sites in the world except for China (241.78, 199.59 and $142.64 \mu\text{eqL}^{-1}$) Tirupati in India ($127.96 \mu\text{eqL}^{-1}$) and Jordan ($112.36 \mu\text{eqL}^{-1}$). In fact, SO_4^{2-} concentrations in Najing and Shanghai were markedly higher than local levels at all other sites, possibly due to China's use of coal as the main fuel source for power generation. The nitrate value ($34.35 \mu\text{eqL}^{-1}$) was comparable with that observed in Tirupati, Ankara, Mexico, Longona and China (Nanjing and Shanghai) but less than Delhi and Jordan. The high sulfate and nitrate concentrations produce low pH values in most events. The concentration of Ca^{2+} and Mg^{2+} is lower than those reported from India, China and Israel. As it can be seen for those countries the pH is alkaline and it shows that the acidity of rainwater has possibly been neutralized by high concentration of crustal ions due to the large contribution of dust. Due to the complex and overlapping nature of source types for Ca^{2+} e.g. desert dust, limestone, calcareous soil, flu ash, biomass burning, construction etc., differences in Ca^{2+} concentrations among the various sites could not be easily attributed. It is interesting to note that the concentration of SO_4^{2-} and Ca^{2+} were much higher in Tirupati, India and Jordan probably due to the large contribution of soil dust.

Compared to Nanjing, Mexico City and Ankara, NH_4^+ concentrations appeared in lower levels in Singapore rainwater. This may be attributed to a much lower local volume of agricultural activities, livestock breeding and biomass burning, which are the main emitters of NH_3 and NH_4^+ .

Table 4-13. A comparison of the average elemental composition of rainwater from a number of urban sites.

City / Country	Element / $\mu\text{g L}^{-1}$									
	<i>Al</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>V</i>	<i>Zn</i>
Al-Hashimya / Jordan [79]	386.00	11.80	6.20	9.90	363.00	48.60	n.a.	26.9	n.a.	1230
Present study (NTU) / Singapore	126.90	0.15	0.49	14.93	23.50	7.14	3.42	4.15	7.68	14.30
Ankara / Turkey [166]	47.00	8.6	0.38	3.70	31.00	n.a.	2.20	3.30	0.92	0.02
NUS / Singapore [165]	18.44	0.33	1.62	5.58	23.91	2.78	3.86	3.37	3.54	7.23
Guaiba / Brazil [163]	16.90	n.a.	n.a.	6.80	22.60	1.40	n.a.	n.a.	n.a.	29.60
Mexico City / Mexico [161]	15.30	0.37	0.26	n.a.	n.a.	8.34	2.98	1.58	4.78	n.a.
Newark / USA [195]	9.54	0.03	0.06	2.82	8.35	n.a.	0.55	0.47	0.28	6.60

n.a. = value not available.

Table 4-13 also shows the comparison of dissolved trace metals in rainwater from NTU, Singapore and other countries. Some of the trace metal values measured in Singapore were higher than other urbane sites, except for Jordon where many of the reported values appear extremely high. The values reported for Singapore in the last published study 10 years ago [165] appear quite similar to the values obtained in this study.

For a better understanding of the of comparisons between the different sampling sites, some parameters such as the Fractional Acidity and Neutralization have been calculated and are presented in Table 4 -14.

Variation in the *pH* of rainwater samples is a result of a complex interplay of acidic and alkaline component at the sampling sites. To explore the quantitative aspects of rainwater acidity, Fractional Acidity (*FA*) was utilized to calculate the capacity of acid neutralization [165]. The formula is given as:

$$FA = \frac{[H^+]}{([NO_3^-] + [SO_4^{2-}])} \quad \text{Eq. 4-24}$$

By this, *FA* assumes firstly, that precipitation acidity was mainly caused by H_2SO_4 and HNO_3 and thus the contribution of organic acids was excluded. Secondly, this equation implies that 100 % of the acidity owing to H_2SO_4 and HNO_3 was not neutralized if $FA = 1$. The extent of neutralization of H^+ by alkaline constituents will thus be represented by deviations of *FA* from unity. Similarly, organic acid components have been excluded in the denominators since their effects are not examined in this study.

Surprisingly the highest fractional acidity was observed for Singapore. It is important to remark that the present findings seem to be consistent with an earlier study [165]. Additionally, SO_4^{2-} ions were mainly responsible for the acidity in rainwater, since they account for 53 %—86 % of the total acidity, approximately twice as much compared to NO_3^- ions (14 %—47 %).

However, because acidity in rainwater will be neutralized by alkaline constituents, measured *pH* values in fact indicate the remaining $[H^+]$ after such neutralization processes, rather than the actual $[H^+]$ in the absence of basic components. According to Galloway, Ca^{2+} and NH_4^+ represent the dominant species present in precipitation accountable for the acid-base reactions and typically originate from airborne aerosols [196]. Thus, assuming that acidity is solely neutralized by Ca^{2+} and NH_4^+ , the original

$[H^+]$ then becomes the sum of measured $[H^+]$, $[Ca^{2+}]$ and $[NH_4^+]$ as shown in the following equations:

$$\begin{aligned}\text{Original pH} &= -\log[H^+]_{\text{original}} \\ &= -\log([H^+]_{\text{remaining}} + [Ca^{2+}] + [NH_4^+])\end{aligned}\quad \text{Eq. 4-25}$$

$$[H^+]_{\text{remaining}} = 10^{-(\text{measured pH})} \quad \text{Eq. 4-26}$$

where all concentration terms, $[Xi]$, are given in units of $\mu\text{eq L}^{-1}$.

Table 4-14. Fractional Acidity, Source of Acidity and pH at sampling sites

Site	Fractional Acidity	Neutralization (%)	Source (%)		pH	
			NO_3^-	SO_4^{2-}	Measured	Original
Jordan	0.00	99.93	0.37	0.63	6.91	3.39
Shanghai, China [190]	0.00	100.00	0.38	0.62	6.62	4.04
Tirupati / India [75]	0.00	100.00	0.24	0.76	6.47	3.49
Tibet [189]	0.01	99.01	0.40	0.60	6.59	3.88
Galilee / Israel [168]	0.01	98.51	0.24	0.76	6.02	-
Delhi / India [192]	0.01	98.73	0.43	0.57	5.70	3.53
NanJing, China	0.01	98.90	0.14	0.86	5.51	3.10
Nagpur / India [191]	0.02	98.38	0.33	0.67	6.30	4.18
Mexico City, Mexico	0.08	92.02	0.41	0.59	5.08	3.81
Guaiba / Brazil [164]	0.1	89.54	0.15	0.85	5.71	4.05
Longone / Italy [194]	0.17	83.49	0.47	0.53	4.80	3.76
Seoul / South Korea [73]	0.21	78.87	0.30	0.70	4.67	3.80
Hong Kong [83]	0.39	61.04	0.28	0.72	4.58	-
Tokyo / Japan [84]	0.46	53.71	0.22	0.78	4.40	3.96
NUS / Singapore [165]	0.61	39.11	0.22	0.78	4.50	3.97
Present Study	0.68	31.74	0.29	0.71	4.35	3.64

As it can be seen from 4-14, it is surprising to note that the original pH , $= -\log ([H^+]_{\text{remaining}} + [Ca^{2+}] + [NH_4^+])$, was around 3.10—4.20 at all sampling sites. These findings may indicate that variations in measured pH were predominantly determined by the varying Ca^{2+} and NH_4^+ that were present in rainwater, rather than differences in $[H^+]$ as the original pH in all sampling sites were very close. The similar original pH also suggests that local precipitation, in the absence of natural and man-made basic constituents, did not vary much in terms of acidity. This possibly arose as a result of the local atmosphere being subjected to approximately equal levels of anthropogenic emissions of acidic nature, which decreased rainwater pH from its natural value of 5.0 – 5.6.

4.8 Statistical Analysis

Statistical analysis was applied to evaluate the relationship between variables. The study used Statistica for Windows v10 and applied the Factor Analysis technique through the Principal Components Method.

4.8.1 Cations and Anions

The raw data was used to produce a correlation matrix and a new set of common factors were determined based on the correlations of the original data. The loading Factors are related to eigen value >1.0 . The factor loadings show that the data produced three factors, explaining about 70 % of total variation. The classification of data into different groups (Common Factors) recommends that the variables listed in the same factor might have the same source. As Varimax rotation was applied, the two factors resulted in factor loads of 43.09 % and 17.46 % for Factors 1 and 2, respectively.

Although factor 1 has high loadings for Mg^{2+} , Na^+ and Ca^{2+} , it also has a high loading factor for SO_4^{2-} , NH_4^+ and NO_3^- . By reviewing the sea salt and non sea salt results, since approximately 60% of Ca^{2+} and 90% of Mg^{2+} have anthropogenic sources, it might explain that this factor is associated with anthropogenic sources beside the high loading of SO_4^{2-} , NH_4^+ and NO_3^- . These ions are usually present in precipitation and their contributions to the acidity of rain is variable. The rate of acidification caused by nitric and sulfuric acids in rainwater samples collected in the *NTU* sampling site was approximately 70%. The contribution of H_2SO_4 found by this study was 40 – 60 %, confirming estimates of global contributions in rainwater. As for HNO_3 , the values observed in the area (20 – 30 %) remained lower than global estimates (30–40%) [167, 185]. The high loading factor of SO_4^{2-} confirms that sulfuric acid is the major acid responsible for acidic rain in Singapore. It might be related to the large scale oil refineries that can potentially release SO_2 into the atmosphere, or coal-fired power plants in nearby Indonesia.

Factor 2 shows high loadings of K^+ and Cl^- . In relation to K^+ , it is believed that the most probable origin of this ion is from biomass burning, because it was found that 82% of K^+ comes from the *NSS* fraction. This hypothesis is supported by the association of K^+ and Cl^- , which can be released as KCl by biomass combustion, since a significant correlation was observed for these ions [187, 197]. Every year Singapore experiences annual fires mainly caused by land clearing and “slash and burn” agricultural practices in Indonesia, particularly Sumatra and Kalimantan. This is done in order to clear or rejuvenate the land for cultivation and planting. These agricultural burning activities are common during the traditional dry season between August 2009 to October 2011.

4.8.2 Trace Elements

The results of factor analysis by method of principal component analysis present three factors that are responsible for 60% of variance (Table 4 -16). Factor 1 was interpreted as high loading of the elements Gd, Sb, and U showing the influence of natural and crustal sources on the composition of the rainwater. It is interesting to note that all these high loading elements has enrichment factors less than 10, which confirms their natural source. This factor represents 34.26 % of total variance.

Table 4-15. Factor Loadings matrix obtained from rainwater samples in Singapore from (August 2009 to December 2011). Extraction: Principal components (Marked loadings are > 0.70000).

Variables	Factor 1	Factor 2
F ⁻	0.55	0.19
Cl ⁻	0.38	0.87
NO ₃ ⁻	0.62	0.10
SO ₄ ²⁻	0.81	-0.01
Na ⁺	0.83	0.14
NH ₄ ⁺	0.60	0.13
K ⁺	0.01	0.97
Mg ²⁺	0.83	0.09
Ca ²⁺	0.83	0.14
H ⁺	-0.01	-0.11
Total Variance	43.10	17.46

Factor 2 showed 27.4 % of the total variance and it represented Fe, Cu, Hg, Sb, W, Cd and Al. This factor might be related to industrial activity (refinery, incinerations, and heavy industrial) nearby the NTU sampling site. This result is supported with EF > 100 that has been reported for these groups. Factor 3 is strongly loaded by Pb, Zn and V and explains 17.43 % of the total variance. However moderate loading of some elements suggest anthropogenic source, and Zn has recently been reported as an index for motor

vehicles [143]. Despite the use of lead free petrol, high concentration of Pb could be due to Pb particles in street dust accumulated for a long time.

Table 4-16. Factor Loadings matrix obtained from rainwater samples in Singapore from (August 2009 to December 2011). Extraction: Principal components.

Elements	Factor 1	Factor 2	Factor 3
Al	-0.12	0.651	0.076
As	-0.02	0.04	0.04
Ba	0.07	0.56	-0.13
Bi	0.22	0.23	0.19
Cd	0.06	0.51	0.13
Ce	0.57	-0.06	0.22
Co	0.22	-0.13	-0.12
Cr	0.16	0.15	-0.09
Cu	-0.01	0.83	-0.04
Cs	0.03	0.015	0.04
Fe	-0.05	0.71	0.09
Gd	0.76	-0.07	0.41
Ga	0.62	-0.08	-0.01
Hg	0.01	0.798	-0.08
Ir	0.13	0.028	0.08
La	0.69	-0.138	-0.00
Mo	0.37	-0.07	0.36
Mn	-0.12	0.56	-0.09
Ni	0.62	-0.08	0.02
Os	0.06	-0.03	0.53
Pb	-0.14	-0.02	0.76
Rb	0.31	-0.04	0.11
Sb	0.05	0.77	-0.08
Se	0.55	-0.09	0.11
Sn	0.28	-0.07	0.10
Sr	0.75	-0.12	0.03
Te	0.24	0.12	0.61
Ti	0.46	-0.08	0.23
Tl	0.19	-0.15	0.82
U	0.80	0.00	0.22
V	0.04	0.11	0.71
W	0.14	0.89	0.06
Zn	-0.14	-0.18	0.81
Total Variance	34.26	27.4	17.43

Chapter 5: : Monitor for AeRosols and Gases

(MARGA)

5.1 Introduction

Over the past several decades, the emission of aerosols and precursor gases from industrial activities has continuously increased due to growing populations and human activities. Research has demonstrated a close relationship between the concentration of certain species in atmospheric aerosols and human mortality/morbidity rates [198, 199].

The impact of aerosols not only causes human health effects, but can also affect atmospheric climatic processes. Long-term aerosol pollution effects air quality, visibility, cloud formation and rainfall [200, 201].

Aerosols can influence the climate by absorbing and scattering light and changing Earth's reflectivity (direct aerosol effects) [202, 203], and they can also alter the climate *via* cloud formation (indirect aerosol effects). Aerosols directly scatter and absorb solar and infrared radiation in the atmosphere. The scattering of radiation causes atmospheric cooling, whereas absorption can cause atmospheric warming. Aerosols alter the properties of clouds through a subset of the aerosol population called Cloud Condensation Nuclei (CCN). The change in droplet concentration caused by increases in aerosol CCN leads to increased cloud albedo, increased light scattering and radiative cooling (first indirect effect), but also leads to reduced precipitation efficiency and increased lifetime of the cloud (second indirect effect). Both aerosol effects are related to the interaction between aerosol particles and water vapor in the atmosphere [204-206].

Aerosol size, composition and distance from origin are closely related parameters that can control the net effect of atmospheric cooling and warming [207-209].

The chemical composition of the atmospheric aerosols is a significant parameter for climatic, health and ecosystem studies. Based on literature reviews, water soluble ions generally account for one-third of particulate matter mass in the urban atmosphere and play an important role in the earth's radiation balance directly by scattering incoming solar radiation and indirectly by altering cloud properties because of the uptake of water vapour [210-213].

Atmospheric aerosols are mixtures of variety of chemical compounds [214, 215]. In general, the most abundant chemical components of atmospheric aerosol are sulfate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon and gaseous precursors.

Pure sulfates and nitrates reflect almost all radiation they meet, cooling the atmosphere. In contrast black carbon absorbs radiation easily, warming the atmosphere but also shading the surface. Organic carbon, sometimes called brown carbon or organic matter, has a warming influence on the atmosphere depending on the brightness of the underlying ground. Dust impacts radiation to varying degrees, depending on the composition of the minerals that comprise the dust grains, and whether they are coated with black or brown carbon. Salt particles tend to reflect all the sunlight they encounter.

The chemical composition and size distributions of aerosols are highly variable and dependent on different factors such as the location, time, meteorological conditions, contribution of specific sources, the origin and altitude. For a few decades, the problems associated with sampling and measurement of semi-volatile aerosol species and related

gaseous precursors have been discussed, especially the collection of HNO_3 [216-218], and NO_3^- [219-222], but also NH_3 [223], NH_4^+ [222, 224], Cl^- [225] and SO_4^{2-} [221, 225]. In addition, the reliable measurement of HNO_3 with good time resolution without interferences is difficult because of its extreme tendency to adsorb on surfaces [226]. The most commonly used procedures for collecting aerosols are filter-based methods, which are simple and easy, but their accuracy has been reported to be very low [227]. Furthermore, the atmosphere evaporation of semi-volatile aerosol species and the possible loss of some compounds due to surface reactions due to the long time-scale sampling periods have been reported [218-220]. Denuder based techniques have been developed to solve the problems related to filter-base methods. Dry-coated diffusion denuders were the first generation of denuders with consistent results, but were tedious and provided only long time-average concentration measurements [228]. To overcome these drawbacks, other researchers have developed wet effluent diffusion denuders, parallel-plate denuders, thermo-denuders and wet-annular denuders [228-231]. The first WAD operating in batch mode and rotating annular denuder was reported and described by Keuken et al. and Wyers et al. respectively [223, 232]. Other techniques such as diffusion scrubber and mist chamber techniques also provide measurements with higher time resolution and are less prone to artifacts.

Researchers have performed many intercomparison experiments for HNO_3 and NH_3 due to problematic sampling and measurement methods [233-235]. In these studies considerable differences were observed between different measurements techniques, which emphasized the need to develop artifact-free sampling and measurement methods.

The replacement of filter-based methods by denuder techniques was a milestone in method development in the last two decades; although the denuder technique has been afflicted with blank problems and restricted to single measurements (gas or aerosol). The desire to find a reliable collection and measurement system with high selectivity, high time resolution and low detection limits for aerosols has encouraged researchers to develop better methodologies such as steam jet aerosol collectors (SJAC) [232, 236], which add steam to sampled air generating condensation droplets [230, 237]. The combination of SJAC with denuder techniques is now the preferred approach for the simultaneous collection of aerosol species and related trace gases. Usually, these collection methods are followed by on-line analysis of the resulting aqueous solutions.

A literature review of many studies indicate that the combination of SJAC with denuder techniques is now the preferred approach for the simultaneous collection of aerosol species and related trace gases [230-237]. Usually, these methods are followed by on-line analysis of the resulting aqueous solution. On-line IC is the main analytical instrument for these sampling systems, with its ability to measure ambient concentrations continuously with low detection limits.

Advancements in aerosol measurement systems and modelling capabilities in the last two decades provide an opportunity to investigate the impact of anthropogenic activities on air quality. An online analyzer for Monitoring for AeRosols and Gases (MARGA) is one of the latest measurement systems for semi-continuous analysis of gases and soluble ions in aerosols.

In the present study, we conducted a 3 month monitoring program in an industrial area containing numerous petrochemical refineries, using MARGA to measure water soluble

ions Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} and gaseous precursors NH_3 , HCl , HNO_2 , HNO_3 and SO_2 in order to investigate the temporal variations and possible sources for these species. The data collected from the MARGA system were compared with ion-chromatography data collected from rain precipitation samples in order to determine how the concentration of aerosol and gaseous precursors (measured in $\mu\text{g m}^{-3}$) were translated into concentrations in present in rainwater (measured in $\mu\text{eq L}^{-1}$).

On the 10th to 15th May during sampling period, Singapore experienced very high haze from Sumatra which was brought in by prevailing winds blowing from the southwest or southeast. These annual biomass burning are mainly caused by land clearing and “slash and burn” agricultural practices in Indonesia, particularly Sumatra and Kalimantan. It will be shown in the discussion below that these high haze events resulted in high atmospheric concentrations of certain molecules in the aerosol and gas samples.

5.2 MARGA Instrument

The Monitor for AeRosols and GAses in ambient air (MARGA) measures the inorganic composition of gases and aerosols in air at an hourly temporal resolution. The MARGA utilizes a Wet Rotating Denuder (WRD) to collect gases, while aerosols are collected by a Steam Jet Aerosol Collector (SJAC). Both the WRD and the SJAC produce aqueous sample streams, which are analyzed by online ion chromatography for anions and cations.

A model ADI 2080 online analyser for Monitoring for AeRosols and Gases (MARGA, Applikon Analytical B.V., the Netherlands) with a $\text{PM}_{2.5}$ sampling inlet was used at Nanyang Technological University in Western Singapore between April 2nd to June 26th,

2011 (close to 3 months continuously, Figure 5 -1). The system was supplied courtesy of Metrohm Singapore Pte Ltd, as part of a collaborative R&D project with NTU.

The development of the MARGA was performed by ECN (the Energy research Centre of the Netherlands) together with Applikon Analytical and Metrohm AG. MARGA consists of sampling and analytical boxes [238], a sample collection box and an analyzer box. Wet Rotating Denuder (WRD) and Steam Jet Aerosol collector (SJAC), which are responsible for absorbing gases and collecting aerosols, are located in the sampling box. Air is drawn through the sampling system (upper box Fig 5. 1) where inorganic gases and aerosols are absorbed and collected into separate absorption liquids.

In the next box that is called detector or analyser box (Figure 5 -1), the inorganic compounds in the gasses and aerosols are determined by ion chromatography. The detector box also contains a laptop to control the instrument through MARGA software. In addition, the system can be operated in the field in remote places easily via an internet or modem connection through Team Viewer software.

5.2.1 Wet Rotated Denuder \ Steam Jet Aerosol Collector

A detailed description of the WAD/SJAC and the analytical procedures are given by Wyers *et al.* and Slanina *et al.* [222, 232, 239]. A simplified sketch of the denuder techniques is shown in Figure 5-2. A mass flow controlled air pump draws 1 m³ ambient air per hour through the sampling box. The size of particulate matter (PM) can be selected by placing special designed cyclones (PM₁₀ or PM_{2.5} µm) before the entrance of the sampling box.

The air sample passes through the impactor and then enters a horizontally aligned WRD that scavenges soluble gaseous species. Water soluble gases are quantitatively

(more than 99.7%) absorbed in the WRD. According to the difference in diffusion velocity of aerosols and gases, the aerosols pass the WRD and are trapped in the SJAC which is connected to the WRD. A peristaltic pump is used to pump the liquid out of denuder at a flow rate $0.5\text{--}0.6\text{ ml min}^{-1}$ [240].

Figure 5-1. MARGA model ADI 2080 in NTU sampling site.

The liquid effluent collects in a sample reservoir. The air enters to SJAC where it is mixed with steam of highly purified water. By steam injection a water supersaturated

condition is created that causes aerosol particles to grow rapidly (within 0.1 s) into droplets of at least 2 μ m diameter (Figure 5-3). These droplets contain the dissolved aerosol species. Aerosol sample transfers into the sample reservoir by a peristaltic pump at a flow rate of 0.5–0.6 ml min⁻¹. Samples collect in exactly one hour in sample reservoirs in the analytical box (Figure 5 -4).

An on-line Metrohm ion chromatograph with two separation columns, A Supp10-75 $\times$ 4mm and C4-100 $\times$ 4mm for anions and cations respectively, and suppressed conductivity detection. Samples were injected *via* loops into 7 mM Na₂CO₃/8 mM NaHCO₃ eluent for anions and 3.2 mM HNO₃ eluent for cations. Changes in retention time and detector response were checked and controlled with internal bromide standard addition for anion chromatograph and an internal lithium standard addition for cation chromatograph, for each sample during the sampling period.

Figure 5-2. (a) Simplified sketch of the WAD, (b) Sampling box, (c) Denuder operation: gases dissolve in liquid film because of its high diffusion rates.

Figure 5-3: (a) Steam Jet Aerosol Collector (SJAC), (b) Simplified sketch of the SJAC

Figure 5-4. Analytical box (Ion Chromatography and sample Reservoirs).

5.3 Results and Discussion

The sampling period was selected from 2nd April to 26th June 2011 covering one haze event (where prevailing winds blew slight haze from central Sumatra towards Singapore between the 12th to 14th May), two month sampling during inter-monsoon conditions (April to May), and one month sampling during southwest monsoon season. Due to an instrument failure no samples were collected from 29 May (21:00 pm) to 30 May (16:00 pm). The Northeast Monsoon is weakened and gives way to Inter-Monsoon conditions from late March. The Inter-Monsoon conditions persisted until May 2012. During the Inter-Monsoon months, light winds, cloudless skies and more direct solar heating occurred. Based on weather information, May 2011 experienced a mean daily maximum temperature of 32.4°C followed by April at 31.9°C. The Southwest Monsoon season lasting from June to September is the traditional dry season for the southern ASEAN region. Interspersed with the occasional thundery showers, "Sumatra" squalls in the predawn and early morning and hotspot activities are common during periods of dry weather. Usually during southwest monsoon Singapore is affected by transboundary smoke haze from Sumatra. The impact of the smoke haze is dependent on factors such as the proximity and extent of the fires, the strength and direction of the prevailing winds and the incidence and amount of rain (<http://app2.nea.gov.sg/index.aspx>). Meteorological conditions of Singapore during this on-line MARGA study period are presented in Table 5-1.

According to validation report for MARGA data, overall measurement uncertainties usually remain below 15% and detection limits values in $\mu\text{g m}^{-3}$ are SO_2 , 0.04; HNO_3 ,

0.10; HNO_2 , 0.02; NH_3 , 0.05; SO_4^{2-} , 0.06; NO_3^- , 0.10 and NH_4^+ , 0.05 [241]. All results of our measurements of gas and aerosol species are presented in μgm^{-3} .

Table 5-1. Meteorological conditions of Singapore during the study period

Month	Season	Temperature			Relative Humidity			Rainfall mm	Surface Wind		PSI		
		Max °C	Min °C	Mean °C	Max %	Min %	Mean %		Direction	Speed	Min	Max	Mean
April	Inter-Monsoon	31.9	24.6	27.9	95.6	65.6	83.9	217.8	NNE	2.4	24	49	34
May	Inter-Monsoon	32.4	25.2	28.5	96.9	66.3	85.3	127	S	1.3	20	60	38
June	South-West Monsoon Season	31.3	25.2	28.4	95.1	69.5	83.7	213	S	1.3	26	56	37

Measurements of 13 different compounds were performed in the present study which resulted in the collection of approximately 10000 data points over 3 months SO_2 was found to be the most abundant gas with an order of magnitude higher concentration than other inorganic trace gases, and reached a maximum value of $331 \mu\text{g m}^{-3}$ on 11th May at 14:00 pm. Correspondingly, SO_4^{2-} was also found to be at least 3 to 10 times higher than other anionic aerosol species.

Figure 5 -5 and Figure 5 -6 show that the highest value (but not the average values) of most gaseous precursors and aerosols were observed in May, suggesting that biomass burning is a strong source of these species (in addition to industrial sources).

Data analysis showed an average trend of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ for aerosol species and $\text{SO}_2 > \text{NH}_3 > \text{HNO}_2 > \text{HNO}_3 > \text{HCl}$ for gases. The lower contributions of Ca^{2+} and Mg^{2+} suggest that they occur mainly as insoluble carbonates, bicarbonates and silicates [242]. Table 5-2 presents monthly statistical data for the target analytes in ambient air.

Figure 5-5. Box-and-whisker plots showing seasonal monthly variations of aerosol species during sampling period.

Figure 5-6. Box-and-whisker plots showing monthly variations of gaseous compounds during sampling period.

Table 5-2. Monthly statistical data ($\mu\text{g m}^{-3}$).

	Parameter	HNO ₂	SO ₂	HNO ₃	NH ₃	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺
April	mean	1.25	7.45	0.42	4.18	0.34	1.74	5.99	0.39	2.17	0.50
	max	4.60	122.51	1.71	25.17	2.46	10.75	34.69	1.12	7.08	2.90
	min	0.03	0.03	0.12	0.47	0.01	0.30	0.43	0.07	0.23	0.08
	std	0.70	14.55	0.21	4.44	0.35	1.22	3.05	0.22	1.07	0.33
	Percentile 25%	0.79	0.92	0.28	1.60	0.09	1.03	4.26	0.22	1.53	0.28
	median	1.11	2.21	0.37	2.46	0.18	1.48	5.57	0.33	2.02	0.39
	Percentile 75%	1.55	5.90	0.51	4.76	0.51	2.04	7.01	0.55	2.54	0.64
May	mean	1.69	25.68	0.84	2.79	0.27	1.56	5.35	0.21	1.87	0.41
	max	7.48	331.03	2.77	25.49	4.60	11.58	19.42	2.01	8.99	2.73
	min	0.06	1.17	0.27	0.29	0.01	0.28	0.53	0.03	0.13	0.06
	std	1.32	37.71	0.49	3.43	0.48	1.47	3.32	0.12	1.41	0.32
	Percentile 25%	0.87	5.35	0.49	0.87	0.06	0.83	3.06	0.14	0.94	0.22
	median	1.26	11.52	0.65	1.62	0.12	1.03	4.45	0.2	1.46	0.32
	Percentile 75%	2.08	27.74	1.00	3.20	0.25	1.60	6.42	0.26	2.28	0.47
June	mean	2.27	32.76	0.84	2.74	0.41	1.53	6.07	0.15	1.94	0.41
	max	7.33	256.17	2.00	20.23	2.64	9.50	21.08	0.75	6.11	1.53
	min	0.22	2.08	0.41	0.24	0.01	0.51	0.92	0.01	0.24	0.05
	std	1.47	32.92	0.24	2.89	0.40	1.08	2.74	0.09	0.92	0.25
	Percentile 25%	1.16	12.42	0.69	0.90	0.13	1.01	4.38	0.09	1.31	0.23
	median	1.72	23.85	0.81	1.67	0.31	1.18	5.58	0.13	1.74	0.36
	Percentile 75%	3.11	41.24	0.95	3.17	0.54	1.45	7.17	0.19	2.45	0.53

5.3.1 Variations of Trace Gases, Anions and Cations

5.3.1.1 HNO₃ and HNO₂

The monthly averaged concentrations of HNO₃ were 0.42, 0.84 and 0.84 $\mu\text{g m}^{-3}$ during April, May June sampling periods, respectively. The maximum values were observed during biomass burning from 12th to 15th May. Figure 5-7 to Figure 5-9 present hourly variation of HNO₃ from 2nd April to 25th May 2011.

The HNO₃ hourly trend showed relatively low values during the night and high values during the day, although there were some exceptions. This pattern has been found in several other studies [240, 243-245].

Nitric acid has been introduced as the main transformation product of NO_x. Three major routes to HNO₃ have been proposed:

It has been suggested that reactions 5-1 and 5-2 are the main route to HNO₃ during daytime and nighttime, respectively [246, 247]

The HNO₃ production rate is generally slower at sunrise and sunset due to the lower concentrations of HO[•] or NO₃[•] radicals during these times [248]. Both meteorology and photochemistry can have an effect on HNO₃ concentration variation. The amount of HNO₃ peaks during the afternoon, most probably because of the increased concentration of hydroxyl radicals. A second reason for the afternoon peaks of nitric acid could be dissociation of ammonium nitrate. It is reported that the higher the ambient temperature, the higher the dissociation constant of ammonium nitrate and thus the higher the observed concentrations of nitric acid [248, 249].

During the day, NO₃[•] is rapidly photolysed, but at night with availability of organic compounds, NO₃[•] reacts to produce HNO₃ by hydrogen abstraction or adding to unsaturated bonds, so reaction 5-3 could be another possibility of HNO₃ formation during night. The atmospheric lifetime of HNO₃ is 10 to 20 days under background conditions to make long distance transport possible, but its lifetime is much shorter in a polluted urban boundary layer [250].

As can be seen from Figure 5 -7, the HNO₃ production rate is generally slower at sunrise and sunset due to the lower concentrations of HO or NO₃ radicals during these

times. Both meteorology and photochemistry can affect the HNO_3 concentration variation. HNO_3 peaks during the afternoon, most probably because of the increased concentration of hydroxyl radicals. A second reason for the afternoon peaks of nitric acid could be dissociation of ammonium nitrate. It is reported that higher ambient temperature increase the dissociation constant of ($K_a = 24$) and thus the higher the observed concentrations of nitric acid [251, 252]. The maximum values ($2.021\text{--}2.77 \mu\text{gm}^{-3}$) observed from 9th to 15th May cover biomass burning period.

HNO_2 plays an important role in atmospheric chemistry because it acts as a source of $\cdot\text{OH}$ radicals through photolysis. Relative to HNO_3 , HNO_2 is expected to be present at lower concentrations. However, as can be seen in Table 5-2, the results show higher values for HNO_2 concentration compared to HNO_3 for the NTU sampling site, with this conversion only observed for heavily polluted areas [253].

As it can be seen from Figure 5-10 to Figure 5-12 the hourly trend of HNO_2 concentration generally showed lower values during the day, which rose to higher levels during the night as expected [254].

Presently the heterogeneous reaction of NO_2 with water on terrestrial surfaces is suspected to be a main HNO_2 source, especially during the night [255, 256].

Figure 5-7. Daily variation of HNO_3 concentration during April 2011.

Figure 5-8. Daily variation of HNO_3 concentration during May 2011.

Figure 5-9: Daily variation of HNO_3 concentration during June 2011.

Figure 5-10: Daily variation of HNO_2 during April 2011.

Figure 5-11: Daily variation of HNO_2 during May 2011.

Figure 5-12: Daily variation of HNO_2 during June 2011.

Singapore's $\text{PM}_{2.5}$ characterization from January through December 2000 showed carbon particles were the main component especially during the haze period [257].

Our results appear to be in agreement with the December 2000 particulate study since a higher concentration of HNO_2 was observed compared to HNO_3 , possibly due to a high concentration of carbon particles, especially during high levels of biomass burning (12th - 15th May 2011). Higher values of HNO_2 were detected at night, reaching maximums of 4 to 8 $\mu\text{g m}^{-3}$. The heterogeneous reaction of NO_2 with water vapor may also be considered as a HNO_2 source due to high humidity of Singapore, or heterogeneous surface reactions with particles in the air [258].

5.3.1.2 NH_3 and NH_4^+

Ammonia is the most important alkaline gas in the atmosphere which plays a key role in the neutralization of atmospheric acid gases. It has been suggested that ammonia is first neutralized by sulfuric acid to form ammonium sulfate or ammonium bisulfate. A high correlation between NH_4^+ and SO_4^{2-} (0.81) at the NTU sampling site appears to agree with this hypothesis. The excess of NH_3 could react with HNO_3 to form NH_4NO_3 (Pearson Correlation of NH_4^+ and $\text{NO}_3^- = 0.77$ in this study) and with HCl to form NH_4Cl [259].

Unlike HNO_3 and HNO_2 which showed typical trends in daytime and nighttime in most studies, ammonia and ammonium ions showed little diurnal variation (Figure 5-13 to Figure 5-15 and Figure 5-16 to Figure 5-18).

Because ammonia gas has an expected lifetime of approximately one day (<http://ammoniabmp.colostate.edu/link%20pages/impacts%20of%20ammonia.html>), its lifetime would be expected to peak in the middle of the day as higher emissions are expected in that period. In contrast, the daily trends for NH_3 during the sampling period

and monthly statistical data indicated that in April NH_3 was relatively low at midday, while it increased from 18:00 to 22:00 hours with a maximum at 20:00 or 21:00 hours in most days, and 4:00 to 7:00 with sharp peaks at 6:00 or 7:00 for some days. Presumably the increasing of NH_3 concentration in early morning could be due to the re-evaporation of deposited NH_3 from wet surfaces because of the increase of temperature after sunrise [240]. It is interesting to note that in most days in May and June, the higher values of NH_3 were observed at midday as expected.

It is reported that NH_4NH_3 generally shows a higher concentration at night due to high relative humidity and lower temperature which results in a shift of the equilibrium in equation 5-4 to the aerosol phase.

A low concentration of NH_4NO_3 is observed during daytime because of evaporation of NH_4NO_3 from the aerosol phase caused by lower relative humidity and higher temperature, consequently raising the gas phase contents. Regarding this hypothesis, ammonium would be expected to exhibit a maximum at night and minimum during the daytime, while in our measured results in some case the daytime value are significantly higher than nighttime. However, in Singapore the temperature and humidity difference between daytime and nighttime are often small, therefore, this may account for the contradiction that was observed between the expected daytime and nighttime levels of ammonium. During the biomass burning period the NH_3 concentration increased to $20 \mu\text{g m}^{-3}$ and consequently the NH_4^+ concentration reached $9 \mu\text{g m}^{-3}$ with a Pearson Correlation of approximately 0.7. Figure 5-19 shows the daily average NH_3 and NH_4^+ concentration cycles for each month. It is interesting that the trend in the amount of NH_4^+

was strongly influenced by NH_3 during May and June (Pearson Correlation ~ 0.5) , while in April the NH_4^+ trends changed inversely with NH_3 over most days (Pearson Correlation ~ 0.05), and a higher mean concentration was obtained in April.

Figure 5-13: Daily variation of NH_3 concentration during April 2011.

Figure 5-14: Daily variation of NH_3 concentration during May 2011.

Figure 5-15: Daily variation of NH₃ concentration during June 2011.

Figure 5-16a: Daily variation of NH_4^+ concentration during April 2011.

Figure 5-17b: Daily variation of NH_4^+ concentration during May 2011.

Figure 5-18c: Daily variation of NH_4^+ concentration during June 2011.

Figure 5-19: Daily averaged NH_3 and NH_4^+ concentration cycles.

Table 5-3 compares sunshine and solar radiation values that were collected over the study period. It is apparent from Table 5-3 that April sunshine duration and total solar radiation were much higher than in May and June. On the other hand the wind direction (Table 5-1) in April was from North and Northeast while for most days in May and June the wind came from the South and Southeast. The observed differences in Meteorological data in April compared to May and June could explain the difference in the NH_3 and NH_4^+ observed in different months.

Table 5-3: Additional Meteorological Data

	Mean Amount Of Cloud (%)	Sunshine Duration (hours)	Total Solar Radiation (mwh/cm ²)
April	86.79	7.16	517.48
		Total: 214.65	
May	88.75	5.9	438.53
		Total: 189	
June	88.75	5.0	400.46
		Total: 150.15	

5.3.1.3 SO₂

The results of this study indicate high concentrations of SO₂ during the sampling period (average values were approximately 22 $\mu\text{g m}^{-3}$). The sources of SO₂ particles are mainly from fuel combustion, power plants and coal burning. SO₂ is considered as a sulfate precursor. In addition to the oxidation of SO₂ by $\cdot\text{OH}$ radicals, the formation of sulfate in clouds could be another important oxidation pathway.

Particularly high maximum values ($\sim 200\text{-}340 \mu\text{g m}^{-3}$) of SO₂ were observed on the 11th, 17th and 18th May. The most smoke effected days (highest recorded PM₁₀ values from biomass burning) occurred between 12th - 15th May, and during these days the SO₂ concentration was almost 120 $\mu\text{g m}^{-3}$ at midday.

Figure 5-20: Variation of SO_2 during biomass burning.

Figure 5-21: Variation of HNO_2 during biomass burning

Figure 5-22. Comparison of SO_2 and HNO_2 Variation during Haze Period.

Continue Figure 5 - 22. Comparison of SO_2 and HNO_2 Variation during Haze Period.

Figure 5-23: Daily variation of SO_2 during April 2011.

Figure 5-24: Daily variation of SO_2 during May 2011.

Figure 5-25: Daily variation of SO_2 during June 2011.

The higher concentrations of HNO_2 during hazy days confirmed strong oxidation ability of the atmosphere which can explain the SO_2 trends during biomass burning. As it can be seen in Figure 5-21, the average HNO_2 concentrations were 1.4 (max=3.02), 1.31 (max=3.22) and 1.31 (max=2.30) μgm^{-3} on the 11th, 17th and 18th May respectively, while during hazy days the average concentration were between 1.40 to 3.2 (max = 5-7) μgm^{-3} . Figure 5 -22 compares the variation of SO_2 and HNO_2 during biomass burning. It is interesting to note that their fluctuations were opposite, except on high haze days where their variation followed the same pattern. Although the Pearson correlation shows quite weak values for whole sampling period (~ -0.1), the value reached -0.6 for hazy days that confirmed these trends.

5.3.1.4 Nitrate and Sulfate

In most other studies, no significant diurnal trend for NO_3^- has been observed, which is in agreement with the observations of this study (Figure 5-26 to Figure 5-28). Since the particulate nitrate has a lifetime of approximately one week, its concentration would be expected to be affected by long range transport.

The scatter plot of nitrate vs. nitric acid (Figure 5-29) shows that there is a very weak positive correlation between these two but the correlation is not significant ($r^2 = 5 \times 10^{-6}$). One possibility could be because the nitrate observed at the site is from long-range transportation whereas the nitric acid is from more local sources [260].

Figure 5-26. Daily variation of NO_3^- concentration during April 2011.

Figure 5-27. Daily variation of NO_3^- concentration during May 2011.

Figure 5-28. Daily variation of NO_3^- concentration during June 2011.

In addition, if both the short lifetime of nitric acid, and the long lifetime of particulate nitrate is considered, the likely conclusion is that one would not expect a relationship between them, especially if the sources are different. Thus, the Pearson correlation between gaseous nitrate and particulate nitrate were found to be very small (0.15). A comparison of particulate nitrates and gaseous nitric and nitrous acid in Figure 5-30 shows that gaseous nitric and nitrous acid were the predominant form in June, while during April and May particulate nitrate was present in almost the same concentration as in the gas phase. In most other urban studies particulate nitrates have been observed in higher concentration compared to gaseous nitrates [260, 261]. It is possible that nitrates present in high amounts in the gas phase could be due to the higher temperature and humidity in Singapore.

Figure 5-29: Relationship of nitrate and nitric acid.

Sulfate is the major component of the aerosols regardless of the metrological conditions, which was expected due to long the lifetime of particulate sulfate (up to approximately ten days). Figure 5-31 to Figure 5-33 show the daily variation of SO_4^{2-} concentration during the sampling period. Thus, the effects of long-range transport and diurnal variation were not observed for particulate sulfate [262]. The only pattern that was observed in daily trends related to the increased biomass burning period which indicated a higher value at midday from 11th to 19th May. However sulfate data collected during this period showed a relatively moderate impact (mean = $5.35 \mu\text{g m}^{-3}$ range = $0.53 - 19.43 \mu\text{g m}^{-3}$) compared to background conditions (mean = $5.79 \mu\text{g m}^{-3}$ with range = $0.4 - 35 \mu\text{g}^{-3}$) which were higher because of the high monthly sulfate levels in April and June.

Figure 5-34 shows the scatter plots for SO_4^{2-} vs. NH_4^+ and NO_3^- vs. NH_4^+ ; the correlations being $r=0.67$ and $r=0.59$, respectively. Contrary to expectations the slope of the regression between SO_4^{2-} and NH_4^+ from the whole data set was 0.31 which indicated a relative moderate neutralization of SO_4^{2-} by NH_4^+ , while the regression between NO_3^- and NH_4^+ from the whole data set was 0.70, which indicated NH_4NO_3 was the major species formed by particulate SO_4^{2-} and NH_4^+ . These findings appear to be in conflict with the hypothesis that firstly NH_4^+ neutralizes SO_4^{2-} , and the excess NH_4^+ reacts to form NH_4NO_3 , which would result in the major component being $(\text{NH}_4)_2\text{SO}_4$ [262]

Figure 5-30: Monthly average variations of particulate nitrate and gaseous nitrate.

Figure 5-31. Daily variation of SO_4^{2-} concentration during April 2011.

Figure 5-32. Daily variation of SO_4^{2-} concentration during May 2011.

Figure 5-33. Daily variation of SO_4^{2-} concentration during June 2011.

Figure 5-34: (a) Scatter plot calculation of SO_4^{2-} vs. NH_4^+ (b) Scatter plot calculation of NO_3^- vs. NH_4^+ .

5.3.2 Total Nitrogen

Total nitrogen was calculated by Eq. 5-5:

$$N_{Tot} = NO_3^- + NH_4^+ + HNO_3 + HNO_2 + NH_3 \quad \text{Eq. 5-6}$$

The distribution of nitrogen into gas and aerosol phases was studied by calculating the contribution of each gas or particulate to N_{Tot} (Figure 5 -35). The variation is complicated but it can be seen that most nitrogen is present in the gas phase, rather than particulate phase. The percentage mean and the 95 percent range (in parenthesis) of the gas-phase nitrogen contribution were 57% (33 - 85%) in April, 60% (36 - 80%) in May and 61% (41 - 79%) in June. Due to uniform temperature and humidity in our sampling site, there were no significant monthly variations.

5.3.3 Distribution of Particulate Matter and Gaseous Compounds

The sulfur oxidation ratio $SOR = \left(\frac{SO_4^{2-}}{SO_4^{2-} + SO_2} \right)$ and nitrogen oxidation ratio $NOR = \frac{NO_3^-}{NO_3^- + HNO_3}$ are available indicators used to quantitatively characterize the secondary transformation reactions of SO_2 and HNO_3 , respectively.

The mean SOR was 0.45 in April and 0.16 in May-June suggesting that the fraction of particulate matter in the atmosphere was low during May-June. It has been reported that SOR values smaller than 0.10 represent conditions of primary source emissions, whereas SOR values above 0.10 occur when sulfate is mainly produced through the secondary transformation of SO_2 oxidation [244]. The NOR showed a similar trend to the sulfur oxidation ratio, with a mean value of 0.80 in April and 0.65 in May - June.

Figure 5-35: Nitrogen fractionation into aerosol and gas phases.

As demonstrated in Figure 5-36, the SOR reached up to 0.60 on high haze days due to secondary pollution and suggesting that the secondary transformation was very significant during the biomass burning. High SO_2 and HNO_3 concentrations and high SOR and NOR values directly resulted in a large amount of secondary sulfate and nitrate particles in the atmosphere at the Singapore sampling site. However, localized meteorological conditions (temperature and humidity) also play a main role in the formation processes of these secondary particulate pollutants.

Figure 5-36: Variation of sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) during the observation period.

5.3.4 Pearson Correlation

The correlation coefficient matrix was used for whole obtained data set in this study. A very high degree of correlation coefficient was observed between NH_4^+ , NO_3^- and SO_4^{2-} (NH_4^+ , NO_3^- =0.77 and NH_4^+ , SO_4^{2-} =0.88), indicating that these ions possibly have a common anthropogenic origin. This correlation also depends on the secondary characteristic of these pollutants which are more dependent on meteorological conditions

than on common anthropogenic sources, like atmospheric stability, wind speed and solar radiation.

The time series of daily averaged data showed similar trends for these particulate ions as well (Figure 5-37). The Pearson correlation was individually applied for obtained data during hazy days. It is interesting to observe that beside the high correlation between NH_4^+ , NO_3^- and SO_4^{2-} , a strong relation (>0.9) was found between K^+ , Cl^- .

The correlation coefficient matrix suggested that during the biomass burning period, NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, KNO_3 , K_2SO_4 , KCl and NH_4Cl are the most abundant compounds respectively, while most other literature reports introduced KCl as the biomass burning index. This finding supports previous research on particulate aerosols in Singapore during the haze period, where it was suggested that forest and peat fires in Sumatra were an important source of sulfate and ammonium in the region [257].

Figure 5-37: Time series of daily averaged concentration of NO_3^- , SO_4^{2-} and NH_4^+ from May 2 to June 25

5.3.5 Acidity of Aerosols

The neutralization ratios (NR) of $\text{NH}_4^+ / (\text{NO}_3^- + 2\text{SO}_4^{2-})$ were calculated in order to estimate the acidity of atmospheric aerosols. A ratio value of 1.0 would indicate neutralization of HNO_3 and H_2SO_4 by atmospheric NH_3 , while NR values lower than unity imply the likely presence of acidic aerosols. Figure 5-38 shows that the observed ratios ranged between 0.02 and 0.47, with a mean of 0.26 indicating that the atmospheric aerosols are strongly acidic.

Figure 5-38: Variation of Neutralization Ratio (NR) during the observation period.

5.3.6 Comparison of Aerosol / Gas Data with Rain Sample Data

Table 5-4 presents statistical data for inorganic ions present in the rain water samples. It can be seen that aerosol data are generally in good agreement with rain data in terms of the relative amounts of the different ions that are present. The concentrations of the ionic species present in rain samples were in the following order: $\text{SO}_4^{2-} > \text{Cl}^- > \text{Ca}^{2+} > \text{NO}_3^- >$

$\text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{F}^-$, with ion percentages 20, 17, 14, 8, 7, 6.6, 5.5, 2.5 and 0.1 respectively. It can be observed that the major ions in rain samples were SO_4^{2-} followed by NO_3^- and NH_4^+ . However, Ca^{2+} was found to be one of the major ions present in rain samples that were not present in significant amounts in aerosols. This difference could possibly be explained by the particle size. For aerosol samples the impactor selects $\text{PM}_{2.5}$, while rain droplets can scavenge particles of all sizes. Thus it appears that the Ca^{2+} , Na^+ and K^+ in rain originate from larger particles in the atmosphere.

A direct comparison between the data obtained from aerosols/gas samples and rain water is complicated because the ions that are detected are measured using different units. Table 5-5 presents a list of the average values over the 3 month sampling period, which gives an indication of how the detection of a certain levels of ions/molecules in the aerosol/gas fraction, can lead to a corresponding amount of ions present in rainwater. Such as correlation assumes that all of the ions present in rainwater are originating from the aerosols and gas molecules, which is not necessarily the case (such as for the Ca^{2+} , Na^+ and K^+ ions).

The distribution of pH revealed that the largest fraction (98%) of all samples had a $\text{pH} < 5.6$, while about only 2% of rain samples had a $\text{pH} > 5.6$. Most pH values ranged between 3.6 and 4.8 (78.5%), while only 2% of the rain samples had pH values between 5.6 and 6.4. The acidic nature of rain samples is consistent with results obtained from aerosols for the acidity and neutralization factor.

Table 5-4. Rain Statistical Data (µeq L-1).

		F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	pH
Apr-11	Average	2.65±0.03 (0.34-5.32)	66.08±3.92 (5.56-390.87)	34.58±1.90 (2.95+125.31)	88.52±2.34 (15.45-193.77)	18.76±0.35 (2.84+68.55)	7.47±0.13 (0.50-25.24)	44.37±3.90 (1.90-335.40)	5.60±0.05 (1.09-21.50)	25.51±0.45 (5.63-91.25)	4.17±0.25 (3.82+4.83)
	Median	2.48	23.54	35.04	84.46	14.21	4.64	6.28	4.28	16.85	4.10
	Percentile 95%	1.53-3.83	15.15-3.73	6.25-47.35	53.62-106.17	11.48-22.24	2.92-10.86	2.9-11.00	3.36-5.91	12.24-28.65	4.06-4.22
May-11	Average	3.47±0.04 (0.72-6.81)	42.66±1.17 (6.63-98.98)	41.70±3.10 (3.17-151.91)	130.81±2.75 (43.80-201.47)	30.59±0.70 (4.92-87.54)	14.27±0.52 (1.23-84.49)	6.22±0.19 (0.87-15.74)	13.41±0.11 (1.01-27.20)	62.44±0.84 (5.54-131.40)	4.11±0.28 (3.70+4.48)
	Median	3.97	32.77	24.67	138.2	22.74	3.57	5.68	14.73	65.92	4.10
	Percentile 95%	1.22-4.96	21.09-53.11	7.05-54-54.61	105.2-165.86	6.92-36.83	1.9-6.76	3.17-7.54	6.17-19.85	34.49-81.16	3.90-4.32
Jun-11	Average	2.93±0.07 (0.33-13.74)	53.11±1.61 (15.73-169.93)	12.85±1.17 (0.33-65.62)	127.25±6.42 (1.88-462.13)	38.01±0.86 (8.07-136.06)	6.45±0.14 (0.55-22.77)	17.41±0.89 (1.83-79.66)	9.92±0.11 (1.04-33.90)	42.79±0.97 (3.18-166.87)	4.23±0.31 (3.90+4.92)
	Median	1.58	38.92	4.55	61.58	32.28	1.70	8.01	6.53	25.67	4.13
	Percentile 95%	0.71-3.43	24.48-59.71	2.57-15.58	51.44-159.21	12.64-45.57	1.23-9.50	5.34-19.49	4.13-13.47	13.16-61.67	4.03-4.39
2010	Average	4.93±0.05 (0.32-31.37)	64.06±4.15 (7.57-644.09)	39.54±1.76 (2.82-323.86)	84.36±1.79 (8.31-413.16)	31.18±0.77 (3.59-229.93)	30.19±0.36 (1.02-345.42)	34.89±3.97 (0.66-533.80)	11.16±0.15 (1.61-76.28)	61.043±0.89 (6.00-340.22)	4.29±0.53 (3.22-6.24)
	Median	3.66	33.09	29.22	72.93	21.81	21.31	12.65	7.15	41.61	4.20
	Percentile 95%	1.55-5.87	19.23-63.23	16.15-47.92	39.25-112.13	13.17-41.16	10.90-38.57	5.69-27.08	4.46-12.82	22.35-87.58	3.93-4.53
2011	Average	3.57±0.12 (0.33-73.80)	83.86±4.09 (0.74-933.20)	30.14±1.99 (0.33-208.81)	81.02±3.54 (1.88-388.04)	32.57±1.08 (1.70-486.82)	18.67±0.40 (0.45-145.68)	23.23±2.96 (0.38-839.90)	10.91±0.17 (1.0-123.53)	63.31±1.69 (3.18-495.63)	4.4±0.53 (3.39-6.22)
	Median	2.24	55.12	20.65	55.83	17.43	12.88	7.642	5.81	33.56	4.27
	Percentile 95%	1.42-4.07	25.14-95.18	9.02-41.18	32.20-102.91	11.07-33.88	3.40-22.34	3.42-15.53	3.94-11.96	16.39-72.07	4.02-7.76
Two Year Data	Average	4.17±0.10 (0.32-73.80)	75.38±3.78 (0.74-933.20)	34.37±2.25 (0.33-323.86)	82.60±3.32 (1.88-413.16)	32.20±0.93 (1.70-486.82)	23.89±0.55 (0.45-345.42)	28.51±2.93 (0.38-839.90)	11.08±0.16 (1.0-123.53)	62.28±1.47 (3.18-495.63)	4.35±0.53 (3.22-6.24)
	Median	2.64	40.72	23.83	64.10	20.35	15.55	9.50	6.58	36.27	4.24
	Percentile 95%	1.42-4.95	22.36-86.94	11.51-44.40	36.80-104.50	12.03-37.31	6.32-30.59	4.32-20.41	4.16-12.41	18.52-79.30	3.99-4.66

Table 5-5. Comparison of the average ($\pm$ standard deviation for whole data) and range (in parenthesis) of chemical data from aerosols and rain water.

Parameters	F⁻	Cl⁻	NO₃⁻	SO₄²⁻	Na⁺	NH₄⁺	K⁺
Rain ($\mu\text{eq/l}$)	4.17 $\pm$ 5.78 (0.32-73.80)	75.38 $\pm$ 106.76 (0.74-933.20)	34.37 $\pm$ 36.35 (0.33-323.86)	82.60 $\pm$ 69.17 (1.88-413.16)	32.20 $\pm$ 40.27 (1.70-486.82)	23.89 $\pm$ 30.30 (0.45-345.42)	28.51 $\pm$ 74.91 (0.38-839.90)
Aerosol ($\mu\text{g/m}^3$)	ND	0.33 $\pm$ 0.42 (0.01-4.62)	1.61 $\pm$ 1.28 (0.28-11.58)	5.79 $\pm$ 3.08 (0.43-34.69)	0.26 $\pm$ 0.19 (0.01-2.01)	1.99 $\pm$ 1.17 (0.13-8.99)	0.44 $\pm$ 0.31 (0.05-2.90)
Parameters	Mg²⁺	Ca²⁺	HCl	HNO₂	HNO₃	SO₂	NH₃
Rain ($\mu\text{eq/l}$)	11.08 $\pm$ 13.12 (1.0-123.53)	62.28 $\pm$ 73.40 (3.18-495.63)	ND	ND	ND	ND	ND
Aerosol ($\mu\text{g/m}^3$)	0.02 $\pm$ 0.12 (<DL-4.80)	0.09 $\pm$ 0.70 (<DL-18.54)	0.04 $\pm$ 0.07 (<DL-1.315)	1.71 $\pm$ 1.27 (0.03-7.48)	0.69 $\pm$ 0.39 (0.12-2.77)	21.49 $\pm$ 31.85 (0.03-331.03)	3.25 $\pm$ 3.73 (0.24-25.49)

ND = No data. DL = detection limit

Chapter 6: Summary and Conclusions

Singapore is an industrially advanced country and over the last few decades, has undergone rapid and extensive industrial growth. This has inevitably led to dramatic increases in pollutant emissions into the atmosphere and consequently increases in deposition of these pollutants. Knowledge of the chemical composition of rain waters can help to distinguish the major sources that contribute to rainwater chemistry and an understanding of the dispersion of elements, whether pollutants or not, and their potential impact on eco-hydrosystems through deposition processes [263].

In this project, we collected rainwater, (wet and dry) from a site in Nanyang Technological University (NTU) between August 2009 to December 2011. In NTU sampling site particulate matter was sampled in two different particle sizes of 10 and 2.5 μm between October 2009 to December 2011.

The elemental part of our sample (PM and Rain) were determined using ICP-OES and ICP-MS. Ion chromatography was employed to measure common ions present in rainwater samples, in addition to pH and conductivity measurements.

The automatic MARGA (Monitor for AeRosols and Gases) sampling system was used to measure the inorganic components Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} in the $\text{PM}_{2.5}$ aerosol phase and the corresponding inorganic molecules HCl , HNO_2 , SO_2 , HNO_3 and NH_3 present in the gas phase. Samples were collected and analysed hourly for 3 months between 2nd April and 25th June, 2011 to determine how the concentration of species in gas and aerosols contribute to the levels found in precipitation.

In this study, a microwave method was developed for sample preparation to determine elemental fractions in airborne particulate matter. The optimization of the method was examined with SRM 2783 based on recovery studies. Further optimization of an ICP–MS method was also performed to quantify a number of elements.

Concentration time series graphs were examined to find out the effect of different local events on the composition of airborne particulate matter at the NTU sampling site and the relationship between different elements. The possibilities of the contribution of anthropogenic sources were estimated using the enrichment factors (EF). The EF calculations were performed using the average crustal profile as a reference.

Source apportionment was carried out with EPA PMF. The PMF model identified 8 factors for PM₁₀ including sea salts, crustal and blown wind dust, refineries and chemicals, oil combustion, electronics and semiconductor industry, high temperature operations (such as incineration, oil and coal combustion and metal industries) and construction. The same factors introduced for PM_{2.5} resulted in the sea salt and crustal factors combining in one factor.

The pH of rainwater over Western Singapore between August 2009 to December 2011 was found to be relatively low in most rain events, with the acidity arising mainly from the presence of sulfuric acid. Considering the high industrialization in Singapore and the surrounding Malay Peninsula, the low pH readings in rainwater are not unusual, and typical of many urbanized areas. An interesting positive correlation was observed between the PSI (PM₁₀) and the conductivity of the rainwater samples, caused by the high haze events increasing the ionic concentration of the water. Several elements (As, Cd, Pb and

Zn) that were detected by ICP-MS measurements were found to be notably enriched beyond their expected background levels.

Enrichment factor calculations indicated the contribution of anthropogenic sources for pollutants in rain water in the NTU sampling site. The results are correlated to a mixture of sources, such as dust, sea salts, vehicles, refinery and chemical, coal-fired power plant agriculture, and biomass burning.

The concentration of particulate and gaseous components in $PM_{2.5}$ aerosols were measured in an industrial area in Singapore between April 2 to June 25 using a MARGA employing a WAD/SJAC coupled with an online IC. The study revealed that the aerosols were very acidic, and were not neutralized by NH_4^+ . The concentration of major ions and related gaseous compound in aerosol samples followed the order of: $SO_4^{2-} > NH_4^+ > NO_3^- > K^+ > Na^+ > Cl^- > Ca^{2+} > Mg^{2+}$ and $SO_2 > NH_3 > HNO_2 > HNO_3$. Sulfate and nitrate were the major acidifying ions in aerosol samples at the NTU sampling site. The maximum values for most of the target analytes were observed during the hazy period in May where there was significant contamination from regional fires.

A strong correlation was observed between the amounts of NH_4^+ , NO_3^- and SO_4^{2-} which suggests that these compounds in the atmosphere were present as NH_4NO_3 and $(NH_4)_2SO_4$.

High SO_2 and HNO_3 concentrations and high SOR and NOR values directly resulted in a large amount of secondary sulfate and nitrate particles in the atmosphere in the NTU sampling site. However, meteorological conditions also play a main role in the formation processes of these secondary particulate pollutants.

The amounts of dissolved elements measured in rainwater were compared with detected elements in particulate matter. Because of the acidic pH of rainwater at the NTU sampling site, the results showed most of elements can be dissolved in rainwater and detected in collected samples, although the dissolution ratio depends on background concentration, rainfall amount and duration, monsoon season and wind direction.

Major elements detected in airborne particulate matter were in good agreement with major ions measured in aerosol samples. The high concentration of Na ($\sim 8 \mu\text{g m}^{-3}$) in airborne particulate matter can be related to high concentration of SO_4^{2-} ($\sim 6 \mu\text{g m}^{-3}$) detected in aerosols and gases.

The amount of major ions present in rain water closely followed the relative amounts detected in the aerosols and gases, except for the inorganic cations (Ca^{2+} , K^+ and Na^+) which were not readily observed in the aerosols ($\text{PM}_{2.5}$) and gases, possibly due to these species originating from larger particles. To examine the effects of growing industrial activities and the population in Singapore air quality, it is planned to perform the same type of monitoring study in subsequent years to identify more reliable source apportionment. A longer-term study of aerosols can help to identify different types of sources and control in order to protect air quality.

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Appendix A - Weather Report

Table I. Rainfall data recorded by NEA over long term period

Rainfall	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Period of Record
Mean Monthly Total (mm)	243.2	159.9	185.7	178.9	171.3	162.1	158.7	175.4	169.2	193.8	256.9	287.4	1869 - 2011 (143 yrs)
Highest Monthly Total (mm)	818.6 (1893)	566.7 (1910)	528.3 (1913)	454.9 (1900)	386.6 (1892)	378.7 (1954)	527.3 (1890)	526.8 (1878)	440.4 (1988)	497.1 (1942)	521.5 (1874)	765.9 (2006)	
Lowest Monthly Total (mm)	15.4 (1997)	6.3 (2010)	18.5 (1912)	16.6 (1977)	41.6 (1997)	21.8 (2009)	18.6 (1997)	18 (1888)	23.7 (1994)	10.8 (2002)	53.5 (1981)	62.5 (1932)	
Highest 1 day Total (mm)	216 30 (2011)	159.3 4 (1995)	122.8 8 (2004)	102.4 27 (2007)	153.7 4 (1990)	121.1 5 (1984)	149.1 27 (1941)	133.9 7 (2008)	187.3 21 (1988)	91.4 8 (1952)	198.6 2 (1995)	512.4 2 (1978)	
Mean Raindays	15	11	14	15	15	13	13	14	14	16	19	19	1891-2011 (121 yrs)
Maximum Raindays	26 (1927)	24 (1964)	23 (1945)	23 (1970)	23 (1991)	26 (1899)	20 (several)	23 (1936)	22 (1986)	23 (several)	24 (several)	26 (several)	
Minimum Raindays	3 (1976)	1 (1983)	3 (1983)	3 (1963)	6 (1997)	4 (1981)	6 (several)	5 (1941, 1961)	3 (1997)	5 (1991)	11 (1998)	8 (1920)	

Table II. Temperature data recorded by NEA over long term period*

Temp (°C)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean Daily Maximum	30.1	31.2	31.6	31.7	31.6	31.3	30.9	30.9	30.9	31.1	30.6	30
Mean Daily Minimum	23.3	23.6	23.9	24.4	24.8	24.8	24.6	24.5	24.2	24.1	23.7	23.5
24-hr Mean	25.9	26.5	26.9	27.4	27.7	27.7	27.4	27.3	27.2	27	26.5	26
Highest Temp	34.3 311979	35.2 262010	36 26 1998	35.8 191983	35.4 1 2005	35 25 1985	34 17 1991 17 1997	34.2 17 1986	34.3 152000	34.6 292002	34.2 262000	33.8 21948
Lowest Temp	19.4 30,31 1934	19.7 23 1951	20.2 12 1933 14 2000	20.7 16 1979	21.2 4 1989	20.8 19 1952	19.7 6 1976	20.2 30 1929	20.7 20 1933	20.6 10 1952	21.1 several	20.6 02 1964

Table III. Relative Humidity data recorded by NEA over long term period*

Relative Humidity %	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean Daily Maximum	95.8	95.7	96.4	96.9	96.4	95.5	95	95.1	95.9	96.5	97.1	96.8
Mean Daily Minimum	65.6	61.2	62	63.4	64.7	64.3	64.9	64.6	63.9	63.3	66.1	68.3
24-hr Mean	84.7	82.8	83.8	84.8	84.4	83	82.8	83	83.4	84.1	86.4	86.9
Lowest Minimum	35 29 1971	38 28 1990	39 06 1990 30 1990	33 1 1966	34 24 1955	36 20 2003	44 17 1991	39 21 1965	35 22 1930	40 Several	37 18 1934	34 1 1950

* data has been collected from 1929 to 1941 and from 1948 to 2011 (over 70 yrs)

Table IV. Surface Wind data recorded by NEA over long term period

Surface Wind	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Period of Record
Mean Wind Direction	N/NE	N/NE	N/NE	Variable	S/SE	S/SE	S/SE	S/SE	S/SE	Variable	Variable	N/NE	1935-1941 1948-2011 (70 yrs)
Mean Daily Wind Speed (m/s)	2.5	2.4	1.8	1.3	1.4	1.6	1.9	1.9	1.7	1.3	1.3	1.9	
Highest 10 minutes	12.2	12.4	14.2	13.4	13.9	12.4	15.4	13.9	13.9	12.9	13.8	11.1	1975-2011 (37 yrs)
Mean Wind Speed (m/s)	6 1986	17 1977	3 1986	11 1981	6 1976	20 1978	5 1975	6 1979	19 1980	3 2010	10 1976	17 1981	

Table IV. Thunderstorm and Lightening data recorded by NEA over long term period *

Thunderstorm, Lightning	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
Mean Thunderstorm Days	5	5	13	19	19	15	13	14	15	18	19
Maximum Thunderstorm Days	13 2001	14 2000	23 2000	26 several	24 2001	21 1999	23 2004	20 1996	20 1986, 1996	24 1993	26 1982
Minimum Thunderstorm Days	0 several	0 1983 1990	3 1990	10 1990	10 2003	9 1982	4 1994	5 1988	4 1994	7 2006	14 1991
Mean Lightning Days	6	5	15	22	22	17	14	13	13	20	24
Maximum Lightning Days	14 2000	14 1988	24 1985	28 1982, 2003	29 1983	24 1988	25 1985	23 1996	24 1984	28 2001	29 Several
Minimum Lightning Days	0 1986	1 1996 2007	2 1983	9 1983	13 2003	10 2004	1 1994	2 1997	0 1994 1997	2 2006	14 2004

*data has been collected from 1982 to 2011 (over 30 yrs).

Appendix B - ICP - MS

Figure B - I. Tuning report - no gas mode.

Tune Report

Tune File : he.u
Comment : 24082011(2)

Integration Time: 0.1000 sec
Sampling Period: 0.3100 sec
n: 200
Oxide: 156/140 0.546%
Doubly Charged: 70/140 1.403%

m/z	Range	Count	Mean	RSD% Background
59	10,000	8336.0	8134.2	3.11 0.20
89	10,000	7786.0	7869.6	3.06 0.80
205	20,000	10326.0	11022.2	3.72 1.70

Tuning Parameters

===Plasma Condition===

RF Power : 1550 W
RF Matching : 1.65 V
Smpl Depth : 8 mm
Torch-H : -0.2 mm
Torch-V : 0.6 mm
Carrier Gas : 1.05 L/min
Dilution Mode : OFF
Makeup Gas : 0 L/min
Optional Gas : --- %
Nebulizer Pump : 0.1 rps
Sample Pump : --- rps
S/C Temp : 2 degC

===Ion Lenses===

Extract 1 : 0 V
Extract 2 : -200 V
Omega Bias : -100 V
Omega Lens : 9.8 V
Cell Entrance : -40 V
Cell Exit : -60 V
Deflect : 1.2 V
Plate Bias : -60 V
===Octopole Parameters===
OctP RF : 190 V
OctP Bias : -18 V

===Q-Pole Parameters===

AMU Gain : 132
AMU Offset : 127
Axis Gain : 1.0005
Axis Offset : 0.03
QP Bias : -15 V

===Detector Parameters===

Discriminator : 4.9 mV
Analog HV : 1622 V
Pulse HV : 956 V

===Reaction Cell===

Reaction Mode : ON
H2 Gas : --- mL/min
He Gas : 4.3 mL/min
Optional Gas : --- %

Figure B - II. Tuning report - He gas mode

Figure B - III. ICP-MS calibration graphs.

Continue Figure B - III. ICP-MS calibration graphs.

Continue Figure B - III. ICP-MS calibration graphs.

Continue Figure B - III. ICP-MS calibration graphs.

Continue Figure B - III. ICP-MS calibration graphs

Figure B - IV. ICP-MS QC graph.

Appendix C - IC

Figure B-I. Cation Calibration Graphs

Figure B-II. Ion Chromatogram of Cations (a) and Anions (b).

Figure B-III. Anion Calibration Graphs.

Appendix D

Particulate Matter data was processed by using Windows based application written in C# programming language in .Net platform.

It provides different type of processing as following:

- Find and highlight data less than Detection Limit value and replace them with the defined value for each element
- Find and highlight data less than background value
- Find and replace missing data(-1) with defined value
- Split different type of particulate matter size
- Calculate the uncertainty data
- Calculate Monthly Maximum, Minimum, Average and Standard deviation of each element
- Calculate result in different units
- Export all result in excel worksheet

Figure D- I. Open Data file (Excel format) in PMDP Application

Figure D- II. Detect (a) and replace (b) data lower than detection limit.

Figure D- III. Detect (a) and replace missing data (b).

	F1	Start Date	End Date	Air Volume	Mass	Sample Volume	particulate size
▶							
	217	29/9/2010	1/10/2010	2736.5	0.04919999999...	100	2.5
	218	29/9/2010	1/10/2010	2781.900000000...	0.07710000000...	100	10
	220	1/10/2010	4/10/2010	4281.899999999...	0.10219999999...	100	10
	222	4/10/2010	6/10/2010	2802.399999999...	0.08890000000...	100	10
	224	6/10/2010	8/10/2010	2691.700000000...	0.12319999999...	100	10
	225	8/10/2010	11/10/2010	4186.200000000...	0.10349999999...	100	2.5
	226	8/10/2010	11/10/2010	4276.5	0.15830000000...	100	10
	227	11/10/2010	13/10/2010	2791.5	0.08749999999...	100	2.5
	228	11/10/2010	12/10/2010	1572.200000000...	0.09020000000...	100	10
	229	13/10/2010	15/10/2010	2772.799999999...	0.05999999999...	100	2.5
	230	13/10/2010	15/10/2010	2763.699999999...	0.10180000000...	100	10
	231	15/10/2010	18/10/2010	3166	0.13200000000...	100	2.5
	232	15/10/2010	18/10/2010	3360.100000000...	0.13710000000...	100	10
	234	18/10/2010	20/10/2010	2487.400000000...	0.16618999999...	100	10
	289	31/12/2010	3/1/2011	4290.099999999...	0.05299999999...	100	2.5
	293	5/1/2011	7/1/2011	2696.800000000...	0.02530000000...	100	2.5
	27	23/11/2009	26/11/2009	4451.61	0.05860000000...	100	2.5
	29	26/11/2009	29/11/2009	4451.61	0.04350000000...	100	2.5
	48	31/12/2009	4/1/2010	5480.909999999...	0.07050000000...	100	2.5
	52	7/1/2010	11/1/2010	5758.389999999...	0.06699999999...	100	2.5
	55	11/1/2010	15/1/2010	5746.5	0.08170000000...	100	2.5
	56	15/1/2010	18/1/2010	2634.5	0.06029999999...	100	2.5
	60	22/1/2010	25/1/2010	4230.699999999...	0.05079999999...	100	2.5
	62	25/1/2010	29/1/2010	5606	0.06389999999...	100	2.5
	218	29/9/2010	1/10/2010	2781.900000000...	0.07710000000...	100	10
	220	1/10/2010	4/10/2010	4281.899999999...	0.10219999999...	100	10
	222	4/10/2010	6/10/2010	2802.399999999...	0.08890000000...	100	10
	224	6/10/2010	8/10/2010	2691.700000000...	0.12319999999...	100	10
	226	8/10/2010	11/10/2010	4276.5	0.15830000000...	100	10
	228	11/10/2010	12/10/2010	1572.200000000...	0.09020000000...	100	10
	230	13/10/2010	15/10/2010	2763.699999999...	0.10180000000...	100	10
	232	15/10/2010	18/10/2010	3360.100000000...	0.13710000000...	100	10
	234	18/10/2010	20/10/2010	2487.400000000...	0.16618999999...	100	10
	290	31/12/2010	3/1/2011	4361.2	0.11709999999...	100	10
	294	5/1/2011	7/1/2011	2732.4	0.05030000000...	100	10
	296	7/1/2011	11/1/2011	5741	0.12789999999...	100	10
	298	11/1/2011	15/1/2011	5014.6	0.14010000000...	100	10
	300	15/1/2011	17/1/2011	2731.3	0.10519999999...	100	10
	302	17/1/2011	19/1/2011	3214.2	0.10460000000...	100	10

Figure D- VI. Separate PM₁₀ and PM_{2.5}.

Appendix E - PSI

PSI distribution graphs during sample collection.

PSI distribution graphs during sample collection.

PSI distribution graphs during sample collection.

PSI distribution graphs during sample collection.

PSI distribution graphs during sample collection.

PSI distribution graphs during sample collection.