Occurrence and Characterization of Atmospheric Trace Gases in Dhaka City, Bangladesh

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Doctor of Philosophy

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A dissertation for the partial fulfillment of the
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DECLARATION

I do hereby declare that the thesis titled "Occurrence and Characterization of Atmospheric Trace Gases in Dhaka City, Bangladesh" has been done by me. I further declare that this work has not been submitted anywhere for any academic degree or diploma.

Date: 14-01-2018

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CERTIFICATE

We have the pleasure to certify that the thesis titled "Occurrence and Characterization of Atmospheric Trace Gases in Dhaka City, Bangladesh" is an original research work by A.T.M. Mustafa Kamal for fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Soil, Water and Environment under the faculty of Biological Sciences, University of Dhaka, Dhaka 1000, Bangladesh. A.T.M. Mustafa Kamal successfully carried out his experimental work during the session 2102- 2013 under our supervision.

To the best of our knowledge no part of this thesis has been submitted elsewhere for any other degree or diploma.

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ABSTRACT

Trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) concentrations were measured at the Dhaka University campus by using automatic direct sense toxic gas monitoring instrument in Dhaka City, Bangladesh from June 2013 to May 2014. Measurements were also done at Karwan Bazar (highly traffic congested and commercial area), Dhaka City; Dhamrai (semi-urban area) in Dhaka district; Jamalganj (rural area) in Sunamganj district and a remote location at Badla Haor (haor area, seasonally submerged for 6 to 7 months) in Kishoreganj district for the comparison. The concentrations of the measured gases at Dhaka University campus varied both within the day and across the year (four seasons). The average concentrations of CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3 were 2603.6 ± 1216.4, 281.5 ± 158.0, 182.7 ± 69.4, 10,068.2 ± 5296.1, 36.6 ± 23.6, 133.8 ± 94.9, 84.8 ± 38.8, and 133.1 ± 37.7 $\mu g/m^3$, respectively in Dhaka City. The concentrations of the measured trace gases showed strong monthly and seasonal variations – (a) CO and NO concentrations were found the highest in winter, (b) TVOC, PH_3 and O_3 concentrations were the highest in monsoon, and (c) NO_2, H_2S and PH_3 concentrations were the highest in pre-monsoon season. The average hourly diurnal concentrations of the measured trace gases (CO and NO_2) were higher in the morning and evening hours due to the emission from a large number of vehicles and atmospheric processes. The diurnal concentrations of NH_3, PH_3 and H_2S were higher in the morning and it might be due to the release of these gases from communal wastes. Concentrations of total volatile organic compounds (TVOC) increased during the day time. From backward air mass trajectory analysis and wind rose plots of two seasons (monsoon vs. winter) indicated that air masses from the south and the southeast direction in monsoon had effects on decreasing the concentrations of most of the trace gases as they pass over the Bay of Bengal. On the other hand, air masses from the north, the northwest and the west direction in winter season had greater influence on the higher concentration of trace gases since they pass over the Indo Gangetic Plain. The ratios of the trace gases of two days (D_1, D_2) from two wind directions (D_1 from the Indo Gangetic Plain, D_2 from the Bay of Bengal) were 2.91 (CO), 1.71 (NO), 1.04 (NO_2), 0.4 (TVOC), 1.11 (O_3), 0.12 (H_2S), 1.08 (PH_3) and 1.85

(NH_3). Among measured gases, NO_2 concentration (182.7 μg/m^3) exceeded annual guidelines value of United States Environmental Protection Agency (USEPA), World Health Organization (WHO), European Union (EU) and Department of Environment (DoE), Bangladesh. Overall, the concentrations of the major trace gases (CO, NO, NO_2, H_2S and O_3) in the Dhaka City (Dhaka University campus and Karwan Bazar) were relatively higher than that of other places (Dhamrai, Jamalganj and Badla Haor) in Bangladesh. Positive matrix factorization (PMF 5.0) model was used to identify the source profile of NOx, TVCO and O_3 gases. Fossil fuel burning and atmospheric processes were identified as the largest contributors of NOx and O_3, while atmospheric process was exclusively recognized as the source of TVOC concentration. Since the atmosphere is a dynamic system, and the concentration of trace gases and their chemistry vary over time, it would need further research to form effective long-term air quality management strategies.

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INTRODUCTION

Atmospheric pollutions play an important role with regard to health effects, climate change, visibility reduction, atmospheric chemistry and agriculture (Mayer *et al*., 2000; Molina and Molina, 2004). Airborne particulate matters and trace gases have important implications through the inhalation, which can be deposited in the tracheobronchial and alveolar regions of the lung (Hileman, 1981). Air pollution is one of the major manmade environmental problems that have gained importance all over the world **(**Ahmed and Hossain, 2008**)**. Emissions of unwanted substances degrade the air quality from either direct emissions or through the production of secondary pollutants in the atmosphere (Schwela *et al*., 2006). Urbanization, industrialization and economic growth resulted in a profound deterioration of urban air quality **(**Wahid, 2006a, b**)**. Modernization and enhanced industrial activities led to the increased use of fossil fuels and their derivatives, particularly in the developing countries. Developing countries are confronted with the great challenge of controlling the air pollution, especially in the rapidly growing mega cities. Concern about air pollution in urban regions is receiving increasing importance worldwide (Salam *et al*., 2003).

A lot of sources (e.g., traffic, industries, construction activities, brick fields, biomass burning, uncovered soil surface, microbial processes, etc.) are responsible for air pollution. Thousands of people are suffering due to air pollution problems. About 7000/year cardiovascular mortality and 2100/year excess case of hospital admissions for chronic obstructive pulmonary disease (COPD) have been reported/ observed in Dhaka city from air pollution problems (Gurjar *et al*., 2010). Unfortunately, there is very limited information in Bangladesh about long term air quality measurements, except few campaign based studies in Bangladesh (Azad and Kitada, 1998; Begum *et al*. 2004; Begum *et al*., 2011; Salam *et al*., 2003; Salam *et al*., 2008; Salam *et al*., 2012). Large-scale emission of trace gases in the urban atmosphere is deteriorating the air quality in Bangladesh. The deteriorating air quality in urban areas is a result of rapid urbanization, tremendous rise in human population, increased industrial emissions and unprecedented growth of passenger and private vehicles (Button and Verhoef, 1998; Longhurst *et al*., 2003).

Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are major pollutants in the ambient atmosphere because of their adverse effects on vegetation and human health; and their contribution to acidification of environment (Legge and Krupa, 1990; Rodhe, 1989) and the role of NO_x in the formation of photochemical oxidants. Oxides of nitrogen (NO_x) contribute to the build-up of tropospheric ozone (O_3), which has potential in positive radiative forcing. Ozone (O_3) is a key precursor of the hydroxyl radical which controls the oxidizing power of the atmosphere (Thompson, 1992). High ozone concentrations have long been known to affect many physiological and biochemical characteristics (Reich and Amundson, 1985) as well as the growth and yield of agricultural crops (Chameides *et al*., 1999; Krupa *et al*., 1995) and natural vegetation (Hogsett *et al*., 1997). Ozone (O_3) is a reactive oxidant gas and its high dose has an adverse effect on human health (Miller, 1995). Hydrogen sulfide (H_2S) is a very poisonous, flammable gas with the characteristic foul odor of rotten eggs. Exposure to even lower concentration of H_2S can result in eye irritation, a sore throat and cough, nausea, shortness of breath, and fluid in the lungs in humans (Elson, 1996; Yu, 2001). Atmospheric NH_3 rapidly reacts with the H_2SO_3 or H_2SO_4 to form ammonium sulfate or ammonium bisulfate (Hobbs, 2000; Yu, 2001). Carbon monoxide (CO) is a toxic poisonous gas affecting human health. Volatile organic compounds (VOCs) work as precursor of photochemical smog reacting with oxides of nitrogen under sunlight. Most of the compounds of VOCs are recognized as carcinogenic to humans if people are exposed for a longer time in their life (Elson, 1996; Yu, 2001).

Dhaka, the capital city of Bangladesh, is a densely populated mega-city in the world. About 16 million inhabitants are living within an area of 390 square kilometers (Salam *et al*., 2011). It is expanding very rapidly due to high influx of people from all over the country. Air quality status of Dhaka has been degrading day by day due to increasing number of vehicles, severe traffic jams, brick kilns, chemical and other industries, construction activities, and also long range transport (Azad and Kitada, 1998; Begum *et al*., 2004; Salam *et al*., 2011). A rapidly growing number of vehicles have worsened the air quality in Dhaka, in spite of major policy interventions, e.g., ban of two-stroke three-wheeled vehicles, phase out of 20 years old vehicles, conversion to compressed natural gas (CNGs), etc. (Salam *et al*., 2011). In recent years, traffic jams in Dhaka city have significantly contributed to impair air quality. As brick is the main material for building construction in Bangladesh, a lot of brick fields are operating throughout the country as well as in and around Dhaka city, especially in the northwest and southeast side of the city, which is another major contributor to severe air pollution in winter season. Emissions from various kinds of ever growing industries in and around Dhaka contribute most of air pollution problems. Crude oil, fossil fuel, coal, natural gas, electricity, and biomass are used as the source of energy and hence emitting huge black carbon and organic carbon along with other gaseous pollutants (Salam *et al*., 2011). The adverse meteorological conditions in winter further aggravate this situation.

In Bangladesh, there is little information of trace gases to ascertain sources and their impact. Thus, this research work has been carried out to study the occurrence and characterization of atmospheric trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) in Dhaka City, Bangladesh.

Objectives of the research work:

- Measurements of the surface concentration of atmospheric trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) for four seasons in Dhaka City, Bangladesh to obtain information on the overall tends of trace gases as well their diurnal, monthly and seasonal variations.
- Analysis of transboundary air mass effects on the measured concentration of trace gases by backward trajectory analysis with Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (National Oceanic and Atmospheric Administration, NOAA).
- Utilization of Positive Matrix Factorization (PMF) model for the source profile analysis of certain trace gases.

CHAPTER TWO

LITERATURE REVIEW

CHAPTER TWO

LITERETURE REVIEW

2.1 Atmospheric Trace Gases

Atmosphere is a mixture of gases and suspended particulate matters that has surrounded the earth's surface. It is very important to life on the earth and does many things to help protect life, and help life to survive. The atmosphere is the air that plants, animals and human beings breathe to survive. It also contains suspended particulate matters (0.001-10 µm in diameter) and these are important contents of the lower atmosphere (i.e., troposphere). Dry air is mostly composed of nitrogen and oxygen (about 99% by volume) and other gases. Moisture content of the air is variable and it can contain as little as 0.01% and as much as 5% water vapor. The atmosphere has 3 categories of gaseous constituents depending on their contents/ concentrations - major, minor and trace. Major gaseous constituent include nitrogen (78.08%) and oxygen (20.95%) which is about 99% by volume of the total gas content. Minor constituents are argon (0.93%) and carbon dioxide (0.037%). The trace constituents of the atmospheric gas comprise the remaining gases whose individual share is very low (i.e., present in very small concentration), and are mostly expressed in terms of ppm by volume, ppb by volume and ppt by volume. Also, the unit of $\mu g/m^3$ is used. The significant trace gases in the atmosphere are neon (18 ppm), helium (5 ppm), Krypton (11 ppm), Xenon (0.90 ppm), methane (1.70 ppm), hydrogen (560 ppb), carbon monoxide (40 - 200 ppb), ozone (0 - 100 ppb), nitrous oxide (310 ppb) ammonia (0 - 0.5 ppb), hydrogen sulfide (0 - 0.5 ppb), sulfur dioxide (0.20 ppb), nitric oxide (0-300 ppt), nitrogen dioxide (0 - 300 ppt) etc. (Barry and Chorley, 2003). Among the gases, noble gases comprise minor (argon) and trace gases (neon, helium, krypton and xenon) which are very inert and do not generally engage in any chemical transformation within the atmosphere. Trace gases (except noble gases), despite their relative scarcity in the earth's atmosphere take part in different chemical reactions and play an important role with regard to health effects, climate change, visibility reduction, atmospheric chemistry and agriculture (Mayer *et al*., 2000; Molina and Molina, 2004).

The density/ concentration of the atmospheric gases decrease with increasing altitude, while the mixed content of nitrogen and oxygen maintains a constant proportion up to about 85 km above the surface. The trace constituents of the lower atmosphere/ troposphere especially carbon monoxide, ozone, nitrous oxide, ammonia, hydrogen sulfide, sulfur dioxide, nitric oxide, nitrogen dioxide, methane, non-methane hydrocarbon, etc. vary considerably due to their addition from both the natural and anthropogenic sources and removal physical and chemical processes (Barry and Chorley, 2003; Godish, 2004; Hobbs, 2000).

2.2 Air Pollution

The presence of one or more materials or contaminants (such as gas, dust, mist, odor, smoke or vapor) in the ambient atmosphere in quantities, of characteristics, and of duration so as to be injurious to human, plant or animal life or to property or which unusually interferes with the comfortable enjoyment of life and property is known as air pollution. When the rate of pollution exceeds the self-purifying capacity of the nature, accumulation of air pollutants takes place, and that may cause severe public and environmental health problems. United States Environmental Protection Agency (USEPA, 1999) defined air pollution as “the presence of contaminants or polluting substances in the air that interfere with the well-being and health of mankind or that produce harmful effects on the environment”. Air pollution refers to the introduction of physico-chemical or biological materials into the atmosphere that may cause harm or discomfort to humans or other living organisms, or deterioration of the natural environment. Any atmospheric condition in which substances (natural or man-made chemical compounds capable of being airborne) are present at concentrations high enough above their normal ambient level to produce a measurable effect on humans and environment are also termed air pollution. Air pollution is hazardous to human health at high concentrations and even can be fatal. The most important atmospheric trace gases of air pollutants are carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NOx), ozone (O_3) and hydrocarbons (HC). In the late 1970s, Environmental Protection Agency of USA added lead (Pb) to this list. Suspended particulate matters (SPM) with an aerodynamic diameter of less than or equal to 10 μm (PM_{10}) was added to the list in 1987, because $PM_{2.5}$ and PM_{10} have effects on human health and also have influences on atmospheric phenomenon (USEPA, 2015).

Air pollutants may enter directly into the atmosphere due to natural events or human activities and these types of pollutants are called primary pollutants, such as SO_2, CO, NOx, SOx, particulates, hydrocarbons, metals etc. Pollutants may also form in the atmosphere while primary air pollutants react with one another or with the basic components of air, and these types of pollutants are termed secondary air pollutants, such as O_3, other photochemical oxidants e.g., PANs, oxidized hydrocarbons. Air pollutants undergo several types of physical and chemical transformations and contribute to a wide range of health and environmental impacts, including deterioration of air quality, toxicological stress on human health and ecosystems, photo - oxidant formation (smog), stratospheric ozone (O_3) depletion, climate change and others (Pennington *et al*., 2004). Air becomes polluted when the concentrations of unwanted gases (CO, NOx, SOx, O_3, VOCs, etc.) and particulate matters (PM) exceed the air quality standards.

2.2.1 Sources of air pollution

Atmospheric trace gases are released both from the natural and anthropogenic sources (Godish, 2004). Air pollution occurs as a consequence of their emissions from natural processes and human activities. Thus, air pollutions are mainly:

(A) Natural air pollution

(B) Anthropogenic/ man - made air pollution

(A) Natural air pollution:

Natural processes that mostly contribute to natural air pollution are:

(a) Volcanic eruption
(b) Forest fire
(c) Storm dust
(d) Ocean spray
(e) Plant and animal decomposition
(f) Microbial processes
(g) Soil erosion and mineral weathering by wind
(h) Volatile hydrocarbons emitted by vegetation
(i) Emission of gases from soil and water surfaces

Some photographs of natural pollution are presented in the Figure 2.1.

Figure 2.1: Some photographs of natural sources of air pollution. (Source: Hoque and Salam, 2016; Mousume and Salam, 2017)

Natural air pollution may cause significant air quality problems when they are generated in significant quantities near human settlement. However, this type of pollution has relatively low significance in causing health and welfare effects, since:

(i) Levels of contaminants are typically very low;
(ii) Large distance from natural pollution sources to human settlements
(iii) Major natural pollutions are episodic and transient (short-lived).

(B) Anthropogenic air pollution:

Man seems capable of releasing - by accident or design - almost all known gaseous species and particulate matters to the atmosphere. Emissions of unwanted trace gases and airborne particulate matters from human activities (Figure 2.2) contribute a serious environmental and public health problem.

Figure 2.2: Photographs of man - made sources of air pollution. (Source: Hoque and Salam, 2016; Mousume and Salam, 2017)

Air pollutants that are emitted from a variety of sources due to human activities are listed below:

(a) Mobile sources: automobiles, trains, aircraft, ships, boats, off- road vehicles etc. due to uses of fossil fuels

(b) Stationary sources:

(i) **Stationary fuel combustion sources**: fossil fuel-fired electricity generating plants, industrial and institutional boilers, home space heaters, domestic cooking etc.

(ii) **Industrial sources**: mineral ore smelting, brick fields, petroleum refining, oil and gas production and marketing, chemical production, paint application, industrial organic solvent use, food processing, mineral rock crushing, construction activities

(iii**) Agricultural production sources**: livestock and paddy-rice production as well as other agricultural practices, destruction of forest, uncovered soil surface, etc.

(c) **Dispersed sources**: solid waste disposal and incineration in open air, biomass burning, etc.

(d) **Atmospheric sources**: production of secondary air pollutants from primary pollutants (man-made source) by atmospheric chemical reactions

2.3 Air Pollutants and their Effects on Human Health and Environment

Hundreds of air pollutants are emitted to the atmosphere. Some air pollutants are present in sufficient quantities in all ambient air especially in urban areas and have potential to threat human health and environment, if they exceed air quality standards. These air pollutants are known as criteria pollutant (WHO, 2006). There are six criteria pollutants and these are:

- CO
- NO_2
- O_3
- SO_2
- PM
- Lead

Other important air pollutants of environmental concern are:

- NO
- Volatile organic compounds
- H_2S
- NH_3
- PH_3

World Health Organization (WHO) also recognizes some air pollutants as carcinogens, such as acrylonitrile, arsenic, benzene, chromium, nickel, poly aromatic hydrocarbons (PAHs), vinyl chloride. The standards of criteria pollutants are set to uphold the air quality for urban dwellers, flora, fauna and materials of that environment. Gaseous pollutants also have major negative impacts on health. They also play an important role in environmental changes and changes in atmospheric chemistry. Effects of criteria pollutants on human health and environment are presented in Table 2.1. Also the effects of other important air pollutants of human health and environmental concern are presented in the Table 2.2.

Table 2.1: Effects of the criteria air pollutants on human health and environment.

Air pollutants	Health effects	Environmental effects
CO	Interferes with oxygen transportation to organs and tissues throughout the body. Thus, it reduces mental alertness, increases heart attack and cardiovascular diseases	Contributes to the formation of some secondary pollutants such as O_3.
SO_2	Causes eye irritation, wheezing, chest tightness, shortness of breath, lung damage.	Contributes to acid rain formation, plant and water damage, aesthetic damage.
NO_2	Increases respiratory diseases such as asthma, coughing, wheezing, shortness of breath	Contributes to the formation of photochemical smog, acid rain, visibility impairment.
O_3	Damages lung tissue, reduces lung function and aggravates asthmatic symptoms	Damages plant and ecosystem, (torpospheric O_3) has role in global warming
Pb	Causes of anemia, high blood pressure, brain and kidney damage, neurological disorders, cancer, lowered IQ	Affects animals and plants, aquatic ecosystems.
PM	Accumulates in the respiratory system and increases asthma, bronchitis and lung damage, and also increases cardiovascular effects leading to unexpected mortality,	Causes visibility impairment, atmospheric deposition, aesthetic damage

(Source: Godish, 2004; Hobbs, 2000; Manahan, 2000; Wayne, 2000)

Table 2.2: Effects of other trace gases on human health and environment.

Air Pollutants	Health effects	Environmental effects
NO	Increases respiratory diseases such as asthma, coughing, wheezing, shortness of breath	Contributes to the formation of photochemical smog, acid rain, visibility impairment
VOCs	Cause eye, nose and throat irritant, worsen asthmatic symptoms, decrease lung function, cause nausea and dizziness, damage kidney and liver (at chronic exposure to high levels of VOCs)	Takes part in the formation of photochemical oxidants, and increases oxidizing capacity of the air
NH_3	Irritants to nose and throat, aggravates asthmatic symptoms	Plays important role in removing SOx and NOx, reduces acid deposition
H_2S	Causes eye irritation, sore throat, coughing, and nausea, increases shortness of breath and fluid in the lungs	Contributes to the formation of SOx and acid formation
PH_3	Respiratory tract irritant , attacks primarily cardiovascular and respiratory systems causing peripheral vascular collapse and cardiac failure, and pulmonary edema	Ignites spontaneously on contact with air

(Source: Godish, 2004; Hobbs, 2000; Manahan, 2000; Wayne, 2000)

2.4 Ambient Air Quality Standards

The atmospheric condition in which substances exist at concentrations higher than the normal background levels or ambient levels is said to be polluted. Air pollution is a major environmental risk to health and is estimated to cause approximately 2 million premature deaths worldwide per year. Exposure to air pollutants is largely beyond the control of individuals and requires action by government bodies and public authorities at the national, regional, and even international levels. The objective of air quality maintenance is to maintain an atmosphere in which pollutants have no negative impact on humans and environment. WHO, for the first time, produced air quality guidelines (AQGs) in 1987 on reducing the health impacts of air pollution, especially criteria pollutants and then updated in 1997. In 2005, WHO recommended a revised limit for the concentrations of O_3, NO_2, SO_2 and particulate matter (PM), based on expert evaluation of scientific evidence (WHO, 2006). The new (2005) air quality guideline of WHO is applicable across all WHO regions (WHO, 2006). Bangladesh has also established an air quality standard to protect human health. Human health protection standards of WHO is also known as primary standards. Secondary standards are set to protect vegetation and other living organisms. WHO guideline standard versus Bangladesh urban ambient air quality standards (μg/m^3) for criteria pollutants are presented in the Table 2.3.

Table 2.3: Guideline standards of WHO versus national ambient air quality standards (NAAQS) for Bangladesh for criteria pollutants in urban area (μg/m^3).

Air Pollutants	Average time	WHO	DoE, BD
CO	15 minutes	100,000	
	30 minutes	60,000	
	1 hour	30,000	40,000
	8 hour	10,000	10,000
NO_2	1 hour	200	-
	annual	40	100
O_3	1 hour	-	235
	8 hour	100 - 120	157
SO_2	10 minute	500	100
	24 hour	20	365
PM_{10}	24 hour	50	150
	annual	20	50
$PM_{2.5}$	24 hour	25	65
	annual	10	15
Pb	Annual	0.50 - 1.00	0.5

(Source: WHO, 2006; DoE, 2016)

2.5 Air Quality Index

Air Quality Index (AQI) is an index number for reporting daily air quality. This is a simple way of describing the air pollution level in a particular area or region that can easily be understood by the public in general. AQI tells how clean or polluted the air is and whether it is healthy or not to breathe this air. AQI focuses on short term health effects that can happen within a few hours or days after breathing polluted air. This index is calculated by comparing the measured concentration of the major air pollutants with their respective health effect. In Bangladesh, the AQI is based on five criteria pollutants such as NO_2, SO_2, O_3, CO, and particulate matter (PM_{10} and $PM_{2.5}$). The Department of Environment (DoE) has also set national ambient air quality standards for these pollutants. These standards aim to protect against adverse human health impacts. AQI is a scale of numbers that runs from 0 to 500. Higher the AQI value, greater is the level of air pollution. For example, an AQI value less than 100 represents good air quality, while an AQI value over 100 represents poor air quality. The AQI scale is divided into six categories. A specific color is assigned to each AQI category (DoE, 2016). These categories are presented in the Table 2.4.

Table 2.4: Air quality index (AQI) for Bangladesh.

Air Quality Index (AQI) Value	Category	Color
0 - 50	Good	Green
51 - 100	Moderate	Yellow Green
101 - 150	Caution	Yellow
151 - 200	Unhealthy	Orange
201 - 300	Very unhealthy	Red
301 - 500	Extremely unhealthy	Purple

(Source: DoE, 2016).

AQI calculation

Concentrations of common air pollutants are measured at a Continuous Air Monitoring Station (CAMS). Each pollutant concentration is converted into an AQI number according to the US EPA methodology (USEPA, 1999, 2016).

AQI is calculated based on five major pollutants:

1. Ozone (O_3)
    - i) 1 - hour average ozone
    - ii) 8 - hour average ozone
2. Carbon monoxide (8 - hour average)
3. Sulfur dioxide (24 - hour average)
4. Nitrogen dioxide (24 - hour average)
5. Particulate Matter
    - i) $PM_{2.5}$ (24 - hour average)
    - ii) PM_{10} (24 - hour average)

AQI for a particular pollutant Ip is calculated using the following equation developed by USEPA (2016).

$$\mathrm{I_P} = \mathrm{I_{Lo}} + (\mathrm{C_P} - \mathrm{BP_{Lo}}) * (\mathrm{I_{Hi}} - \mathrm{I_{Lo}})/(\mathrm{BP_{Hi}} - \mathrm{BP_{Lo}})$$

Where,

Ip = The Index Value for Pollutant P

Cp = Concentration of Pollutant P

BPHi = The Break Point that is greater than or equal to Cp

BPLo = The Break Point that is less than or equal to Cp

IHi = The AQI value that is corresponding to BPHi

ILo = The AQI value that is corresponding to BPLo

2.6 Overview of Air Pollution in Dhaka City

Dhaka, the capital city of Bangladesh is situated between 23° 42' and 23° 54' North latitude and 90° 20' and 90° 28' East longitude (BBS, 2016). Over 16 million people are living within 390 square kilometers of Dhaka city and it is one of the most densely populated cities in the world (Salam *et al.*, 2011). According to the Far Eastern Economic Review, Dhaka will be the home of 25 million people by the year 2025

(Davis, 2006). Presently, more than half of the world's population is living in urban areas and about 70% will be city dwellers by 2050 (United Nations, 2014). Many of the urban centers are ever expanding, leading to the gradual growth of mega cities. The expansion of urbanization, industrialization and motorization with increasing population in Dhaka city (Zaman *et al*., 2010) has unexpectedly increased fossil fuel combustion, and urban infrastructure development, which are causing huge emission of pollutants into the ambient air (Sharma *et al*., 2014; Tie *et al*., 2006). Megacities are hotspots of atmospheric trace gaseous and particulate pollutants. The understanding of the air pollutants in urban areas remains complex being the diversity of their emission sources (unequally distributed in space and time) as well as their formation and transformation processes.

Dhaka city is congested with aging vehicle fleet, and the total number of motor vehicle is 1,739,357 (BBS, 2016). Moreover, operation of many factories, construction of roads and buildings are taking place continuously throughout the city (Zaman *et al*., 2010). There are four important sources of trace gases and aerosols into the atmosphere in the urban area and these are - (i) emissions from motor vehicles due to combustion and evaporation of automotive fuels (ii) emissions from industrial units, brick kilns and construction of buildings, infrastructure in and around urban area, (iii) emissions from domestic sources, and (iv) import of emissions through down winds (Andreae and Merlet, 2001; Khare, 2012). All of these are applicable for the Dhaka city. Motor vehicle discharge an appreciable amount of exhaust emission which consists of air pollutants such as carbon monoxide (CO), sulphur dioxide (SOx), nitrogen oxides (NOx), volatile organic compounds (VOCs), PM and lead (Pb) (WHO, 2006). Traffic congestion and low traffic speed increase fuel consumption and enhance emissions of carbon monoxide (CO) and volatile organic compounds (VOCs) per vehicle - km by 200% or more. The problems are common in the Dhaka city due to the inadequate road space, poor road conditions, indiscriminate use of speed breakers, water logging during monsoons, political or religious processions on busy roads, and encroachment of roads by pavement dwellers and street hawkers. Past studies showed that traffic congestion is the main reason behind the high level of pollutant concentrations at roadside of Dhaka city (Faiz *et al*., 1996). In the winter of 1996 - 97, air pollution in the city was most severe, when lead in the air was reported to be higher than in any other place in the world (Ahmed and Hossain, 2008). Sikder *et al*. (2010) observed the measurement of CO, O_3, NOx and O_3 in Dhaka city, and stated that all measured had peak in winter and base in monsoon period, and motorized vehicles and brick kilns were the main contributors of these gases (Begum *et al*. 2010). A study was conducted on air quality of Dhaka city in the year 2000, which revealed that traffic congestion, fuel quality and brick field emission are the main reasons of air pollution in Dhaka city (Begum, 2004). Salam *et al*. (2008) carried out a study on trace gases (SO_2, NO_2, CO and O_3) and aerosol particulate matter (PM_{10} and $PM_{2.5}$) at five locations in and around Dhaka city from January to April 2006, and found that the total average concentrations of SO_2 and NO_2 were much lower than the annual average guideline values of the World Health Organization. The total average O_3 concentration was also much lower than the daily maximum values established by WHO (average of 100 $\mu g/m^3$ for an 8-h sample).The vast majority of kilns used in Bangladesh is outdated and use energy-intensive technologies that are highly polluting (World Bank, 2011). The kilns are located in Keraniganj, Savar and Dhamrai of Dhaka district, Gazipur and Naraynganj clusters. Tanvir and Begum (2010) in their work revealed that air pollution level at traffic congestions considerably improved as was evidenced by the concentration level of CO within the limit of National Ambient Air Quality Standards for Bangladesh (DoE, 2016), but the concentrations of NOx in the ambient air exceeded the standard values. The PM_{10} level was alarming. Air pollution level at traffic congestions has considerably improved due to the large scale introduction of CNG vehicles in Dhaka city, introducing lead free petrol (from July 1999) (DoE, 2001) and banning 2-strokes 3-whleers within city limits (by January 01, 2003) (CAI-ASIA, 2008).

2.7 Air Pollution in Bangladesh

Bangladesh, with an area of about 147,570 square kilometers, is located in the tropics between $20^0$34' and $26^0$38' north latitudes and $88^0$1' and $92^0$41'' east longitudes in South Asia, is bounded by India on the west, north, and northeast, and Myanmar on the southeast as well as by the Bay of Bengal on the south (BBS, 2016). Bangladesh has been experiencing a phase of growth and economic development reflected by urbanization, industrialization, rise in income and motorized vehicle use. The continuing growth reflects ongoing migration from rural to the urban areas in search of better job opportunities and to gain access to urban amenities especially in Dhaka city, the capital of Bangladesh (Zaman *et al*., 2010). Dhaka is the center of economic, political, and cultural activities in Bangladesh. Chittagong, Khluna, Gazipur, Barisal, Narayangonj, Rajshahi and Sylhet are other biggest cities in Bangladesh. The expansion of urbanization, industrialization and motorization with population rise in urban areas unexpectedly increases fossil fuel combustion, and urban infrastructure development, which are causing huge emission of pollutants into the ambient air (Sharma *et al*., 2014; Tie *et al*., 2006).

Atmospheric trace gases with ambient fine particles are one of the challenging environmental issues in urban and industrial areas (Wang and Hao, 2012). The rate of increase of pollutant concentrations in the developing countries is higher than that in the cities of the developed countries (Begum *et al*., 2009). Excessive emissions are released by the vehicles if they are not well maintained and are not properly driven. This results in increase in fuel consumption, decrease in mileage, increased expense, wastage of precious fuel, and also the pollution of the environment. Emission from vehicles is a deadly mixture of poisonous gases and particulates which affects the human beings, vegetation, agriculture and buildings (Begum *et al*., 2009; Dockery and Pope, 1994; Prince and Ubokobong, 2014). All these affects have been associated predominately with criteria pollutants that are routinely measured to assess air quality in most cities around the world. About 1200 brick kilns are operating around Dhaka city. Brick making kilns operate in dry season all over Bangladesh. This industry emits huge amounts of gases and PM (Begum *et al*., 2006; Begum *et al*., 2009). The air pollution situations in Dhaka city have been explained in the section 2.6. Some research works were done about air pollution level in Dhaka city. There is little research work on other urban areas in Bangladesh. The concentrations of $PM_{2.5}$ and PM_{10} in the air of Pabna, Bangladesh were investigated in five locations and found that PM concentrations in Pabna were higher than the ambient air quality standards in Bangladesh. Brick kiln emission, minibus and long range transports were the sources of particulate matter in Pabna (Hasan *et al*., 2016).

Biomass burning at the cooking stoves for daily meal preparation in the suburban and rural areas is one of the largest contributors to the air quality in Bangladesh. About 70% of the rural people in Bangladesh are using cow dung, woods, dry leaves, rise husk and straw, jute stick, bamboos in the cooking stoves. Indoor air pollution in rural areas is mainly associated with the use of biomass fuels during cooking with poor ventilation (Sarkar *et al*., 1998).

2.8 Air Quality Monitoring and Regulation in Bangladesh

Air pollution has adverse impacts on human health, material, agricultural production, ecosystems and regional and global climate, thus adversely affecting quality of life and economic output. The air quality monitoring, management and regulation in Bangladesh is relatively recent one. Ambient air quality standards of Bangladesh were first familiarized in 1997 under the environmental conservation rules (ECR) 1997. The Air Quality Management Project (AQMP) was the first major project towards air quality management in Bangladesh, and it was implemented by the Department of Environment (DoE) during 2000-2007 with support from the World Bank. The objectives of the AQMP were to reduce vehicular emissions in the metropolitan areas, setting standards, enforcing pilot programs towards cleaner technologies, as well as implementing air quality monitoring and evaluation. Other important projects taken towards air quality management included certain component of the clean and sustainable environment (CASE) Project supported by the World Bank. The overall objective of the CASE project is to introduce Sustainable Environment Initiatives (SEIs) in vital polluting sectors such as urban transport and brick making with a focus to abate air pollution and generate co-benefits through introducing energy efficient technology in brick sector and lay the foundation of introducing mass transit projects such as Bus Rapid Transit in Dhaka (DoE, 2012).

Air quality monitoring is the key to understand and develop strategies for reducing air pollution. In 2002, a continuous air quality monitoring station (CAMS) was first established at the premise of the national parliament building (the Jatiyo Sangsad) under AQMP and then another CAMS was set up in Bangladesh Agricultural Research Council (BARC), Farmgate, Dhaka (DoE, 2012). Since 2006, other continuous air quality monitoring stations (CAMS) were set up in Chittagong, Rajshahi, Khulma, Barisal, Narayanganj and Gazipur in view of rising air pollution in these cities under the clean and sustainable environment (CASE) Project (DoE, 2016). The CAMS provides continuous measurement of CO, NOx, SO_2, O_3, non-methane hydrocarbons and meteorological parameters. Batch sampling of PM_{10} and $PM_{2.5}$ is also carried out in parallel. The findings of the AQMP then led to the revision of ambient air quality standards for Bangladesh in July 2005 (DoE, 2012).

Bangladesh has set an ambient air quality standard and a number of specific strategies were undertaken in order to reduce the concentration of the criteria air pollutants. Lead (Pb) was an important air pollutant in the urban cities of Bangladesh due to the use of leaded fuels. High concentrations of Pb in blood and in ambient air were identified from motorized vehicle sources. Lead emissions in the 1980s and 1990s received much attention from national and international media. This resulted in the government decision to phase out Pb from petrol in the mid -1990s. By 1998, Pb content in petrol was dropped down to 0.4 g/L from a high value of 0.8 g/L in 1980. Regular petrol was made free of Pb by 1998, while the remaining Pb from premium petrol (locally known as octane) was made Pb free on July 1, 1999. To mitigate this problem, phasing out of Pb from fuels was one of the major decisions towards air pollution regulation in Bangladesh (DoE, 2012). Two-stroke three-wheeled baby taxis were identified as a major source of PM and other criteria pollutants emissions in Dhaka city due to their incomplete and inefficient combustion mechanism. The Government of Bangladesh banned the use of two-stroke three-wheelers in Dhaka from January 1, 2003 (Begum *et al*., 2006). Around 12,000 existing two-stroke baby taxis were replaced by 9,000 new four-stroke CNG baby taxis. The air quality at various locations in Dhaka improved significantly due to the banning of two-stroke three-wheelers in Bangladesh and then in Chittagong city (DoE 2012). Compressed natural gas (CNG) used in vehicles as fuel has multiple environmental benefits in reducing criteria air pollutant emissions and improvement of local air quality, reduction in greenhouse gas emissions and improving financial benefit due to local production of natural gas. All of these benefits encouraged the Government of Bangladesh in 2002 to endorse conversion of petroleum vehicles to run on CNG. The ambient PM concentration remained stable for the past few years despite a significant growth in vehicle numbers in Dhaka, indicating the success of CNG conversion in mitigating air pollution. Moreover, CNG run vehicles have a lower operating cost per km, and therefore, more converted CNG vehicles run than the original petrol vehicles (DoE, 2012). The older buses and trucks run primarily on diesel with no emissions mitigation technologies and banning them could have significant air quality benefits. Old vehicles were responsible for a disproportionately larger amount of emissions from motor vehicles. In 2002, rules were proposed to ban buses older than 20 years or trucks older than 25 years from Dhaka city (DoE, 2012). Almost all of the personal vehicles plying in the streets in Bangladesh are reconditioned vehicles, imported from Japan, although new vehicles are slowly emerging. Government of Bangladesh has banned the import of vehicles older than 5 years, and also reduced import duties on newer vehicles. New vehicles generally have better emissions performance. Bangladesh had a vehicle emissions standard since 1977, which was strengthen in 2005 to correspond to Euro 2 standards. The standards are legally binding, and any vehicle fails to meet the emissions standard is theoretically barred to ply on the roads. Bangladesh Road Transport Authority (BRTA) is an organization, which is responsible for issuing vehicle 'fitness' certificate. Since Bangladesh imports vehicles from Japan, it is easy to adopt Japanese standards (or Euro) (DoE, 2012). Industrial sources are gradually being regulated. There are a number of emissions standards regulations about pollutant emissions to the ambient air from various sources. In addition to motor vehicles, these emissions standards cover brick, cement, fertilizer, power plant and sugar industries. In 2013, the Government of Bangladesh passed the brick manufacturing and brick kilns establishment (control) act to establish control over brick manufacturing and brick kilns. This act came into force from 1st July 2014, and permitted two years' time limit to convert the brick kilns into modern technology and relocate them (Shams, 2017).

Bangladesh has adopted an air quality index (AQI) to be used for increasing the awareness of public on the quality of air they breathe (DoE, 2012; DoE, 2016). The AIQ for Bangladesh is primarily based on USEPA's system but with some modification. It is an index number for reporting daily air quality. This is a simple way of describing the air pollution level in a particular area or region that can easily be understood by the public in general. AQI tells how clean or polluted the air is in breathing and whether it is healthy or not to breathe this air. AQI focuses on short term health effects that can happen within a few hours or days after breathing polluted air. This index is calculated by comparing the measured concentration of the major air pollutants with their respective health effect. These pollutants are NO_2, SO_2, O_3, CO, and particulate matter (PM_{10} and $PM_{2.5}$).

2.9 Descriptions of Some Important Atmospheric Trace Gases

The concentrations of the atmospheric gases varied both horizontally and vertically. The trace constituents of the lower troposphere especially carbon monoxide, ozone, nitric oxide, ammonia, hydrogen sulfide, sulfur dioxide, nitric oxide, nitrogen dioxide, methane, non-methane hydrocarbon, etc. vary considerably due to their addition from both the natural and anthropogenic sources and removal by physical and chemical processes (Barry and Chorley, 2003; Godish, 2004; Hobbs, 2000;). A description of the following important trace gases regarding this research interest is presented in the sub - sequent subsections:

(1) Carbon monoxide (CO)
(2) Nitric oxide (NO)
(3) Nitrogen dioxide (NO_2)
(4) Total volatile organic compound (TVOC)
(5) Ozone (O_3)
(6) Ammonia (NH_3)
(7) Hydrogen sulfide (H_2S)
(8) Phosphine (PH_3)

2.9.1 Carbon monoxide (CO)

Carbon monoxide is an important atmospheric constituent affecting air quality, human health and climate (Buchwitz *et al.*, 2006). It is a colorless, odorless, tasteless, non-irritating (at low concentration) and poisonous (at high concentration) gas which is formed when carbon in fossil fuel and biomass is not burned completely (incomplete oxidation). The major sources of CO emission are from fossil and biofuel combustion, biomass burning, and oxidation of hydrocarbons [methane (CH_4) and non-methane hydrocarbons (NMHCs)] and organic compounds (Crutzen and Andreae, 1990; Logan *et al.*, 1981,). The largest contributors of CO are motor vehicle exhaust, industrial processes (chemical and metallurgical) and open burning activities (Buchwitz *et al.*, 2007; Theodore, 2008). The situation becomes worsen for the countries/ regions with the intensive fuel consumption and the increasing energy demand. The primary natural source is oxidation of methane (20 - 50%) with the remainder from oxidation of other carbohydrates and from oceans. This gas is an important source for local and regional air pollution. It has an average lifetime of 2 - 4 months in the atmosphere (McMillan *et al*., 2005).

The highest levels of CO in the ambient air usually occur during the colder months of the year when inversion conditions are more frequent. The air pollution becomes trapped near the ground beneath a layer of warm air (Badarinath *et al*., 2007). Globally, about 50% of CO emission comes from anthropogenic sources while the remainder is coming from biomass burning and oxidation of naturally occurring volatile hydrocarbons such as CH_4 and isoprene (McMillan *et al*., 2005; Seinfeld and Pandis, 2006). Biomass burning is responsible for about one quarter of CO emission to the atmosphere and its concentrations in the Northern Hemisphere are much higher than in the Southern Hemisphere because human population and industry are much greater (Liu *et al*., 2005). In the Southern Hemisphere, on an average over 50% of atmospheric CO is indirectly sourced from oxidation of CH_4 and volatile organic compounds (VOCs) (Logan *et al*., 1981).

Carbon monoxide has adverse effects on the heaths of humans and animal (WHO, 1999). It binds strongly to hemoglobin in red blood corpuscles resulting in the production of carboxyhemoglobin. This impairs the transport of oxygen within the blood and can result in adverse effects on tissues with high oxygen needs such as the cardiovascular and nervous systems. A recent study has shown that chronic exposures to CO may cause adverse birth outcomes such as reduced birth weight and intrauterine growth retardation (Salam *et al*., 2005). The levels of normal carboxyhemoglobin in an average person are less than 5%, whereas cigarette smokers (two packs/day) may have to levels up to 9% (Delaney *et al*., 2001). It also involved in producing harmful tropospheric ozone which moreover affects human health and crop yield (Buchwitz *et al*., 2006).

Carbon monoxide is mainly lost by reaction with the OH radical (the most abundant cleaning agent in the atmosphere) (Duncan *et al*., 2007; Holloway *et al*., 2000; Logan *et al*., 1981), absorption by some plants and microorganisms and washout by rain. It is not a significant greenhouse gas because of its weak absorption of terrestrial infrared radiation. It acts as an important indirect source of greenhouse gases, because it has significant influence on the budgets of hydroxyl radicals (OH•) and thus indirectly affects the concentrations of CO_2 and ozone (O_3). Hydroxyl (OH) radical is available in abundant quantities in the lower atmosphere (Wayne, 2000) and a larger fraction of it is used to oxidized CO into CO_2 (a greenhouse gas) and also to produce hydrogen atom (H).

$$OH\bullet + CO \rightarrow CO_2 + H$$

The H atom reacts rapidly with O_2 to produce HOO• radical.

$$H + O_2 + M \rightarrow HOO\bullet + M$$

Net reaction: $CO + HO\bullet + O_2 + M \rightarrow CO_2 + HOO\bullet + M$

The HOO• radical then reacts with NO• to generate $NO_2\bullet$ and HO• radical.

$$HOO\bullet + NO\bullet \rightarrow NO_2\bullet + HO\bullet$$

In turn, $NO_2\bullet$ photolyzes [$NO_2\bullet + h\nu$ ($\lambda < 420$ nm) $\rightarrow NO\bullet + O$] again to produce NO• and O, and subsequently, the O produced reacts with molecular oxygen (O_2) to form O_3 molecule (a greenhouse gas).

$$O_2 + O + M \rightarrow O_3$$

It is about 75 % of OH• sinks, which is capable to influence the concentration of greenhouse gases and finally contributes to climate change (Daniel and Solomon, 1998). Although it does not have a direct greenhouse effect like methane and carbon dioxide, its role in atmospheric chemistry is estimated to cause an indirect radiative forcing of 0.23 (0.18–0.29)W/m^2 (IPCC, 2013).

Bangladesh is experiencing a severe air pollution problems, because of increasing anthropogenic emissions associated with biogenic emissions from different sources. Maximum air pollutant levels occurs over South Asian subcontinent in the late months of dry season due to strong regional biomass burning and long-range transport of air masses from the western Asia and Middle East. The tropical biomass burning in South and Southeast Asia is a major source of atmospheric pollutants and strongly influenced by anthropogenic post - agricultural waste burning (Pochanart *et al*., 2003). Andreae and Merlet (2001) estimated the annual emission of CO from vegetation fires in tropical forests and savannas which is 342 Mt (1 Mt = 109 kg) CO per year, while the total CO emission for all non-tropical forest fires is 68 Mt CO per year. A concentration of as little as 400 ppm (0.04%) CO in the air can be fatal.

2.9.2 Nitric oxide (NO)

Nitric oxide is a colorless, odorless, tasteless and relatively nontoxic gas. It is a primary pollutant. It is produced naturally in soil through biological nitrification, denitrification and chemodenitrification processes (Williamas *et al.*, 1992) and as a result of biomass burning, lightning, and oxidation of NH_3 by photochemical reaction (Godish, 2004). Nitric oxide is produced anthropogenically in high-temperature combustion processes of N_2 and O_2 or though combustion of the nitrogen content of the fuel.

$$N_2 + O_2 \rightarrow 2NO$$

The above reaction is endothermic and thus, equilibrium moves to the right at high temperatures and to the left al low temperature. If cooling of NO through emission is rapid, equilibrium is not maintained and significant NO emissions occur. High combustion temperature and rapid cooling are associated with gas flows from chambers, and instantaneous dilution contributes to high NO emissions (Jacob, 1999; Godish, 2004). Major anthropogenic sources of NO include gas- and diesel-powered vehicles, fossil fuel-fired electricity generating stations, industrial boilers, municipal incinerators, and home space heating.

Nitric oxide and NO_2 along with other N-containing compounds are emitted to the atmosphere from both the natural and anthropogenic sources. The sum of NO and NO_2 is called NOx. Light-duty vehicles emit NOx mostly in the form of NO, but diesel vehicles tend to emit higher NO_2 fractions (Carslaw, 2005; Herner *et al.*, 2009; Heywood, 1988; Lloyd and Cackette, 2001). Additionally, catalytic converters used in heavy-duty diesel trucks convert much of the NO to NO_2 during combustion process. This exhaust is used to oxidize soot particles and continuously clean particle filters, and partially converting the NO_2 back to NO (Herner *et al.*, 2009; Van Setten *et al.*, 2001).

In the atmosphere, NO is also formed from the photo-dissociation of NO_2 and $NO_3•$ radical:

$$NO_2 + h\nu\ (280\text{-}\ 420\ nm) \rightarrow NO + O$$

$$NO_3• + h\nu\ (\lambda < 700\ nm) \rightarrow NO + O_2$$

Nitric oxide released from both the anthropogenic and natural sources is a significant contributor to the NOx mixing ratio in the atmosphere and may directly be involved in influencing the oxidizing capacity of the atmosphere. NO is oxidized to nitrogen dioxide (NO_2) in the atmosphere on reaction with HOO• or other peroxy radicals, and it is the primary chemical removal process of NO. It (NO) may directly be involved in the production of HO• in daytime, thus stimulating the oxidizing capacity of the atmosphere (Delon *et al.*, 2008; Steinkamp *et al.*, 2009).

$$NO + HOO\bullet \rightarrow NO_2 + OH\bullet$$

$$ROO\bullet + NO \rightarrow NO_2 + RO\bullet$$

$$RC(O)OO\bullet + NO \rightarrow NO_2 + RC(O)O\bullet$$

Nitric oxide reacts with ozone (O_3) to produce NO_2. It locally titrate ozone (O_3) via the following reaction to form NO_2. At night, NO is also converted to NO_2 by reacting with O_3 molecule.

$$NO + O_3 \rightarrow NO_2 + O_2$$

Nitric oxide can be converted to NO_2 by a relatively slow, direct oxidation reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

Nitric oxide is a reactive gas that plays an important role in the atmospheric chemistry by influencing the production [$NO + O_3 \rightarrow NO_2 + O_2$, $NO_2 + hv\ (\lambda \leq 420\ nm) \rightarrow NO + O$, $O_2 + O + M \rightarrow O_3 + M$] and destruction of ozone [$O_3 + NO \rightarrow NO_2 + O_2$], and thereby the oxidizing capacity of the atmosphere (Godish, 2004; Hobbs, 2000; Wayne, 2000). It also contributes by its oxidation products to the formation of acid rain (especially at night).

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O_3 \rightarrow NO_3\bullet + O_2$$

$$NO_3\bullet + NO_2 + M \rightarrow N_2O_5 + M$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Nitric oxide (NO) concentrations peak maximizes during the early morning (6 to 9 a.m.) in the urban areas, and then depletes rapidly by oxidation to NO_2. Nitric oxide concentration is not generally reported separately from that of NO_2.

2.9.3 Nitrogen dioxide (NO_2)

Nitrogen dioxide (NO_2) is a colored gas that varies from yellow to brown depending on its concentration in the atmosphere. It has pungent and irritating odor; and is relatively toxic and corrosive due to its high oxidation potential. It has effects on human health, if it exceeds health based standard. Long-term exposures to this irritant gas may reduce immunity and lead to respiratory infections. Nitric oxide and NO_2 along with other N-containing compounds are emitted to the atmosphere from both the natural and anthropogenic sources. Reactive nitrogen is largely emitted as NO by anthropogenic sources and then oxidized quickly to NO_2 (Stehr *et al*., 2000). Both NO and NO_2 are subjected to chemical transformation in the atmosphere from one form to another. Anthropogenic NOx (= NO + NO_2) is produced in high-temperature combustion processes of N_2 and O_2 or though combustion of the nitrogen content of the fuel (Hoobs, 2000; Wayne, 2000). NO is the principal product of this process along with NO_2 and other gases.

$$N_2 + O_2 \rightarrow 2NO$$

Major anthropogenic sources of NOx include gas- and diesel-powered vehicles, fossil fuel-fired electricity generating stations, industrial boilers, municipal incinerators, and home space heating. Light-duty vehicles emit NOx mostly in the form of NO, but diesel vehicles tend to emit higher NO_2 fractions (Carslaw, 2005; Herner *et al*., 2009; Heywood, 1988; Lloyd and Cackette, 2001). Moreover, catalytic converters are used in heavy-duty diesel trucks which significantly increase NO_2 emission through the oxidation of NO with excess oxygen in the exhaust. Furthermore, this exhaust (NO_2) is used to oxidize soot particles in combustion chamber and continuously clean particle filters, partially converting the NO_2 back to NO (Herner *et al*., 2009; Van Setten *et al*., 2001) and thus, reduces the direct emission of NO_2.

Upon released into the troposphere, nitric oxide (NO) (primary pollutant) reacts rapidly with the molecular oxygen (O_2) to form nitrogen dioxide (NO_2) (secondary pollutant), a yellowish-brown gas with a choking odor.

$$2NO + O_2 \rightarrow 2NO_2$$

The NO_2 gas is responsible for the brownish haze that hangs over many cities during afternoon of sunny days. Thus, photochemical smog is sometimes called brown-air smog. It is also called Los Angeles smog, because such smog in 1944 caused most severe air pollution in Los Angeles city and thus, named (Hobbs, 2000).

Nitrogen dioxide is also produced more rapidly, primarily by photochemical oxidation of NO with O_3, ROO• and odd hydrogen species (HO•, HOO•, H_2O_2, etc.)

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(both day and night)}$$

$$ROO\bullet + NO \rightarrow NO_2 + RO\bullet$$

$$HOO\bullet + NO \rightarrow NO_2 + HO\bullet$$

$$RC(O)OO\bullet + NO \rightarrow NO_2 + RC(O)O\bullet$$

Nitric oxide can locally titrate ozone (O_3) via the reaction to form NO_2.

$$NO + O_3 \rightarrow NO_2 + O_2$$

At night, NO is converted to NO_2 by reacting with O_3 molecule.

$$NO + O_3 \rightarrow NO_2 + O_2$$

In the morning, both N_2O_5 and $NO_3\bullet$ compounds rapidly photolize to give the troposphere a morning boosts of NOx.

$$N_2O_5 + h\nu \rightarrow NO_3\bullet + NO_2$$

$$NO_3\bullet + h\nu \rightarrow NO + O_2 \,/\, NO_2 + O$$

In the upper troposphere, NO_2 is produced from HNO_3 by photolysis.

$$HNO_3 + h\nu \rightarrow NO_2 + HO\bullet$$

Nitrogen dioxide can also be produced from NO by a relatively slow, direct oxidation reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

Nitrogen dioxide is an important atmospheric trace gas since (i) it absorbs visible solar radiation and contributes to impaired atmospheric visibility; (ii) as an absorber of visible radiation it could have a potential direct role in global climate change if its concentrations become high enough; (iii) it is, along with nitric oxide (NO), a chief regulator of the oxidizing capacity of the free troposphere by controlling the build-up and fate of radical species, including hydroxyl radicals; and (iv) it plays a critical role in determining ozone (O_3) concentrations in the troposphere, because the photolysis of

NO_2 is the only key initiator of the photochemical formation of O_3 both in polluted or unpolluted atmospheres (Wayne, 2000).

Nitrogen dioxide involves in different chemical and photochemical reactions that convert NO_2 to other N-Compounds. In daytime, NO_2 is oxidized by HO• radical to produce HNO_3.

$$NO_2 + HO\bullet + M \rightarrow HNO_3 + M$$

$$RC(O)OO\bullet + NO_2 \rightarrow RC(O)OONO_2 \text{ (at low temperature)}$$

At night, NO_2 is converted to HNO_3 by reactions involving O_3.

$$NO_2 + O_3 \rightarrow NO_3\bullet + O_2$$

$$NO_2 + NO_3\bullet + M \rightarrow N_2O_5 + M$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

In daytime, NO_2 is also oxidized by HO• radical to produce HNO_3.

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

Nitrogen dioxide can be absorbed in water droplets.

$$NO_2 + H_2O \rightarrow 2H^+ + NO_3^- + NO_2^-$$

Nitrogen dioxide (NO_2) is an odd-electron molecule and thus can act as a free radical. It is already a problem for many cities due to its toxicity and key role in the formation of tropospheric ozone (Seinfeld and Pandis, 2006). The NO_2 to NOx emissions ratio affects ozone production and spatial distribution (Heeb *et al.*, 2010). O_3 is a secondary pollutant formed in the troposphere from NO_2 photolysis that produces oxygen atom. If NOx is emitted as NO, it will locally titrate ozone via the following reaction and must react with a species (e.g., ROO•, HOO•, H_2O_2) other than O_3 to form NO_2 before net ozone production can occur.

$$NO + O_3 \rightarrow NO_2 + O_2$$

However, direct NO_2 emission is immediately available for ozone production via the photolysis of NO_2 as per following reactions

$$NO_2 + h\nu \text{ (280- 420 nm)} \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

This pathway results in ozone (O_3) production closer to the NOx emission source and a higher final O_3 concentration later takes part in oxidation of all the emitted NOx.

Nitrogen dioxide concentration measurement was carried out at Dayalbagh, a suburban site and at St. John's, an urban site at Agra (India) by Kumar *et al*. (2004) which showed that seasonally highest concentrations of NO_2 were observed during winter and lowest during monsoon. This is because of high fuel usage during winter. Also, during winter months, the pollutants emitted from various anthropogenic and natural sources are trapped in the boundary layer due to frequent temperature inversions.

Adon *et al*. (2016) observed higher concentration of NO_2 in the dry season (35.4 ppb) and lower concentration in the wet season (24.1 ppb) during the period of January 2008 to December 2009 at Dakar, Senegal. And also explained that intense urban traffic with aged vehicle and the predominant use of diesel at Dakar could be the reason of high levels of NO_2 concentrations.

2.9.4 Total volatile organic compound (TVOC)

Total volatile organic compounds (TVOC) consist of various classes of carbon-containing organic compounds that under normal temperature and pressure quickly evaporate into the atmosphere once emitted. Volatile organic compounds (VOC) include non-methane hydrocarbons (NMHC), oxygenated NMHC (e.g., alcohols, aldehydes and organic acids), aromatic hydrocarbons and halogenated hydrocarbons. They have fractions of a day to months of atmospheric lifetime (Matsumoto *et al*., 2010; You *et al*., 2007).

Volatile organic compounds are released into the environment from both the natural and anthropogenic (man-made) sources. They can originate from natural sources such as fossil fuel deposits (e.g., oil sands), and can be emitted from volcanoes, vegetation, oceans and biological processes. Vegetation is the largest natural source of VOCs emission. Isoprene has the largest emission rate and is only emitted during plant photosynthesis (Lerdau and Keller, 1997). Natural emissions occur predominantly in the tropics (23°S to 23°N).

Man-made VOCs are characteristically petroleum-based and are a major component of gasoline. In this condition, VOCs are emitted through gasoline vaporization and vehicle exhaust (Cetin *et al*., 2003; Nguyen *et al*., 2009). Burning of fuels such as gasoline, wood, coal or natural gas can also release VOCs. Major sources of VOCs include emissions from combustion, biomass burning, vehicles, industrial production processes and biological processes (Parra *et al*., 2006). Volatile organic compounds are used in solvents and can be found in paints, paint thinners, varnish thinners, air fresheners, wood preservatives, dry cleaning fluids, cleaning solutions, adhesives, inks, and sometimes in pesticides. Pesticides containing solvents normally release higher levels VOCs. The active component in certain pesticides may also contain VOCs. Solid formulations release the lowest amount. Anthropogenic emissions of most VOC have increased since pre-industrial times due to increased use of gasoline and other hydrocarbon products. The amount of VOCs release in an urban area increases with its urbanization, and also the amount of VOCs ingresses from surrounding areas (due to industrial production processes, biological processes, agricultural activities and natural plant growth). Trees produce different types and amounts of VOCs through a variety of processes such as release from leaves, decomposition of organic matter by anaerobic bacteria. In urban areas, nearly 60% of the non-methane VOC mass consists of Benzene, Toluene, Ethylbenzene and Xylene which are released from traffic sources (Hoque *et al*., 2008; Liu *et al*., 2009). Although anthropogenic VOC pollution is a problem, about 74% of VOC emissions in the US are from natural biogenic emissions. The variability in VOC concentration levels is controlled by a combination of factors including source strengths (e.g., emissions), dispersion and dilution processes as well as photochemical reaction rates with OH radicals and other oxidants (Filella and Peñuelas, 2006).

Volatile organic compounds are important fraction of air pollution. They have harmful effects on human health and welfare (Hunt *et al*., 1986; Tam and Neumann 2004).The harmful effects of exposure to VOCs vary depending on the specific compounds - ranging from no effects to highly toxic effects. This variance is related to the nature of the VOC, the level of exposure to the VOC, and the length of exposure to the VOC. With short-term exposure, the consequences can be eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment. Long-term contact with VOCs can damage the liver, kidneys and central nervous system. Some VOCs (e.g., benzene) are hematotoxic, neurotoxic, leukemogenic, mutagenic and carcinogenic (Sun *et al*., 2010; Whaysner *et al*., 2004).

Volatile organic compounds (VOCs) have great scientific interest because they influence climate through their production of organic aerosols and also their involvement in photochemistry, i.e., production of O_3 in the presence of NO_x and light (Chiang *et al*., 2007; Louie *et al*., 2013; Monod *et al*., 2001).

$$ROO + NO \rightarrow NO_2 + RO$$

$$RC(O)OO + NO \rightarrow NO_2 + RC(O)O$$

$$NO_2 + h\nu\ (<420\ nm) \rightarrow NO + O$$

$$O_2 + O \rightarrow O_3$$

Volatile organic compounds can also form organic nitrates, oxidized hydrocarbons, peroxyacyl nitrates and peroxy benzoyl nitrates (PBN) by photochemical oxidation (Ng *et al*., 2007; Pachauri *et al*., 2013), which has significant adverse effects on human health (Hou *et al*., 2015; Zhang *et al*., 2012).

$$R(CO)OO\bullet + NO_2 + M \rightarrow R\text{-}(CO)\text{-}OO\text{-}NO_2 \text{ (peroxyacyl nitrates, PANs)]} + M$$

The seasonal variation of VOCs was measured in urban area of Dallas, USA from 1996 to 2004 (Qin *et al*., 2007), where the time series of anthropogenic hydrocarbons emission showed an obvious seasonal cycle with relatively high concentration in winter and low concentration in summer, which was connected with source emissions and meteorological conditions. The rapid growth of vehicle population and energy consumption had also greatly aggravated the levels of atmospheric pollutants in recent years (Lang *et al*., 2012).

Baudic *et al*. (2016) studied the seasonal variability of atmospheric VOCs and their various associated emission sources in the French megacity. The largest contributors to the VOC concentrations were traffic-related activities (including motor vehicle exhaust, 15% of the total mass on the annual average, and evaporative sources, 10%), with the remaining emissions from natural gas and background (23%), solvent use (20%), wood-burning (18%) and a biogenic source (15%). Wood-burning, especially in winter represents up to about 50% of the total mass of VOCs. Biogenic emissions also unexpectedly contributed up to about 30% in summer. The mixed natural gas and background source exhibited a high contribution inspiring (35%, when continental air influences were observed) and in autumn (23%, for home heating consumption).

The concentrations of VOCs in the atmosphere in Hong Kong were mainly affected by direct emissions from vehicles, evaporation of fuels, photochemical reactions and few industrial emissions. Ho *et al*. (2004) measured ambient VOCs concentration at three locations [PolyU campus (PU), Kwun Tong (KT), HokTsui (HT)] in Hong Kong during the periods of November 2000 - February 2001 and June 2001 - August 2001 and observed higher VOCs concentration in summer than in winter at the PU station, which was close to a main road. Regional physical dispersion/ transportation and mixing depth may be the reasons for higher VOC concentrations in winter at HT. Volatile organic compound removal is faster in summer than in winter as more sunlight and higher temperatures produce higher chemical removal reaction rates. Therefore, the winter VOC concentrations were higher than those in the summer, as found in many other cities (Hartwell *et al*., 1987; Wathne, 1983).

2.9.5. Ground level ozone (O_3)

Ozone is a triatomic molecule, consisting of three oxygen atoms. It is pale blue gas and slightly soluble in water. Ozone (O_3) is a trace gas of secondary origin which produces in the troposphere by photochemical reactions from its precursor gases - nitrogen oxides (NOx) and non-methane volatile organic compounds (including alkanes, alkenes, aromatics and multifunctional compounds), methane (CH_4) or carbon monoxide (CO) in the presence of sunlight (Atkinson, 2000; Chameides and Walker, 1973; Monks *et al*., 2009; Zhang *et al*., 2008). O_3 is also supplied to the troposphere by transportation from the stratosphere (relatively minor source) (Hocking *et al*., 2007; Lefohn *et al*., 2011).

Ground level ozone (O_3) is an important reactive oxidant. High concentrations of ground-level ozone are harmful to human health, vegetation and ecosystems, manufactured goods, building materials and the global climate (Cooper *et al*., 2010; Santurtun *et al*., 2015). It has adverse effects on human health such as increased morbidity and mortality and alteration in the respiratory, cardiovascular and cerebrovascular systems (Larsen *et al*., 2010;; Lippmann 2009, Sicard *et al*., 2011;

WHO, 2008;). Ozone affects vegetation and ecosystems which are manifested as visible leafy symptoms, defoliation, senescence and reduction in crop productivity (Paoletti, 2006; Sicard *et al.*, 2011). Ozone-sensitive plants are damaged when WHO recommended limit value of ozone; 65µg/m^3 is exceeded (Hollaway *et al.*, 2012). It acts as a corrosive agent for natural and synthetic rubbers, surface coatings, buildings and plastic materials (de Leeuw, 2000; Screpanti and Marco, 2009). Finally, tropospheric ozone also acts as a greenhouse gas absorbing earth's outgoing infrared radiation of 9.60 µm wavelength (Akimoto, 2003) and contributing to global warming (with estimated globally-averaged radiative forcing of 0.40 ± 0.20 W/m^2) (IPCC, 2013) and climate change (Kulkarni *et al.*, 2011). Ozone takes part in different chemical processes such as oxidation, acidification, formation of aerosols, and photochemical smog (Lin *et al.*, 2014; Zheng *et al.*, 2008). Additionally, it plays a critical role in the tropospheric chemistry, since it is a key precursor of hydroxyl radical (HO•) and maintains oxidizing power of the lower atmosphere (Thompson, 1992; Sitch *et al.*, 2007). Hydroxyl radical (HO•) (in the relatively unpolluted troposphere) is produced from the oxidization of water vapor by the energetically excited oxygen atom (O*), where in O* is produced from the photolysis of O_3 molecule (Hobbs, 2000).

$$O_3 + hv\ (\lambda\ 320 - 300\ nm) \rightarrow O_2 + O^*$$

$$O^* + H_2O \rightarrow OH\bullet + OH\bullet$$

The net reactions is: $O_3 + H_2O + hv\ (\lambda\ 320\text{-}300\ nm) \rightarrow O_2 + 2OH\bullet$

The ozone concentration variations mostly depend on the precursor emission characteristics, concentration of different pollutants, chemical processes, and meteorological conditions (Jacob, 2000; Santurtun *et al.*, 2015; Stathopoulou *et al.*, 2008).

In the troposphere, O_3 concentration generally increases with increasing emissions of precursor gases - nitrogen oxides (NOx) [mainly from fossil fuel combustion and biomass burning] and non-methane volatile organic compounds (VOCs), CH_4 or CO [mainly from human activities such as fossil fuel and biomass combustion, fuel evaporation, solvent use and chemical manufacturing] (Jacob, 2000). They mostly augment in the urban areas due to increasing motorized traffic, industrial and agricultural activities (Brown *et al.*, 2006; Sicard *et al.*, 2009; Sicard *et al.*, 2013,).

Vehicle emissions are one of the most important sources of ozone precursors in Beijing, New York, Tokeyo (Song *et al.*, 2007). These precursors also originate from natural sources including biogenic volatile organic compounds (BVOC) emissions, wildfires, lightning NOx and biogenic NOx emitted from soils (Brown *et al.*, 2006). However, NOx emissions from anthropogenic sources exceed natural sources (Godish, 2004).

Nitrogen oxides (NOx) play an important role in controlling the levels of O_3. NO is emitted from combustion processes or natural sources, is oxidized to produce NO_2, because of short lived. In the presence of sunlight, NO_2 phytolyzes to produce NO and oxygen atom (O), and then O combines with O_2 to form O_3 (Godish, 2004).

$$NO_2 + h\nu\ (<420\ nm) \rightarrow NO + O$$

$$O_2 + O \rightarrow O_3$$

Once formed, O_3 quickly reacts with NO regenerating NO_2 in the absence of VOCs, CH_4 or CO. This is called titration reaction (Munir *et al.*, 2015). This is also called ‘null cycle’, which does not lead to a net production or destruction of O_3.

$$O_3 + NO \rightarrow NO_2 + O_2$$

Nitrogen oxides (NOx), particularly NO_2 is considered one of the precursors of O_3 formation. On the other hand, freshly emitted NOx, especially NO is a sink of O_3. So, NOx have correlated both positively and negatively with O_3 (Munir *et al.*, 2015).

$$NO_2 + h\nu <420\ nm \rightarrow NO + O$$

$$O_2 + O \rightarrow O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

Ozone (O_3) formation depends on the speed of NO_2 photolysis and on the NO_2/NO ratio. An increase in NO_2/NO ratio is associated with reduce titration of O_3 by NO. This reflects that the atmosphere is effectively “NOx - saturated with respect to NO_2” to form O_3. If there is no other processes that transform NO to NO_2, the concentration of O_3 will not increase significantly (Junior *et al.*, 2009).

In the troposphere, VOCs, CH_4 or CO react with OH radicals and form intermediary peroxyradicals compounds like hydroperoxy (HOO•) and organic peroxy radicals [ROO•, RC(O)OO•, etc.].

$$RH \text{ (hydrocarbon)} + OH\bullet + O_2 \rightarrow ROO\bullet + H_2O$$

$$R + O_2 \rightarrow ROO\bullet$$

$$CO + HO\bullet \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HOO\bullet + M$$

These radicals oxidize NO to NO_2 without consumption of O_3 and the photolysis of the resulting NO_2 by sunlight leads to an increase in the accumulation of O_3 (CETESB, 2003; Seinfeld and Pandis, 2006). Obviously, VOCs compete with ozone to oxidize NO to NO_2 and hence, they help in the formation and retaining ozone concentrations (Jacob, 2000).

$$ROO\bullet + NO \rightarrow NO_2 + RO\bullet$$

$$NO_2 \rightarrow NO + O$$

$$O_2 + O \rightarrow O_3$$

In urban areas, the relation between photochemical O_3 production and the concentration of its precursors is not linear. It depends upon the concentrations of NOx and VOCs, the ratio of NOx to VOCs, and the intensity of solar radiation (Tie *et al.*, 2009; Zhang *et al.*, 2004). In some cases, O_3 formation is controlled almost entirely by NOx and is largely independent of the amount of VOC (NOx - sensitive), while in other cases, it increases with increasing VOC (VOC - sensitive) (Sillman, 1999). Increasing the concentration of VOCs always increases O_3 formation (Guicherit and Roemer, 2000; Sadanaga *et al.*, 2003). NOx emissions are mainly responsible for O_3 formation in rural areas, whereas VOCs are primarily responsible for O_3 formation in urban areas. Average ozone concentrations at the rural background site is normally high than the urban background station, because lower NO concentrations in rural areas prevent ozone titration. Sometimes, O_3 concentrations decrease at the motorized road possibly due to the increased chemical O_3 reaction with NO (NO scavenging).

The concentration of ground level O_3 in an area is also dependent on meteorological parameters such as sunshine, ambient temperature, relative humidity, rainfall, wind speed and direction. Ozone formation, chemical/ physical removal, transportation/ dispersion, dry deposition and mixing are influenced by meteorological conations (Andersson *et al*., 2007; Reddy *et al*. 2010; Santurtun *et al*., 2015; Stathopoulou *et al*., 2008). Large variations in meteorological conditions can exert a large impact on O_3

concentration (Duenas *et al*., 2002). Meteorological conditions also enable the movement of O_3-forming precursor gases, and other air pollutants (Andersson *et al*., 2007; Reddy *et al*., 2010). Thus, variations in ozone concentration occur on local, regional and global scales (Reddy *et al*., 2010). Precursor emissions (NOx and VOCs) can lead to elevated levels of surface O_3 locally and downwind, and cause large diurnal, day-to-day, seasonal and year-to-year variations in O_3 levels as a result of complex meteorological influences and photochemical mechanisms (Solomon *et al*., 2000).

The ozone concentration slowly rises after the sun rises and attains its maximum during daytime (especially afternoon), and then again decreases until the next morning. This is due to photochemical O_3 formation. The afternoon peak and night-time low concentrations of O_3 are typical characteristics of the diurnal cycle of ozone (Han *et al*., 2011; Pudasainee *et al*., 2006; Roberts-Semple, *et al.* 2012).

The afternoon peak in O_3 concentration is produced by the reactions of NOx and volatile hydrocarbon compounds in the presence of solar radiation, while low concentration at night-time is caused by turbulent mixing induced by both wind shear and thermal convection (AQEG, 2009). The shape and amplitude of ozone cycles are strongly influenced by temperature, solar radiation and prevailing levels of precursors (NOx and volatile organic compounds).

Photochemical reactions are the most intensive on sunny, humid and warm days (high temperature), hence the higher tropospheric ozone concentrations commonly occur at afternoon and during the spring and summer season (Nishanth *et al*., 2012; Richards *et al*., 2013; Tecer *et al*., 2003), while during winter its concentration is relatively low due to less intensive solar radiation. Wet and rainy weather with high relative humidity is typically associated with low levels of O_3 due to the less intensive photochemical oxidation and perhaps wet deposition of ozone with the water droplets (Nishanth *et al*., 2012; Tarasova *et al*., 2003). Temperature is one of the most important meteorological parameters that control the speed and amount of photochemical production of O_3. Generally, the concentration of O_3 is high both in the winter and summer season and follow the following order:

Winter> summer> post-monsoon> pre-monsoon

It is observed that windy weather can influence ozone concentration near the surface. Strong wind disperses and transports away air pollutants and decreases the concentrations of ozone precursors, while calm/ mild-to-lower wind is favorable for the production of O_3 (Elminir, 2005). Both regional transport and local ozone production play key roles in ozone accumulation (Laurila, 1999; Thompson *et al.*, 2001). High levels of O_3 might be registered within a city or at a distance downwind due to the high emissions of O_3 precursors in urban areas (Garcia *et al.*, 2005). Since photochemical production of O_3 is higher in urban area (Atkinson, 2000); the highest O_3 levels in rural areas are observed downwind to urban plumes. Significant variation of ozone concentration also takes place up to 250 meters from the ground level due to the variation of vertical mixing (Lin *et al.*, 2014; Zheng *et al*. 2008).

The strongest positive correlation of ground-level ozone production with ambient temperature has been observed. While the correlation among ozone production and wind velocity and direction, pressure, and cloud abundance is weaker and negative (Camalier *et al.*, 2007; Dawson *et al.*, 2007). In Europe, the highest ozone concentrations take place in summer under stable high-pressure systems with clear skies (Valuntaite *et al.*, 2009).

Shanghai is one of the largest megacities in eastern China, experiencing rapid urbanization and industrialization and thus are conducive to significantly increased emissions of VOCs and NOx as well as subsequently influence production of O_3 (Zhao *et al.*, 2015). Zhao *et al*. (2015) found the highest monthly average O_3 concentration in June (41.1 ppbv) which was nearly three times higher than the lowest level recorded in December (15.2 ppbv) due to seasonal and diurnal variation patterns in association with meteorological factors. Vehicle emissions are one of the most important sources of ozone precursors in Beijing (Song *et al.*, 2007).

Ran *et al.*, (2009) found that spring was the most productive season for ozone, with the highest daily maximum (128 ppbv) in May 2007 in Shanghai due to the photochemistry. In Shanghai, summer monsoon introduced oceanic air that significantly affects atmospheric pollution via air mass transport and thus ozone concentration is low (Wang *et al.*, 2006).

Chelani (2009) assessed the persistence of ozone concentrations in an urban setting and concluded that, O_3 concentration in ground level is affected by the photochemistry, which in turn is dependent on the amount of solar radiation. Ground level O_3 concentration is expected to be high during daytime due to the photochemical reactions and thus its concentration is high during longer sunshine hours of summer season in comparison to the concentration of winter season.

The variability of ground level O_3 against temperature and wind speed data for a period from October 2013 to September 2014 at Karaikal, Union Territory of Puducherry, a coastal region along south east India was assessed by Punithavathy *et al.* (2015). It was found that the ozone cycles in the study area were strongly influenced by meteorological conditions. Ambient temperature, wind speed along with solar radiation together can contribute to about 93% of the observed ground level ozone concentration. Seasonal characteristics reveal that formation of ozone is high during the summer and pre-monsoon period compared with north-east and winter period which is due to the favorable ambient temperature and solar radiation. Correlation between O_3 and wind speed shows not much significance relationship ($r^2 = 0.1816$).

Average annual cycle of ground level O_3 in Makkah, KSA during the period of 1997 - 2007, showed the highest concentration in September and lowest in December. O_3 concentrations are lower in colder months probably due to lower solar radiation levels, while highest concentrations were observed in September. The concentrations of O_3 decreased in hottest months - June and July probably due to chemical and biophysical responses (Munir *et al*., 2015).

The residence time-scale of O_3 varies from season to season, a few days at the surface to a few weeks in the free troposphere (Finlayson-Pitts *et al*., 1986). It was observed that the O_3 concentration is rising with the rate of 0.50 - 2 % per year over the Northern Hemisphere due to the increased anthropogenic activities (Vingarzan, 2004).

In northern Europe, variability and trends of surface O_3 have been extensively studied (Derwent *et al*., 2007; Parrish *et al*., 2012; Sicard *et al*., 2009; Vingarzan, 2004;), and it is found that ozone levels reach the highest levels in the Mediterranean region (Cristofanelli and Bonasoni, 2009; Sicard *et al*., 2013). In southern Europe, meteorological factors such as high temperatures, intense solar radiation and frequent dry spells favor O_3 formation. Additionally, anthropogenic emissions of precursors across the continent have been found to be responsible for the elevated levels of O_3 in the Mediterranean area (Adame *et al.*, 2012) due to frequent biomass burning in dry summer conditions (Pace *et al.*, 2005; Tressol *et al.*, 2008) as well as due to large emissions of natural and anthropogenic precursors in Central and Eastern Europe while continental air masses are transported towards the Mediterranean region (Duncan *et al.*, 2008). Finally, long-range transport of O_3 and its precursors from North America (Auvray and Bey, 2005) and Asia over the Mediterranean has been shown influence on the elevated levels of O_3.

In addition to photochemical formation of O_3, long-range transports of air masses contribute to the high O_3 levels (Nishanth *et al.*, 2012). Hassan *et al.*, (2013a) found that air masses had strong marine influence for the enhancement of ground level O_3 during a study period of 12 months in the city of Jeddah from December 2011 to December 2012. A similar pattern of back trajectory was observed in other areas of the world (Khemani *et al.*, 1995; Nishanth *et al.*, 2012).

At regional or global reception sites, the impact from long-range transportation and long-term emission changes are extraordinarily important to understand ozone pollution and its temporal trends (Wang *et al.*, 2011).

2.9.6 Atmospheric ammonia (NH_3)

Ammonia (NH_3) is the most abundant and only basic/alkaline gas species in the atmosphere. It is the third most abundant nitrogen compound after nitrogen gas and nitrous oxide in the atmosphere (Seinfeld and Pandis, 2006).

The major sources of NH_3 in the atmosphere include anaerobic decomposition of N-containing organic matter, emissions from domesticated animals and their wastes, biomass burning (including forest fires), losses from soils under native vegetation and agricultural crops, and production and application of N-containing (nitrate/anhydrous NH_3) fertilizer to cropland (Amaral and Rodrigues, 2007; Bates *et al.*, 2013; Bates *et al.*, 1997). Since NH_3 is produced by biological processes and hence, exists in both clear and polluted atmosphere. Other NH_3 sources include fossil fuel combustion and emissions from vehicles, industrial activities, wetlands, wastewater treatment plants and human residents (human excreta) (Anderson *et al*., 2003; Aneja *et al*., 2012; Olivier *et al*., 1998; Walker *et al*., 2004; Zhang *et al*., 2008). Traffic exhausts are considered to be the main source of NH_3 in the urban environment (Battye *et al*., 2003; Livingston *et al*., 2009). Ammonia emission from road traffic happens because of the use of three-way catalytic (TWC) converters in gasoline-driven automobiles which contribute in decreasing NOx and CO emissions (Kean *et al*., 2000). In the three-way catalytic (TWC) converters, NH_3 is formed via steam reforming from hydrocarbons (Whittington *et al*., 1995) and/or via reaction of nitrogen monoxide (NO) with molecular hydrogen (H_2) (through reaction ii or iii) produced from a water–gas shift reaction between CO and water (i) (Barbier and Duprez, 1994; Bradow and Stump, 1977).

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(i)$$

$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2 \ldots\ldots\ldots..(ii)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots(iii)$$

Kean *et al*. (2009) reported that the highest average ammonia emission rates were observed for 10-year-old vehicles. Overall, the agriculture sector contributes 80.6 % to the total global NH_3 emissions, followed by 11 % from biomass burning and 8.3 % from the energy sector, including industries and traffic. The regions with the highest emission rates are located in Europe, the Indian subcontinent and China. South America reflect the patterns of animal densities and the type and intensity of synthetic fertilizer uses (Behera *et al*., 2013).

The background concentrations of NH_3 vary from 100 pptv over remote oceans to 1-10 ppbv over continents (Godish, 2004). The atmospheric lifetime of H_2S is relatively short (about 10 days). It can be transported over 10 to 100 km from the source depending on the meteorological conditions, however atmospheric lifetime of NH_4^+ is about 1 - 15 days and may be transported to much longer distance (100 to >1000 km) (Asman *et al*., 1998; Sutton *et al*., 2000). Thus, atmospheric NH_3 contributes to transboundary air pollution issues on long range transboundary pollution (Fowler *et al*., 1998).

Atmospheric ammonia (NH_3) has great environmental implications due to its important role in the nitrogen cycle in ecosystems, the neutralization of acids in the air, the formation of particulate matter ($PM_{2.5}$) and climate change with associated health effects (Behera *et al.*, 2013). In the atmosphere, NH_3 reacts primarily with acidic species and neutralizes a substantial part of the acid produced by sulphur oxides (SOx), nitrogen oxides (NOx) and hydrochloric acid (HCl). These processes form ammonium-containing secondary particulate matter including ammonium sulphate, ammonium nitrate and ammonium chloride (Kulmala *et al.*, 2004, Ianniello *et al.*, 2011; Schiferl *et al.*, 2014; Yao *et al.*, 2007; Yao and Zhang, 2012).

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$
$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$
$$NH_3 + HCl \rightarrow NH_4Cl$$

Thus, ammonium (NH_4^+) is a major component of atmospheric aerosols and also contributes significantly to aerosols mass ($PM_{2.5}$, PM_{10}) (Asman *et. al.*, 1998). Particulate ammonium species contribute to the degradation of air quality which have effects on human health (Brunekreef and Holgate, 2002; Verma *et al.*, 2009). These materials have effects on the reduction of atmospheric visibility and modification of the global radiative balance of the atmosphere through scattering the incoming solar radiation (IPCC, 2007, Erisman *et al.*, 2007) as well as to act as cloud condensation nuclei and indirectly increase cloud lifetime (Bauer *et al.*, 2007; Behera *et al.*, 2013; Charlson *et al.*, 1990; Myhre *et al.*, 2009; Shukla and Sharma, 2010; Xue *et al.*, 2011).

Ammonia levels are also affected by several factors such as NH_3 emissions, NH_3 - NH_4^+, partitioning, and meteorological conditions (Hu *et al.*, 2014; Reche *et al.*, 2012; Sutton *et al.*, 2002; Yao and Zhang, 2012). In summer time, NH_4^+ will be transformed to NH_3 due to high temperature and low relative humidity (Seinfeld and Pandis, 2006). Atmospheric NH_3 and ammonium salt-aerosols can be transported through downwind and eventually undergo dry and wet deposition to natural ecosystems (Asman, 1995; Beem *et al.*, 2010; Krupa, 2003; Sutton and Fowler, 2002). Excessive NH_3 deposition may lead to terrestrial deposition and eutrophication in aquatic ecosystems and thus threaten the biodiversity (Aneja *et al.*, 1986; Asman *et al.*, 1998; Beem *et al.*, 2010; Bobbink *et al.*, 2010; Erisman *et al.*, 2005; Erisman *et al.*, 2007; Galloway *et al.*, 2003; Krupa, 2003; Pinder *et al.*, 2012).

Ammonia can also be oxidized on reacting with HO•. It is readily absorbed by H_2O (rainwater, fog, etc.) and soil surfaces.

$$NH_3 + H_2O \rightarrow NH_3\,(aq)/\,NH_4OH$$

When ammonia reaches on the soil surface, it usually reacts with water in the soil and is converted into ammonium (NH_4^+) ion and then adsorbed by soil particles. The ammonium in the soil eventually dissociates or nitrifies into nitrite (NO_2^-) or nitrate (NO_3^-) by nitrifying bacteria, releasing H^+ ions into the soil (Williams *et al*., 1992).

The concentrations of ammonia in Santiago, Chile are among the highest, due to the large number and variety of sources (mobile sources, wastewater treatment plants, agricultural activities in the southwestern part of the city, rivers and channels with loads of organic matter, and wetlands) and adverse geographical and meteorological conditions for dispersion of gases and particles (Toro *et al*., 2014).

Pandolfit *et al*. (2012) measured the ambient concentrations of gas-phase ammonia (NH_3) in an urban background (UB) traffic-influenced area and in an historical city centre (CC) in Barcelona (NE Spain) during summer (low humid weather), between May and September 2011. The levels of NH_3 were higher at CC (5.60 ± 2.10 μg/m^3 or 7.50 ± 2.80 ppbv) compared with UB (2.20 ± 1.0 μg/m^3 or 2.90 ± 1.30 ppbv). This difference is attributed to the contribution from non-traffic sources such as waste containers, sewage systems, humans and open markets in the densely populated historical city centre. Under high temperatures in summer these sources had the potential to increase the ambient levels of NH_3 well above the urban-background-traffic-influenced UB measurement station.

According to Zhou *et al*. (2015), more than 60% of total ammonia emission in Beijing comes from livestock and farm - land. Other sources included were human excrement, waste disposal, biomass burning, chemical industry and traffic.

Ambient NH_3 concentration was measured from 24 to 27 February 2014 at Kolkata city of India by Sharma *et al*., (2016). They revealed by analyzing surface wind direction and wind speed that the local activities like agriculture, livestock, drainage, vehicles etc. might be the possible sources of ambient NH_3 at the observational site of

Kolkata. They also concluded that the variation of ambient NH_3 region may be due to variation in source strength and meteorological conditions of the observational sites.

Ammonia concentration measurement was carried out at Dayalbagh, a suburban site and at St. John's, an urban site at Agra (India) by Kumar *et al*. (2004) and showed that highest values of NH_3 were recorded during the monsoon and lowest during the winter. The high concentration during monsoon may be due to more vegetation and favorable conditions for microbial activity.

2.9.7 Hydrogen sulfide (H_2S)

Hydrogen sulfide (H_2S) is a relatively toxic and flammable colorless gas. It has a characteristic odor of rotten eggs and human can detect its presence while the concentration is even as low as 500 pptv (Godish, 2004). It is an air pollutant. It has effects on human health and also has role in atmospheric chemistry. Commonly, H_2S is emitted both from natural sources and anthropogenic activity. It naturally occurs in the atmosphere from volcanoes, sulfur springs, under sea vents, swamps, stagnant water bodies and also from crude petroleum and natural gas field. There are substantial natural emissions of H_2S and other reduced sulfur compounds into the troposphere from biological activity in vegetation, soils and water ecosystems. Bacteria, fungi, and actinomycetes release H_2S during the anaerobic decomposition of sulfur-containing organic matters and by the direct reduction of sulfate (SO_4^{2-}) (Finlayson and Pitts, 1986; WHO, 2012). Anthropogenic sources of H_2S in the atmosphere include oil and gas extraction, petroleum refining, municipal sewage pumping and treatment plants, landfilling, animal containment and manure handling, pulp and paper production, construction in wetlands, asphalt roofing, pelt processing, animal slaughter facilities, tanneries, petrochemical synthesis, coke production plants, viscose rayon manufacture, sulfur production, iron smelting, and food processing (Godish, 2004; Schoor and Valdez, 2005). The human body produces small amounts of H_2S. Yet, anthropogenic sources produce less than 5% of global emissions; highest ambient concentrations take place near anthropogenic sources. In industrial and surrounding ambient environments H_2S concentrations are usually above the odor threshold of 500 pptv. The background concentrations of H_2S are in the 30 to 100 pptv range (Godish, 2004). The lifetimes for H_2S are probably more than usually a few hours and it may be only a few days for the highest concentrations observed (Wayne, 2000).

Hydrogen sulfide gas often produces inflammation of the eyes, skin burns and respiratory diseases such as rhinitis, bronchitis and pneumonia in humans. When inhaled in small amounts, the gas produces headaches and nausea; a large amount produces paralysis (Schorr and Valdez, 2005). H_2S is very toxic and rapid death ensues from exposure to air containing > 1000 ppm H_2S owing to asphyxiation since it paralyses the fephorphirin molecule in the human respiratory system. Lower doses cause dizziness and excitement due to damage of the central nervous system (Schorr *et al*., 2006). According to the WHO air quality guideline (WHO, 2000), the maximum allowable concentration of H_2S for ambient air is 150 $\mu g/m^3$ (average value in 24 h), although it should not exceed 7 $\mu g/m^3$ (average value in 30 min) to avoid significant odor annoyance due to its typical rotten-egg smell (detectable at 0.70 - 42.0 $\mu g/m^3$, depending on individual sensitivity; (Schiffman and Williams, 2005). Long-term exposures to low H_2S concentrations can have severe public health consequences on respiratory, cardiovascular and nervous systems (Bates *et al*., 2002; Legator *et al*., 2001; Manahan, 2000; Schorr *et al*., 2006). At 15 mg/m^3, H_2S incites eye irritation, while at slightly higher concentrations it prompts damage to the upper respiratory tract and causes loss of smell, whereas coma occurs after a single breath when the H_2S values are $\geq$1400 mg/m^3 (McManus, 1999; Schorr and Valdez, 2005; WHO, 2000; WHO, 2003).

In the atmosphere most of the H_2S is readily oxidized and rapidly converted to first SO_2 and subsequently to sulfuric acid and sulfates (Finlayson and Pitts, 1986; Wayne, 2000). Hydrogen sulfide is oxidized by HO• radical to produce H_2O and thiol radical.

$$H_2S + HO\bullet \rightarrow H_2O + SH\bullet$$

Further, oxidation of thionyl (SH•) radical by O_2, O_3 or NO_2 leads to SO_2 production.

$$SH\bullet + O_2 \rightarrow SO + HO\bullet$$

$$SH\bullet + O_3 \rightarrow SHO\bullet + O_2$$

$$SHO\bullet + O_2 \rightarrow SO + HOO\bullet$$

$$SO + (O_2, O_3 \text{ and } NO_2) \rightarrow SO_2 + \text{other products}$$

2.9.8 Atmospheric phosphine (PH_3)

Phosphine (PH_3) is a colorless reactive-reducing trace gas in the atmosphere with a fishy or garlic-like odor. It ignites spontaneously on contact with air. Gaseous PH_3 has been found worldwide and is ubiquitously present in the low terrestrial troposphere (Glindemann *et al*., 1996a, Liu *et al*., 1999).It is a significant part of an atmospheric link of the phosphorus biogeochemical cycle on the earth (Zhu *et al*., 2009). In nature, PH_3 exists in two different forms - free gaseous PH_3 (De´vai *et al*., 1988; Glindemann *et al*., 1996a) and matrix-bound PH_3 (MBP) (Gassmann, 1994). Matrix-bound PH_3 (MBP) is considered to be the major sources responsible for the emission of phosphine (D´evai and Delaune, 1995; Han *et al*., 2000; Liu *et al*., 1999; Zhu *et al*., 2006a) and producing enough PH_3 into the atmosphere to influence the biogeochemical cycles of phosphorus (Glindemann *et al*., 2005a).

Matrix-bound PH_3 has been detected in many terrestrial media such as river and lake sediments (De´vai *et al*., 1988), marsh soils (De´vai and Delaune, 1995), landfills and communal waste (Jenkins *et al*., 2000; Roels and Verstraete, 2004), animal slurry or human feces (Ding *et al*., 2005; Glindemann and Bergmann, 1995; Glindemann *et al*., 1996b; Zhu *et al*., 2006b), paddy fields (Eismann *et al*., 1997, Han *et al*., 2000) and natural rocks rich in phosphorus (Glindemann *et al*., 2005a). It is also found in the marine sediments, for instances in Hamburg Harbor (0.20 - 55.6 ng per kg) in Germany and Jiaozhou Bay (maximum 685 ng per kg) in China, indicating that marine biospheres are significant sources for atmospheric PH_3 (Gassmann and Schorn, 1993; Gassmann, 1994; Yu and Song 2003). Phosphine can easily transfer into air from the solid or water-phase. Wet-land ecosystems are thought to be the major sources of phosphine emissions in the atmosphere (D´evai and Delaune, 1995; Han *et al*., 2000; Liu *et al*., 1999; Zhu *et al*., 2006a). Several reports suggest that phosphine can be produced by biochemical processes (such as bacterial reduction of phosphate or natural organophosphorus compounds) (Eismann *et al*., 1997; Gassmann and Glindemann, 1993; Jenkins and Morris, 2000; Roels and Verstraete, 2001). Therefore, phosphine emissions and its forming biochemical processes support a gaseous link to the phosphorus cycle in the global environment (Glindemann *et al*., 2003; Glindemann, 2005; Roels and Verstraete, 2001).

In atmospheric air, the concentration of PH_3 is in the range pg/m^3 to ng/m^3. Gaseous phosphine has been found worldwide in the earth's atmosphere, even at such remote locations at the 1.00 ng/m^3 range in the lower troposphere (Glindemann *et al*., 1996a) and higher troposphere (Glindemann *et al*., 2003); a diurnal night-time maximum of phosphine in the lower troposphere (Glindemann *et al*., 1996b); in surface air of the Northern Sea (Gassmann *et al*., 1996); and in the urban air of Beijing at the range of 100 ng/m^3 (Liu *et al*., 1999). The concentration of PH_3 is significantly higher near paddy fields then in urban residential areas (Glindemann *et al*., 2005). The ambient atmospheric levels of phosphine in Beijing are relatively high as compared with those in Germany and South America due to emissions from vast paddy fields and numerous eutrophic water bodies (Liu *et al*., 1999).

Wetland ecosystems are important locations for free PH_3. Production and emission fluxes of free phosphine from four wetlands types in southern China were observed in different seasons by Han *et al*. (2010). The emission concentrations of different wetlands followed the sequence: paddy field (51.83 ± 3.06) ng/m^3> marsh (46.54 ± 20.55) ng/m^3> lake (37.05 ± 22.74) ng/m^3> coastal wetland (1.71 ± 0.73) ng/m^3; the positive phosphine emission flux occurred in rice paddy field (6.67 ± 5.18) ng/m^2.hr and marsh (6.23 ± 26.9) ng/m^2.hr, while a negative phosphine flux of (- 13.11 ± 35.04) ng/m^2.hr was observed on the water-air interface of Lake Taihu, indicating that paddy field and marsh may be important sources of phosphine gas production and emission in the atmosphere, while lake may be served as a pool of atmospheric PH_3 gas. Phosphine might be an important gas pathway for phosphorus transport in eutrophicated lakes. The negative flux of PH_3 in the lake also may be the reason of the low atmospheric PH_3 concentration. Atmospheric phosphine levels and emission flux from Yancheng marsh and rice paddy field varied in different seasons, since the release of PH_3 in study areas correlate with temperature and water. Furthermore, the atmosphere can carry gaseous phosphorus to other places.

Phosphine is a reactive atmospheric trace gas. Hydroxyl-radicals induced by UV from daylight cause its cleavage ($PH_3 \rightarrow H\bullet + \bullet PH_2$) and oxidation (WHO, 1988). It competes with methane and other greenhouse gases for hydroxyl radicals, and thus, augments an indirect greenhouse effect or the so-called coupling effect (Prinn, 1994). PH_3 can dissipate over a wide area and accumulate at night because it is not autoxidable. It undergoes auto-ignition at 100^0C and thus is a potential hazard in industrial processes and in the laboratory. It is flammable and highly toxic gas at its higher concentration.

Phosphine gas poisoning in humans causes respiratory tract irritation, cardiac failure, pulmonary edema, depression of the central nervous system, fatigue, vomiting and painful breathing. Even a short exposure to an acute amount of phosphine can lead to chronic neurological problems (Manahan, 2000). Phosphine itself is a toxic substance, which inhibits the growth of soil microorganisms and damages crop roots. These toxic effects would not only influence the emission fluxes of other greenhouse gases from soil, but also could cause disturbance in the rhizosphere (Han *et al*., 2000).

2.10 Effects of Meteorological Conditions on the Distribution of Air Pollutants

Meteorological factors have a significant influence on air quality in cities (Gong *et al*., 2015). Some meteorological parameters such air temperature, relative humidity, average rainfall, wind speed and wind direction have effects on the distribution of atmospheric trace gases/air pollutants. Meteorological variables such as wind speed, wind direction, temperature, humidity, rainfall should be recorded, and a brief description of meteorological conditions (such as temperature inversions, prevailing wind direction, height above sea level) that are likely to affect air quality at the monitoring site should also be incorporated (Larsen and Schaug, 1995; WMO, 1992; USEPA, 1987). Meteorological conditions may contribute to the diurnal and seasonal variability of different trace gases.

2.10.1 Diurnal variation

During the day-time, over the land especially in urban areas, the chemicals are generally well mixed up to the planetary boundary layer (PBL) by turbulence/convection due to the effects of solar radiation. The PBL extends up to a height of about 1 km from the earth’s surface (depending on the location and season). Some of the trace gases with a long residence time may escape PBL and follow the global circulation pattern. So, the concentrations of trace gases are usually low during day-time at or close to the earth’s surface. At night, mixing is less efficient, and the depth of the PBL may be only a few hundred meters. Thus, the concentrations of some chemicals over the land tend to be greater at night than during the day (Hobbs, 2000).

The diurnal cycles of CO, SO_2 and NOx follow daily social activities. CO, SO_2 and NOx concentrations increases in the early morning and evening due to rush hours of traffics and then, their concentrations decrease or maintain low during noon periods. At night their concentrations are low due to lower height of the mixing layer and weak wind speed (Sikder *et al.*, 2010). The concentration of volatile organic compounds (VOCs) is generally high during noon period due to their availability both from natural and anthropogenic sources than other period of the day-time; however its concentration is higher at night. Ozone concentrations are normally high in afternoon, since they are formed from their precursor gases (NOx and VOCs) under the influence of sunlight (Hobbs, 2000; Jacob, 1999). The diurnal concentrations of H_2S, NH_3 and PH_3 are generally higher in the morning may be due to the release of these gases from communal wastes and then decrease with increasing day-light hours, and at night their concentrations again increase because of less mixing after sunset.

2.10.2 Seasonal variation

The temporal trends of the concentrations of trace gases and particulate matter indicate that during the winter (dry) season their concentrations increase than the rainy season. This was happened not only for seasonal fluctuations of air pollutants emission, but also for meteorological effects. Calm, mist, drizzle, and temperature inversion (which is mostly observed at night, when the weather is calm and fine) provide favourable conditions for concentrating the pollutants near the ground level, so that air pollution may significantly increase in such cases (Psiloglou *et al.*, 2013). In Bangladesh, winter season is characterized by low humidity, no or scanty rainfalls, less solar intensity, dry weather, and low northwesterly wind speed and direction. This situation favors the trace gases and particulate matter to be higher during winter season. The highest levels of CO in air typically occur during the colder months of a year when inversion conditions are more frequent near the ground, beneath a layer of warm air (Badarinath *et al.*, 2007).

2.11 Effects of Air masses on the Concentrations of Trace Gases

Back trajectories trace an air parcel's path back in time and indicate where air parcel has been, before it reaches the site where it is analyzed. The applications of such a capability are extensive and in many studies backward trajectory have been used as a tool their research. Anastassopoulos *et al.* (2004) used HYSPLIT model to study air quality in the city of Windsor (42.16^{o}N, 82.58^{o}W), Ontario, Canada. In this regard, 2-day back trajectory simulations were conducted in 2003 to investigate the regional transport of air pollutants. The results identified that air masses from Ontario and neighboring American states including Michigan, Ohio and Wisconsin had greater influence on the air quality of Windsor, primarily due to the prevailing wind directions. Jaffe *et al.* (1999) used back trajectories to verify that anthropogenic emissions from Asia could have a significant impact on the concentrations of chemical species arriving in North America. Cheng *et al.* (2013) showed that the transboundary PM_{10} transport played a critical role in the formation of PM_{10} pollution events in Guangzhou, China. Wang *et al.* (2016) observed that air masses transported from south areas affected many cities in the south side of Beijing with a serious air pollution episode specially the VOCs. Baudic *et al.* (2016) observed air mass trajectories in the Paris megacity, France for the year 2010, and termed that air masses arriving from different directions in different seasons contained VOCs and other pollutants from origin sources and en route transportation

2.12 Source Profile Study of Trace Gases and Characterization

Identifying important pollution sources that contribute to ambient concentrations of pollutants is essential for developing an effective air quality management plan. Air quality models use mathematical and numerical techniques to simulate the physical and chemical processes that affect air pollutants as they disperse and react in the atmosphere. Based on inputs of meteorological data and source information such as emission rates and stack height, these models are designed to characterize primary pollutants that are emitted directly into the atmosphere and, in some cases, secondary pollutants that are formed as a result of complex chemical reactions within the atmosphere. These models are important to the air quality management system because they are widely used by agencies tasked with controlling air pollution to both identify source contributions to air quality problems and assist in the design of effective strategies to reduce harmful air pollutants. For example, air quality models can be used during the permitting process to verify that a new source will not exceed ambient air quality standards or, if necessary, determine appropriate additional control requirements. Air quality models can also be used to predict future pollutant concentrations from multiple sources after the implementation of a new regulatory program, in order to estimate the effectiveness of the program in reducing harmful exposures to humans and the environment. Air pollution models are powerful tools for policy makers as they can be used to relate emissions and concentrations. Hybrid Single particle Lagrangian Integrated Trajectory - HYSPLIT (Draxler and Hess, 1997; Stein *et al*., 2015) and Positive Matrix Factorization (Norris and Duvall, 2014; Begum *et al*., 2004) are using from sources characterization of atmospheric pollutants for chemical components.

CHAPTER THREE

RESEARCH METHODOLOGY

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3.1. Description of the Experimental Sites

The study was performed in the Dhaka University campus, Dhaka 1000, Bangladesh for four seasons (1 year). The sampling location was chosen to be away from the direct local pollution sources. It was about 50 meter away from the nearby road. It is located at $23^0$43.497' N latitude and $90^0$24.194' E longitude. An automatic direct sense toxic gas monitoring instrument (Model TG-501 and TG-502, GrayWolf, Ireland) was installed at the roof-top (20 meter above the ground level) of the “House Tutor Quarter”, Amar Ekushey Hall, Dhaka University to analyze trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) and meteorological data (temperature and humidity). The concentrations of the same trace gases were also measured at Karwan Bazar (highly traffic congested and commercial area) in Dhaka city, Dhamrai (semi-urban area) in Dhaka district, Jamalganj (rural area) in Sunamganj district and Badla Haor (haor area, seasonally submerged for 6 to 7 months) in Kishoreganj district. The measured concentrations of the trace gases of these different locations had been compared with the concentrations of trace gases measured at the Dhaka University campus. The different sampling locations are indicated in the map of Bangladesh (Figure 3.1).

3.1.1 Dhaka University campus

An automatic direct sense toxic gas monitoring instrument (Model TG-501, and TG-502, GrayWolf, Ireland) was installed at the roof-top (20 meter above the ground level) of the “House Tutor Quarter”, Amar Ekushey Hall, Dhaka University to analyze trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) and meteorological data (temperature and humidity) for four seasons (1 year). It is located at $23^0$43.497' N latitude and $90^0$24.194' E longitude (Figure 3.1 and Figure 3.2).The sampling location was chosen to be away from direct local pollution sources.

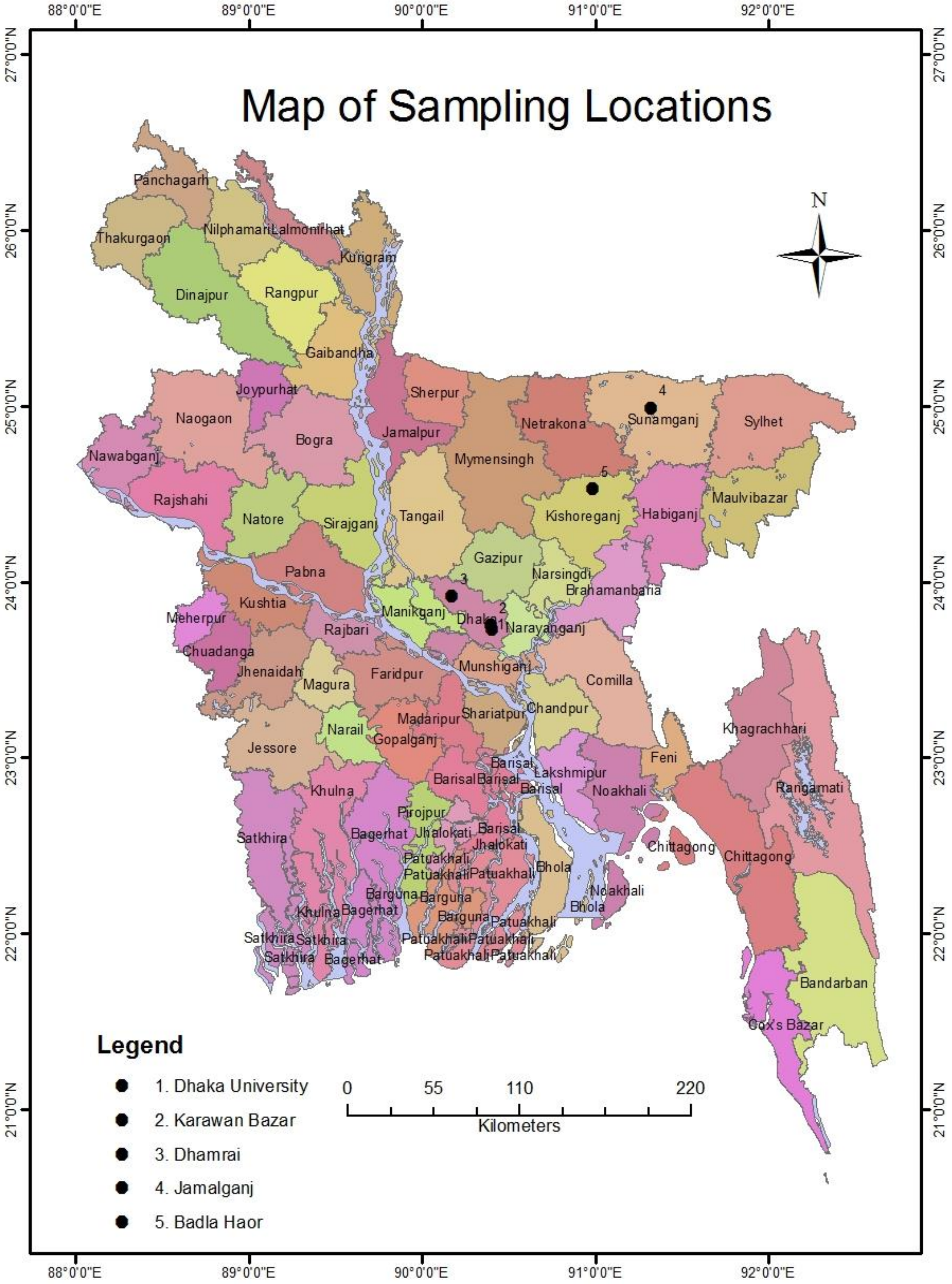


Figure 3.1: Map of Bangladesh showing the sampling locations.

It was about 50 meter away from nearby road. The “House Tutor Quarter”, Amar Ekushey Hall is situated on the north side of Old Secretariat road, and different kinds of vehicles such as cars, auto-rickshaws (motorized three-wheeler), buses, man-paddled rickshaws, trucks and other types of vehicles pass through this road. It is also located on the south of Curzon Hall (where a part of the department of sciences remains), Shahidullah Hall and Fazlul Hoque Muslim Hall area. On the east, south and north side of “House Tutor Quarter”, some commercial spots such as Banga Bazar, Andanda Bazar, Chankharpul business area and Dhaka medical hospital are situated within about 500 meter close to the sampling location. These neighboring areas are one of the busiest and most crowded areas of the Dhaka city.

3.1.2 Karwan Bazar

Karwan Bazar is a commercial area of Dhaka City, Bangladesh. A main road, named Nazrul Islam Avenue runs on the west side of it. It is a one of the busiest road in Dhaka city. Most of the vehicles ply through it, and the road experiences traffic congestion in most of the time. A rail road is situated on the eastern side of Karwan Bazar. It is one of the largest wholesale kitchen-market places in Dhaka city. Most of the main offices of newspapers (The Prothom Alo, The Daily Star, and The Independent), offices and studios of television channels (Ekushey Television, NTV, ATN Bangla, Bangla Vision and ATN News), corporate offices, hotels, educational institutes, electronic market and overseas offices are located here. This is one of the busiest and most crowded areas of the Dhaka city. Neighboring places of Karwan Bazar are Pantapath, Bangla Motor, Farmgate etc. The major emission sources in Dhaka City are motor vehicles and also brickfields (working around) during winter and dry season (November to May), which have large contribution to air pollution in Dhaka. Moreover, meteorological conditions spread emissions over the surrounding atmosphere from brick kilns. Sikder *et al*. (2010) observed that the concentrations of the cycles of O_3, CO, NOx and SO_2, and concluded that their concentrations were the highest during winter season, and lowest in the monsoon season in Dhaka over the period from April 2002 to December 2005. To observe the concentration levels of trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) in a commercial cum traffic congested area, an automatic direct sense toxic gas monitoring instrument (Model TG-501, and TG-502, GrayWolf, Ireland) was put in on the road side of

"Nazrul Islam Avenue". It is located at $23^0$45'08.7"N latitude and $90^0$23'33.2"E longitude (Figure 3.1 and Figure 3.2). The measured concentrations of trace gases were then used to compare with the measured values of the Dhaka university campus.

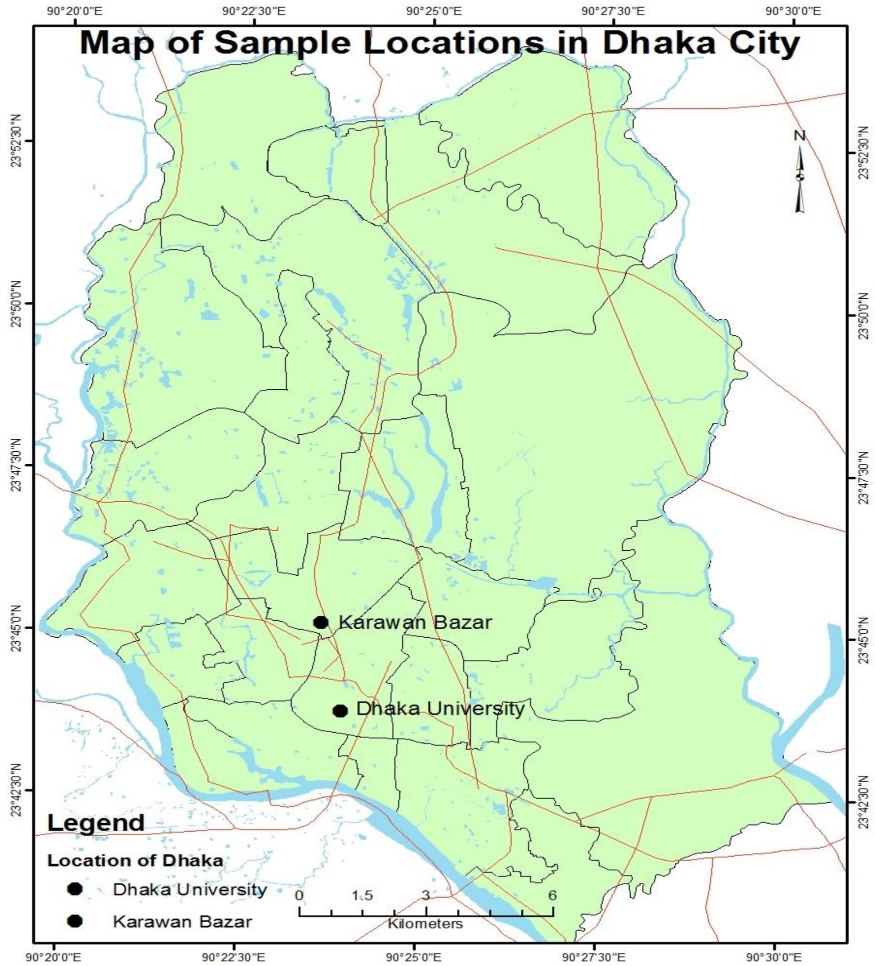


Figure 3.2: Map of Dhaka City showing the sampling locations.

3.1.3 Dhamrai

The study location is situated at Kalampur of Dhamrai upazila in Dhaka district, Bangladesh. Dhamrai is an upazila, located about 40 kilometers north-west of the Dhaka city. The upazila is surrounded by the upazilas of Mirzapur and Kaliakair and Nagarpur on the north, Singair on the south, Savar in the east and Saturia on the west. It is a semi-urban area and consists of one municipality (densely populated), 16 unions and 398 villages (Banglapedia, 2015). There are 139 government primary schools; 15 high schools; 25 junior high schools; 109 schools run by NGOs; 11 madrasahs, 6 colleges and 1 agriculture college in Dhamrai upazila. Main sources of income are agriculture, non-agricultural labourer, industry, commerce, transport and communication, service, construction and others. Different manufacturing industries such as ceramic industry, jute industry, aluminium industry, pharmaceutical industry, textile industry, embroidery, brickfield, saw mill, rice mill, leather factory, shoe factory, cold storage and small cottage industries (such as goldsmith, blacksmith, potteries, handicraft etc.) are situated in Dhamrai. A highway has passed through Dhamrai to connect Dhaka with Manikganj district. The study location ($23^0$55'09.3"N latitude and $90^0$10'13.4"E longitude) (Figure 3.1) is about 1 kilometer far from the highway, but there are some brick kilns and other industries around 500 meters distance.

3.1.4 Jamalganj

The study location is situated at Jaynagar of Jamalganj upazila in Sunamganj district, Bangladesh. Jamalganj upazila with an area of 338.74 km^2, is bounded by Tahirpur and Bishwamvarpur upazilas on the north, Khaliajuri and Derai upazilas on the south, Sunamganj Sadarupazila on the east, Mohanganj and Dharmapasha upazilas on the west (Banglapedia, 2014). Sunamganj is the border district of Bangladesh with north-eastern part of India. The study site is a rural area, and population density of this area is very low. A road has run about 500 meters far from the study location ($24^0$59'20.23"N latitude and $91^0$19'00.15"E longitude) (Figure 3.1), which has connected Jamalganj upazila with Sylhet-Sunamganj highway. A small number of vehicles such as such buses, auto-rickshaws (motorized three-wheeler), man-paddled rickshaw and trucks pass through this road.

3.1.5 Badla Haor

Trace gases sampling location ($24^0$31'50.5"N latitude and $90^0$58'50.4"E longitude) (Figure 3.1) is situated in Badla Haor of Itna upazila in Kishoreganj district, Bangladesh. It is a semi-permanent water body that remains submerged for 6 to 7 months of the year. Only in dry season, from November to April, this area support mostly paddy cultivation and occasional maize production. The population density of Itna upazila is very low. Most of the people are engaged in paddy cultivation during dry season and fishing in submerged period. Badla Haor is connected with upazila town by a narrow road that supports small number of vehicles movement from Itna to Kishoreganj.

3.2. Meteorology of Dhaka City

Air pollution status of an area in addition to emission sources is governed by meteorological conditions, since they contribute to the diurnal, monthly and seasonal variability of different gases. Thus, the measurements of meteorological parameters of the Dhaka city were also done in addition to the measurement of trace gases concentrations of interest. Bangladesh has a tropical monsoon climate characterized by high temperature, excessive humidity and fairly marked seasonal variations of precipitation. Meteorologically, the year of Bangladesh is divided into 4 distinct seasons: pre-monsoon (March-May), monsoon (June-August), post-monsoon (September-November) and winter (December-February). The pre-monsoon is a hot and muggy season characterized by high temperatures and the occurrence of thunderstorms. A hot, humid and rainy monsoon season begins in June which continues up to November i.e., the end of post-monsoon season with little variability in temperature and humidity. The cool and dry winter season exists from December to February. A brief summary of the average meteorological conditions (June 2013-May 2014) of Dhaka City (BMD, 2016) for different seasons is given in Table 3.1.

Table 3.1: A brief summary of the average meteorological conditions (June 2013 - May 2014) of Dhaka City.

Season	**Temperature (^{0}C)**		**Average relative humidity (%)**	**Average rainfall (mm)**	**Average wind speed (Knot)**	**Prevailing wind direction**
	Maximum	**Minimum**				
Monsoon (June-August)	32.7	25.7	88.27	1.14	1.87	S, SE, E
Post-monsoon (September-November)	31.5	22.6	80.86	0.4	0.69	S, SE, E, NE
Winter (December-February)	28.8	15.1	68.87	0.02	0.99	N, W, NW
Pre-monsoon (March-May)	36.8	23.2	64.23	0.33	1.63	NW, W, SW, S

3.3 Air Quality Monitoring Instrument

Atmospheric trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) along with temperature and humidity were measured with an automatic direct sense toxic gas monitoring instrument (Model TG-501 and TG-502, GrayWolf, Ireland). Few photographs of the toxic gas monitoring instrument are presented in Figure 3.3.

Figure 3.3: Photographs of the toxic gas monitoring instrument installed at the roof-top (20 meter above ground level) of the "House Tutor Quarter", Amar Ekushey Hall, Dhaka University, Dhaka, Bangladesh. The same instrument was used in all the locations for trace gases measurement.

3.3.1. Instrument operation and working principles

An automatic direct sense toxic gas monitoring instrument (Model TG-501 and TG-502, Gray Wolf, Ireland) was used to measure the concentrations of atmospheric trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) along with temperature and humidity. The instrument comprises two probes - TG 501 (measures CO, NO, NO_2, O_3) and TG 502 (measures TVOC, NH_3, H_2S and PH_3, temperature and humidity). These probes contain 4 kinds of sensors for measuring trace gases (CO, NO, NO_2, O_3, TVOC, NH_3, H_2S and PH_3) along with temperature and humidity. The sensors are:

Electro-chemical sensors
Photo ionization detector (PID) sensor
Pt100 RTD sensor
Thin-film capacitive sensor

A brief description of the working method of each sensor of the automatic direct sense toxic gas monitoring instrument is presented in Table 3.2.The probes were run with dry cells and were connected with a micro-computer for monitoring and storing air quality data with date, location and time interval. This microcomputer operates with GreyWolf sense (TM) application software which takes the reading of trace gases along with temperature and humidity. The microcomputer comprised rechargeable battery and that can run for about 6 hours while fully charged. It can also run with direct electricity. Before starting trace gases monitoring in every time, data lodging file name along with desired time interval of data collection were set in the microcomputer, and also battery level, display of parameters (gases, temperature and humidity) and units of measurement were checked.

Table 3.2: A brief description of the working method of each sensor of the automatic direct sense toxic gas monitoring instrument.

Element	Measuring sensor	Working method
CO	Electrochemical sensor	The electro-chemical toxic sensor comprises two electrodes: sensing and counter, separated by a thin layer of electrolyte. This is enclosed in a plastic housing that has a small capillary to allow gas entry to the sensing electrode and includes pins which are electrically attached to both electrodes. While gas diffuse into the electrochemical sensor, the working (sensing) electrode either oxidizes (CO, NO, H_2S, PH_3, NH_3 gases) or reduces (O_3, NO_2) the target gas with the counter electrode balancing the generated current. The rate of gas entry into the sensor is controlled by the capillary diffusion barrier; the current generated is proportional to the concentration of gas present outside the sensor and gives a direct measure of the toxic gas present.
NO	Electrochemical sensor	
NO_2	Electrochemical sensor	
O_3	Electrochemical sensor	
NH_3	Electrochemical sensor	
H_2S	Electrochemical sensor	
PH_3	Electrochemical sensor	
TVOC	Photo ionization detector (PID) sensor	The PID operates on molecules of interest by generating VUV (vacuum ultraviolet) radiation from a gas discharge lamp. As a result, some percentages of these molecules are ionized and a pair of electrodes in the PID sensor creates a small current which is amplified and converted to be displayed by the instrument.
Temperature	Pt100 RTD sensor (Resistance Temperature Detector)	RTD is a sensor that contains a resistor made up of a length of fine platinum wire wrapped around a glass core. It has an accurate resistance/ temperature relationship and the resistance value changes as its temperature changes. "Pt" is the symbol for platinum, "100" for the resistance in ohms at 0 °C.
Relative humidity	Thin-film capacitive sensor	Thin-film capacitance sensor operates on the principle that changes in relative humidity cause the capacitance of a sensor to change in a detectable and repeatable fashion.

3.3.2 Probe calibration

The probes of the measuring instrument have been designed to be maintenance-free and stable for long periods, since they collect gases via molecular diffusion. The probe works on "factory mode" and it does not require calibration at each measurement. The probe was calibrated at the factory during its manufacturing according to Gray-Wolf standard. Whenever this instrument is used a calibration data is produced that includes date, last factory calibration and settings for each parameter. The calibration data is stored in the probe and a copy is made (along with the measurement data) in every data location file of the micro-computer.

3.4. Data Collection and Analysis

3.4.1. Data collection

The concentrations of the atmospheric trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) along with temperature and humidity were measured with an automatic direct sense toxic gas monitoring instrument (Model TG-501 and TG-502, GrayWolf, Ireland) at the roof-top (20 meter above the ground level) of the "House Tutor Quarter", Amar Ekushey Hall, Dhaka University, Dhaka 1000, Bangladesh for a period of 1 year, i.e., June 2013 to May 2014. Ten-minute average trace gas concentrations as well as temperature and relative humidity were measured for 4 to 5 hours (8:00 to 13:00 hour local time) for 3 days in a week over a year (4 seasons). Data were collected in both the working and weekend days as it would represent the overall scenario of the trace gases in a year. To observe the diurnal tends of trace gases (CO, NO_2, TVOC, NH_3, H_2S and PH_3) also data were collected for twenty four hours.

The meteorological data of Dhaka city such as rainfall, wind direction and wind speed had been obtained from the Bangladesh Meteorological Department (BMD), Dhaka, Bangladesh for the study period of 1 year, i.e., June 2013 to May 2014. Also sunny days, rainy days, cloudy days and fogy days were observed during the investigations.

The concentrations of the same trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) were also measured at Karwan Bazarin in Dhaka city, Dhamrai in Dhaka district, Jamalganj in Sunamganj district and Badla Haor in Kishoreganj district for short period (one to three days). The measured concentrations of the trace gases of these different locations had been compared with the concentration measured at the Dhaka University campus.

3.4.2. Data analysis

From the collected data overall trends (time series analysis), monthly and seasonal variations of the concentrations of measured trace gases (CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3) were studied. Statistical analyses were also done. Microsoft Excel and SigmaPlot (an advanced scientific graphing and statistical analysis platform) were used for data interpretation. The overall trends of the temperature and humidity data from June 2013 to May 2014 were studied to find relationships with the concentration of trace gases.

3.4.3. Air mass trajectory analysis

3.4.3.1. HYSPLIT model

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) (Draxler and Hess, 1997, 1998; Rolph *et al.*, 2017; Stein *et al.*, 2015;) model by Air Resources Laboratory (ARL) of National Oceanic and Atmospheric Administration (NOAA), USA is a commonly used air modeling program that can calculate air mass paths from one region to another, and thus demonstrate whether the vector for air pollutant transport is indeed present (Perkauskas, 2000). It is a complete system for computing atmospheric trajectories as well as complex transport, dispersion, chemical transformation, and deposition simulations of pollutants and hazardous materials (NOAA, 1999). A common application is a backward trajectory analysis to determine the origin of air masses and establish source-receptor relationships. Other applications include backward/forward air mass trajectories analysis for tracking and forecasting the release of radioactive material, wildfire smoke, windblown dust, pollutants from various stationary and mobile emission sources, allergens and volcanic ash. HSYPLIT model uses gridded meteorological data obtained from the archived data sources to drive the trajectories and concentrations either backwards or forwards in time at regular time intervals. HYSPLIT calculates advection and dispersion using either puff or particle approaches under a Lagrangian framework (Draxler and Hess, 1997). In the puff model, puffs expand until they exceed the size of the meteorological grid cell (either horizontally or vertically) and then split into several new puffs, each with its share of the pollutant mass. In the particle model, a fixed number of particles are advected about the model domain by the mean wind field and spread by a turbulent component. The model's default configuration assumes a 3-dimensional particle distribution (horizontal and vertical). The model calculation method is a hybrid between the Lagrangian approach, using a moving frame of reference for the advection and diffusion calculations as the trajectories or air parcels move from their initial location, and the Eulerian methodology, which uses a fixed three-dimensional grid as a frame of reference to compute concentrations of air pollutants (Draxler, 2003). The trajectory calculation is achieved by the time integration of the position of an air parcel as it is transported by the 3-D winds (Draxler and Hess, 1997). By moving backward in time, the resulting back trajectory indicates air mass arriving at a receptor at a particular time, thus identifies the source region. The HYSPLIT model has been used in numerous air quality applications (Hsu *et al*., 2003; Poissant, 1999).

3.4.3.2. Experimental procedure for air mass backward trajectories

The backward trajectories were calculated by the NOAA HYSPLIT model (Rolph *et al*., 2017; Stein *et al*., 2015). Trajectories are colour-coded to show the altitudinal variations of the air parcels along their path. To prepare HSYPLIT’s back trajectories at the trace gas data sampling location ($23^0$43'30.25"N latitude and $90^0$24'11.91"E longitude), Dhaka University campus, archived gridded meteorological data sources of Air Resources Laboratory (ARL), USA were used. Back trajectories of air masses arriving to the data sampling site were calculated 96 hours backwards in time that moved on 500 m, 1000 m and 3000 m above the ground surface. After every 6 hours trajectory points were located. NOAA HYSPLIT models were run to create backward trajectories at 04:00 UTC (10:00 a.m. local time) on the 10th July 2013 (monsoon season) and 10th January 2014 (winter season) to observe the influence of air masses in the two extreme opposite seasons on the concentrations of trace gases.

3.4.4 Wind rose plot

Generally local wind direction and speed have influence on the measured concentrations of trace gases, because prevailing wind can carry air pollutants if they have presence on the way of the blowing air. In this regard, wind directions and speeds prevailed in the four seasons, from June 2013 to May 2014, in Dhaka City, Bangladesh were collected from the Bangladesh Meteorological Department (BMD). Then, rose plots of prevailing wind directions and speeds for different seasons were created with the collected data. Also wind rose plot had been created at 10:00 hour local time on the 10th July 2013 (monsoon season) and 10th January 2014 (winter season) to observe whether local wind direction and speed had any influence on the measured concentrations of trace gases.

3.4.5 Positive Matrix Factorization (PMF) Model

The Positive Matrix Factorization (PMF) developed by the Environmental Protection Agency (EPA) of USA is a widely implemented multivariate factor analysis receptor model and has been widely used in air pollution research community in many air pollutants source apportionment studies. The fundamental principle of PMF is the conversion of mass analysis. By using the species concentration of the samples, the model could obtain sources of chemical composition and contributions that affecting the sampling point. In this research work, factor contribution/profile of different sources of O_3, TVOCs and NOx gases was measured using US EPA PMF 5.0 model of the United States Environmental Protection Agency (US EPA) as suggested by Norris and Duvall (2014). Detailed descriptions of PMF application are given at US EPA 5.0 fundamentals and user guide.

Positive matrix factorization (PMF) model is a multivariate factor analysis tool that decomposes (factorizes) a matrix of speciated sample data into two matrices: factor contributions and factor profiles. The corresponding two-way factor (two matrices) model can be expressed through the following equation:

$$X = GF + E$$

Here, any matrix X of data of dimension n rows and m columns (where n and m are the number of samples and the number of species, respectively) can be factorized into two matrices, namely G(n×p) and F(p×m), and the unexplained part of X, i.e., E [where p represents the number of (independent source) factors extracted].

or,

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

Here, i =1,...,n; j =1,...,m; k =1,...,p; i = number of sample (number of data), j = number of species (what kinds of gases), k = number of independent source/factor, X is the n×m data matrix consisting of n rows of n samples and m columns containing the m detected species; G is a n×p matrix of source contributions and F is a p×m matrix of source profiles. The remaining un-modeled part of the data is represented by the residual matrix E. The values g_{ik} and f_{kj} (required to be non-negative) are adjusted until a minimum (value is obtained) for the objective function Q, i.e. the sum of squares of the ratio of the residuals and the user defined uncertainty matrix S_{ij} for a given number of factors (sources) p is found:

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

The theoretical Q (Qexpected) can be approximated as

$$Qexp = nm - p\,(n+m)$$

It is the goal to find solutions with a minimum for Q/Qexp.

Positive matrix factorization (PMF) model is a mathematical factor based on receptor model that interprets source types with a robust uncertainty estimate. Two sets of data were run through the PMF model: (1) concentration data file (excel file) and (2) uncertainty file (excel file). The concentration of each element (gas data) was pretreated and validated on the outliers, missing values or values below MDL (method detection limit). Species (gas) with concentration below MDL (method detection limit) were replaced with the half of the MDL. Zeroes and negatives are not permitted for either the detection limit or the percent uncertainty. The uncertainty (Unc) is calculated using a fixed fraction of the MDL.

$$\mathrm{Unc} = \frac{5}{6} \times \mathrm{MDL}$$

If the concentration is greater than the MDL provided, the calculation is based on a user provided fraction of the concentration and MDL.

$$\mathrm{Unc} = \sqrt{(\mathrm{Error\ Fraction} \times \mathrm{concentration})^2 + (0.5 \times \mathrm{MDL})^2}$$

The uncertainty value of each variable (each gas) of each sample (data value, concentration of gas) was calculated following the empirical formula:

$$\sigma_{ij} = 0.01\,(X_{ij} + \overline{X}_j)$$

Where, σ_{ij} is the estimated measurement error for j^{th} species (up to the last or the jith sample value of the last gas species) in the sample, X_{ij} is the observed elements (gases) concentration, and $\bar{X}_j$ is the mean value (of each gas). Thus, the measurement of uncertainty (S_{ij}) can be computed using the following equation:

$$S_{ij} = \sigma_{ij} + C_3 X_{ij}$$

In this study, a value of 0.4 for C_3 (calibrated data or span data) was used. An additional 5% uncertainty was added to cover any methodological errors. To show the stability of the results, the error of the concentration for each variable was estimated using bootstrap (BS), displacement (DISP), and a combination of BS-DISP.

In preparing PMF model, it also needs to provide a number of sources, and the source types are identified through trial and error by comparing them to measured factor profiles. Source contributions are used to determine how much each source contributed to a sample (gas species). Factor profiles need to be interpreted to identify the source types that may be contributing (%) to the sample using measured source profile information, and emissions or discharge inventories. The model calculates source contributions and source profiles or fingerprints. PMF 5.0 model was run for O_3 TVOCs and NOx for the source apportionment study.

CHAPTER FOUR

RESULTS

AND

DISCUSSION

CHAPTER FOUR
RESULTS AND DISCUSSION

Atmospheric trace gas concentrations vary widely, and the variability of the concentration of different trace gases is controlled by a combination of factors including emission source strengths, meteorological conditions, dispersion and dilution processes as well as chemical and photochemical reaction rates (Filella and Peñuelas, 2006). Firstly, the comparison of the concentrations of measured trace gases has been figured out. Then, the variations of the meteorological data during the study period as well as the paradigm of the variation of trace gas concentrations are discussed with time series, monthly and seasonal variations basis, depending on the measured concentrations. Also the diurnal variations of the concentrations of trace gas have been discussed for a whole day. Finally the measured concentrations of the trace gases at the Dhaka University campus were compared with the concentrations measured in semi-urban, rural and remote locations.

4.1 Comparison of the Trace Gases

4.1.1 Concentrations of trace gases measured at different locations

The main study was performed in the Dhaka University campus, Dhaka 1000, Bangladesh to measure trace gases (CO, NO, NO_2, TVOC, O_3, H_2S, PH_3 and NH_3) from June 2013 to May 2014. The concentrations of the same gases were also measured at Karwan Bazar (urban Dhaka), Dhamrai (semi-urban Dhaka), and in remote locations (Jamalganj in Sunamganj district, and Badla Haor in Kishoreganj district). The measured concentration of the trace gases of these locations had been compared with the concentration of trace gases measured at the Dhaka University campus. A comparison between the measured concentrations ($\mu g/m^3$) of different gases at different location is presented in Table 4.1.

Table 4.1: Comparison of the measured concentration (µg/m^3) of trace gases (CO, O_3, NO, NO_2, TVOC, H_2S, PH_3, and NH_3) of different locations in Bangladesh.

Locations	Concentration (µg/m^3)							
	CO	O_3	NO	NO_2	TVOC	H_2S	PH_3	NH_3
Dhaka University, Dhaka (urban area)	2603.6	36.6	281.5	182.7	10,068.2	84.8	133.1	133.8
Karwan Bazar, Dhaka (Commercial area)	5048.0	15.9	617.7	393.0	12042.0	131.8	151.3	50.9
Dhamrai, Dhaka (Semi-urban)	1773.2	30.1	279.8	265.6	19995.9	68.1	99.5	102.4
Jamalganj, Sunamganj (rural area)	1636.4	16.4	197.4	189.5	13520.6	99.5	197.8	361.3
Badla Haor, Kishoreganj (Semi-permanent water body)	1492.2	19.1	247.1	260.3	14828.9	104.5	110.4	486.1

At the Dhaka University campus, O_3 concentration was the highest that might be due to the availability of the high amount of O_3 precursors as well as the high photochemical reaction as the sampling device was placed on the roof-top (20 meter above ground level). It is evident that the concentration of the trace gases such as CO, NO, NO_2 and H_2S were the highest in Karwan Bazar, Dhaka due the presence of direct emission sources such as huge number of vehicles and severe traffic congestions. TVOC concentration was the highest in Dhamrai, the semi-urban area of Dhaka district. In Badla Haor, Kishoreganj district the NH_3 concentration was the utmost among the sampling sties because of the presence of vast paddy fields and enormous aquatic areas. PH_3 concentration was the highest in Jamalganj rural area, sunamganj might be due to the existence of vast paddy fields and nearby river system.

4.1.2 Comparison of the concentrations of trace gases with air quality standards

The annual average concentration levels of the measured CO, NO_2 and O_3 gases at the Dhaka University campus along with the standard limits of USEPA, EU, WHO and DoE, Bangladesh have given in Table 4.2. Only three gases were compared with the limit value as there no guide line value for other measured gases.

Table 4.2: Comparison of the estimated concentrations ($\mu g/m^3$) of different gases (CO, NO_2 and O_3) with air quality standards.

Pollutants	Average time	Concentration ($\mu g/m^3$)				
		USEPA	EU	WHO	DoE	Dhaka University campus
CO	15 minutes			100,000	-	2,603.6
	30 minutes			60,000	-	
	1 hour	40,075 (35 ppm)		30,000	40,000	
	8 hour	10,305 (9 ppm)	10,000	10,000	10,000	
NO_2	1 hour	188 (100 ppb)	200	200	-	182.7
	annual	99.64 (53 ppb)	40	40	100	
O_3	1 hour			-	235	36.1
	8 hour	140 (0.07 ppm)	120	100	157	

(Source: USEPA, 2015; Kryzanowski and Cohen, 2008; WHO, 2006; DoE, 2016)

It can be said that annual average concentration of CO (2,603.6 $\mu g/m^3$) is within the standard limit set by US EPA, EU, WHO and DoE, Bangladesh. But, the annual average concentration of NO_2 (182.7 $\mu g/m^3$) in the ambient air exceeded the annual standard values set by US EPA, EU, WHO and DoE, Bangladesh. The annual average concentration of O_3 did not exceed any standard values of 1 hour and even 8 hour average time. However, the concentrations trace gases (CO and O_3) were within the standard limits, though elevated level of concentration of trace gases were observed.

4.2 Variation of the Meteorological Conditions

Meteorological parameters are known to be the key factors governing diurnal, monthly and seasonal variations of different gases (Filella and Peñuelas, 2006). The measurements of the meteorological parameters in Dhaka City were also done in addition to the trace gases. The principal meteorological conditions observed were temperature, relative humidity, wind speed and wind directions. The overall trends of the temperature and relative humidity during the study period of June 2013 and May 2014 have in Figure 4.1 and Figure 4.2. The 10-minute average minimum and maximum air temperatures were 15.1^{0}C and 36.8^{0}C in January 2014 and May 2014, respectively with an average of 27.01 ± 4.18^{0}C (Figure 4.1). The 10-minute average lowest relative humidity was recorded in April 2014 (25%), while the highest one was recorded in August 2013 (96%) with an average value, 75.71 ± 17.99% (Figure4.2).

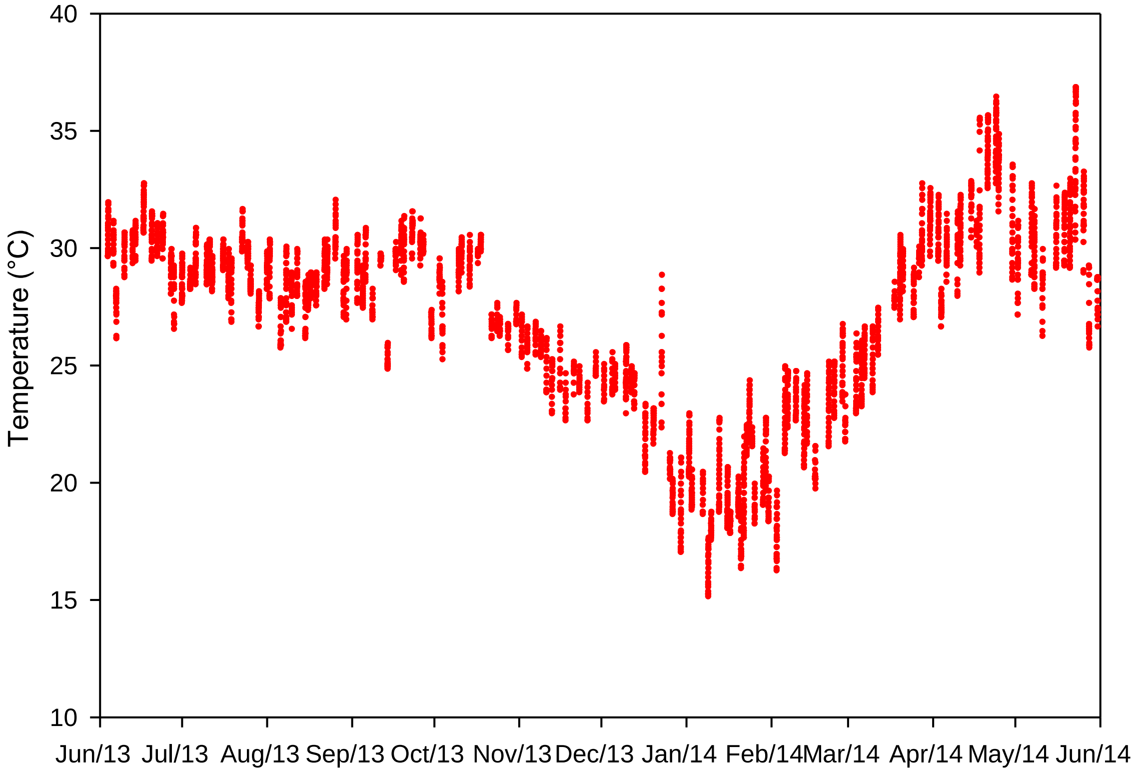


Figure 4.1: Overall trends of the temperature in Dhaka University campus, Dhaka, Bangladesh from June 2013 to May 2014.

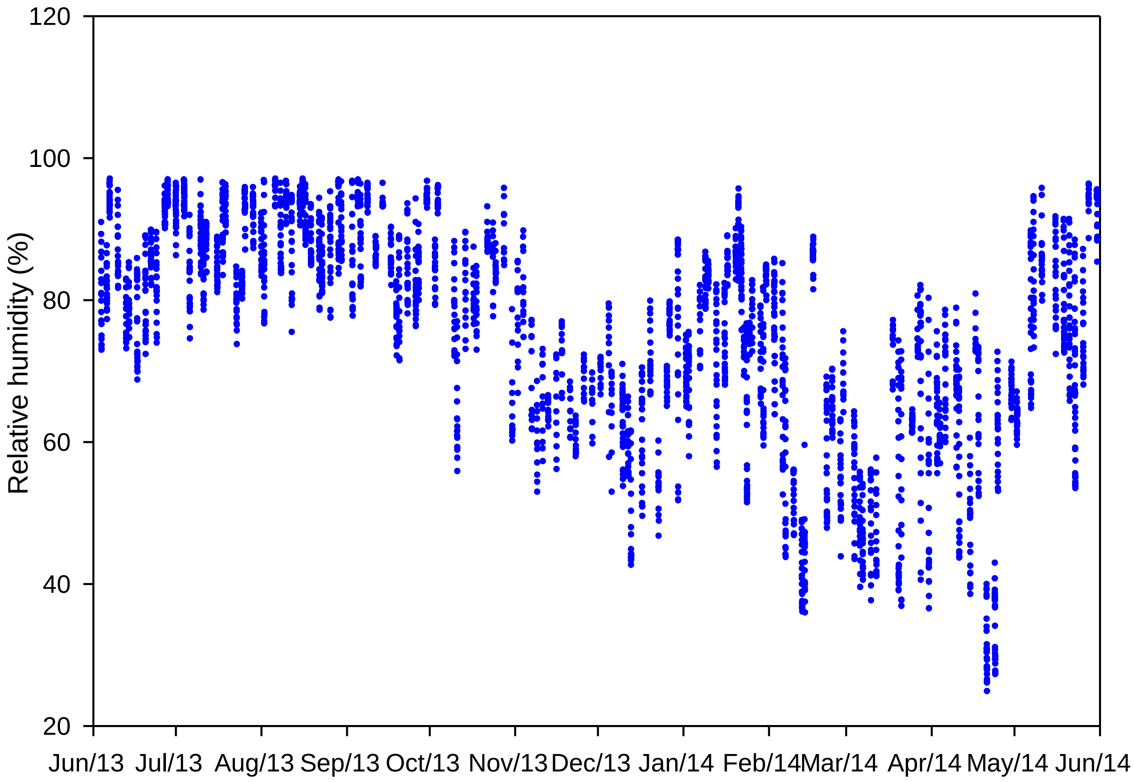


Figure 4.2: Overall trends of the relative humidity in Dhaka University campus, Dhaka, Bangladesh from June 2013 to May 2014.

Monthly average temperature and relative humidity variations were also calculated from the 10-minute averages of each month. From the figure it has been observed that the April 2014 was the hottest (31.6^{0}C) (Figure 4.3) and August 2014 was the most humid month (relative humidity 90%) (Figure 4.4) in Dhaka, Bangladesh.

The overall seasonal trends of the prevailing wind direction and speed (3 hour average) from June 2013 to May 2014 are shown in Figure 4.5(a) and in Figure 4.5(b). Strong prevailing wind reduces air pollutant concentrations and the downwind locations usually have higher concentrations than the upwind sites. During monsoon season, most of the prevailing winds were from the south-east, south and east directions (Figure 4.5a) with the average wind speeds up to 7.5 knot.

Figure 4.3: Monthly average temperature from June 2013 to May 2014 in Dhaka University campus, Dhaka Bangladesh.

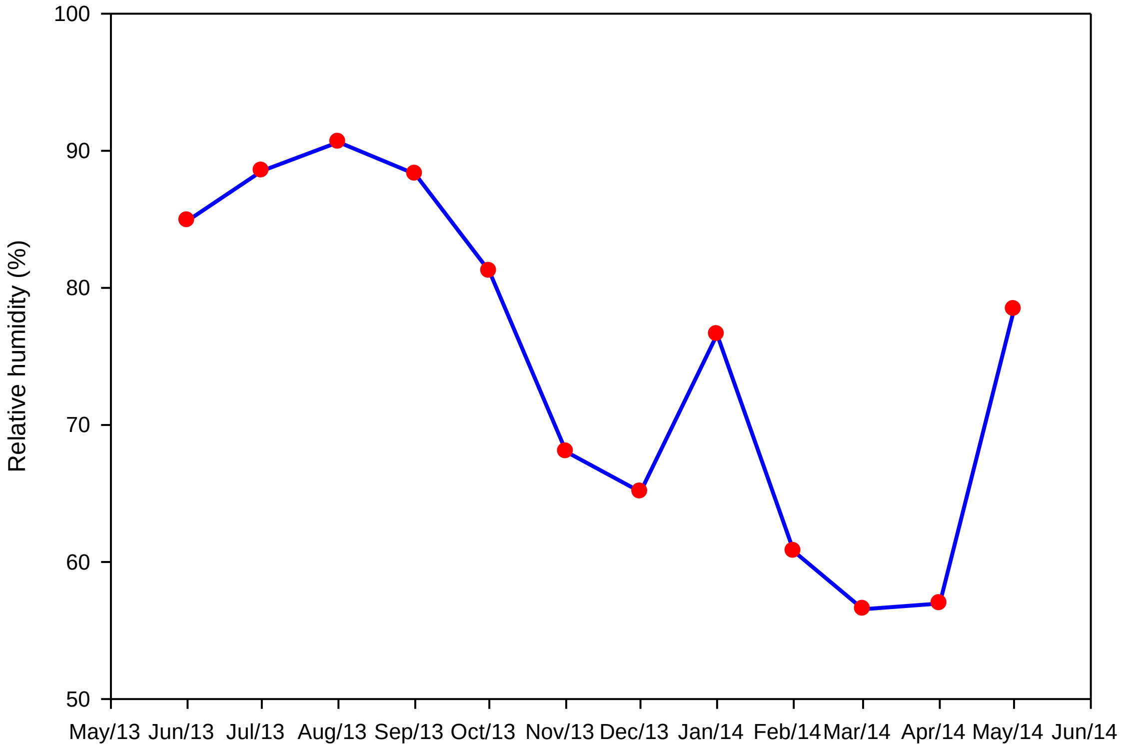
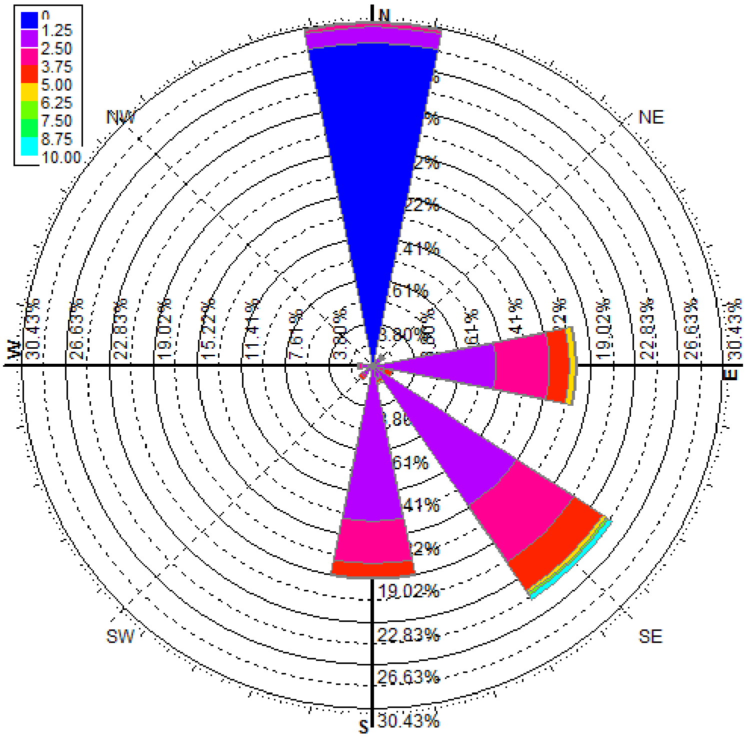
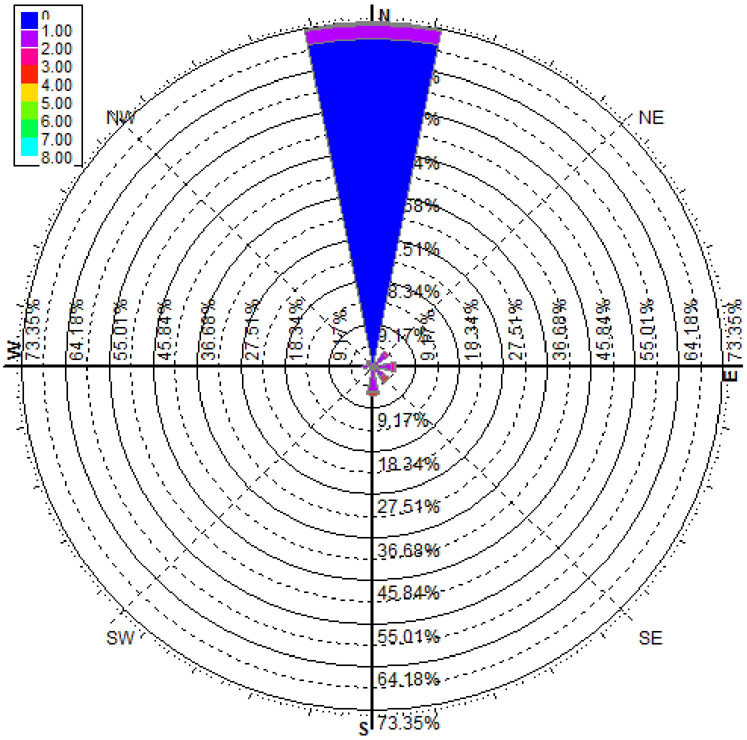


Figure 4.4: Monthly average relative humidity (%) from June 2013 to May 2014 in Dhaka University Campus, Dhaka, Bangladesh.

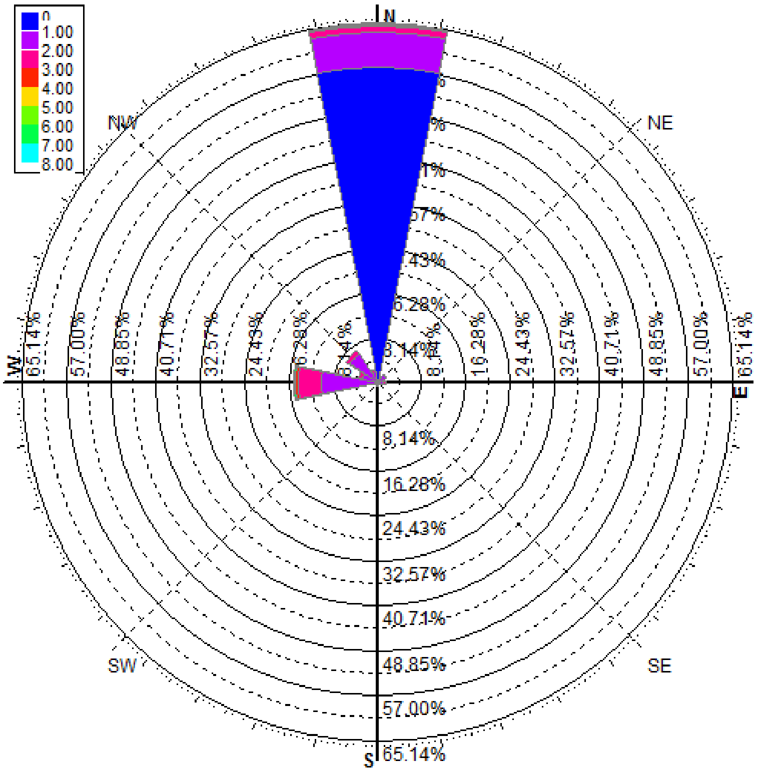


Monsoon

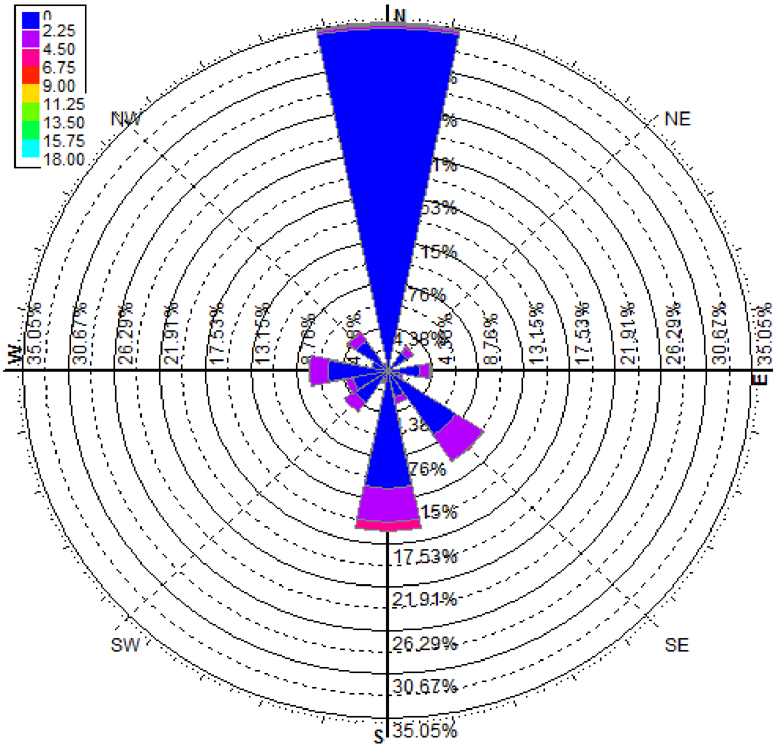


Post-monsoon

Figure 4.5(a): Wind rose plot showing the trends of wind direction and wind speed measured in monsoon (June 2013 - August 2013) and post-monsoon (September 2013 – November 2013) in Dhaka, Bangladesh.



Winter



Pre-monsoon

Figure 4.5 (b): Wind rose plot showing the trends of wind direction and wind speed measured in winter (December 2013 – February 2014) and pre-monsoon (March 2014 – May 2014) in Dhaka, Bangladesh.

While wind velocity was least (up to 2 Knot) in the post monsoon with prevailing wind direction mostly from the north (Figure 4.5b). During the winter season, wind velocity was up to 3 Knot with prevailing wind mainly from the north, west and north-west directions. In the pre-monsoon, wind directions were diverse with wind speed up to 6.75 knot.

4.3 Variation of CO Concentrations in Dhaka University Campus, Bangladesh

4.3.1 Time series of CO concentrations

Time series of the 10-minute average CO concentrations measured at Dhaka University campus during the study period of June 2013 and May 2014 has given in Figure 4.6. The average concentrations were highly variable both within the day and across the year (Appendix 1). The measured CO concentration ranged from 864.6 μg/m^3 (February 2014) to 17,047.4 μg/m^3 (February 2014) with an average of 2603.6 ± 1216.4 μg/m^3 (Appendix 1). Average higher values were observed in most of the days in August 2013, September 2013 and winter months (December 2013, January

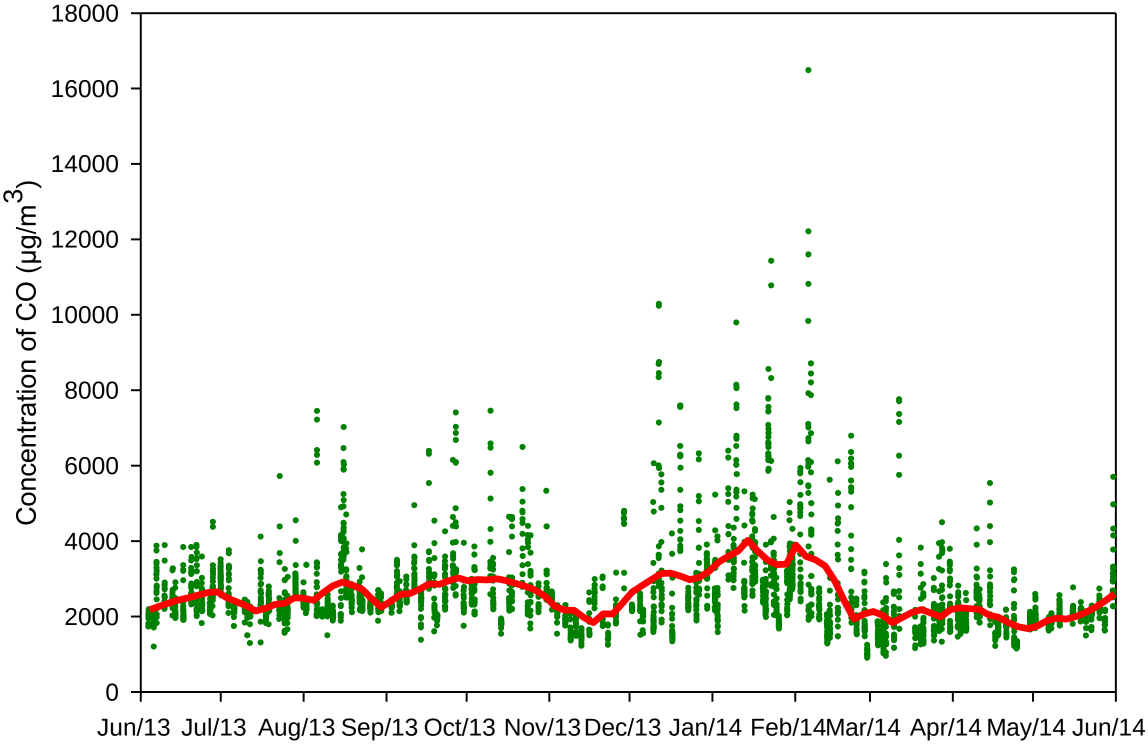


Figure 4.6: Time series of the measured concentrations of CO from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

2014 and February 2014) with a wide range of diversity within the sampling days. In pre-monsoon months, the concentrations came down to lower values. The changes in CO concentrations within the same day might be due to the variation in emission of sources. Traffic is considered to be the main source of CO in Dhaka city. Emissions from industrial sources and the oxidation of hydrocarbons in the urban environment are additional sources that brought changes in CO concentration in Dhaka.

The average concentration of CO (2603.6 µg/m^3) in Dhaka University area was about half of the measured value found in Kawran Bazar in Dhaka city, but about 1.5 times higher than Dhamrai, Dhaka; 1.6 times higher than Jamalganj, Sunamganj; and 1.8 times higher than Badla Haor, Kishoreganj (Table 4.1). One year average of CO concentration in New Delhi was 3366.8 µg/m^3 (Chelani *et al*., 2012), which was about 30% higher than the current measurement. The average concentration of ten cities in Northern China was 1362.8 µg/m^3 (Wang *et al*., 2014). One year average concentration of CO in large Russian cities was found 493.9 µg/m^3 (Elanshy *et al*., 2016).

4.3.2 Monthly average concentrations of CO

The monthly average variation of the CO concentrations calculated from the 10-minute average concentration during the study period from June 2013 to May 2014 is shown in Figure 4.7. The measured concentrations varied from 1,867.3 to 3,486.5 µg/m^{3}with an average value of 2,569.6 ± 498.0 µg/m^3. The higher concentrations of CO were recorded in September 2013, October 2013, December 2013, January 2014 and February 2014 with the highest value of 3,486.5 µg/m^3 in January 2014. The monthly average concentrations of CO were lower in March 2014, April 2014 and May 2014 with the lowest value of 1867.3µg/m^3 in April 2014. Intermediate values were found in other months of the study period.

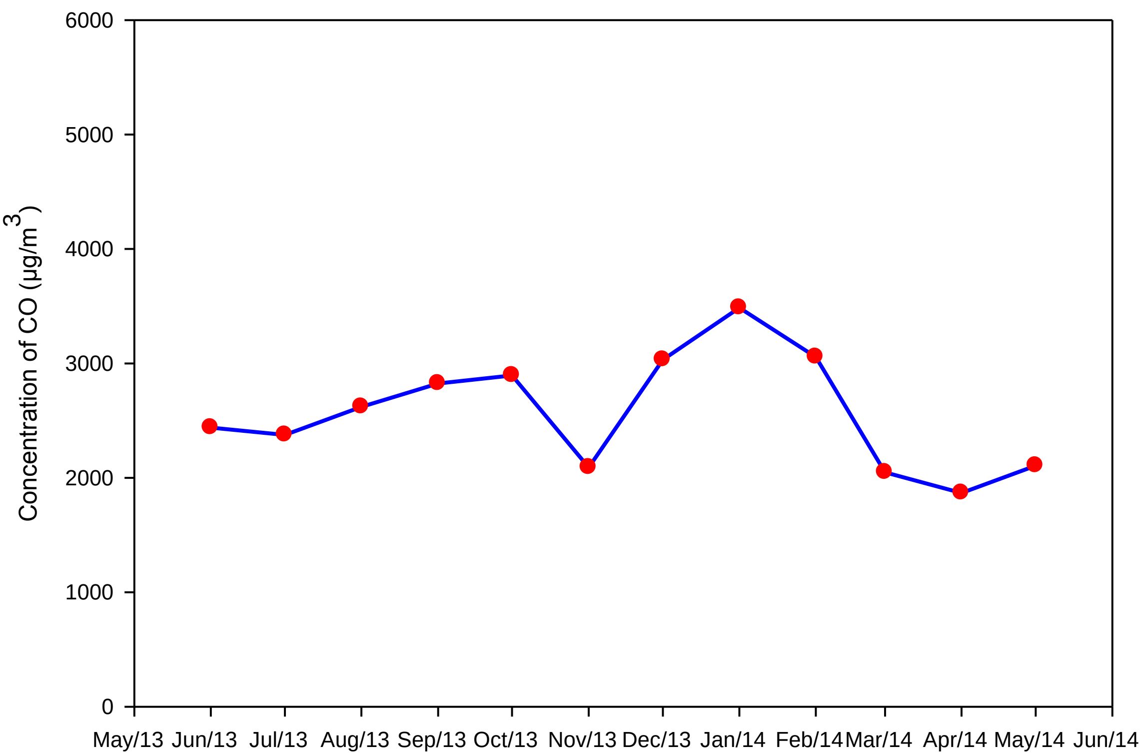


Figure 4.7: Monthly average concentrations of the measured CO gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

4.3.3 Seasonal variation of CO concentrations

The behavior of CO levels as a function of the season is presented in Figure 4.8. The seasonal trends of CO revealed that the highest level of CO (3237.9 µg/m^3) was detected in winter season. The lowest seasonal average was recorded 2030.8 µg/m^3 in pre-monsoon. The concentrations of CO then augmented in monsoon (2,485.3 µg/m^3) and post-monsoon (2,665.0 µg/m^3) seasons. The seasonal average of the CO concentration was 2,604.8 ± 499.4 µg/m^3.

The highest concentration of CO in the winter season occurred due to the emissions from traffics and industries along with biomass burning (heating and cooking purposes, and post-agricultural burning) and brick kiln operations around Dhaka city especially in winter. Ahmed and Begum (2010), and Motalib and Lasco (2014) observed higher CO concentration in winter season in Dhaka city and claimed traffic congestion and brick field were the sources of emission. Pochanart *et al.* (2003) observed that biomass burning, particularly post-agricultural waste burning in South and Southeast Asia was a major source of atmospheric pollutants, especially CO.

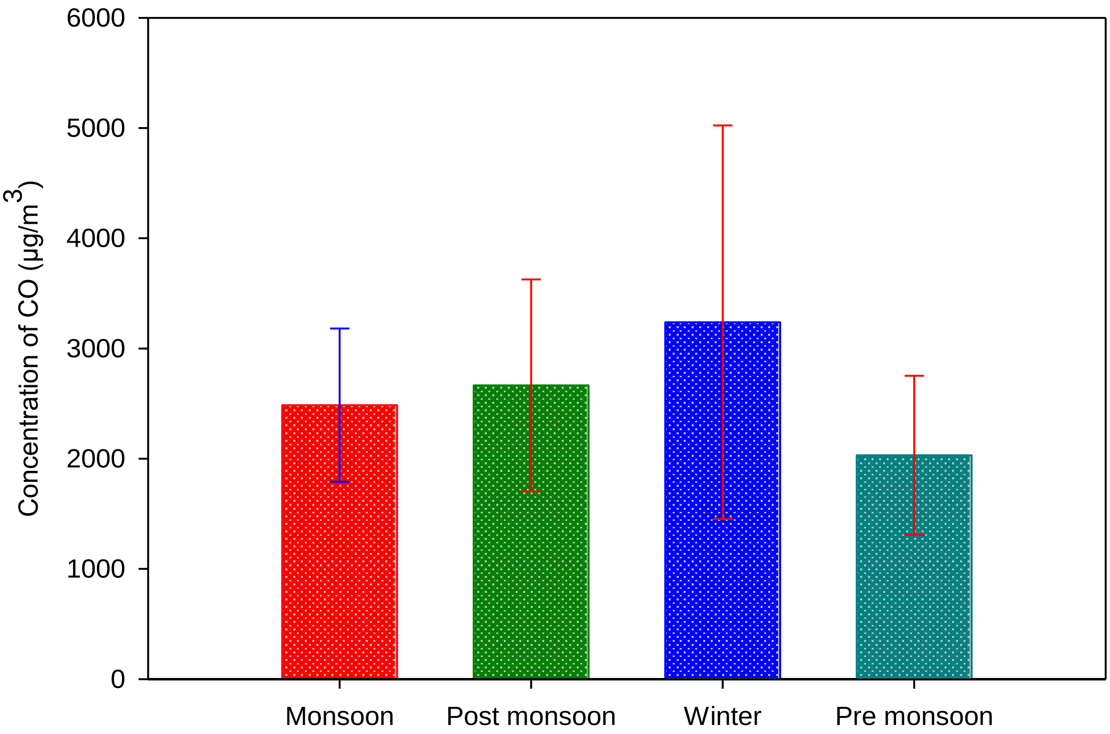


Figure 4.8: Seasonal variations of the concentrations of CO from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

During winter season, the dispersion and dilution effects on gases are low due to low wind effects and less photochemical activity, and this also could be a cause of higher CO concentration. Higher CO level in the winter (cold season) has also been reported by many researchers (Bigi and Harrison, 2010; Jang *et al*., 2017). Elansky *et al*. (2016) in Russian cities observed that the highest concentration of CO was strongly dependent on anthropogenic sources. In pre-monsoon season, the solar intensity and temperature are very high in favoring the formation of HO radical, and which then causes the chemical decomposition/removal of CO (Duncan *et al*., 2007; Holloway *et al*., 2000; Logan *et al*., 1981).

$$CO + HO\bullet + M \rightarrow CO_2 + HOO\bullet + M$$

So the measured CO concentration in the pre-monsoon season was very low.

4.3.4 Diurnal variation of CO concentrations

The mean hourly diurnal variations of CO concentration for 24-hour period have been presented in Figure 4.9. The diurnal CO concentration was higher in the morning hours (6:00-11:00 hour local time). The diurnal course of CO concentrations exhibited single peak in the morning (08:00 hour local time) and the peak value was 2066.8 μg/m^3. Then, the diurnal concentration of CO declined at noon hours and again, it increased in the evening (17:00 - 20:00 hour local time). After the evening, concentration peak showed declining tendency and the lowest diurnal value was 1453.2μg/m^3 at 04:00 hour local time. None of the measured 1-hour CO concentration exceeded the 1-hour limit value set by WHO (30,000.0 μg/m^3) and DoE, (Bangladesh) (40,000.0 μg/m^3). During the morning and evening hours, CO concentration was higher because of increased emissions from large number of vehicles on roads and industrial operations. While in the afternoon, CO concentration decreased due to diffusion of gas being high temperature and oxidation of CO by OH radical.

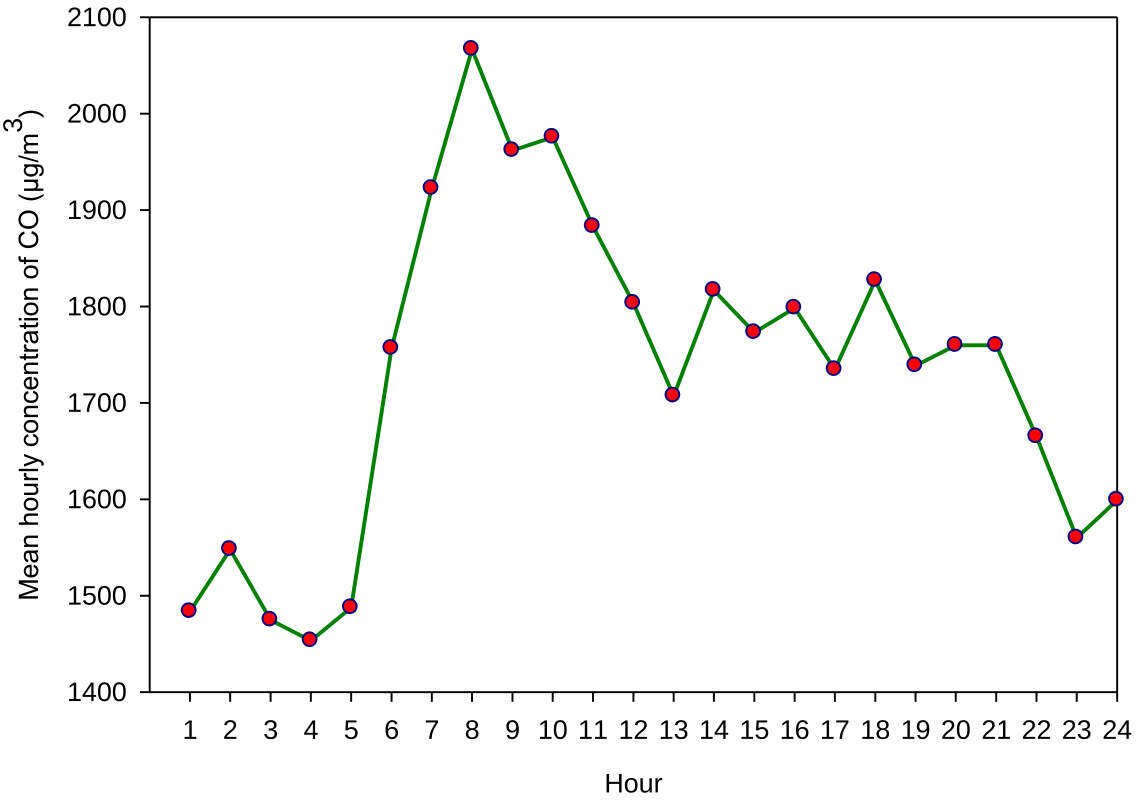


Figure 4.9: Mean hourly diurnal variation of CO concentrations in Dhaka University campus, Bangladesh.

Chandra *et al*. (2016) also made the same kind of observation. At the evening its concentration again increased due to thermal inversion. Yin *et al*. (2017) had observed two peaks at morning and evening rush hours due to the effect of on-road motor vehicles in China. Chandra *et al*. (2016) also observed two peaks at morning and at the end of evening in Ahmedabad, India.

4.4 Variation of NO Concentrations in Dhaka University Campus, Bangladesh

4.4.1 Time series of NO concentrations

Figure 4.10 presents the time series of 10-minute average NO concentrations during the study period from June 2013 to May 2014. The measured concentrations varied widely both within the day and across the year. In this study, 10-minute average NO concentration ranged from 5.2 to 731.7 µg/m^3 with an average of 281.5 ± 158.0µg/m^3

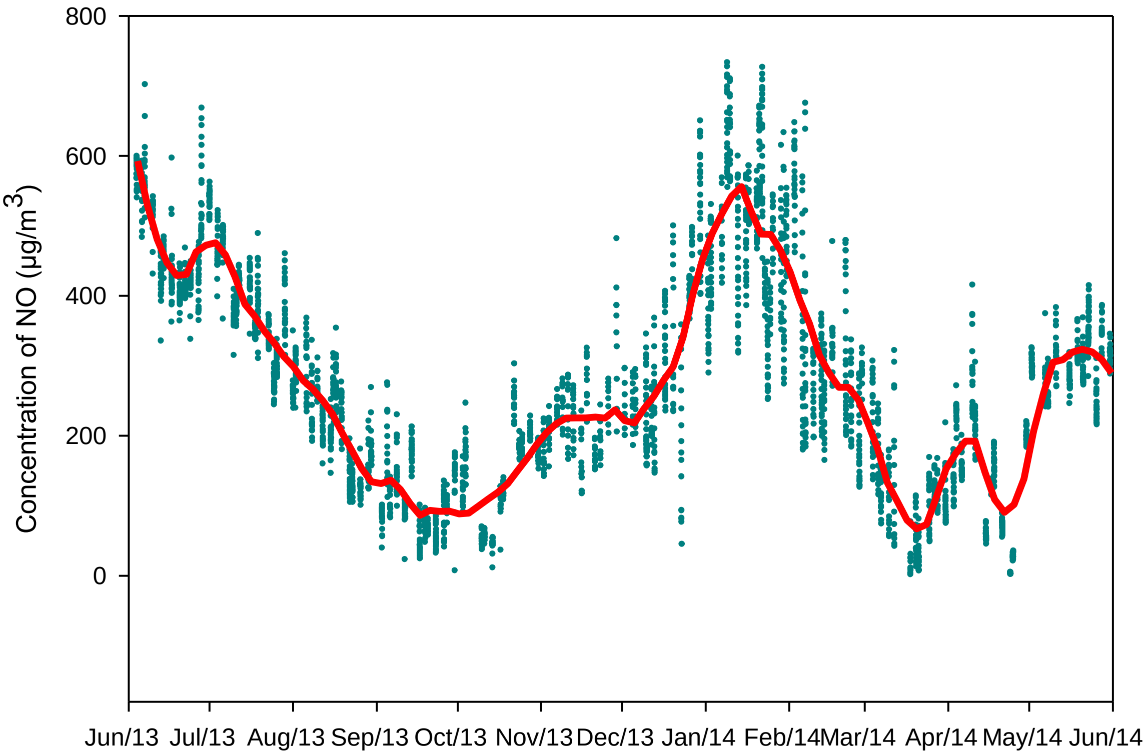


Figure 4.10 Time series of the measured concentrations of NO from June 2013 to May 2014 in Dhaka University campus, Bangladesh

(Appendix 1). Higher NO concentrations were observed during the months of June 2013, December 2013, January 2014 and February 2014 with the maximum value of 731.7 µg/m^3 in January 2014. However, lower NO concentrations were observed during the months of September 2013and March 2014 with the lowermost value of 5.20 µg/m^3 in March 2014.

The average concentration of NO was 281.5 µg/m^3 in Dhaka University area. While NO concentration was 617.7µg/m^3 in Kawran Bazar, Dhaka city; about 279.8 µg/m^3 in Dhamrai, Dhaka; 197.4µg/m^3 in Jamalganj, Sunamganj; and 247.1 µg/m^3 in Badla Haor, Kishoreganj (Table 4.1). One year average (2013-2014) concentration of NO in Busan, South Korea was 67.6 µg/m^3 (Jang *et al.*, 2017), whereas one year average in large cities in Russia was 13.1 µg/m^3 (Elansky *et al.*, 2016).

4.4.2 Monthly average concentrations of NO

The monthly average concentrations of NO gas (Figure 4.11) were calculated from the 10-minute average concentrations of the respective months, ranged from 103.6 to 491.4 µg/m^3 with an annual average of 268.7 ± 135.9 µg/m^3. The lowest and highest concentrations of NO were observed in September 2013 and January 2014, respectively. There are two peaks (in June 2013 and January 2014) and two lowermost values (in September 2013 and March 2014) of NO concentrations during the study period.

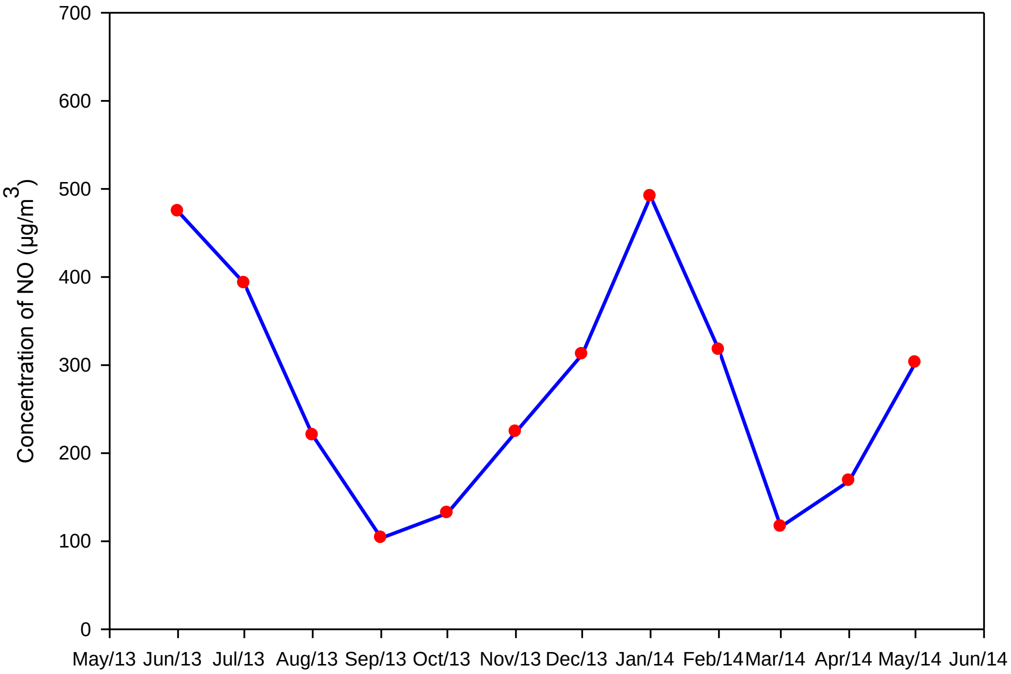


Figure 4.11: Monthly average concentrations of the measured NO gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

The increasing trend of NO concentrations was found from September 2013 to January 2014; then declined till March 2014 and afterward increased. Furthermore, NO concentration declining tendency was also observed from June 2013 to September 2013.

4.4.3 Seasonal variation of NO concentrations

The seasonal pattern of NO concentrations is illustrated in Figure 4.12. The NO concentration differed from one season to another. The highest level of NO concentration (392.1 µg/m^3) was observed in winter and the lowest (142.4 µg/m^3) in post-monsoon i.e., winter concentration was 2.75 times higher than in post-monsoon. Monsoon season exhibited the second highest value of NO (351.1 µg/m^3) and then pre-monsoon (188.3 µg/m^3). The average seasonal value was 268.5 ± 121.7µg/m^3.

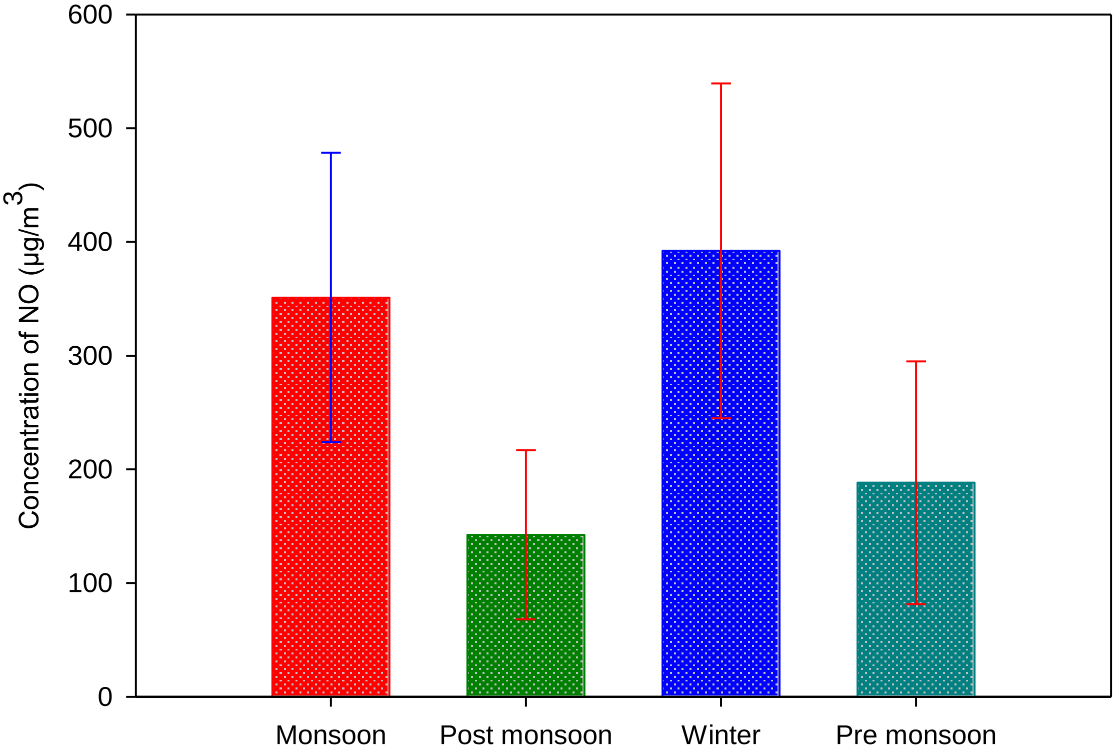


Figure 4.12: Seasonal variations of the concentrations of NO from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

Nitric oxide is produced anthropogenically in high temperature combustion processes of N_2 and O_2 or though combustion of the nitrogen content of the fuel.

$$N_2 + O_2 \rightarrow 2NO$$

Major anthropogenic sources of NO include gas- and diesel-powered vehicles, fossil fuel-fired electricity generating stations, industrial boilers, municipal incinerators, and home space heating. Light-duty vehicles emit NOx mostly in the form of NO, but diesel vehicles tend to emit higher NO_2 fractions (Carslaw, 2005; Herner *et al*., 2009; Lloyd and Cackette, 2001). It is produced naturally in soil through biological nitrification, denitrification and chemodenitrification processes (Williams *et al*., 1992) and as result of biomass burning, lightning, and oxidation of NH_3 by photochemical reaction (Godish, 2004). Nitric oxide concentration primarily depends heavily upon on the traffic. The highest concentration of NO in the winter season occurred due to the emissions from traffics and industries along with biomass burning. It could also be due to a lower mixing highest and less intensive photochemical reaction under at a low ambient temperature (Bielaczyc *et al*., 2014; Dandiots *et al*., *201*3; Henschel *et al*., 2015). Elansky *et al*. (2016) in Russian cities observed that the highest concentration of NO was strongly dependent on anthropogenic sources.

Moreover in winter, Dhaka city experiences higher rate of pollution due to emissions from brick kilns and other industries. During the monsoon NO concentrations were lower than winter season and that might be due to the removal of NO by precipitation. In the pre-monsoon and post monsoon season NO concentrations were lower, which might have happened due to the intense solar radiation that favor photochemical oxidation of NO to NO_2 (Hobbs, 2000; Roberts-Semple *et al*., 2012).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(both day and night)}$$
$$ROO\bullet + NO \rightarrow NO_2 + RO\bullet$$
$$HOO\bullet + NO \rightarrow NO_2 + HO\bullet$$
$$RC(O)OO\bullet + NO \rightarrow NO_2 + RC(O)O\bullet$$

Nitric oxide concentration is not only influenced by the anthropogenic activities such as rush-hour traffic, but also by the atmospheric mixing ratio during the daylight hours (Mayer, 1999).Thus, the seasonal pattern of NO levels differed between winter and monsoon.

4.5 Variation of NO_2 Concentrations in Dhaka University Campus, Bangladesh

4.5.1 Time series of NO_2 concentrations

The time series of the 10-minute average concentration of NO_2 during the study period, from June 2013 to May 2014 is presented in Figure 4.13. From the figure it is found that the 10-minute average concentration of NO_2 varied both within the day and throughout the year. The lowest concentration was measured as low as 10.2 µg/m^3 in January 2014 and the highest value was 399.3 µg/m^3 in April 2014 with an annual average value of 182.7 ± 69.4 µg/m^3 (Appendix 1). The 10-minute average of NO_2 concentrations was very scattered within every sampling day, except the days in November 2013.The average concentrations of NO_2 mostly remained high in September 2013, October 2013, February 2014 and March 2014.

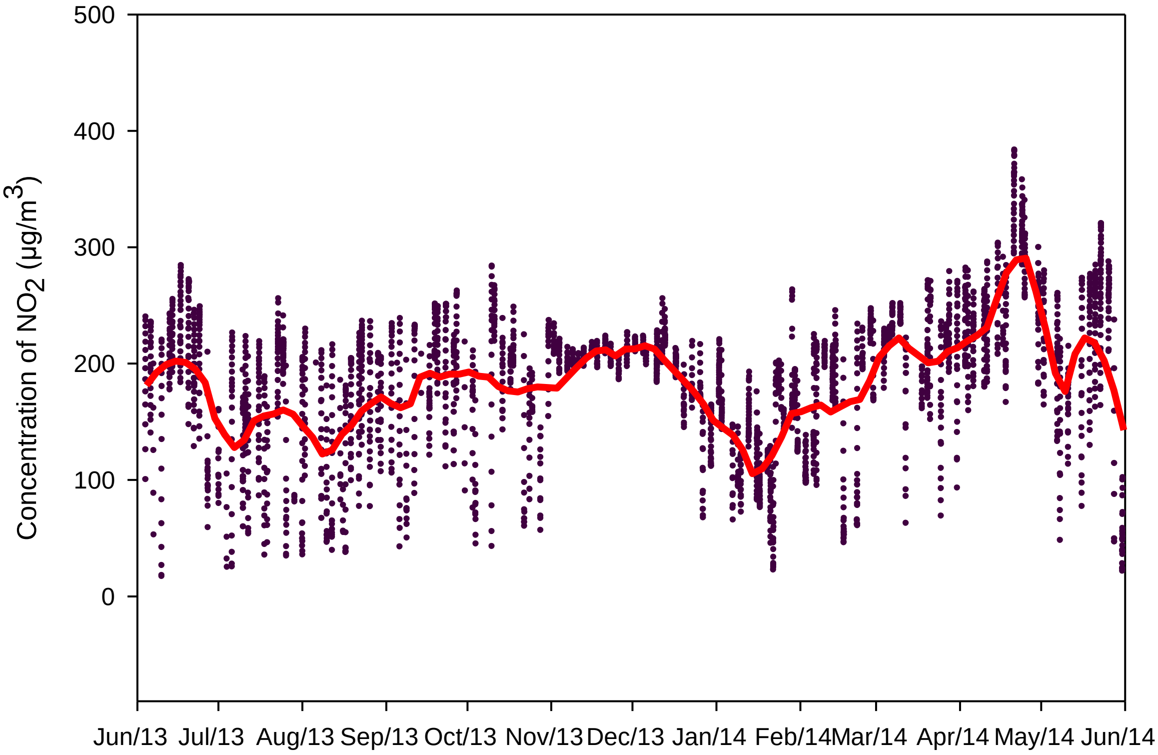


Figure 4.13: Time series of the measured concentrations of NO_2 from June 2013to May 2014 in Dhaka University campus, Bangladesh.

The average concentration of NO_2 (182.7 µg/m^3) in Dhaka University area was about 2.15 times lower than that measured value found in Kawran Bazar, Dhaka city; 1.45 times lower than Dhamrai, Dhaka and 1.42 times lower than Badla Haor, Kishorerganj; but the concentration of Jamalganj, Sunamganj was almost the same as the measured value obtained in Dhaka University campus area (Table 4.1). The average annual (2013 - 2014) concentrations of NO_2 in the traffic and commercial sites of urban air in Busan, South Korea were 59.5 µg/m^3 and 48.0 µg/m^3, respectively (Jang *et al*., 2017). They both were about one third of the concentration found in Dhaka University campus areas. One year average concentration of NO_2 in in large Russian cities was 20.7 µg/m^3 (Elansky *et al*., 2016). The average concentration of NO_2 in ten cities of Northern China was 44.4 µg/m^3 (Wang *et al*., 2014), which was four times lower than the current measurement in Dhaka University campus.

4.5.2 Monthly average concentrations of NO_2

The average monthly variation of NO_2 concentrations is shown in Figure 4.14. The monthly average NO_2 concentrations ranged from 106.0 to 237.8 µg/m^3, with an average value of 184.4 ± 33.4µg/m^3 (Appendix 1). The lowest concentration was observed in August 2013, and also lower values were found in July 2013 and January 2014. After January, NO_2 concentration showed increasing tendency till the maximum value in April 2014.

The rising tendency of NO_2 concentration might be due to the photochemical oxidation of NO by O_3, ROO• and odd hydrogen species (HO•, HOO•, H_2O_2, etc.) along with increasing intensity of solar radiation (Goddish, 2004; Jacob 1999,). Subsequently, a declining trend of monthly average NO_2 concentration was observed during monsoon months because some portion of it might be removed by precipitation. In winter months (December 2013, January 2014 and February 2014) the probable decrease of NO_2concentration could be the lower rate of NO oxidization to NO_2 byO_3, ROO•, HOO•, etc. as all reactions are dependent on the sunlight.

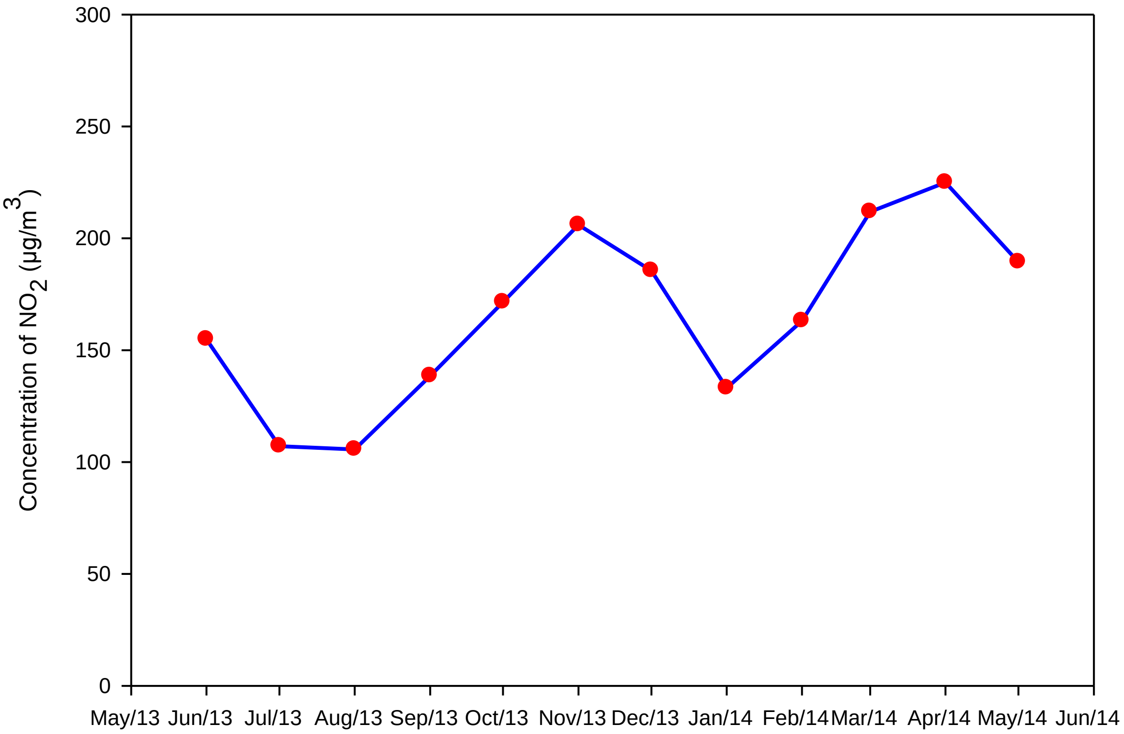


Figure 4.14: Monthly average concentrations of the measured NO_2 gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

4.5.3 Seasonal variation of NO_2 concentrations

The seasonal variations of NO_2 concentrations were assessed from June 2013 to May 2014, and the variation pattern is presented in Figure 4.15. The seasonal highest (223.2 µg/m^3) and lowest (163.1 µg/m^3) values were noticed in pre-monsoon and winter seasons, respectively. Monsoon (159.9 µg/m) and post-monsoon (185.7 µg/m) seasons showed increased value than winter season.

In Dhaka city, motor vehicles and industrial emissions are the main sources of NO_2 along with brick kilns operation especially in winter and pre-monsoon season. Azad and Kitada (1998) observed NO_2 concentration in winter 1995 - 1996 and speculated that motor vehicles and brick fields were the major emission sources. In pre-monsoon season and post-monsoon, the higher concentrations of NO_2 might be due to direct emission of NO_2 from diesel-runner vehicles, oxidation of NO by oxygen molecule (slow process), and also mainly by increased secondary production by photochemical oxidation of NO with O_3, ROO•, HOO•, etc.) (Hobbs, 2000; Jacob, 1999; Jang *et al.*, 2017; Mavroidis *et al.*, 2012).

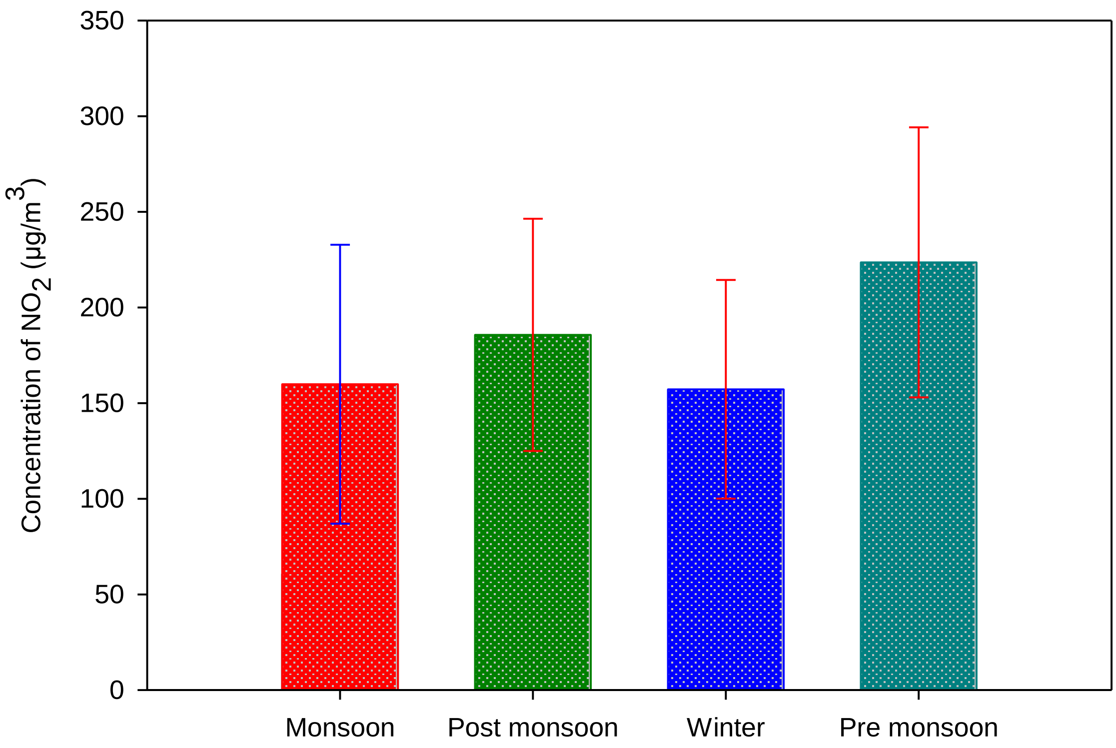


Figure 4.15: Seasonal variations of the concentrations of NO_2 from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

Thus, NO concentrations during post-monsoon and pre-monsoon season were measured lower in this experiment (Figure 4.12). Adon *et al.* (2016) also observed higher concentration of NO_2 in the dry season and lower concentration in the wet season during the period of January 2008 to December 2009 in Dakar, Senegal. In this experiment nitric dioxide concentration was observed lower in monsoon and post monsoon seasons than pre-monsoon because some portion of it might be removed by precipitation. Elansky *et al.* (2016) in Russian cities observed that the highest concentration of NO_2 was strongly dependent on anthropogenic sources. The lowest concentration of NO_2 in winter season might be lower rate of photochemical oxidation of NO to NO_2 (since NO_2 is mainly a photochemical pollutant), oxidation of NO_2 to a variety of products such as HNO_3, NO_3, N_2O_5, PAN (peroxy acyl nitrates), and partial removal of NO_2 by dry deposition at surface by under no precipitation (Azad and Kitada, 1998; Mavroidis and Llia, 2012). Also, at low temperature NO_2 may combine with organic peroxy radicals to form peroxy acylnitrates (Hobbs 2000; Jacob, 1999).

$$NO_2 + HO\bullet + M \rightarrow HNO_3 + M$$

$$RC(O)OO\bullet + NO_2 \rightarrow RC(O)OONO_2 \quad \text{(at low temperature)}$$

In contrast, in the winter season, higher NO_2 concentration of was observed by many researchers. Kumar *et al*. (2004) carried out NO_2 concentration measurement at Dayalbagh, a suburban site and at St. John's, an urban site at Agra (India) and showed that seasonally highest concentrations of NO_2 were observed during winter and lowest during monsoon. This is because of high fuel usage during winter. Also, during winter months, the pollutants emitted from various anthropogenic and natural sources are trapped in the boundary layer due to frequent temperature inversions.

4.5.4 Diurnal variation of NO_2 concentrations

The mean hourly diurnal distribution of NO_2 concentrations for 24-hour period is presented with in Figure 4.16. It is observed that the average hourly concentrations of NO_2 were higher in daytime hours than at night. The daytime peak value was 298.3 µg/m^3 at 15:00 hour local time and then declined gradually. The lowest value was 118.0 µg/m^{3}at 24:00 hour local time. Hourly NO_2 concentrations were augmented with increasing daytime due to the rise of emissions from vehicles and industrial sources.

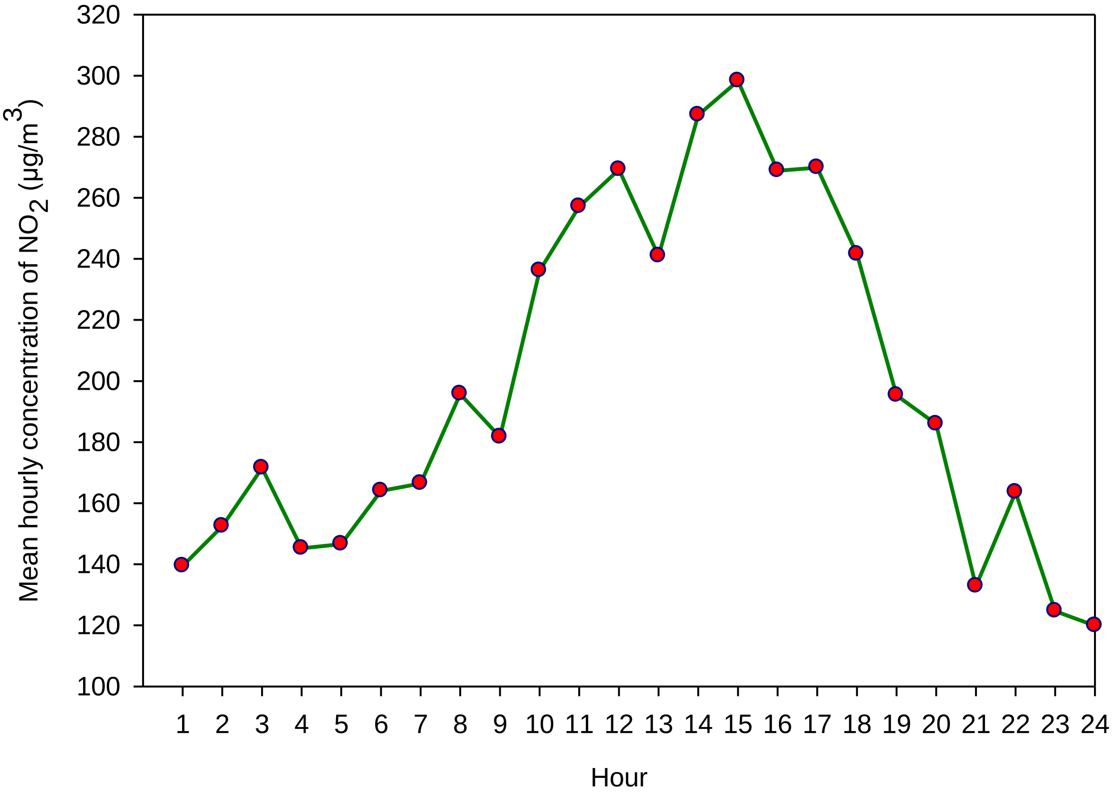


Figure 4.16: Mean hourly diurnal variation of NO_2 concentrations in Dhaka University campus, Bangladesh.

The expansion of urbanization, industrialization and motorization with increasing population in Dhakacity (Zaman *et al.*, 2010) has unexpectedly increased fossil fuel combustion, and urban infrastructure development, which might be the cause of huge emission of NO_2 and other pollutants especially into the ambient air (Sharma *et al.*, 2014; Tie *et al.*, 2009).In the morning, both N_2O_5 and $NO_3•$ compounds rapidly photolize to give the troposphere a morning boosts of NO_2.

$$N_2O_5 + hv \rightarrow NO_3• + NO_2$$

$$NO_3• + hv \rightarrow NO + O_2 / \; NO_2 + O$$

During daytime NO_2 production also increased primarily by photochemical oxidation of NO with O_3, ROO• and odd hydrogen species (HO•, HOO•, H_2O_2, etc.) (Hobbs, 2000; Wayne, 2000).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(both day and night)}$$

$$ROO• + NO \rightarrow NO_2 + RO•$$

$$HOO• + NO \rightarrow NO_2 + HO•$$

$$RC(O)OO• + NO \rightarrow NO_2 + RC(O)O•$$

The 1-hour NO_2 concentration exceeded the 1-h WHO guides line value (200 µg/m^3) from 10:00 to 18:00 hour local time. Yin *et al.* (2017) observed two peaks of NO_2at morning and evening rush hours due to the effect of on-road motor vehicles in China.

4.6 Variation of TVOC Concentrations in Dhaka University Campus, Bangladesh

4.6.1 Time series of TVOC concentrations

The time series of the 10-minute average TVOC concentrations during the study period from June 2013 to May 2014 is presented in Figure 4.17. The 10-minute average concentrations of TVOC varied both within the day and throughout the year. In this study, TVOC concentration ranged from 501.1 (February 2014) to 24,204.5 µg/m^3 (July 2013) with an average of 10,068.2 ± 5296.1 µg/m^3 (Appendix 1). 10-minute average TVOC concentrations were very scattered within every sampling day due to the variations of emission concentrations.

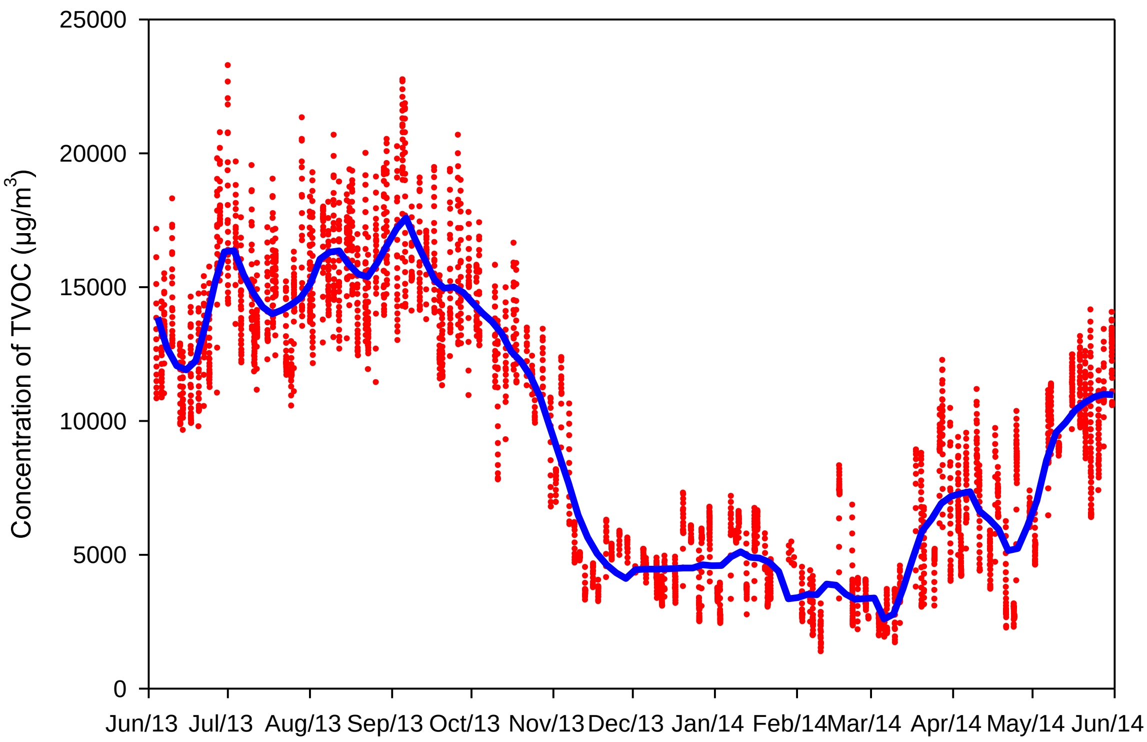


Figure 4.17: Time series of the measured concentrations of TVOC from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

The average concentration of TVOC was 10,068.2 µg/m^3 in Dhaka University area. The TVOC concentration was found 12,042.0 µg/m^3 in Kawran Bazar, Dhaka city; 19,995.9 µg/m^3 in Dhamrai, Dhaka; 13,520.6 µg/m^3 in Jamalganj, Sunamganj, and 14,828.9 µg/m^3 in Badla Haor, Kishoreganj (Table 4.1).

4.6.2 Monthly average concentrations of TVOC

The monthly average concentration of TVOC calculated from the 10-minute average concentration during the study period from June 2013 to May 2104 is presented in Figure 4.18. The measured concentrations varied widely, 2,393.1 to 15,927.7 µg/m^3 with an average value of 9384.7 ± 4336.4 µg/m^3. The increase level of TVOC was also found to be higher during June 2013 to September 2013, mainly due to the high emission from vegetation and plants sources (since vegetation growth and biological processes are high in monsoon due to high temperature and rainfall) along with anthropogenic sources.

Figure 4.18: Monthly average concentrations of the measured TVOC gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

Additionally, the prevailing wind (south and south easterly) directions in Bangladesh and long range air mass transportation (south and south easterly, from the Bay of Bengal) especially in monsoon months might have influenced the increase of TVOC concentration. The highest value was measured 15,927.7 µg/m^3 in September 2013. Then the monthly average TVOC concentration was found to be declined till February 2014, largely might be due to the decline in emissions from the natural vegetation and agricultural sources, other than anthropogenic sources, (such as motor vehicle exhausts. The lowest concentration was measured 2393.1 µg/m^3 in February 2014. However, the rise in concentration was found up to May 2014 because of an increase of emission from potential volatile sources due to high temperature.

4.6.3 Seasonal variation of TVOC Concentrations

Figure 4.19 shows the seasonal trends of TVOC concentrations. The seasonal TVOC concentration the highest was in monsoon season (14,817.9 µg/m^3), followed by post monsoon (12,307.1 µg/m^3) and then pre-monsoon (7,269.2 µg/m^3). The seasonal concentration of TVOC was found be the lowest in winter (3,296.7 µg/m^3). The seasonal average value was 9384.7 ± 4336.4 µg/m^3. The TVOC concentration of monsoon season was about 4.5 times higher than winter season.

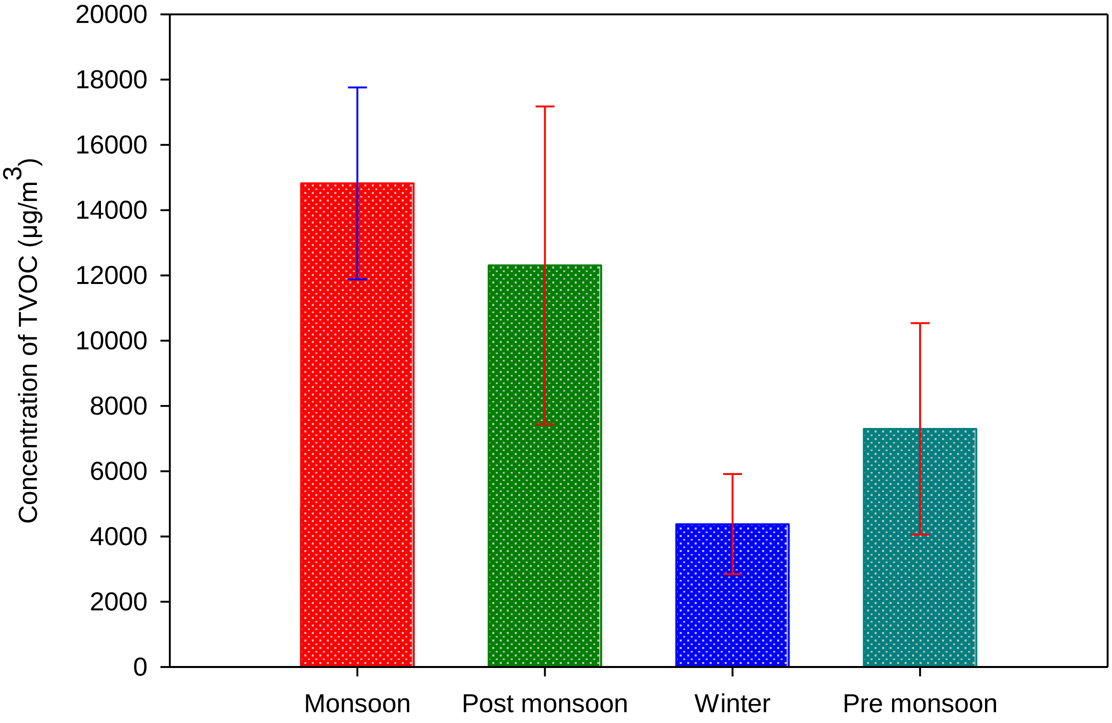


Figure 4.19: Seasonal variations of the concentrations of TVOC from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

Most of the VOCs were emitted to the atmosphere from anthropogenic activities such as motor vehicle exhausts and evaporation of petrol vapors from motor vehicles along with release from natural vegetation and agricultural sources (Cetin *et al.*, 2003; Nguyen *et al.*, 2009; Parra *et al.*, 2006). Baudic *et al.* (2016) observed that biogenic emission contributed up to 30% of VOCs in summer. Some VOCs have higher atmospheric concentrations in summer than in winter because of temperature dependent evaporation. Physical transportation of VOCs from remote sources could also be the cause of higher concentration of TVOC in monsoon than in winter. As the prevailing winds in Bangladesh are from south and south easterly directions, especially in monsoon and post monsoon, the transportation of TVOC and other pollutants could be one of the possible sources for the higher concentrations. On the other hand, several factors such as high atmospheric mixing depth, washout by rains and photochemical oxidation have dilution effect on the concentrations of VOCs in the monsoon and post-monsoon than in winter, but physical transportation of VOCs by long range air mass and prevailing wind direction might be high enough to cause of higher concentration during these seasons. Several researchers also found that long range air masses have influence on the local and regional concentration of VOCs. Wang *et al*. (2016) observed that air masses transported from south areas affected many cities in the south side of Beijing with a serious air pollution episode specially the VOCs. Baudic *et al*. (2016) observed air mass trajectories in Paris, France for the year 2010, and explained that air masses arriving from different directions in different seasons contained VOCs and other pollutants from origin sources and en route transportation. The seasonal concentration of TVOC pollutants was found to be the lowest in winter might be their less emission from natural vegetation and agricultural sources. Ho *et al*. (2004) measured ambient VOCs concentration at three locations [PolyU campus (PU), Kwun Tong (KT), HokTsui (HT)] in Hong Kong during the periods of November 2000 - February 2001 and June 2001- August 2001, and observed higher VOCs concentration in summer than in winter at the PU station, which was close to a main road.

4.6.4 Diurnal variation of TVOC concentrations

The mean hourly diurnal variation of TVOC concentrations is present in Figure 4.20. The diurnal variations ranged from 6,061.8 to 11,396.0 µg/m^3. Lower concentrations were observed during 08:00 -10:00 hour local time and then concentrations increased with time up to 13:00 hour local time, then the concentration dropped at 14:00 hour local time and again, the concentration levels increased and remained higher. The higher levels might be the effects of emission from vehicles and industrial operation. At night, higher concentration might be due to the temperature inversion.

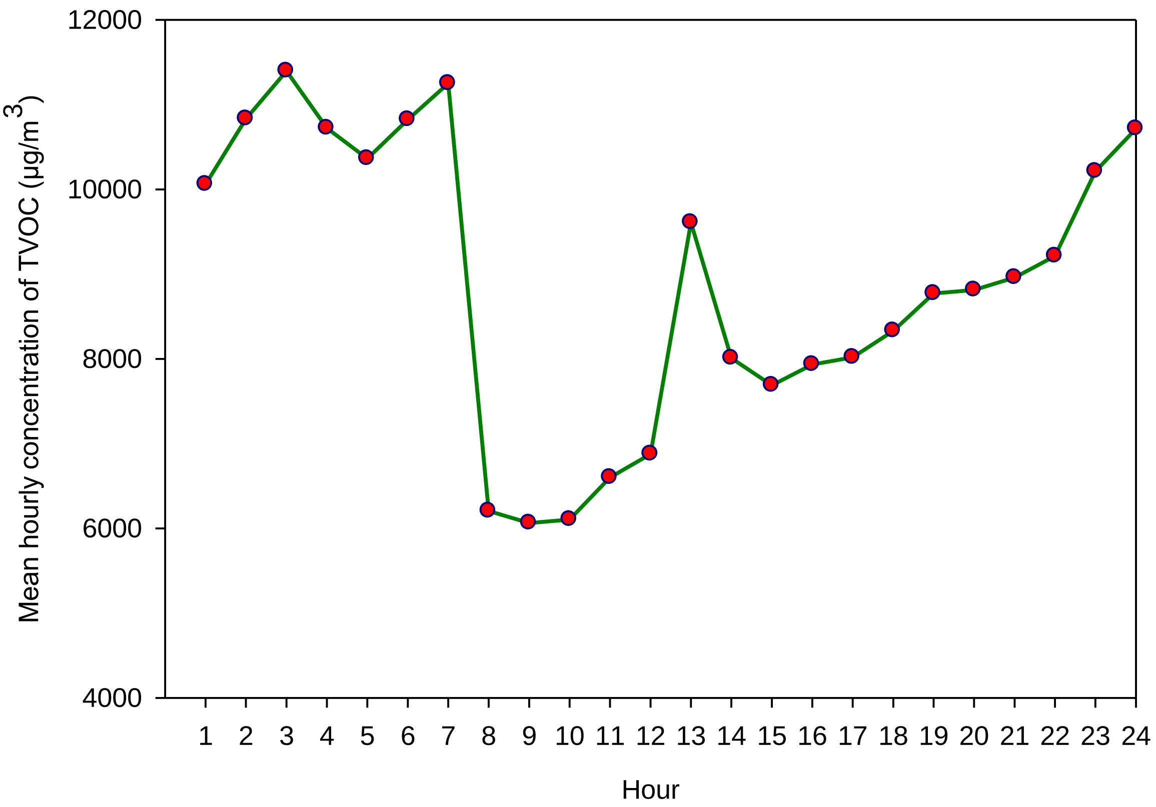


Figure 4.20: Mean hourly diurnal variation of TVOC concentrations in Dhaka University campus, Bangladesh.

4.7 Variation of O_3 Concentrations in Dhaka University Campus, Bangladesh

4.7.1 Time series of O_3 concentrations

The time series of O_3 concentrations from June 2013 to May 2014 is presented in Figure 4.21. The measured O_3concentrationvaried widely both within the day and throughout the year, and ranged from 3.52 to 178.0 µg/m^3 with an average of 36.6 ± 23.6 µg/m^3 (Appendix 1). Higher concentrations were detected from June 2013 to September 2013 with a wide range of diversity within the sampling days. From November 2013 to May 2014, the dispersion of O_3concentrations within the sampling days was not high.

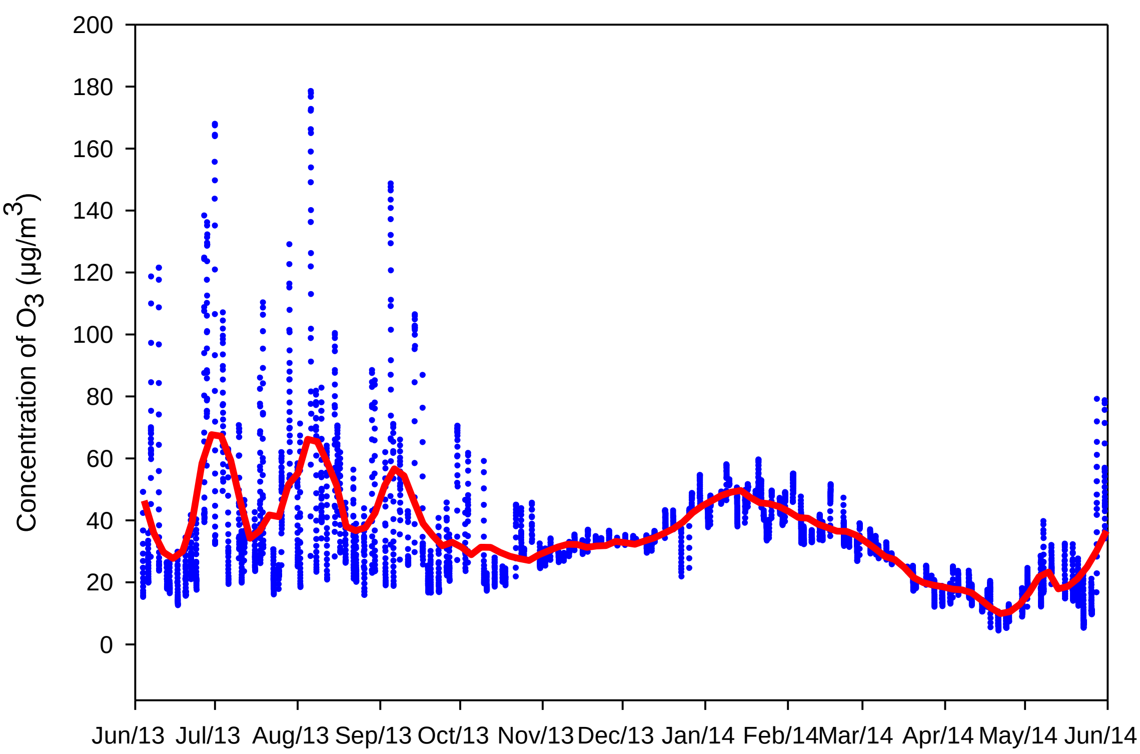


Figure 4.21: Time series of the measured concentrations of O_3 from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

The average concentration of O_3 (36.6 µg/m^3) in Dhaka University area was about half of measured value found in Kawran Bazar, Dhaka city; Badla Haor, Kishoreganj; and Jamalganj, Sunamganj. Almost similar value was observed in Dhamrai, Dhaka (Table 4.1). One year average concentration of O_3 in large cities in Russia was 46.2 µg/m^3 (Elansky *et al.*, 2016). The average concentration was 62 µg/m^3 in New Delhi, India (Chelani *et al.*, 2012) and 57.0 - 112.2 µg/m^3 in Anantapur, India (Reddy *et al.*, 2012). The average annual (2013 - 2014) concentration of O_3 in the traffic and commercial sites of urban air in Busan, South Korea were 35.7 µg/m^3 and 52.2 µg/m^3, respectively (Jang *et al.*, 2017). The average concentration of O_3 in ten cities of Northern China was 78.4 µg/m^3 (Wang *et al.*, 2014).

4.7.2 Monthly average concentrations of O_3

The monthly average variations of O_3 concentrations calculated from the 10-minute concentration during the study period from June 2013 to May 2014 is shown in Figure 4.22. The monthly average O_3 concentrations ranged from 19.7 to 48.8 µg/m^3, with an average value of 35.9 ± 10.2 µg/m^3. The highest concentration was observed in

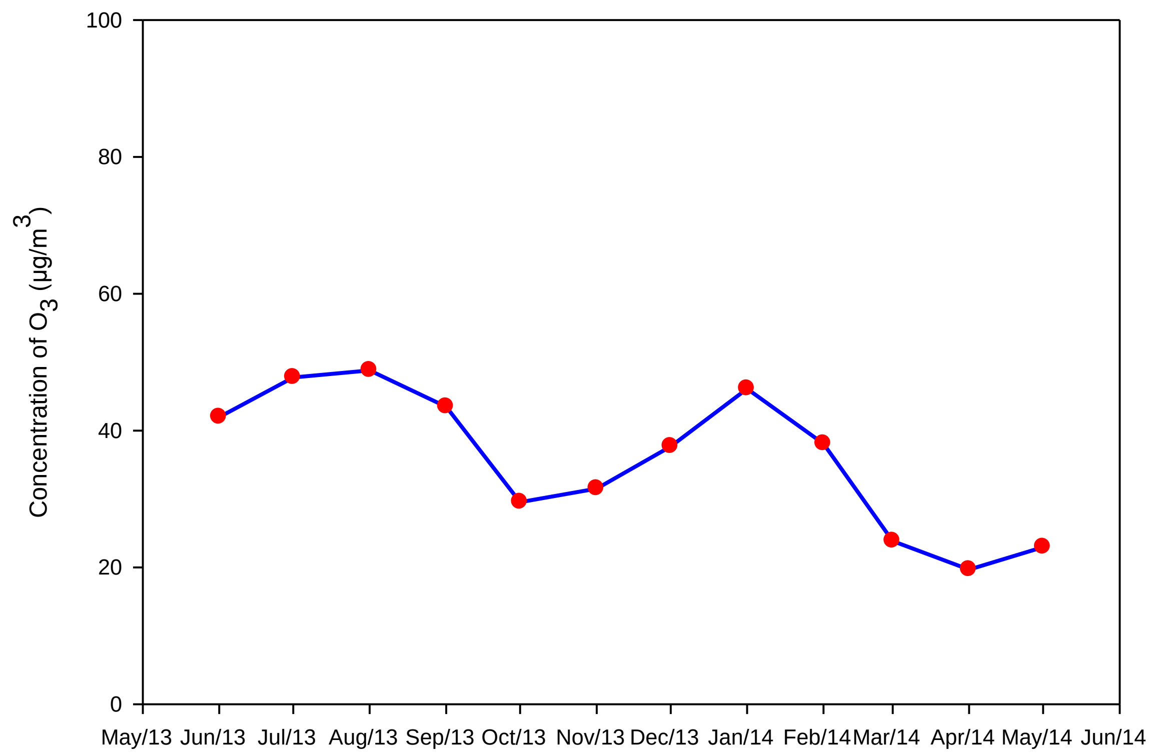


Figure 4.22: Monthly average concentrations of the measured O_3 gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

August 2013 and afterward showed a decreasing order up to October 2013, and which then showed a rising tendency till January 2014. Subsequently, the declining trend of monthly O_3 concentrations were observed till April 2014 and later the value increased.

4.7.3 Seasonal variation of O_3 concentrations

The seasonal variations of the O_3 concentrations are presented in Figure 4.23. The average seasonal O_3 concentration was 36.0 ± 11.6 µg/m^3, with the highest value (46.5 µg/m^3) in monsoon through a decline into post-monsoon (36.1 µg/m^3) and for a second spell high value of 41.5µg/m^{3}was found in the winter season, while the lowest value was observed in pre-monsoon (20.10 µg/m^3). In urban areas, O_3 variations are apparently caused by varying effects of precursor sources (NOx and VOCs), activity of photochemical reactions and meteorological conditions among different seasons(Brown *et al*., 2006; Sicard *et al*., 2009;Sicard*et al*., 2013).Meteorological conditions enable the movement of O_3-forming precursor gases, and other air pollutants (Andersson *et al*., 2006; Reddy *et al*., 2010).

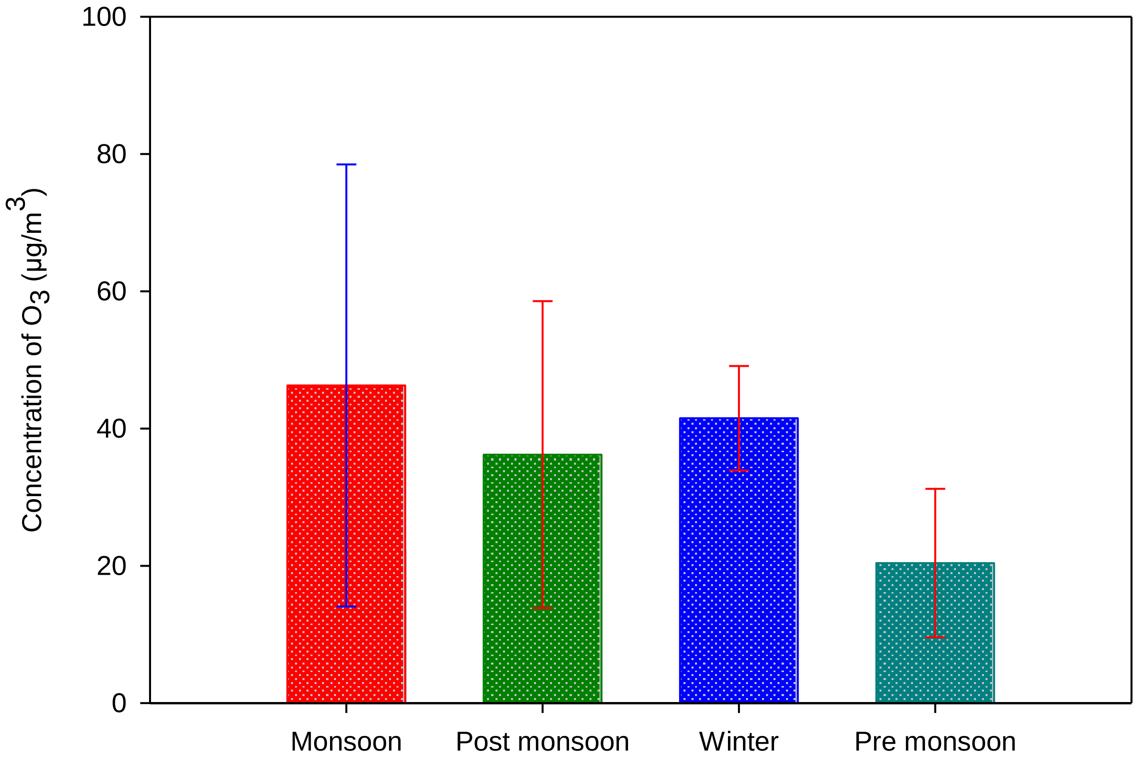


Figure 4.23: Seasonal variations of the concentrations of O_3 from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

During the monsoon, O_3 concentration was the highest because of intense solar radiation (although cloudy conditions prevailed), humidity and availability of precursor gases. In this study, NO concentration was the second highest (351.1 μg/m^3) (Figure 4.12) and TVOC concentration was the highest (14,817.9 μg/m^3) (Figure 4.20) that could be the causes of the highest level of O_3 concentration. (Louie *et al.* (2013) observed that the volatile organic compounds (VOCs) are important precursors to the formation for O_3 in the presence of solar radiation. Liu *et al.* (2005) estimated that vehicular exhaust was the major contributor of VOC, followed by painting operations, gasoline vapor, and liquefied petroleum gas. The higher O_3 concentration in monsoon indicated that VOCs in the atmosphere might be due emission from vehicles and natural vegetation sources. In Houston, USA the main reason of high O_3 concentration was observed from the highly reactive composition of VOCs emitted from petrochemical enterprise (Ryerson *et al.*, 2003). This kind of observation was also made by many scientists (Brown *et al.*, 2006; Seinfeld and Pandis, 2006; Song *et al.*, 2011). Wet scavenging in summer monsoon does not directly reduce O_3as its solubility in water is low (Girach *et al.*, 2017), so the concentration of O_3 was the highest in monsoon. On the other hand, Tarasova *et al*. (2003) and Nishanth *et al*. (2012) observed that wet and rainy weather with high relative humidity was typically associated with low levels of O_3 due to the less intensive photochemical oxidation and perhaps wet deposition of ozone with the water droplets.

In winter season, the subsequent second highest O_3 concentration (41.5 µg/m^3) might be due to O_3 accumulation owing to mild to low wind, and oxidation of NO to $NO_2$by O_3. In winter season, in this experiment NO concentration was observed as the highest (392.1 µg/m^3) (Figure 4.12), and TVOC concentration was the lowest (4,376.8 µg/m^3) (Figure 4.20), that (higher NO concentration) could be the causes of lower (i.e., second highest) level of O_3. Liao *et al*. (2014) indicated that the reduced emission of VOCs in the Northeastern U.S. decreased O_3 concentration effectively. Other researchers (Song *et al*., 2007; Tang *et al.*, 2009; Xu *et al*., 2008) also observed that O_3 concentration in Beijing was controlled by VOCs in recent years. The lowest concentration of O_3 (20.1 µg/m^3) was found in pre-monsoon and that might happen due to lower availability of precursor gases (NO and TVOC). On contrary, Ran *et al*. (2009) found that spring was the most productive season for ozone, with the highest daily maximum (128 ppbv) in May 2007 in Shanghai due to the photochemistry.

4.8 Variation of NH_3 Concentrations in Dhaka University Campus, Bangladesh

4.8.1 Time series of NH_3 concentrations

The 10-minute average NH_3 concentrations varied widely both within the day and across the year during the study period from June 2013 to May 2014 (Figure 4.24). The lowest concentration of NH_3 was recorded, 2.3 µg/m^3 (April 2014) and the highest value was 524.4 µg/m^3 (May 2014). The average concentration of NH_3 during the study period was 133.8 ± 94.9 µg/m^3 (Appendix 1). The NH_3 concentration changed dramatically within the same day probably as a result of the strong influence of emission sources in the vicinity. The transitory intensive ammonia exhausts from vehicles and industries might have strong effects on the ambient NH_3 levels.

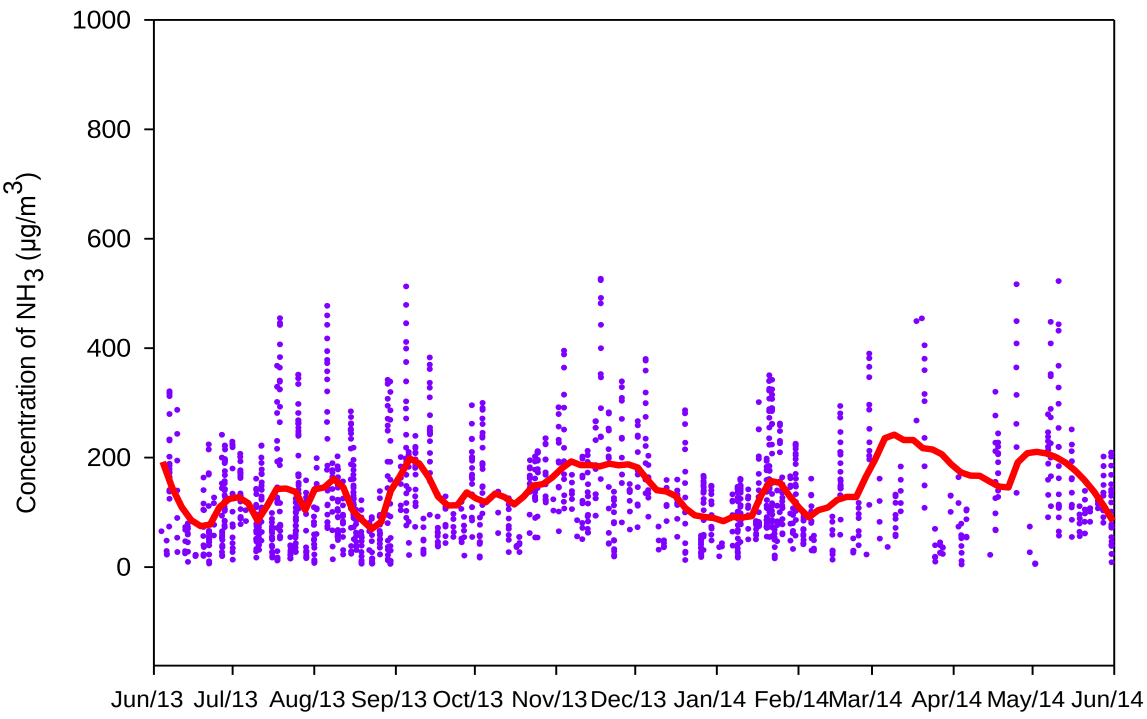


Figure 4.24: Time series of the measured concentrations of NH_3 from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

Traffic exhausts are considered to be the main source of NH_3 in the urban environment by several researchers (Battye *et. al.*, 2003; Livingston *et. al.*, 2009). The higher NH_3levels were influenced by heavy traffic emissions and high population density along with weather pattern, and these factors enhanced the contribution of biological sources (Pandolfi *et al.*, 2012; Reche *et al.*, 2012).Ammonia volatilizations from surrounding agricultural non-point sources, N-related fertilizer application in crop land, wastes in and around Dhaka city might have influenced NH_3 level too (Reche *et al.*, 2012). The temporal assessment of urban NH_3 levels and potential emission sources in six major Spanish cities (Barcelona, Madrid, A Coruña, Huelva, Santa Cruz de Tenerife and Valencia) confirmed that NH_3 sources in Spanish urban environments were vehicular traffic, biological sources (e.g. garbage containers), sewerage system, wastewater treatment plants, solid waste treatment plants and industry (Reche*et al*. 2012).

The average concentration of NH_3 (133.8 µg/m^3) in Dhaka University area was 2.70 and 1.31 times higher than that obtained in Kawran Bazar (Dhaka city) and Dhamrai (Dhaka district), respectively. The concentration of NH_3 in Jamalganj (Sunamganj) and Badla Haor (Kishoreganj) were 2.70 and 2.63 times, respectively higher than the measured concentration in Dhaka University campus area (Table 4.1). Urban atmospheric NH_3 concentration in the Santiago City, Chile was 15.25 µg/m^3 (Toro *et al*., 2014), which was about 9.0 times lower than the obtained value in the Dhaka University campus. The average annual (2013 - 2014) concentration of NH_3 in Shanghai megacity, China was 4.31 µg/m^3 (Wang *et al*., 2015). One year average (April 2002 - March 2003) NH_3 concentration in Thessaloniki urban area of Greece was 2.3 µg/m^3 (Anatolaki and Tsitouridou, 2007).

4.8.2 Monthly average concentrations of NH_3

The monthly average NH_3 concentrations from June 2013 to May 2015 are presented in Figure 4.25. The highest monthly average concentration was 182.7 µg/m^3 in November 2013, which is 1.66 times higher than in June 2013, the lowest monthly

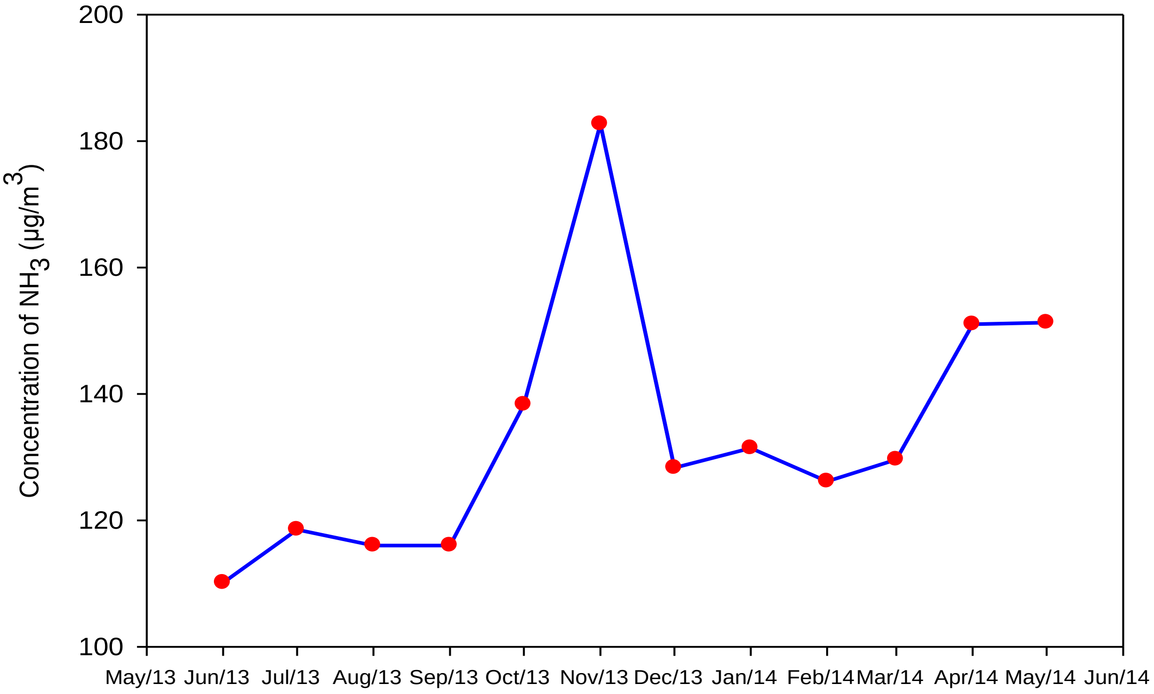


Figure 4.25: Monthly average concentrations of the measured NH_3 gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

average NH_3 concentration in the year (110.1µg/m^3). The monthly average concentration was 133.3 ± 20.3 µg/m^3. In October 2013, April 2014 and May 2014 NH_3 concentrations were also higher than other months of the experimental period. The monthly average concentrations were always low from June to September 2013, especially during monsoon season than in post-monsoon months (October and November 2013).

4.8.3 Seasonal variation of NH_3 concentrations

The behavior of NH_3 levels as a function of the season is presented in Figure 4.26. The seasonal trends of NH_3 reveal that the highest level of NH_3 (146.7 µg/m^3) was detected in pre-monsoon season. The lowest seasonal average was recorded 115.7 µg/m^3 in monsoon, which then augmented (138.9 µg/m^3) in post-monsoon and afterward it slightly declined to 129.6 µg/m^3 in winter. The seasonal average value of NH_3 concentration was 132.7 ± 13.3 µg/m^3.

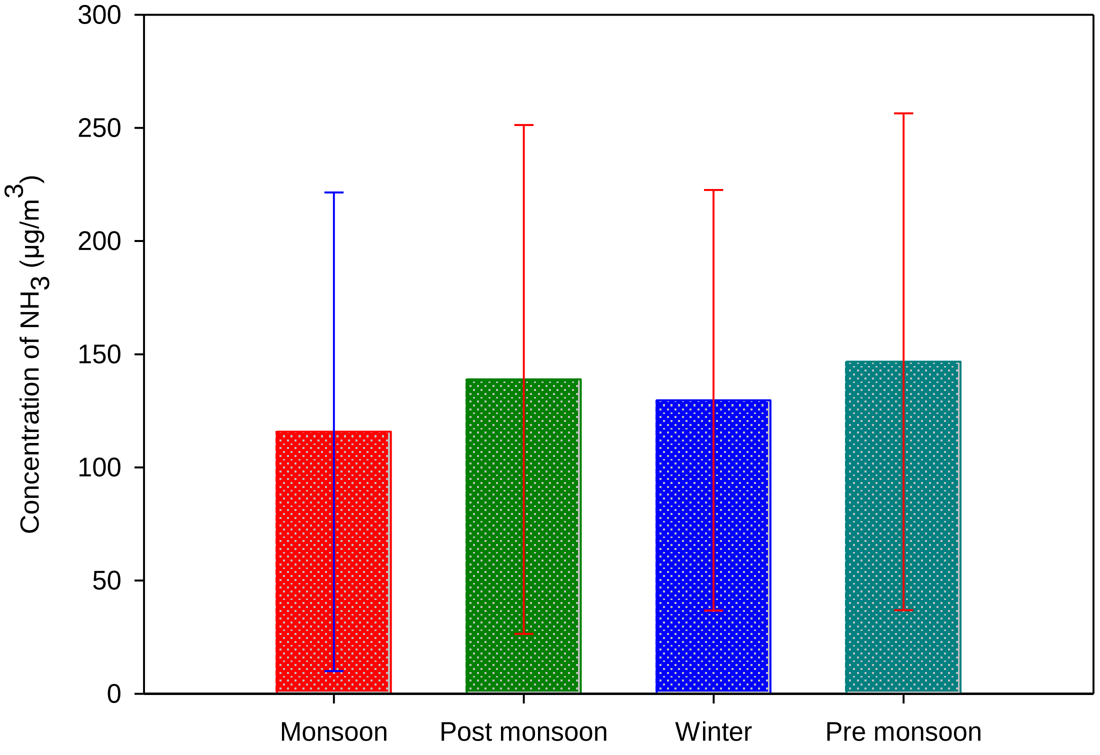


Figure 4.26: Seasonal variations of the concentrations of NH_3 from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

In the urban environment, traffic exhausts are considered to be the main source of NH_3 (Battye *et al*., 2003; Livingston *et al*., 2009). Kean *et al*. (2009); Burgard *et al*. (2006) reported about the highest average ammonia emission rates from 10-year-old vehicles. Other sources of NH_3 in urban areas include industrial activities and nitrogen-containing biological sources (e.g. solid waste disposal, landfills, communal wastes, human feces) (Anderson *et al*.,2003; Aneja *et al*., 2012; Olivier *et al*. 1998,Walker *et al*., 2004; Zhang *et al*. 2008). The concentration of NH_3 in urban areas also increases as prevailing wind can bring it from N-fertilized cropland, livestock, drainage system etc. from surrounding areas (Sharma *et al*., (2015).

The highest level of NH_3in pre-monsoon could be due to the potential volatilization NH_3 from N-containing biological sources (decomposable organic wastes, landfills, communal wastes, human feces) at relatively higher temperatures along with emissions from vehicles. The atmospheric NH_3 concentration may be indirectly affected by air temperature (Robarge *et al.*, 2002). In the atmosphere, NH_4^+ generally combines with NO_3^- and SO_4^{2-} and forms ammonium nitrate and ammonium sulfate, respectively (Appel *et al.*, 1981; Utsunomiya and Wakamatsu, 1996), however ammonium salts is transformed to NH_3 due to the high temperature (Seinfeld and Pandis, 2006) and low relative humidity. This might be the cause of high NH_3 concentration in pre-monsoon season. Throughout the monsoon season, the NH_3concentration was the lowest, which might happen due to washout by heavy precipitation and absorption within clouds. During winter its concentration was also low due to the less emission of NH_3 from biological sources and also for the higher rate of formation of particulate ammonium nitrate owing to low temperature (Stelson and Seinfeld, 1982).NH_3 concentration measurement was carried out at Dayalbagh, a suburban site and at St. John’s, an urban site at Agra (India) by Kumar *et al*. (2004) which showed that highest values of NH_3 were recorded during the monsoon and lowest during the winter. In fact, seasonal variations in NH_3 concentrations were associated with changes in temperatures in some studies (Gupta *et al*., 2008; Hassan *et al*., 2013b). Zhou *et al*. (2015) observed that more than 60% of total ammonia emission in Beijing came from livestock and farm-land. Ambient NH_3 concentration was measured from 24 to 27 February 2014 at Kolkata city of India by Sharma *et al*. (2015), which revealed by analyzing surface wind direction and wind speed that the local activities like agriculture, livestock, drainage, vehicles etc. may be the possible sources of ambient NH_3 at the observational site of Kolkata. They also concluded that the variation of ambient NH_3 region may be due to variation in source strength and meteorological conditions of the observational sites (Sharma *et al*., 2014).

4.8.4 Diurnal variation of NH_3 concentrations

The diurnal variations of NH_3concentration for 24-hour period are presented in Figure 2.27. In the morning (05:00 to 08:00 am local time) and the after sunset, the diurnal NH_3 concentration peaks were observed higher than during the other sunlight period. The highest concentration was measured 686.7µg/m^3 at 01:00 hour local time. The lowest diurnal value was 2.1 µg/m^3 in the daytime (09:00 hour local time).In the morning the higher values (at 05:00 to 08:00 local time) of NH_3might be due to the emissions from communal wastes, garbage and traffic sources. NH_3 emissions from the same kinds of sources were reported by Aneja *et al*. (2012) and Walker *et al*. (2004).

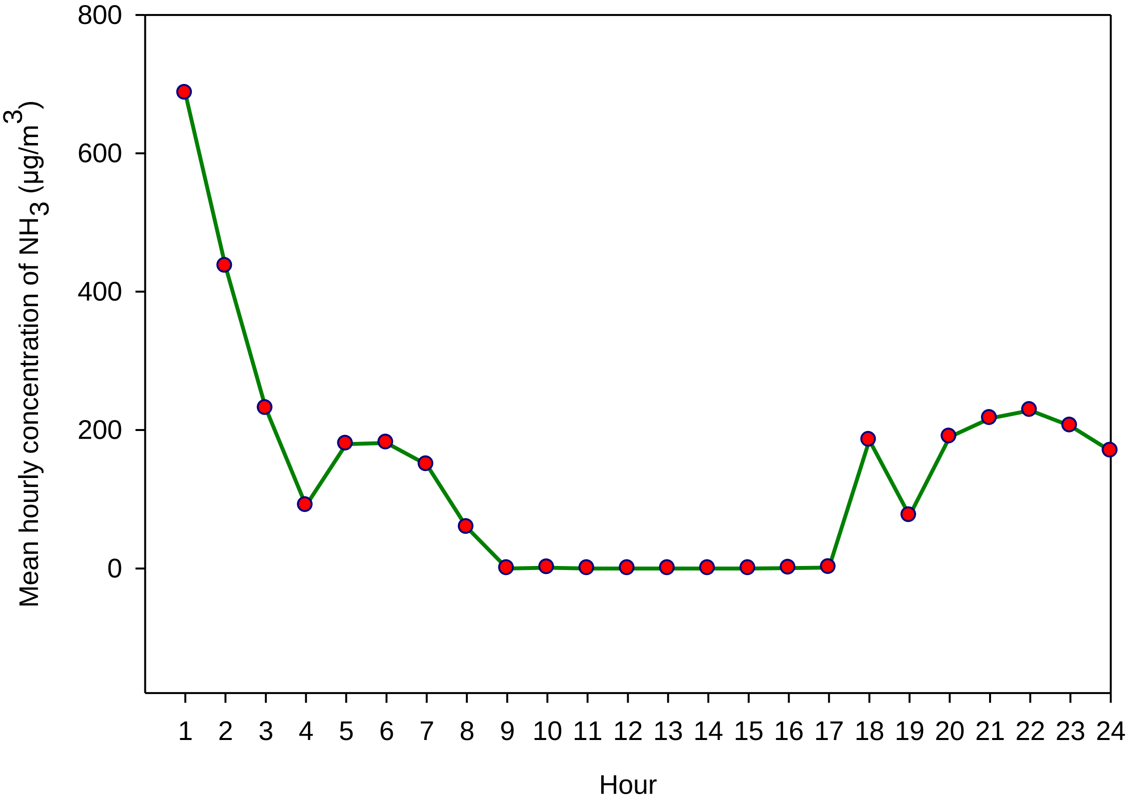


Figure 4.27: Mean hourly diurnal variation of NH_3 concentrations in Dhaka University campus, Bangladesh.

The surface NH_3 concentration decreased from the morning higher values and kept it in stable state until evening, might be due to the increasing dispersion and dilution caused by high temperature. During daytime NH_3 can also be oxidized reacting with HO• and it might also be the cause of its low concentration. At night, the hourly concentrations were always higher than daytime. This clearly suggests that accumulation of NH_3 in ambient air happens during the night time (Kapoor *et al.*, 1992). The atmospheric stability during the night time might have attributed to the higher concentration of NH_3during the night hours (Cadle *et al.*, 1982; Kapoor *et al.*, 1992).

4.9 Variation of H_2S Concentrations in Dhaka University Campus, Bangladesh

4.9.1 Time series of H_2S concentrations

The time series of the 10-minute-average concentration of H_2S gas measured from June 2013 to May 2014 is presented in Figure 4.28. From the figure it is evident that the measured concentrations varied widely both within the day and throughout the year. During the study period, the concentration varied from 4.00 to 301.8 µg/m^3 with an annual average of 84.8 ± 38.8 µg/m^3 (Appendix 1). In the pre-monsoon months,

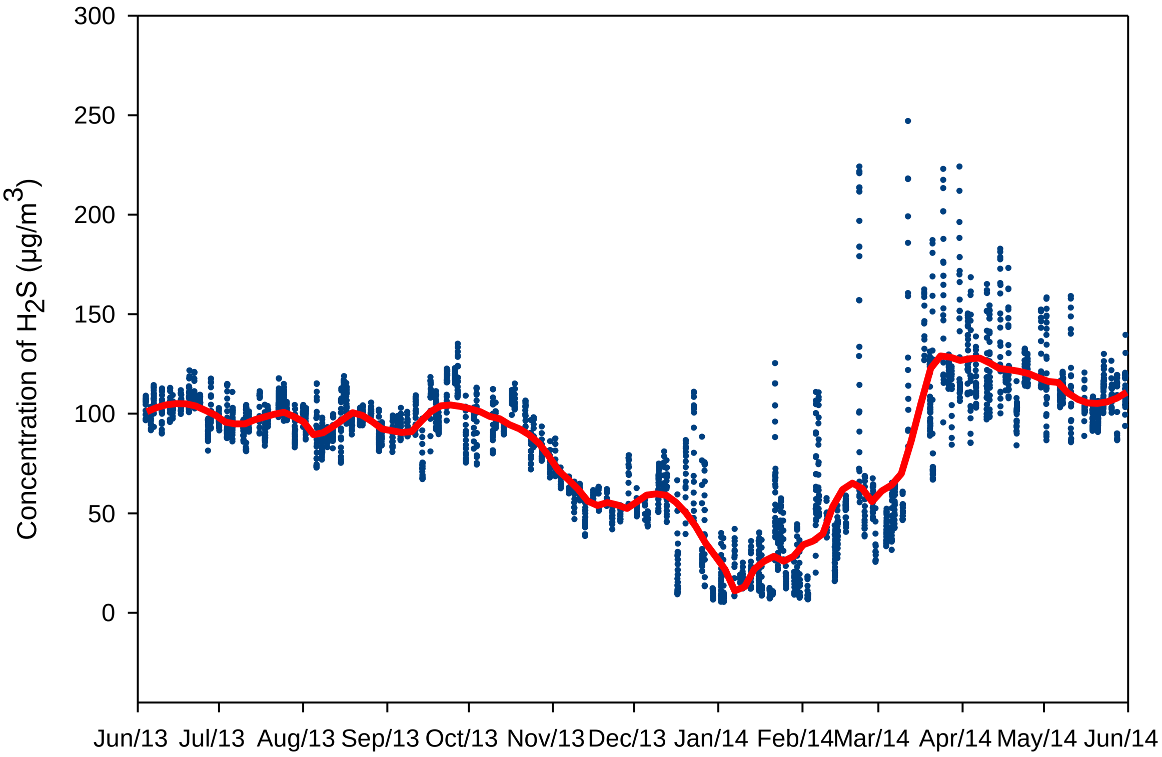


Figure 4.28: Time series of the measured concentrations of H_2S from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

10-minute average concentrations were higher, and within those days their variations were pronounced as well. In the other months, 10-minute average concentrations were low, with further lower values in January 2014.

The average concentration of H_2S (84.8 µg/m^3) in Dhaka University area was lower than the measured values in Kawran Bazar (131.8 µg/m^3), Dhaka city and Badla Haor (104.5 µg/m^3) (Kishoreganj), but the concentrations of H_2S in Dhamrai (Dhaka district) and Jamalganj (Sunamgnj district) were lower than that of Dhaka University area (Table 4.1). One full year ambient H_2S concentration in the City of Thessaloniki, Greece was 8.0 µg/m^3 (Kourtidis *et al*., 2008), which was about 10.6 times lower than the value found in Dhaka University area. The average concentration of H_2S during the study period, 2003 - 2009 in the Reykjavik capital area, Iceland was 3.35 µg/m^3 (Finnbjornsdottir *et al*., 2015).

4.9.2 Monthly average concentrations of H_2S

The monthly average concentrations of the measured H_2S gas are presented in Figure 4.29. The average monthly variations occurred due to emission variations from the

Figure 4.29: Monthly average concentrations of the measured H_2S gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

monthly average concentrations of H_2S were at lower levels during the winter months (December 2013, January 2014 and February 2014) and among them the lowest value was 20.9µg/m^3 in January 2014. After January 2014, the monthly average value increased gradually and the highest value (122.3 µg/m^3) was recorded in April 2014. During monsoon (June, July and August 2013) and post-monsoon (September 2013, October 2013 and November 2013) months, the monthly average values were lower than pre-monsoon months, but remained higher than winter months. The average monthly concentration of H_2S was 83.7 ± 30.1 µg/m^3.

4.9.3 Seasonal variation of H_2S concentrations

The seasonal variations of H_2S concentrations are presented in Figure 4.30. Seasonal average concentration of H_2S was 83.9 ± 31.3 µg/m^3. The highest concentration (117.2 µg/m^3) of H_2S was observed in the pre-monsoon season, while monthly mean values were higher too. The lowest seasonal average concentration was 39.4 µg/m^3 in the winter season. In the monsoon H_2S concentration was 98.1 µg/m^3, but it was higher than post-monsoon value of 87.0 µg/m^3. H_2S concentration may vary considerably due to the emission source variations along with meteorological conditions specially temperature.

In and around urban areas, it comes from traffic emission (storage of sulfur during fuel lean condition and its subsequent release as H_2S during fuel rich conditions), municipal garbage rotting, stagnant polluted water bodies, sewage system, landfills, animal manure handling, tanneries, iron smelting, and food processing industries (Godish, 2004; Kourtidis *et al*., 2008; Schoor and Valdez, 2005). All of these sources are common in Dhaka city. Moreover, emissions from biological activities and anaerobic decomposition of sulfur-containing organic matters (Finlayson and Pitts, 1986; WHO, 2012) might be additional sources. Venturi *et al*. (2016) observed that both natural and anthropogenic sources were the causes of H_2S emission in the urban and non-urban areas of Italy. Existing emission sources could be the main contributor of H_2S in the Dhaka city. The emission intensifies with temperature and this could be the cause of higher levels of H_2S in the hot pre-monsoon season. In monsoon season, its concentration was also higher, since wet and hot weather prevail in Bangladesh which favored the decomposition of S-containing organic materials.

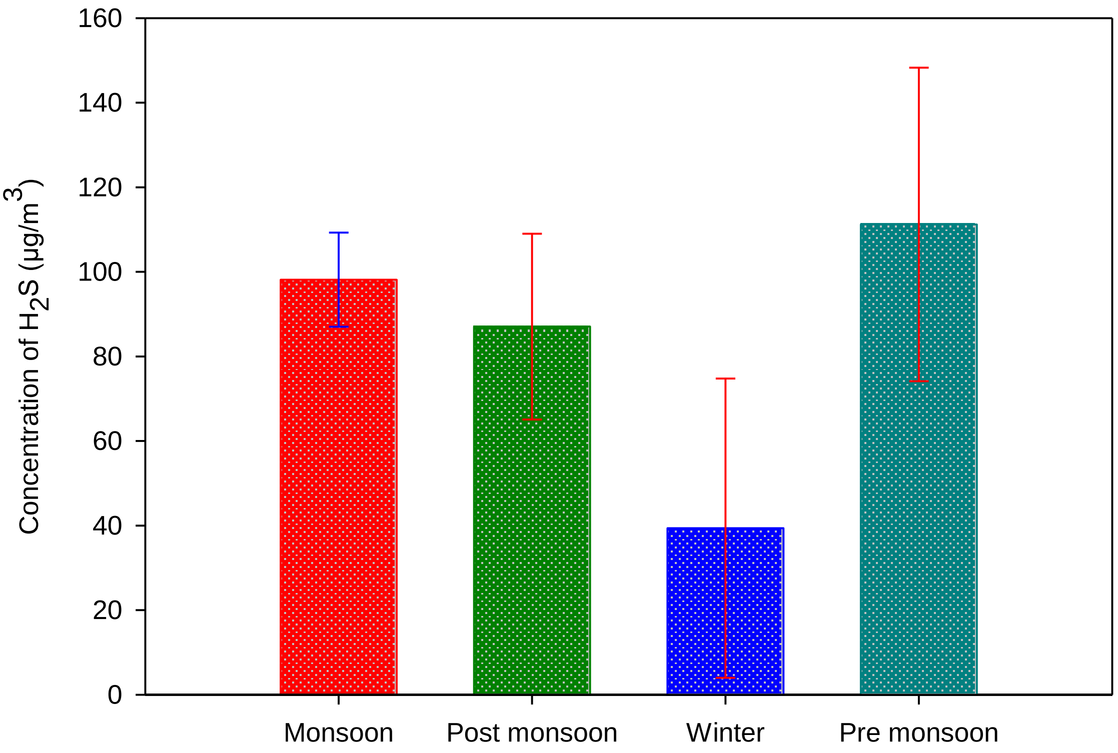


Figure 4.30: Seasonal variations of the concentrations of H_2S from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

During pre-monsoon and monsoon months, a combination of factors, such as hot induced vertical air mixing and photochemical oxidation of H_2S by OH levels accelerate the decrease of H_2S concentration (Finlayson and Pitts, 1986; Wayne, 2000). But the concentration of H_2S remained high, since the rate of emissions from sources might be higher than its destruction. The concentration of H_2S was the lowest in winter season, might be due to lower emission rate. Kourtidies *et al.* (2008) measured H_2S concentration in urban traffic site of Thessaloniki, Greece and observed ambient higher concentration in winter season. It might happen due to different climatic condition.

4.9.4 Diurnal variation of H_2S concentrations

The diurnal variations of H_2S concentration for 24-hour period are presented in Figure 4.31. In the morning (06:00 to 09:00 hour local time) the diurnal NH_3 concentration peaks were observed higher, and then declined and yet again from 16:00 to 20:00 hour local time, concentration peaks were observed higher. The highest concentration was measured 217.5 µg/m^3 at 07:00 am local time. The lowest diurnal value was 72.7

µg/m^3 at 23:00hour local time. In the morning the higher values (at 06:00 to 09:00 local time) of H_2S were might be due to the emissions from communal wastes, garbage and traffic sources.

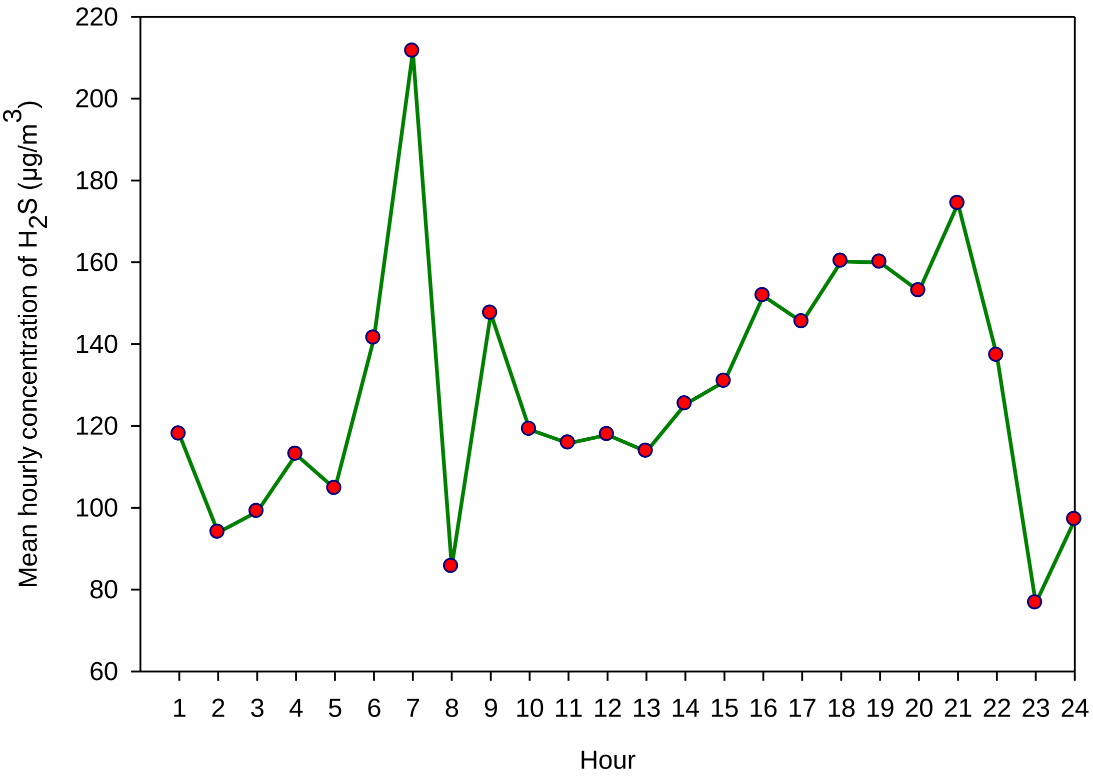


Figure 4.31: Mean hourly diurnal variation of H_2S concentrations in Dhaka University campus, Bangladesh.

The H_2S concentration remained low from 10:00 to 15:00 hour local time that might be due to the increasing dispersion caused by high temperature and loss of H_2S through oxidation by higher levels of HO radical produced photochemically (Finlayson and Pitts, 1986; Wayne, 2000).

4.10 Variation of PH_3 Concentrations in Dhaka University Campus, Bangladesh

4.10.1 Time series of PH_3 concentrations

The 10-minute average PH_3 concentrations varied widely both within the day and throughout the year during study period from June 2013 to May 2014 (Figure 4.32). The concentrations of PH_3 varied from 53.8 µg/m^3 (April 2014) to 296.0 µg/m^3 (May

2014) with an average concentration of 133.1 ± 37.7 μg/m^3 (Appendix 1). The minimum values were observed during the months of November 2013, March 2014and April 2014.In the monsoon months (June 2013 to August 2013), the maximum values of PH_3 were recorded.

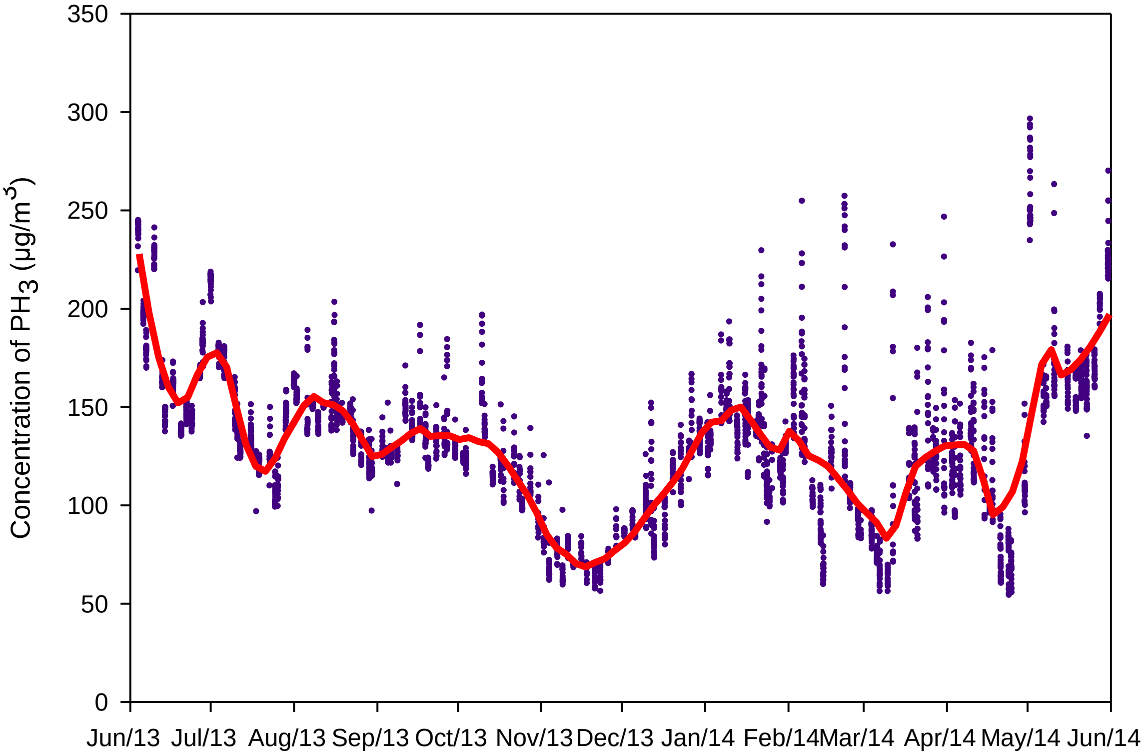


Figure 4.32: Time series of the measured concentrations of PH_3 from June2013to May 2014 in Dhaka University campus, Bangladesh.

The average concentration of PH_3 (133.1 μg/m^3) in Dhaka University campus was lower than that measured in Kawran Bazar (Dhaka city) (151.3 μg/m^3) and Jamalganj (Sunamganj) (197.8 μg/m^3); but the concentrations of PH_3 in Dhamrai (Dhaka district) (99.5 μg/m^3), and Badla Haor (Kishoreganj) (110.4 μg/m^3) were lower than the values obtained in Dhaka University area (Table 4.1). The information regarding phosphine in the urban atmosphere is still very limited. Generally people study phosphine level in the paddy field, coastal and wetland areas. The average concentration of phosphine in the atmosphere varies from pg/m^3 to ng/m^3 (Glindemann *et al.*, 2005b). The average phosphine concentration of an urban location in Berlin, Germany was observed 0.16 μg/m^3 (Glindemann *et al.*, 2005b), which was very low (about 831 times lower) compared to the obtained value at the Dhaka University campus. This might be due to the open garbage dumping in the city area and the presence of river around Dhaka city.

4.10.2 Monthly average concentrations of PH_3

The average monthly variation of PH_3 concentrations is shown in Figure 4.33. The concentrations varied from 72.7µg/m^3 (November 2013) to179.9 µg/m^3 (May 2014) with an average of 130.0 ± 27.0µg/m^3. The monthly average PH_3 concentrations were higher in June, July, August, September and October 2013 and then in January 2014 and May 2014.

Figure 4.33: Monthly average concentrations of the measured PH_3 gas from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

During winter months especially November and December 2013, lower values of PH_3 were observed.

4.10.3 Seasonal variation of PH_3 concentrations

The seasonal trends of PH_3concentrations are show in Figure 4.34. The highest concentration NH_3 of was found 154.8 µg/m^{3}in monsoon. The lowest seasonal average was 115.3 µg/m^3 in post-monsoon, which then augmented with value 125.6 µg/m^3 in winter and then 132.5µg/m^3 in pre-monsoon. The seasonal average value was 131.3±15.4 µg/m^3.

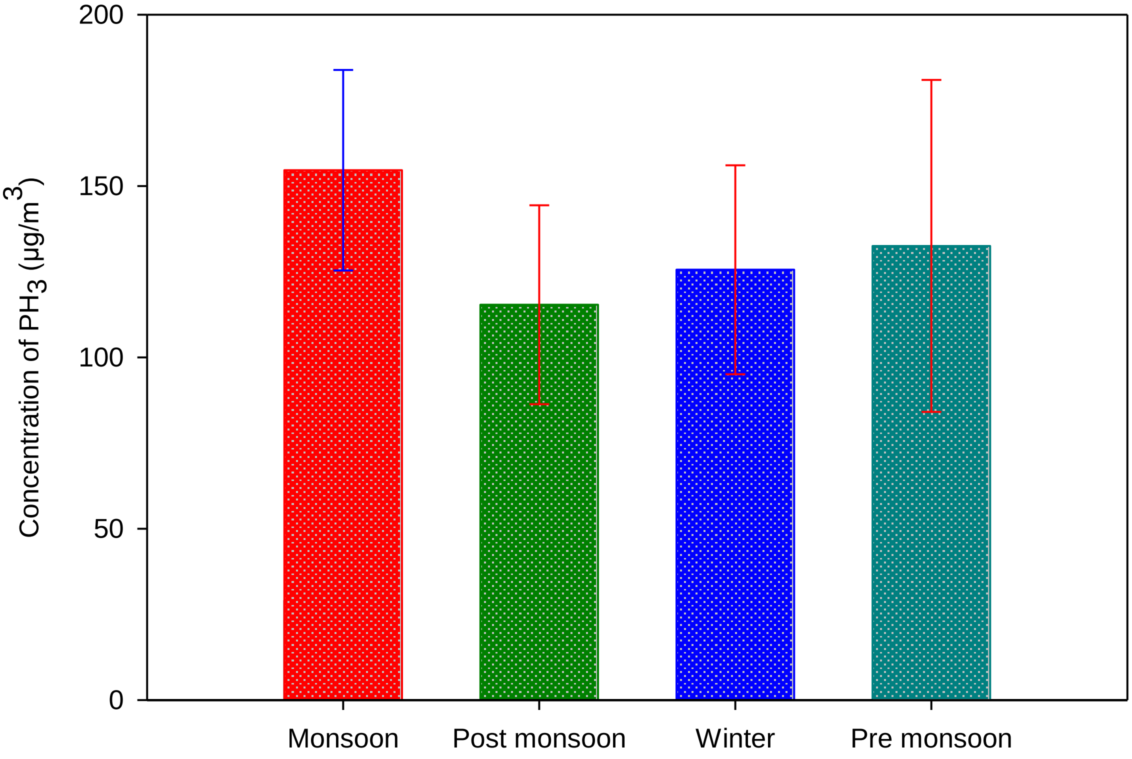


Figure 4.34: Seasonal variations of the concentrations of PH_3 from June 2013 to May 2014 in Dhaka University campus, Bangladesh.

Phosphine emits mostly from landfills, communal wastes (Jenkins *et al*., 2000, Roels and Verstraete, 2004), animal slurry or human feces, solid waste disposal sites (Ding *et al*., 2005; Glindemann and Bergmann, 1995; Glindemann *et al*., 1996a; Zhu *et al*., 2006b) and marsh soils (De´vai and Delaune, 1995). Emission of PH_3 is high at higher temperature. In the pre-monsoon and monsoon season high, temperature favored PH_3 emission and this might be the cause of higher level of PH_3. Glindemann *et al.* (2005) observed that the concentration of PH_3 is significantly higher near Paddy fields then in urban residential areas (Glindemann *et al.* 2005). The ambient atmospheric levels of phosphine in Beijing are relatively high as compared with those in Germany and South America due to emissions from vast paddy fields and numerous eutrophic water bodies (Liu *et al*. 1999).

Wetland ecosystems are important locations for free PH_3. Production and emission fluxes of free phosphine from four wetlands types in southern China were observed in different seasons by Han *et al.* (2010). Bangladesh is predominantly an agricultural country with large areas of paddy fields, and also has numerous unmanaged waste dumping sites in and around cities, which might have been favoring the gaseous phosphorus (PH_3) emissions. This cloud be the cause of PH_3 concentration variation in Dhaka city during different seasons. During monsoon season fields become flooded due to heavy rainfall and hence, anaerobic conditions favor the anaerobic fermentation of phosphorus-containing organic matter. When phosphine formation rate is high, or gas transport is efficient, a substantial amount of phosphine is able to reach the atmosphere, and the emission flux is high (Han *et al.*, 2000). This might be the cause of highest level of PH_3 during monsoon period. Throughout the monsoon season the oxidation of PH_3 is delayed under the rain and overcast weather conditions (Zhu *et al.*, 2007), which would be the cause of PH_3 accumulation and the highest level of this gas.

4.10.4 Diurnal variation of PH_3 concentrations

Figure 4.35 presents the mean hourly diurnal variations of PH_3 for 24-hour. In the morning, the diurnal PH_3 concentration peak was about 235.8 µg/m^3 at 07:00 hour local time, while it dropped down to a minimum of 104.7 µg/m^{3}at afternoon (at 15:00

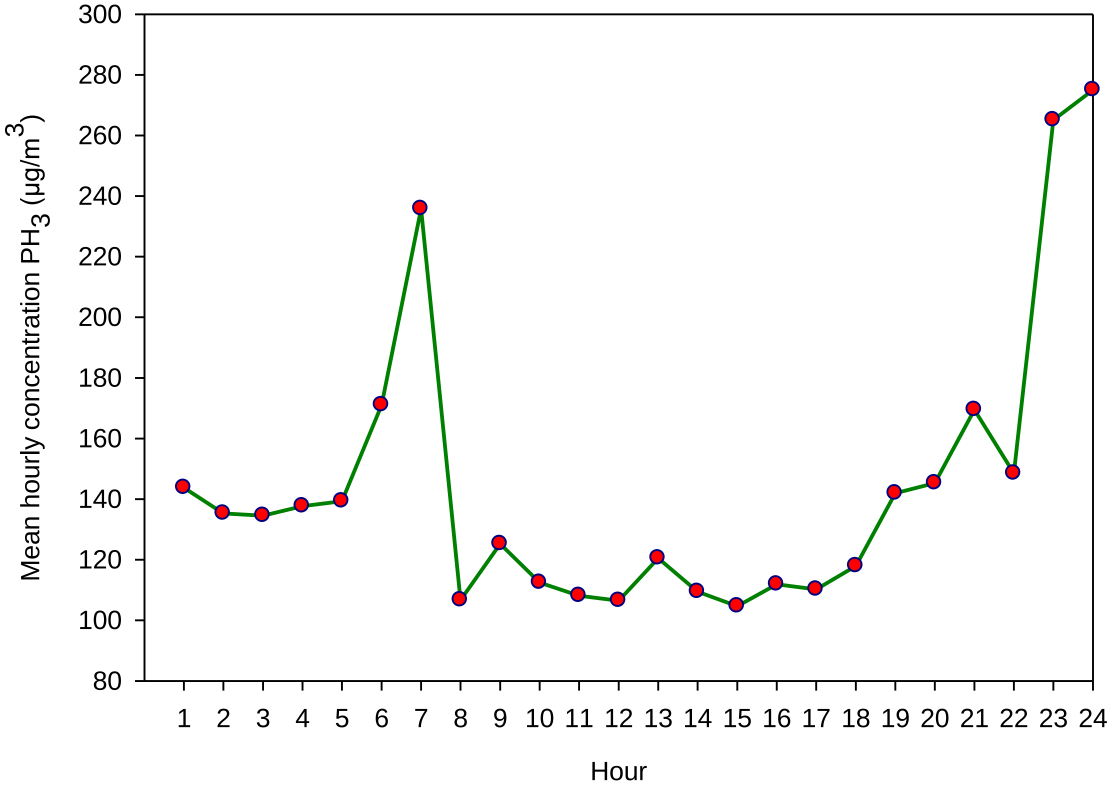
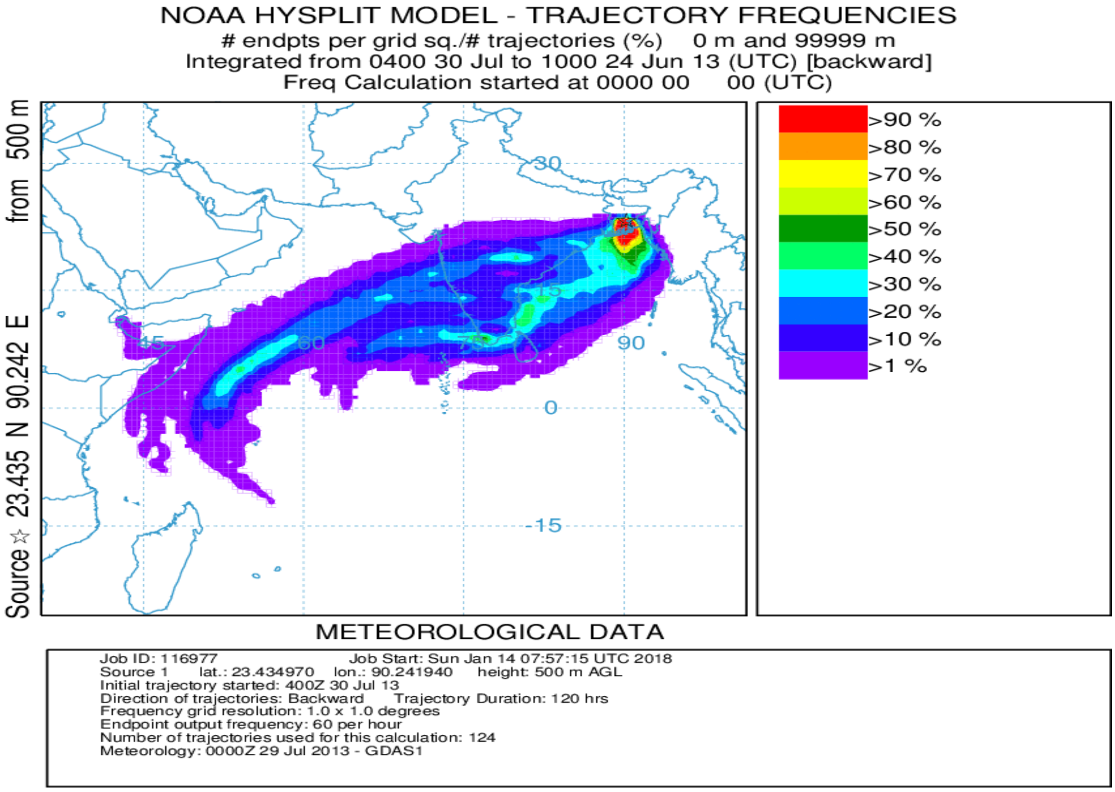


Figure 4.35: Mean hourly diurnal variation of PH_3 concentrations in Dhaka University campus, Bangladesh.

hour). The higher concentrations were observed after the sunset and it was the highest (275.0 µg/m^3) at 24:00 local time. At night the concentrations were always higher than daytime except in the morning. This clearly indicated that PH_3 accumulated in ambient air during the night time. In the morning, the higher values (06:00 - 7:00 local time) of PH_3 were due to the emissions from communal wastes, human feces, solid waste disposal sites (Ding *et al*., 2005; Glindemann and Bergmann, 1995; Glindemann *et al*., 1996a; Zhu *et al*., 2006b). The night-time/daytime difference of PH_3 concentration supports the hypothesis of phosphine fluxing from terra into the atmosphere. Phosphine is a reactive atmospheric trace gas. Hydroxyl-radicals induced by UV from daylight cause its cleavage (PH3 --> H. + .PH_2) and oxidation (WHO, 1988) and thus its concentration decreased during the daytime. At night the concentration of PH_3 increased because it is not autoxidable. Glindemann *et al.* (1996a) observed higher concentrations of PH_3 at night than during daytime in Germany. Zhu *et al.* (2006a) observed daytime variation of PH_3 and concluded that increasing light intensity promoted PH_3 oxidation and resulted in low concentration in the atmosphere of Coastal Antarctica. The same diurnal variation of PH_3 at ambient levels over paddy field at different stages of rice growth was observed by Han *et al*. (2000) and got the similar results.

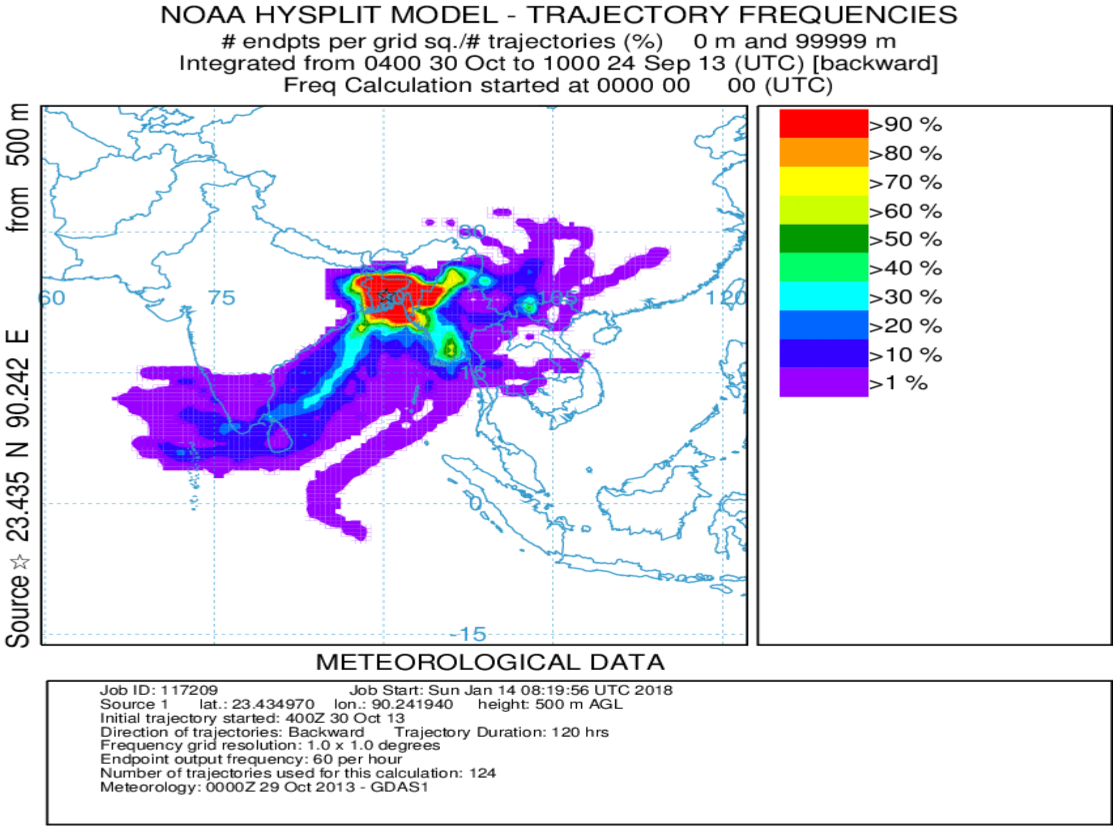
4.11 Air Mass Trajectory Analysis: Influence of Air Mass and Wind Direction

The origin of air masses is an important parameter as the concentration of atmospheric trace gases is dependent on the transport path (direction) of air. To understand the origin of the air masses, the frequencies of the backward air masses had been modeled with HYSPLIT for the four seasons (monsoon, post-monsoon, winter and pre-monsoon) in Dhaka University Campus, Bangladesh ($23^0$43.497'N latitude and $90^0$24.194'E longitude, height 500 m, at 0040 UTC - 10:00 a.m. local time). Four different types of backward air mass trajectories were observed [Figure 4.36(a) and 4.36(b)]. Air masses were originating above 90% from south that means directly from the Bay of Bengal in monsoon season [Figure 3.36(a)]. During post monsoon, backward air masses were from the surrounding region of Dhaka city and also had significantly greater influence from the eastern region of Bangladesh and India [(Figure 3.36(a)]. Winter time air masses (about 90%) were originating from north and northwest of Indo Gangetic Plain (IGP). [(Figure 4.36(b)]. Whereas, during the pre-monsoon season, air masses (about 90%) were mostly from the Bay of Bengal (mostly south and southwest) but very near to the Indian coastal region [(Figure 4.36(b)]. However, the frequency of the backward air masses showed that Dhaka University campus had strong influence either from south/southwest or north/northwest. As a case study, two days (in monsoon and winter) were selected to observe the differences of the pollutant concentrations from south/southwest (i.e., the Bay of Bengal) (on July 10, 2013) or north/northwest (i.e., from IGP) (on January 10, 2014) directions. Therefore, 96-hour air mass back trajectories arriving at 500, 1000 and 3000 meter above ground level at the sampling location ($23^0$43.497'N latitude and $90^0$24.194'E longitude), Dhaka University campus, at 0400 UTC (10:00 a.m. local time) on the 10th July 2013 (monsoon) and 10th January (winter) were calculated [Figure 4.37(a) and Figure 4.37(b)].


NOAA HYSPLIT MODEL - TRAJECTORY FREQUENCIES
endpts per grid sq./# trajectories (%) 0 m and 99999 m
Integrated from 0400 30 Jul to 1000 24 Jun 13 (UTC) [backward]
Freq Calculation started at 0000 00 00 (UTC)

Job ID: 116977 Job Start: Sun Jan 14 07:57:15 UTC 2018
Source 1 lat.: 23.434970 lon.: 90.241940 height: 500 m AGL
Initial trajectory started: 400Z 30 Jul 13
Direction of trajectories: Backward Trajectory Duration: 120 hrs
Frequency grid resolution: 1.0 x 1.0 degrees
Endpoint output frequency: 60 per hour
Number of trajectories used for this calculation: 124
Meteorology: 0000Z 29 Jul 2013 - GDAS1

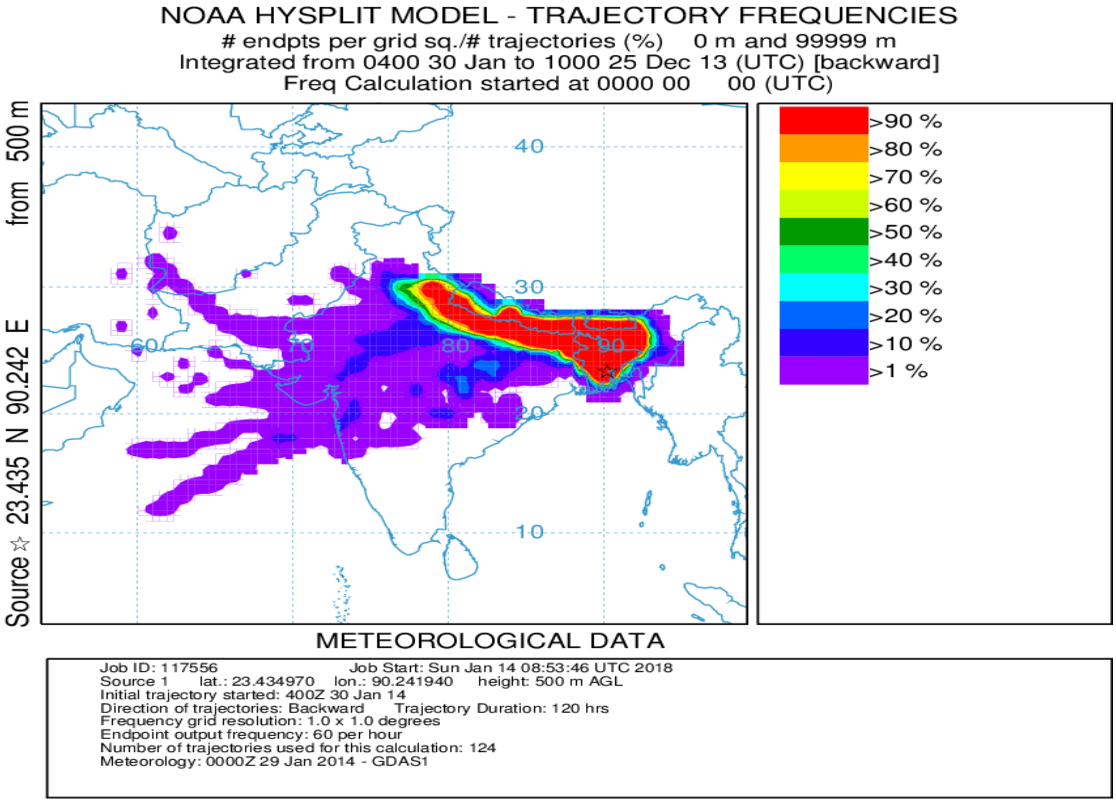
Monsoon


NOAA HYSPLIT MODEL - TRAJECTORY FREQUENCIES
endpts per grid sq./# trajectories (%) 0 m and 99999 m
Integrated from 0400 30 Oct to 1000 24 Sep 13 (UTC) [backward]
Freq Calculation started at 0000 00 00 (UTC)

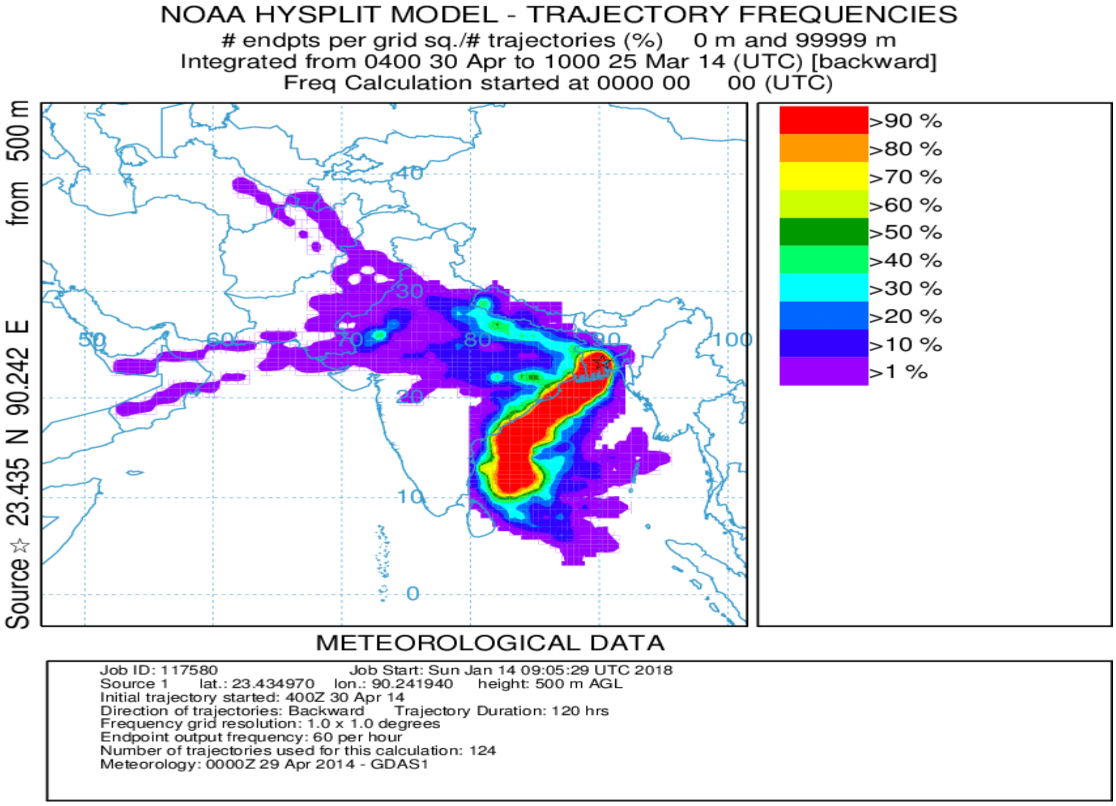
Job ID: 117209 Job Start: Sun Jan 14 08:19:56 UTC 2018
Source 1 lat.: 23.434970 lon.: 90.241940 height: 500 m AGL
Initial trajectory started: 400Z 30 Oct 13
Direction of trajectories: Backward Trajectory Duration: 120 hrs
Frequency grid resolution: 1.0 x 1.0 degrees
Endpoint output frequency: 60 per hour
Number of trajectories used for this calculation: 124
Meteorology: 0000Z 29 Oct 2013 - GDAS1

Post-monsoon

Figure 4.36(a): Backward air mass trajectories showing frequencies and wind directions in the monsoon season (top) and post-monsoon season (bottom) at Dhaka University campus, Bangladesh.



Winter



Pre-monsoon

Figure 4.36(b): Backward air mass trajectories showing frequencies and wind direction in the winter season (top) and pre-monsoon season (bottom) in Dhaka University campus, Bangladesh.

According to the Figure 4.37(a), air masses arriving at Dhaka University campus at 0400 UTC (10:00 a.m. local time) on the 10th July 2013 were in south directions, of them two were originated (500 and 1000 meter above ground level) in the Indian Ocean and then flew over the Indo Gangetic Plain and afterward passed over the Bay of Bengal. Air mass originated in the Indo Gangetic Plain (3000 meter above ground level) flew over the Bay of Bengal (Indian Ocean) in arriving the sampling location. During the summer monsoon, relatively cleaner marine air masses from the Bay of Bengal are transported to Bangladesh and Indian subcontinent. These air masses bring some trace gases of marine origin and also pick up trace gases discharged from natural and man-made sources along en route. These air masses also bring water vapor which cause cloudy conditions and enough rainfall in monsoon. Also wind rose plot [(Figure 4.37(a)] on the 10th July 2013, indicated that at 0400 UTC (10:00 a.m. local time) the wind was in south direction (180^0) with an average speed of 1.5 to 2 Knot. All the air mass and wind directions might had effects on the trace gas concentration. The concentration of the trace gases (CO, NO, NO_2, TVOC O_3, NH_3, PH_3 and H_2S) measured on the July 10, 2013 are presented in Table 4.3.

On the 10th January 2014, air masses arriving at the sampling location (Dhaka University campus) at 0400 UTC (10:00 a.m. local time) had different air flow directions as well as they were originated in different regions [Figure 4.37(b)]. One air mass (500 meter above ground level) was coming from the north direction and was originated at the north-east part of Ingo Gangetic Plain. Another one (1000 meter above ground level) originated in the north-west part of Ingo Gangetic Plain, was coming from the north-west direction. Another air mass was originated (3000 meter above ground level) in the far west of Ingo Gangetic Plain and traveled a long way. All of the air masses were originated in the continental parts and would have abundance in air pollutants due to the probable presence of emission sources. Wind rose plot at 0400 UTC (10:00 a.m. local time) on the 10th January 2013 [(Figure 4.37(b)], indicated that wind was coming from the north-east direction with an average speed of 2 knot. All the air mass and wind directions might had effects on the trace gas concentration. The concentration of the trace gases (CO, NO, NO_2, TVOC O_3, NH_3, PH_3 and H_2S) measured on the 10th January 2014 are presented in Table 4.3.

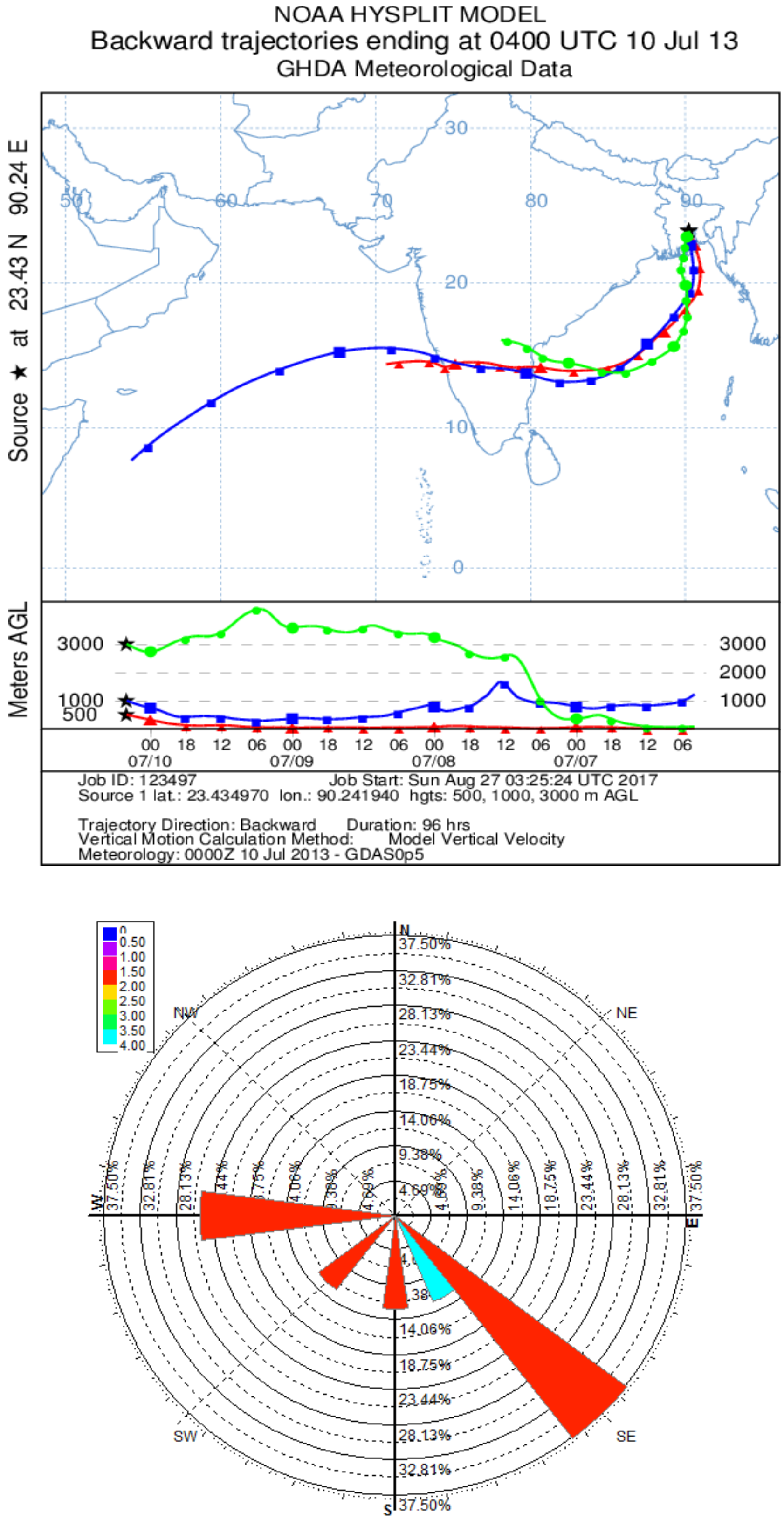


Figure 4.37(a): Backward air mass trajectories (top) and wind rose plot (bottom) in the monsoon season at 10:00 a.m. local time on 10th July2013 in Dhaka University campus, Bangladesh.

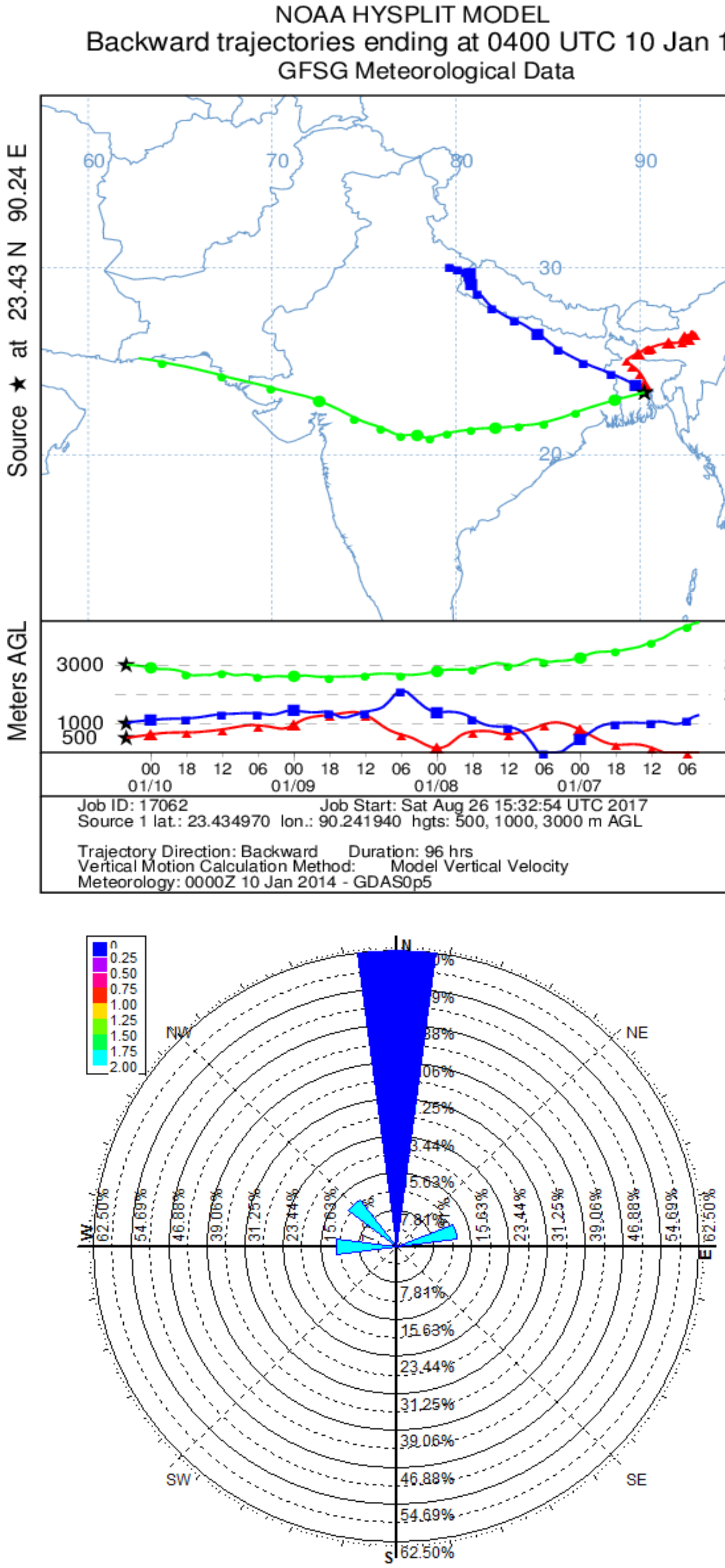


Figure 4.37(b): Backward air mass trajectories (top) and wind rose plot (bottom) in the winter season at 10:00 a.m. local time on 10th January 2014 in Dhaka University campus, Bangladesh.

Many researchers also observed air mass trajectories to study air quality since they typically represent local and regional pollution conditions. Anastassopoulos et *al*. (2004) used HYSPLIT model to study air quality in the city of Windsor (42.16°N, 82.58°W), Ontario, Canada. The results identified that air masses from Ontario and neighboring American states including Michigan, Ohio and Wisconsin had greater influence on the air quality of Windsor, primarily due to the prevailing wind directions. Jaffe *et al*. (1999) used back trajectories to verify that anthropogenic emissions from Asia which had a significant impact on the concentrations of chemical species arriving in North America. Wang *et al*. (2016) observed that air masses transported from south regions affected many cities in the south side of Beijing with a serious air pollution episode specially the VOCs. Baudic *et al*. (2016) observed air mass trajectories in the Paris megacity, France for the year 2010, and termed that air masses arriving from different directions in different seasons contained VOCs and other pollutants from origin sources and en route transportation.

From the Table 4.3, it is observed that the concentrations of all the trace gases, except TVOC and H_2S were in higher orders on the 10th January 2014 (D_1) (winter season) than on the 10th July 2013 (D_2) (monsoon season).

Table 4.3: Concentrations of trace gases of the two selected days - 10th July2013 (monsoon) and 10th January 2014 (winter season).

Trace gas	**Concentration (μg/m³)**		**D_1/D_2 ratio**
	10th January 2014 (D_1)	10th July 2013 (D_2)	
CO	6,490.1	2,228.2	2.91
NO	632.0	369.0	1.71
NO_2	102.3	98.0	1.04
TVOC	6,325.6	15,745.2	0.40
O_3	51.7	46.7	1.11
H_2S	11.1	90.6	0.12
PH_3	160.1	148.1	1.08
NH_3	128.8	69.6	1.85

In winter season, high concentrations of the trace gases (CO, NO, NO_2, O_3, NH_3 and PH_3) at the study location would be the cause of less dispersion and dilution effects on pollutants, origin of air masses on the terrestrial parts and picking up of pollutants on en route transportation. However, on the 10th July 2014, TVOC and H_2S concentrations were high, since air masses blowing over the ocean were relatively clear and only contained marine origin gases and they also brought enough moisture to cause precipitation. Marine origin air mass also might have indirect effect on the TVOC emission since vegetative growth increase in rainy season. Rainy season also favors H_2S emission from organic matter due to the anaerobic decomposition. Moreover, marine origin air masses were strong enough to reduce the concentrations of other trace gases in the monsoon season.

4.12 Correlation Coefficient among Different Trace Gases and Temperature and Relative Humidity

Correlation coefficients were measure to see the degree of correlation among the trace gases, temperature and humidity. These coefficients always lie between - 1 and 1. Table 4.4, 4.5, 4.6 and 4.7 showed the correlation coefficient (r) among the measured trace gases (CO, O_3, NO, NO_2, TVOC, H_2S, PH_3, and NH_3), temperature and humidity during the monsoon (June 2013 - August 2013), post-monsoon (September 2013 - November 2013), winter (December 2013 - February 2014) and pre-monsoon (March 2013 - May 2014), respectively.

CO concentrations had positive correlation with O_3, TVOC, H_2S, PH_3, and humidity in the monsoon (Table 4.42); with TVOC, H_2S, PH_3, temperature and humidity in post-monsoon (Table 4.5); with O_3, NO, TVOC, H_2S, PH_3, and NH_3 in winter (Table 4.6) and with NO, H_2S, and PH_3 in pre-monsoon (Table 4.7). The correlation coefficients ranged from 0.088 to 0.115, and CO showed highly significant (at the level of 0.01) correlation coefficient with H_2S and PH_3since they may come from reduce sources.

O_3 had highly significant (at the level of 0.01) correlation with CO, TVOC, PH_3, NH_3 and humidity in the monsoon (Table 4.4); with NO, TVOC, PH_3, NH_3 and humidity in post-monsoon (Table 4.5); with CO, NO, TVOC, PH_3, NH_3 and humidity in winter (Table 4.6) and with NO, TVOC, PH_3 and NH_3 in pre-monsoon (Table 4.7). NO and

TVOC are precursors of O_3 and thus their effects on O_3 production were pronounced here. O_3 also had significant correlation (at the level of 0.05) with PH_3 in post-monsoon season (Table 4.3). O_3 was negatively correlated with NO_2 in all seasons.

NO showed highly significant (at the level of 0.01) correlation coefficient with H_2S, PH_3 and temperature in the monsoon (Table 4.4); with O_3 and NH_3 in post-monsoon (Table 4.5); with CO, O_3, TVOC, PH_3, NH_3 and humidity in winter season (Table 4.6) and with CO, O_3, TVOC, PH_3 and temperature in pre-monsoon (Table 4.7).

Table 4.4: Correlation coefficient (r) among the measured trace gases (CO, O_3, O, NO_2, TVOC, H_2S, PH_3, and NH_3), temperature and relative humidity during the monsoon season (June 2013 - August 2013).

	CO	O_3	NO	NO_2	TVOC	H_2S	PH_3	NH_3	Temperature	Relative humidity
CO	1									
O_3	0.249**	1								
NO	-0.082	0.076	1							
NO_2	-0.247	-0.803	0.033	1						
TVOC	0.237**	0.650**	-0.117	-0.711	1					
H_2S	0.501**	-0.344	0.165**	0.375**	-0.247	1				
PH_3	0.208**	0.136**	0.535**	-0.080	0.103**	0.142**	1			
NH_3	0.046	0.665**	0.023	-0.651	0.385**	-0.237	-0.198	1		
Temperature	-0.229	-0.743	0.245**	0.843**	-0.598	0.451**	0.088*	-0.634	1	
Relative humidity	0.267**	0.813**	-0.106	-0.923	0.705**	-0.368	0.006	0.703**	-0.905	1
** Correlation is significant at the level of 0.01 (0.115) * Correlation is significant at the level of 0.05 (0.088)										

NO_2 have positive correlation coefficient with H_2S and temperature in the monsoon (Table 4.4); with temperature in post-monsoon (Table 4.5), winter (Table 4.6) and pre-monsoon (Table 4.7). The correlation coefficients (r) ranged from 0.088 to 0.115 and NO_2 showed highly significant (at the level of 0.01) correlation coefficient.

TVOC had highly significant (at the level of 0.01) correlation with CO, O_3, PH_3, NH_3 and humidity in the monsoon (Table 4.4); with CO, O_3, H_2S, PH_3, temperature and humidity in post-monsoon (Table 4.5); with CO, O_3, NO, PH_3, NH_3 and humidity in winter (Table 4.6) and with O_3, NO, H_2S, PH_3, NH_3 temperature and humidity in pre-monsoon (Table 4.7).

Table 4.5: Correlation coefficient (r) among the measured gases (CO, O_3, NO, NO_2, TVOC, H_2S, PH_3, and NH_3), temperature and relative humidity during the post-monsoon (September 2013 - November 2013).

	CO	O_3	NO	NO_2	TVOC	H_2S	PH_3	NH_3	Temperature	Relative humidity
CO	1									
O_3	0.030	1								
NO	-0.089	0.274**	1							
NO_2	0.009	-0.832	-0.202	1						
TVOC	0.327**	0.437**	-0.462	-0.536	1					
H_2S	0.575**	-0.147	-0.626	0.053	0.634**	1				
PH_3	0.564**	0.099*	-0.647	-0.185	0.745**	0.779**	1			
NH_3	-0.092	0.617**	0.575**	-0.553	-0.011	-0.383	-0.258	1		
Temperature	0.312**	-0.299	-0.827	0.232**	0.576**	0.858**	0.717**	-0.639	1	
Relative humidity	0.228**	0.611**	-0.162	-0.758	0.821**	0.398**	0.587**	0.373**	0.216**	1
** Correlation is significant at the level of 0.01 (0.115) * Correlation is significant at the level of 0.05 (0.088)										

TVOC with H_2S, PH_3 and NH_3 reflected the influence of emissions from biological and rotten-waste sources (e.g., communal wastes, landfills, polluted river water and paddy fields around Dhaka City).

Hydrogen sulfide had highly significant (at the level of 0.01) correlation with CO, NO, NO_2, PH_3 and temperature in the monsoon (Table 4.4); with CO, TVOC, PH_3 temperature and humidity in post-monsoon (Table 4.5); with CO, PH_3 and temperature in winter (Table 4.6) and with CO, TVOC, PH_3, NH_3, temperature and humidity in pre-monsoon (Table 4.7).

The results of the correlation analysis showed that PH_3 had highly significant (at the level of 0.01) correlation with CO, O_3, NO, TVOC and H_2S in the monsoon (Table 4.4); with CO, TVOC, H_2S, temperature and humidity in post-monsoon (Table 4.5); with CO, O_3, NO, TVOC, H_2S, NH_3 and temperature in winter (Table 4.6) and with

CO, O_3, NO, TVOC, H_2S, NH_3, NH_3 and humidity in pre-monsoon (Table 4.7). PH_3 had also significant (at the level of 0.01) correlation with temperature in monsoon (Table 4.4) and with O_3 in post-monsoon (Table 4.5).

Table 4.6: Correlation coefficient (r) among the measured gases (CO, O_3, NO, NO_2, TVOC, H_2S, PH_3, and NH_3), temperature and relative humidity during the winter season (December 2013 - February 2014).

	CO	O_3	NO	NO_2	TVOC	H_2S	PH_3	NH_3	Temperature	Relative humidity
CO	1									
O_3	0.232**	1								
NO	0.385**	0.913**	1							
NO_2	-0.364	-0.741	-0.719	1						
TVOC	0.236**	0.308**	0.255**	-0.376	1					
H_2S	0.314**	-0.568	-0.447	0.021	0.039	1				
PH_3	0.646**	0.533**	0.640**	-0.713	0.305**	0.180**	1			
NH_3	0.173**	0.421**	0.423**	-0.407	0.217**	-0.125	0.108**	1		
Temperature	-0.216	-0.982	-0.936	0.707**	-0.266	0.579**	-0.544	-0.388	1	
Relative humidity	0.345	0.802**	0.801**	-0.682	0.460**	-0.339	0.557**	0.621**	-0.779	1
** Correlation is significant at the level of 0.01 (0.115) * Correlation is significant at the level of 0.05 (0.088)										

Ammonia had highly significant (at the level of 0.01) correlation coefficient with O_3, TVOC and humidity in monsoon (Table 4.4); with O_3, NO and humidity in post-monsoon (Table 4.5); with CO, O_3, NO, TVOC, PH_3 and humidity in winter (Table 4.6) and with O_3, TVOC, H_2S, PH_3 and humidity in pre-monsoon (Table 4.7).

Meteorological parameters (temperature and relative humidity) influence trace gases. Temperature had highly significant (at the level of 0.05 and 0.01) correlation with NO, NO_2, H_2S and PH_3 in the monsoon (Table 4.4); with CO, NO_2, TVOC, H_2S, PH_3 and humidity in post-monsoon (Table 4.5); with NO_2 and H_2S in winter (Table 4.6) and with NO_2, TVOC and H_2S in pre-monsoon (Table 4.7). The association between temperature and CO and NO, was found to be weak or insignificant in all seasons, except highly significant correlation with NO in the monsoon (Table 4.4) and with CO in the post-monsoon (Table 4.5).

Table 4.7: Correlation coefficient (r) among the measured gases (CO, O_3, NO, NO_2, TVOC, H_2S, PH_3, and NH_3), temperature and relative humidity during the pre-monsoon season (March 2014 - May 2014).

	CO	O_3	NO	NO_2	TVOC	H_2S	PH_3	NH_3	Temperature	Relative humidity
CO	1									
O_3	-0.069	1								
NO	0.124**	0.207**	1							
NO_2	-0.111	-0.819	-0.317	1						
TVOC	0.025	0.190**	0.502**	-0.429	1					
H_2S	0.405**	-0.101	0.004	-0.329	0.258**	1				
PH_3	0.328**	0.190**	0.620**	-0.484	0.506**	0.495**	1			
NH_3	-0.083	0.425**	0.045	-0.529	0.293**	0.246**	0.157**	1		
Temperature	-0.033	-0.677	-0.061	0.528**	0.201**	0.273**	-0.018	-0.211	1	
Relative humidity	0.001	0.541**	0.600**	-0.711	0.837**	0.218**	0.574**	0.466**	-0.210	1

** Correlation is significant at the level of 0.01 (0.115)
* Correlation is significant at the level of 0.05 (0.088)

Relative humidity had highly significant (at the level of 0.01) correlation with CO, O_3, TVOC and NH_3 in the monsoon (Table 4.4); with CO, O_3, TVOC, H_2S, PH_3, $NH_3$and temperature in post-monsoon (Table 4.5); with O_3, NO, TVOC, PH_3 and NH_3 in winter (Table 4.6) and with NO, TVOC, H_2S, PH_3 and NH_3 in pre-monsoon (Table 4.7).The correlation coefficient between relative humidity and NO was found negative in monsoon (Table 4.4) and in post-monsoon season (Table 4.5). Relative humidity had negative correlation with NO_2 in all seasons.

Several studies were also reported the correlation co-efficient among different gaseous pollutants. Wang *et al*., 2014 reported correlations among CO, SO_2, O_3 and NO_2 pollutants in different seasons and also found O_3 had positive correlation with other pollutants. All other pollutants were still correlated with each other, but the correlations were lower than in winter and the fall (Wang *et al*., 2014). AL-Awadhi (2014) measured air pollution in Kuwait city during March 2011 to February 2012 and showed that NH_3 was strongly correlated with O_3 in winter season, while in summer NH_3 was strongly correlated with NO. The association between NOx and CO was found weak or insignificant, while O_3 followed a positive correlation with temperature except in post-monsoon season (Gaur *et al*., 2014). Wang *et al*. (2016) indicated that VOCs had good correlation with CO. Carbon monoxide was often used as indicator for vehicle exhaust (Liu *et al*., 2009), and the higher correlation reflected the influence of vehicle emission on the ambient VOCs concentrations. However, the temperature is one of the most important meteorological parameters that control the rate and amount of photochemical production of O_3. So, the higher O_3 concentrations commonly occur at afternoon and during the spring and summer season, while during winter its concentration is relatively low due to less intensive solar radiation (Nishanth *et al*., 2012; Richards *et al*., 2013; Tecer *et al*., 2003). In the present study a negative correlation between O_3 and temperature was observed in all season, which might be caused by the reduced generation of O_3 and increased consumption. AL-Awadhi (2014) also found strong negative correlation between O_3 and ambient temperature in winter season and strong positive correlation in fall season.

4.13 Source Profile Analysis of O_3, TVOC and NOx by PMF 5.0 Model

Positive matrix factorization (PMF 5.0) is a receptor model that quantitatively estimates the contributions from specific sources. PMF is widely used for source appointment study of the chemical composition of the atmospheric particulate matters (e.g., Begum *et al*., 2004), volatile organic carbons (Wang *et al*., 2016; Baudic *et al*., 2016). There is no or very limited information of the source apportionment study of atmospheric trace gases with PMF. In this study a 93 × 3 (93 samples with 3 gases - NOx, O_3 and TVOC) data set was introduced into the PMF 5.0 model to estimate the source contributions of the gases (NOx, O_3 and TVOC) in Figure 4.38, 4.39 and 4.40. Two source profiles of gases were analyzed from the PMF5.0 model. Two factors contributed for NOx and O_3 and one exclusively for total volatile organic compound (TVOC).

Factor 1: Factor 1 is the atmospheric processes (e.g., photochemical reactions, formation of secondary air pollutants, physical transportation, etc.) which contributed 35.5% in ozone (with about 30% ambiguity), exclusively 100% in TVOC and 10.1% in NOx.

Factor 2: Factor 2 is the fossil fuel burning that contributed 64.5% in ozone and 89.9% in NOx.

The sources and their contributions analyzed by PMF are shown by pie chart (Figure 4.38), finger print region for the sources are presented in Figure 4.39, and the source profile of O_3, TVOC and NOx gases in Dhaka City is shown in Figure 4.40.

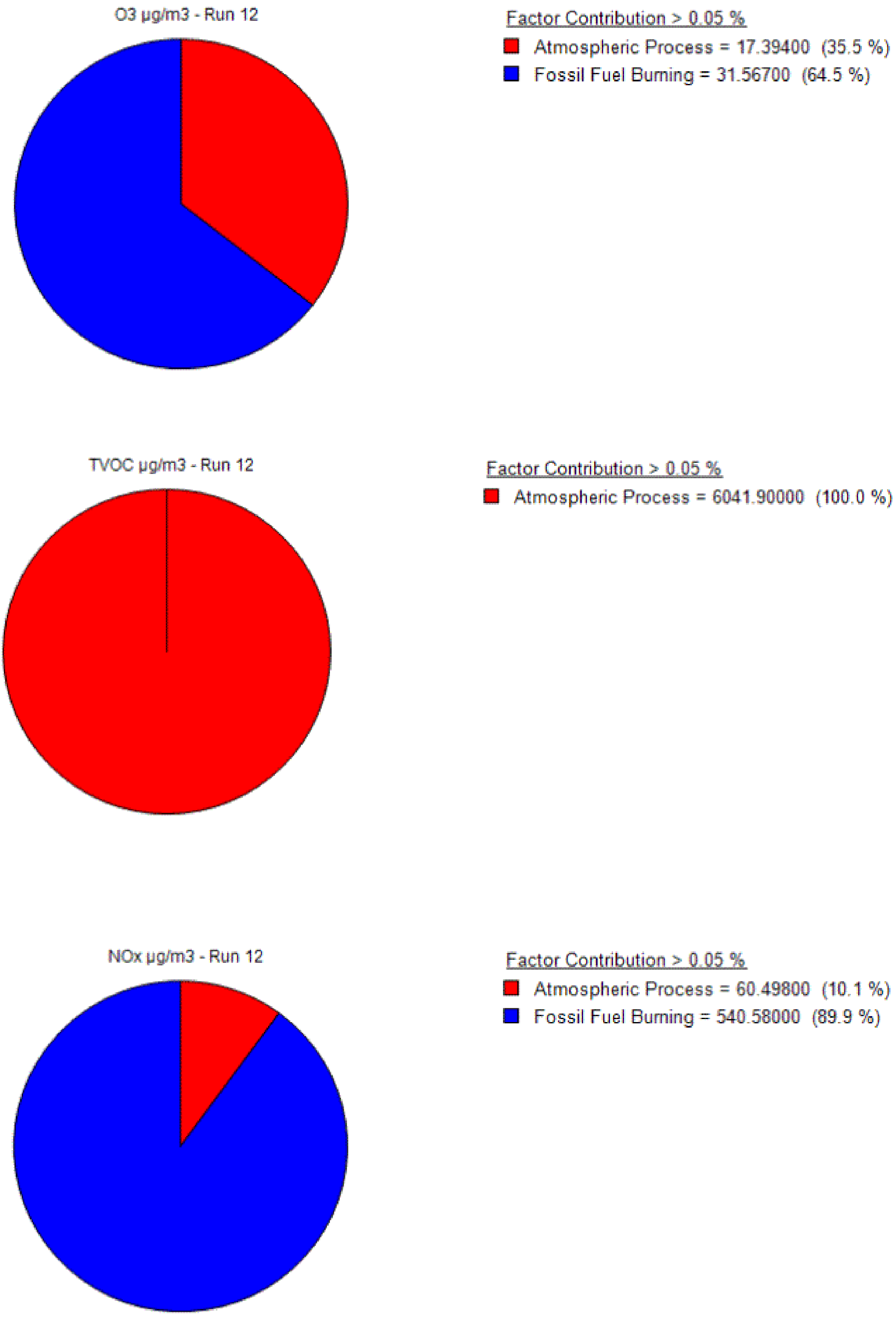


Figure 4.38: Sources contribution for O_3, TVOC and NOx gases in Dhaka City, Bangladesh.

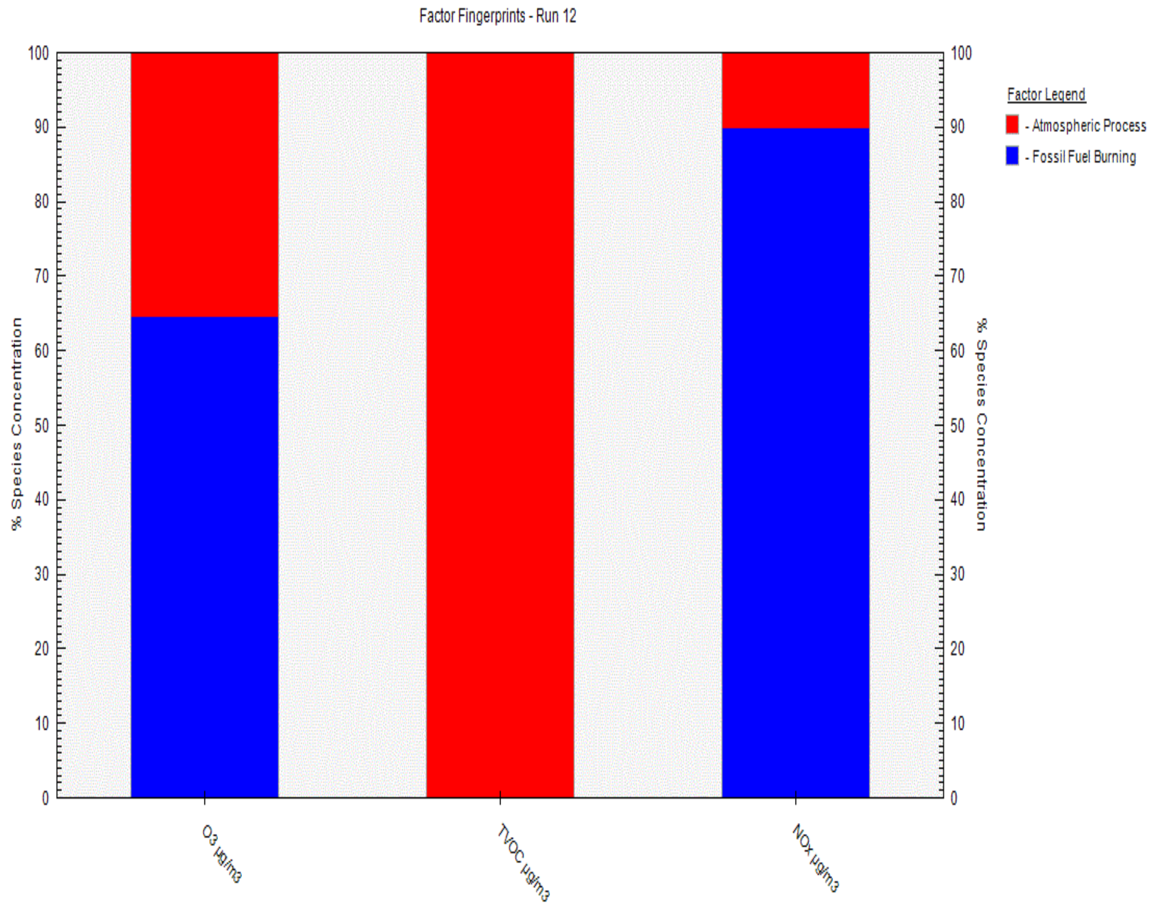


Figure 4.40: Factors finger print region for the sources in Dhaka City, Bangladesh

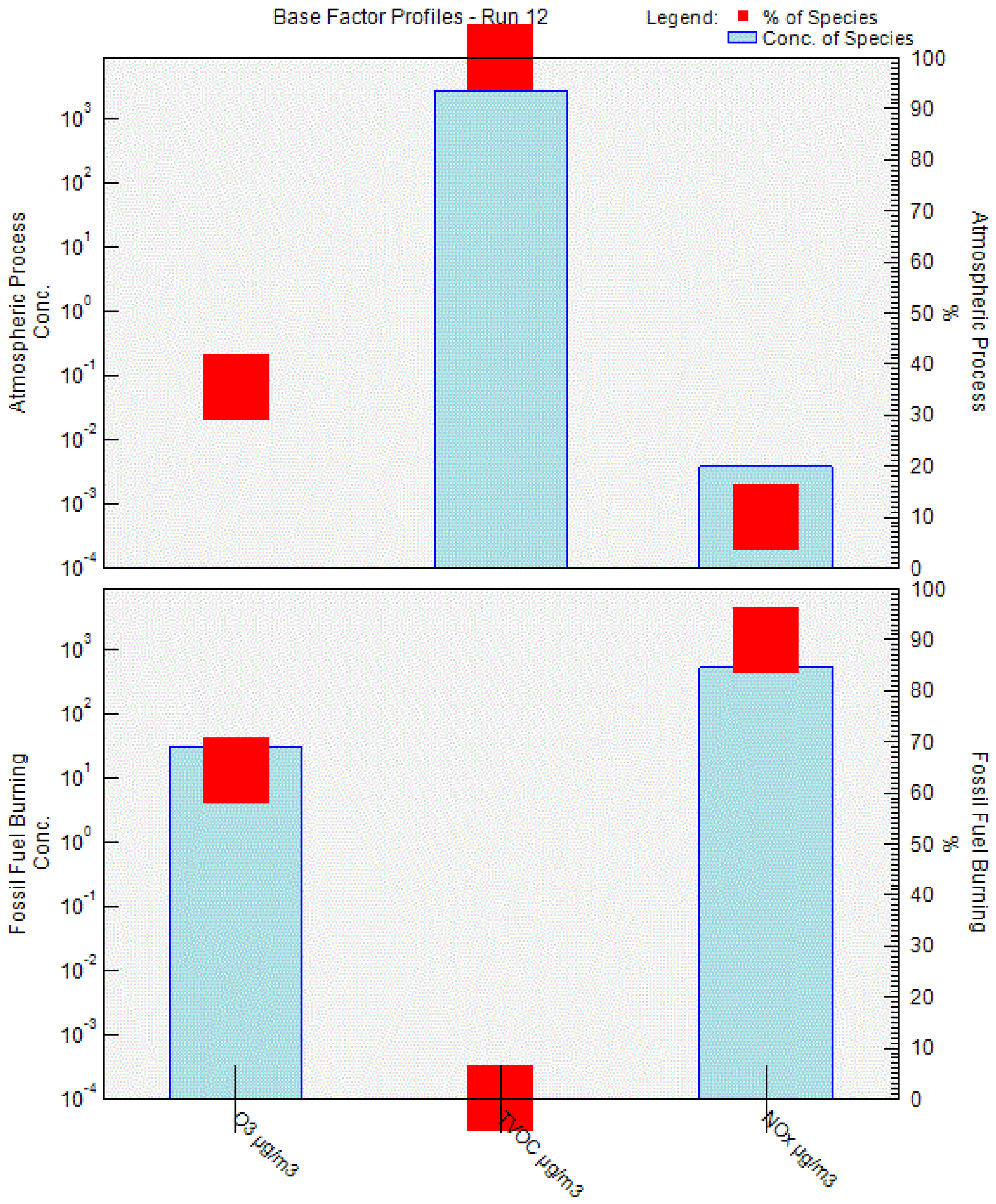


Figure 4.40: Source profile of O_3, TVOC and NOx gases by PMF 5.0 in Dhaka City, Bangladesh.

CHAPTER FIVE

CONCLUSION

CHAPTER FIVE

CONCLUSION

Atmospheric pollution has significant impact on human health, climate change, visibility reduction, atmospheric chemistry and ecosystem. Gaseous pollutants are important component of the atmospheric pollution and these are emitting from both natural and anthropogenic sources. Very limited information of the trace gases, sources, and impacts are available in Bangladesh. However, this research work was accomplished to study the occurrence and characterization of selected atmospheric trace gases such as CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3 in the central part of Dhaka city in Bangladesh between June 2013 and May 2014. Same trace gases were also measured at Karwan Bazar in Dhaka, Dhamrai in Dhaka district, Jamalganj in Sunamganj district and Badla Haor in Kishoreganj district for the comparison. The annual average concentrations of CO, NO, NO_2, TVOC, O_3, NH_3, H_2S and PH_3 were 2603.6 ± 1216.4, 281.5 ± 158.0, 182.7 ± 69.4, 10068.2 ± 5296.1, 36.6 ± 23.6, 133.8 ± 94.9, 84.8 ± 38.8, and 133.1 ± 37.7 $\mu g/m^3$, respectively in Dhaka University campus, Bangladesh. The observed elevated concentrations of these trace gases were much higher than the values in other cities of the world. But they are still below the guideline values of US EPA and WHO except NO_2. The concentrations of the traffic emitted trace gases (e.g., CO, NO, NO_2) in Dhaka University campus, however, were much lower than the traffic intersection of Karwan Bazar, Dhaka but much higher than the other locations in Bangladesh. The average concentrations of these gases varied from month to month. For example, the monthly average concentration of CO was 2,569.6 ± 498.0 $\mu g/m^3$ with the highest value (3,486.5 $\mu g/m^3$) in January 2014 and the lowest value (1,867.3 $\mu g/m^3$) in April 2014. Whereas, the highest TVOC concentration was observed in September 2013 and the lowest was in February 2014. The variations of these trace gases were not same in all season. Some gases (CO and NO) showed peak concentrations in winter, whereas TVOC, PH_3 and O_3 showed peak in monsoon, and NO_2, H_2S and PH_3 concentrations were the highest in pre-monsoon season. The diurnal variation of CO showed a good agreement with density of vehicles in the street of Dhaka city. Interestingly the TVOC concentration was gradually increased from morning to evening hours. The NOAA HYSPLT analyses showed that the frequency of the backward air masses arriving at the sampling location of Dhaka University campus was from four different directions, e.g., during winter air mass was coming from Indo-Gangetic Plain (IGP) region, and during monsoon from the Bay of Bengal. As a case study, the concentrations of trace gases during two wind directions (monsoon vs winter) were characterized. It was found that the concentrations of most trace gases were 1 to 3 times lower during the air mass originated from the Bay of Bengal than that of the air mass originated from IGP region. The correlation coefficients of the measured components were studied for four different seasons. The results indicated that CO has good positive correlation with O_3, TVOC, H_2S, PH_3 and relative humidity in monsoon season. Phosphine had strong correlation with TVOC (0.745) and H_2S (0.779) in post monsoon season. Ozone had strong correlation with NO (0.913) only in winter season. The PMF 5.0 model was running for O_3, TVOC and NOx for the source apportionment study. It showed that there were two main sources (fossil fuel burning and atmospheric photochemical activities) for O_3 and NOx, whereas atmospheric photochemical activity was mainly responsible for TVOC. This study was the first time systematic measurement of atmospheric trace gases for four seasons in Bangladesh, which will provide a baseline data for the policy makers and also for the long term study in future.

CHAPTER SIX

REFERENCES

CHAPTER SIX

REFERENCES

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APPENDIX

Appendix 1: The overall minimum, maximum, average, median and standard deviation of the atmospheric trace gases (µg/m^3) in Dhaka University campus, Bangladesh.

	CO	**NO**	**NO_2**	**TVOC**	**O_3**	**NH_3**	**H_2S**	**PH_3**
Minimum	864.6	5.4	10.2	501.1	3.5	2.3	4.0	53.7
Maximum	17047.4	731.7	399.3	24204.5	178.0	848.5	301.8	296.0
Average	2604.0	281.7	182.7	10068.3	36.6	133.8	84.8	133.1
Median	2260.6	265.1	196.2	10328.0	32.1	121.0	93.5	133.1
Standard deviation	1218.5	157.8	69.4	5277.1	23.3	120.8	38.8	37.7