EXPLORING THE POTENTIAL OF MAX-DOAS INSTRUMENT FOR ATMOSPHERIC MONITORING OF NO_2 CONCENTRATION DURING THE TIME PERIOD OF 2014-2018

Hafiz Ahsan Mehmood

(00000170838)

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

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By

Hafiz Ahsan Mehmood
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THESIS ACCEPTANCE CERTIFICATE

It is certified that the contents and form of the thesis entitled “Exploring the potential of MAX-DOAS instrument for atmospheric monitoring of NO_2 concentration during the time period of 2014-2018” submitted by **Mr. Hafiz Ahsan Mehmood (Reg # 00000170838)** has been found satisfactory for the requirements of the degree of Master of Science in Environmental Science.

Supervisor: ____________

Dr. M. Fahim Khokhar

IESE, SCEE, NUST

Head of Department: ________

Dr. Muhammad Arshad

IESE, SCEE, NUST

Principal: ________________

Dr. Tariq Mahmood

SCEE, NUST

CERTIFICATE

It is certified that the contents and forms of the thesis entitled **"Exploring the potential of MAX-DOAS instrument for atmospheric monitoring of NO_2 concentration during the time period of 2014 - 2018"** submitted by Mr. Hafiz Ahsan Mehmood has been found satisfactory for the requirements of the degree of Master of Science in Environmental Science.

Supervisor:____________________
Dr. Fahim Khokhar
Professor
IESE, SCEE, NUST

Member:

____
Dr. M. Zeeshan Ali Khan
Assistant Professor
IESE-SCEE, NUST

Member:

____
Dr. Muhammad Arshad
Associate Professor
IESE-SCEE, NUST

I dedicate this thesis to my beloved Father and siblings who have
been always a source of inspiration for me and stood beside me
at every moment in my life

بسم الله الرحمن الرحيم

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Thanks to Allah Almighty, the "Most Beneficent" and the "Most Merciful" Who blessed us with ability, skills and wisdom to accomplish this thesis. I express my sincere gratitude to my Family for their affection and moral support throughout my academic career.

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Hafiz Ahsan Mehmood

LIST OF ABBREVIATIONS

$\mu g/m^3$	Microgram per Cubic meter
AMF	Air Mass Factor
ArcGIS	Arc Geographic Information System
DOAS	Differential Optical Absorption Spectroscopy
DOASIS	Differential Optical Absorption Spectroscopy Intelligent System
DSCD	Differential Slant Column Densities
FTIR	Fourier Transform Infrared Spectrometry
FWHM	Full Width Half Maximum
GOP	Government of Pakistan
HNO_3	Nitric Acid
JICA	Japan International Cooperation Agency
LTV	Light Transport Vehicle
MAX-DOAS	Multi-axis Differential Optical Absorption Spectroscopy
NDIR	Non-Dispersive Infra-Red
NGO’s	Non-Government Organizations
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_2 SCD	Nitrogen Dioxide Slant Column Density
NO_2 VCD	Nitrogen Dioxide Vertical Column Density
NO_2^-	Nitrites
NO_3^-	Nitrates
NO_x	Oxides of Nitrogen
O_3	Ozone
OMI	Ozone Monitoring Instrument
OSHA	Occupational Safety & Health Administration
Pak-EPA	Pakistan Environmental Protection Agency
Pak-NEQs	Pakistan National Environmental Quality Standards

PAN	Peroxy Acetyl Nitrile
PCTs	Pollution Control Techniques
PM	Particulate Matter
SFP	Slit function Parameter
USEPA	United States Environmental Protection Agency
UTC	Coordinated Universal Time
UV	Ultra-Violet
VOCs	Volatile Organic Compounds
WHO	World Health Organization
WinDOAS	Windows Differential Optical Absorption Spectroscopy
ppb	Parts per Billion
RMS	Root Mean Square
OMI	Ozone Monitoring Instrument
OSHA	Occupational Safety & Health Administration
Pak-EPA	Pakistan Environmental Protection Agency
Pak-NEQs	Pakistan National Environmental Quality Standards

PCTs	Pollution Control Techniques
PM	Particulate Matter
SFP	Slit function Parameter
USEPA	United States Environmental Protection Agency
UTC	Coordinated Universal Time
UV	Ultra-Violet
VOCs	Volatile Organic Compounds
WHO	World Health Organization
WinDOAS	Windows Differential Optical Absorption Spectroscopy
ppb	Parts per Billion
RMS	Root Mean Square

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ABSTRACT

Air pollution is one of the emerging issues in most of the urban centers of Pakistan. Increasing traffic load, power generation, industrial, and construction activities are contributing to air pollution. Air quality standards are regulated by monitoring criteria air pollutants such as NO_2. It's a major contributor in the formation of acid rain, tropospheric ozone and several other secondary pollutants. This study was designed to monitor the tropospheric NO_2 in Islamabad, Pakistan during the time period of September 2014 to September 2018 by using MAX-DOAS. Besides continuous monitoring, field campaigns by using MAX-DOAS were conducted in different forest types in Pakistan were also incorporated in the present study. NO_2 diurnal, weekly, and annual cycles were observed. Results show that NO_2 concentration was higher in morning and evening but lower during the noon time due to higher photolysis rate of NO_2. It was also observed that NO_2 was lowest on Friday (business holiday), while annual cycle shows highest average concentrations in winters and lowest in summers. During field campaigns conducted in different forest areas, the NO_2 concentrations were found within permissible limit (42.5ppb). NO_2 MAX-DOAS measurements were also compared with the OMI instrument observations and a similar spatial distribution of NO_2 was identified by the both data sets. A good correlation was observed when MAX-DOAS data was averaged for 01-02 pm (PST) and compared with OMI observations, as the satellite passes over Pakistan between 01-02 pm (PST). However, the OMI instrument tends to underestimate the NO_2 concentration as compared to ground based MAX-DOAS observations.

INTRODUCTION

1.1. Background

Air pollution is one of the major environmental issues in Pakistan classified as one of the top most polluted region among his countries (WHO 2016). According to the pollution index of NUMBEO 2017(Mid-year), the mega cities of Pakistan such as Lahore and Karachi have very hazardous air quality and falls in top sixty cities of the world. The number of Lahore is fifty-eight and Karachi is at seventh number with the pollution index of 79.71and 95.67, respectively (NUMEBO, 2017).

Nitrogen dioxide is one of the major criteria pollutant and extremely reactive gas that impacts the physical health and visibility in human beings. No doubt in the troposphere NO_2 is present in trace amounts but both Short and long-term exposure effects the human health such as short-term causes restriction in airway while long-term exposure causes respiratory infections and immune system malfunction of the humans (US Environmental Protection Agency, 2003). For the control of air pollution levels the formulation of public policy is direly needed (DEFRA, 2003). The monitoring stations should be present in every populated area particularly in mega cities. In addition to these stations for the measurement of NO_2 there must be many other ground-based remote sensing instruments and satellite remote sensing techniques are also be available.

The color of Nitrogen dioxide is reddish brown above 21.2 °C (70.2 °F; 294.3 K) with an acidic odor and a pungent smell, below 21.2 °C (70.2 °F; 294.3 K) it becomes a yellowish-brown liquid, and below −11.2 °C (11.8 °F; 261.9 K) it is converted into dinitrogen tetroxide (N_2O_4) which is a colorless gas. In the troposphere Nitrogen oxides (NO_x=NO+NO_2) are among the most important trace components of the atmosphere playing a key role (e.g., Seinfeld and

Pandis, 1998). In the lower troposphere the oxides of nitrogen affect the radiative forcing and oxidation capacity by controlling the formation of ozone, contributing to nitrate radical and nitric acid formation and also by affecting the levels of hydroxyl (Solomon et al., 1999; Finlayson-Pitts and Pitts, 1999). The major sources of NO_2 includes biomass burning, combustion of fossil-fuel, microbiological processes in the soil, aircraft emissions and lightning processes (Lee et al., 1997; Jaeglé et al., 2005). The major anthropogenic sources are the combustion processes occurring at high temperature in vehicle engines, power plants and industrial activities (EEA, 2013). So the industrial areas as well as roads with heavy traffic such as urban areas are characterized by different in spatio-temporal patterns for the concentrations of oxides of nitrogen.

Direct emissions of NO_2 are very minute but the major proportion of nitrogen dioxide is produced by the oxidation of nitrogen monoxide (NO) (Hewitt and Jackson, 2009). The contribution of diesel vehicles is much higher of directly emitted nitrogen dioxide to the total nitrogen oxide emissions, so it results in an enormous increase of NO_2 concentrations during recent years in urban locations it contribute to frequently breaching of NO_2 air quality limits (Grice et al. 2009; Keuken et al., 2012).

Both terrestrial and aquatic lives are affected by oxides of nitrogen. When O_3 reacts with NO it converts it into NO_2 and produce a molecular oxygen, after that catalytic conversion of NO_2 into NO. So this cyclic activity continue in the atmosphere with an equilibrium until disturbed by anthropogenic activity. The larger number of vehicles leads to more emissions which ultimately affect the communities /habitats. The conversion of these emissions into nitric acid intensifies the formation of acid rain and photochemical smog (Fowler, Ashmore, Cape, & Derwent, 2012).

NO_2 acts both as a primary and secondary pollutant. The incomplete combustion causes the direct exposure of NO_2 in the atmosphere which is termed as primary pollutant, while when it reacts with ozone it is termed as secondary one. The primary and secondary both are harmful for the environmental health and services.

Air is very important component of life on this planet, so without air life is impossible on this planet termed as Earth. Normally a human breathes about 22,000 times on daily basis, the amount of air taken is 20 times higher than the food taken by a normal individual in a day (Yadav, 2008).

By seeing these extensive impacts of nitrogen dioxide, the monitoring of this trace gas were planned. The concentrations of nitrogen dioxide was monitored with the help of MAX-DOAS instrument within Islamabad, Pakistan and annual/seasonal, monthly, weekly and diurnal cycles are discussed. At the end ground-based MAX-DOAS observations were compared with the satellite observations.

1.2. MAX-DOAS- the instrument:

For the monitoring of trace gases in the atmosphere need great care and proper planning either directly from primary sources or from secondary sources. Samples can be taken directly from the vehicle tails, industrial stacks and emission pipelines of factories and can be interpreted on the spot. But there is a great need of properly designed instrument for the fractional distribution of gases in the atmosphere. For the monitoring of pollutants (NO_2, HCHO, SO_2, and O_3) etc. slant column densities one of the best instrument is MAX-DOAS. MAX-DOAS works on the principle of “Lambert Beer Law” at different elevation angles the scattering sunlight being captured and gives information about the vertical distribution of different trace species. The mini MAX-DOAS instrument is mounted on the roof top of IESE-NUST (longitude= 72.9835° E, latitude=33.6416° N) for the purpose of point base observations of different trace gases.

Figure 1.1. MAX-DOAS on rooftop of IESE

Absorbance in shallow atmosphere the MAX-DOAS instrument is very sensitive for the reterival of vertical profile of traces gases by merging the measurement with Radiative Transfer Model calculations (Rivera, Stremme, & Grutter, 2013).

1.3. Methods for Monitoring of Air Quality:

Since the 19th century a number of ambient air quality monitoring methods have been devised and improved. In the field of research and development innovations and discoveries have opened new ways of monitoring with better instrument precision (~99%) and accuracy, such as MAX-DOAS. If we want to find out details about local conditions then MAX-DOAS data profile is being used. MAX-DOAS can be used for both stationary as well as mobile measurements, to get Maximum absorption in the spectrum, it is mounted at a certain height and specific elevation viewing angles.

The working principle of MAX-DOAS is “Lambert- Beer Law”, measurement are taken at various predefined elevation, zenith, and recalculated azimuth angles during daily operations.

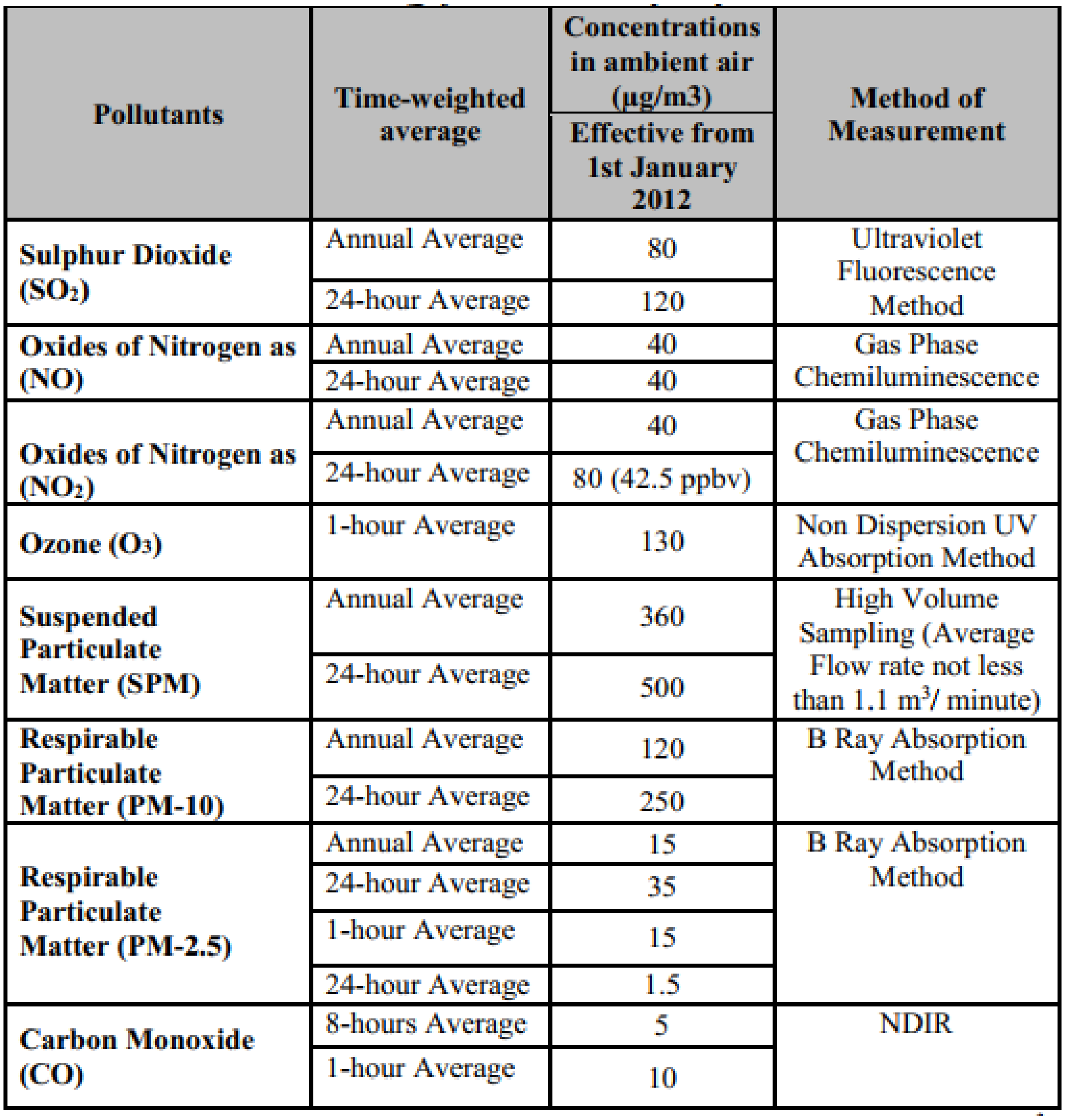
The trace gas species in the lower troposphere have greater absorption as the greater part of optical path is in the lower troposphere (Takashima, Kanaya, & Taketani, 2016). The trace gas absorptions in the atmospheric spectra of scattered sun light are examines by the DOAS (differential Optical Absorption Spectroscopy) technique. To find out the column densities of different trace gases such as NO_2, HCHO, SO_2, and O_3etc instantaneously in the atmosphere the most advanced technique till date. So we can find out the tropospheric vertical column densities with the help of AMF (Air Mass Factor) (Donner et al., 2016).

A new technique known as I-DOAS (Imaging Differential Optical Absorption Spectroscopy) has also been used for the calculation of differential slant column densities (DSCS) in the atmosphere. For the atmospheric trace gases the I-DOAS technique offer two-dimensional distribution measurement. NO_2 and other gases quantitative details for temporal variations are provided by I-DOAS. In urban areas it facilitates and points the directions of emission sources of the major trace gases. (Chong et al., 2016).

1.4. For Ambient Air National Environmental Air Quality Standards of Pakistan (Pak-NEQS):

Pakistan National Environmental Air Quality has formulated the standards (as listed below in table 1.1) for certain pollutant in the ambient air for controlling the quality of ambient air. Emission coming from industries and other sources are regulated by these quality standards in the ambient air, so air quality of ambient air are maintained in this way.

Table 1.1: Pak- NEQS for ambient air



Pollutants	Time-weighted average	Concentrations in ambient air (µg/m3)	Method of Measurement
		Effective from 1st January 2012	
Sulphur Dioxide (SO_2)	Annual Average	80	Ultraviolet Fluorescence Method
	24-hour Average	120	
Oxides of Nitrogen as (NO)	Annual Average	40	Gas Phase Chemiluminescence
	24-hour Average	40	
Oxides of Nitrogen as (NO_2)	Annual Average	40	Gas Phase Chemiluminescence
	24-hour Average	80 (42.5 ppbv)	
Ozone (O_3)	1-hour Average	130	Non Dispersion UV Absorption Method
Suspended Particulate Matter (SPM)	Annual Average	360	High Volume Sampling (Average Flow rate not less than 1.1 m^3/ minute)
	24-hour Average	500	
Respirable Particulate Matter (PM-10)	Annual Average	120	B Ray Absorption Method
	24-hour Average	250	
Respirable Particulate Matter (PM-2.5)	Annual Average	15	B Ray Absorption Method
	24-hour Average	35	
	1-hour Average	15	
	24-hour Average	1.5	
Carbon Monoxide (CO)	8-hours Average	5	NDIR
	1-hour Average	10	

Nitrogen Dioxide (NO2) WHO conversion factor 1 ppbv = 1.88 µg/m3.

1.5. Study Area:

Air pollution is an emerging issue in Pakistan as Pakistan is ranked in the top polluted countries of the region. The major contributors of the air pollution is lack of any satisfactory measures and constant rapid economic development. So these factors are responsible for projecting towards worst air quality. One of the very important environmental issue in Pakistan is the degraded ambient air quality (Ilyas 2007). By keeping in view this important environmental issue the monitoring of air quality of following areas were planned.

The study areas for monitoring are included Islamabad (lat:33.7294° N, lon:73.0931° E), Pine Park Hotel (lat:34.3837° N, lon:73.2811° E) (Shogran, KPK) Pakistan forest institute field station (lat:34.4724254° N, lon:73.2662724° E) and National tea garden (lat:34.28° N, lon:73.1629° E) (KPK),Rama (lat:35.2131° N, lon:74.4841° E) Bata kundi (lat:34.566° N, lon:73.4549° E), and deosai national park (lat:34.5934° N, lon:75.1513° E) (GB).

1.6. Objectives of the Present study:

- long-term analysis of MAX-DOAS observations for atmospheric monitoring of NO_2 concentration during the time period of 2014 to 2018
- To compare the results of satellite observation for NO_2 concentration with Ground based MAX-DOAS measurements.

1.7. Expected outcomes of the study:

The health of the residents of Islamabad are negatively impacting by air pollution and deteriorated air quality (Aziz and Bajwa 2007; Hyder et al., 2006).

In the field of air pollution and air quality monitoring this study will be very supportive for assessing the NO_2 pollution levels over Islamabad and developing an inventory of NO_2 pollution levels for more research over the area.

To counter the effects of air pollution and public health this study may help to find out some indigenous solutions. The present study will also be helpful to find out the sources of local emissions and their effects on the environment.

Beside this, the data obtained by this research can be used as a baseline by research institutes, environmental issue, Non-Governmental Organizations (NGO’s) and other departments concerning about health impacts and monitoring of air quality (Khwaja et al., 2005).

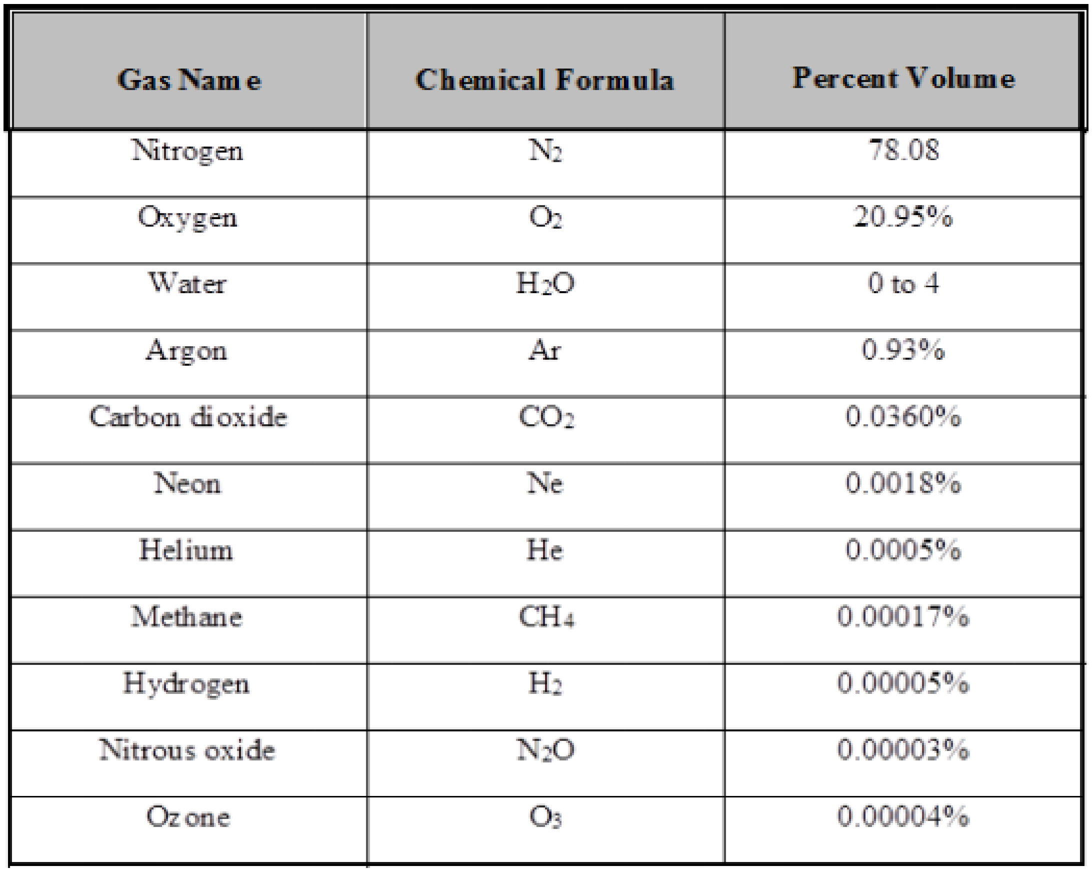
By comparing the ground-based MAX-DOAS results with satellite NO_2 observations in the study area will help to identify the emission sources of NO_2 and transboundry percentage over the designated area. Proper proposed pollution control techniques (PTCs) can impart their role in the reduction of air pollution in Pakistan after identification of these potential air pollution sources.

LITERATURE REVIEW

2.1. Composition of atmosphere:

A layer of gases that surrounds the earth is called atmosphere. Atmosphere is very thick and concentrated near the surface of the earth and its thickness is decreases as we move in vertical (upward) direction in atmosphere. Atmosphere contains a large number of gases in which some are present in small amounts and others are in larger amounts. The atmosphere keeps the earth accountable for producing different weathers and habitable for different lives. The major atmospheric composition are 78% Nitrogen, Oxygen covers 21% of the atmosphere and 0.9% argon according to the relative abundance. The trace gases like N_2O, O_3, CO_2, CH_4, NO, etc. covers only 1/10th part of the atmosphere by percentage (Rasool, S., 2012).

Table 2.1. Composition of atmosphere



Gas Name	Chemical Formula	Percent Volume
Nitrogen	N_2	78.08
Oxygen	O_2	20.95%
Water	H_2O	0 to 4
Argon	Ar	0.93%
Carbon dioxide	CO_2	0.0360%
Neon	Ne	0.0018%
Helium	He	0.0005%
Methane	CH_4	0.00017%
Hydrogen	H_2	0.00005%
Nitrous oxide	N_2O	0.00003%
Ozone	O_3	0.00004%

2.2. NO_2 Sources and Sinks:

Nitrogen presents in the atmosphere 78% naturally. It is released by both natural and anthropogenic sources such as by thunder-light, microbial processes, organic growth and decay and forest fires, and fuel combustion by vehicles engine and power sector, industry and by cooking activities respectively. Basically during the combustion processes the nitrogen is emitted in the form of NO and is instantly converted into NO_2 in the atmosphere by combining with atomic oxygen (O).

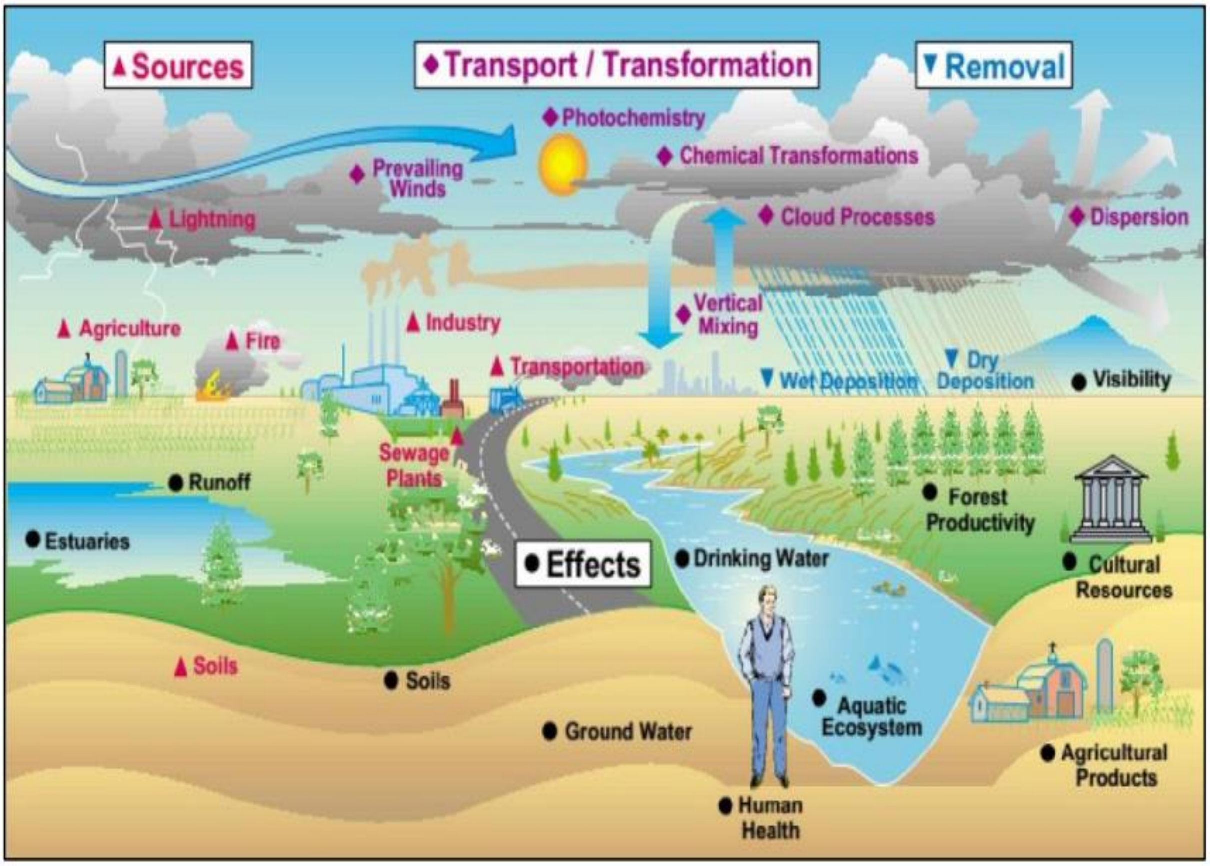


Figure 2.1. Representing the NO_2 sink and sources in the atmosphere adopted from (Lindvall, 1985).

In the atmosphere NO_2 gets involve in a chain of reactions by Oxygen and UV radiations that leads to the formation of "Photochemical smog" and eventually the formation of secondary pollutants like Nitrates (NO_3-), Nitrites (NO_2-), Ammonia (NH3) etc. (Lindvall, 1985).

The photochemistry is very important for the formation of oxides of nitrogen (NOx). Due to vertical mixing and wind turbulence locally as well as globally transport of NOx takes place. The lifetime of NO_2 ranges from some days (Seinfeld and Pandis, 2006) to a few hours (Crutzen, 1970).

The removal of nitrogen oxides is occur by two processes, which is wet and dry deposition. In the process of wet deposition the species present in the air are precipitated down on the surface of earth in an aqueous form i.e., rain, fog and snow. While during the dry deposition the airborne species are settled down without precipitation (Seinfeld and Pandis, 2006).

2.3. NO_2 as a criteria pollutant:

NO_2 has a pungent and irritating smell with a reddish-brown color. It usually looks yellowish brown haze over the major cities as it has the ability to absorb the light. NO_2 also plays very important role in the formation of photochemical smog. Nitrogen is one of the criteria pollutant which is out of control since the beginning of air quality regulations. It is because of the diversity of NO_2 sources i.e., emissions from power-stations and automobiles, etc. The most contributing air pollution source over worldwide is the upsurge of automobiles (Han & Naeher, 2006). For preventing the sensory irritation in the population the daily (24 hours) guideline of 80 µg/m3 for NO_2 is suggested (*Pak NEQs*, 2010).

2.4. Relevant literature about NO_2 in Pakistan

The major source of NO_2 in Pakistan is transportation followed by industry and power plants (GOP/IUCN, 1992). From 1995 to 2005 the number of motor vehicle increased by 33.61% annually that leads to worsened the air quality of the region (Ilyas et al., 2007).

For regulation of ambient air quality a very little work is being done as NEQS implementation strategy is very poor. Pak-EPA and JICA in order to monitor the ambient air quality of Pakistan conducted air sampling in three major cities of Pakistan including Islamabad, Lahore and Rawalpindi in 2000. Monitoring purpose was to measure all criteria pollutants including PM, Oxides of Nitrogen, Carbon Monoxide, Sulphur Dioxide, Hydrocarbons and Ozone. In all that it was noted that most abundant specie was Oxides of Nitrogen due to traffic congestion mainly. The air quality of Lahore was most poor (JICA, 2000).

Along N5 Highway at various point Ali et al. in 2006 monitored ambient air quality. Criteria pollutants were monitored by adopting different techniques to find out the ambient air quality of the region. In Lahore the NO_2 levels were highest.

NO_2 pollution levels in two major cities including Islamabad and Rawalpindi of the Pakistan was studied by Zafar et al. in 2012. Sampling was completed in two phases by taking samples at different locations in two different seasons first was winter and the second was the spring. Industrial activities and traffic congestions were linked with the pollution level of NO_2 in twin cities.

Indoor Air quality (NO_2) was monitored by Jahangir et al. in 2013 of different hospitals including both public and private in twin cities Islamabad-Rawalpindi. They found that Hospitals have higher levels of NO_2 which were located at the traffic congested roads.

Several studies were carried out at IESE-NUST to find out the ambient air quality. Mini MAX-DOAS was mounted on the roof-top of IESE for the purpose of monitoring. In twin cities Islamabad-Rawalpindi by mobile monitoring NO_2 VCDs have been calculated. Furthermore with the help of MAX-DOAS placed on roof top of IESE, NUST Ozone and Formaldehyde was also monitored by research students (Nisar et al., 2013).

To check special and temporal trends of NO_2 pollution levels over Pakistan a database has been established for NO_2 VCDs from satellite observations. During the winter seasons especially an enhanced NO_2 levels were found near the urban centers of Pakistan according to obtained results (Khokhar et al,. 2015).

2.5. Chemistry of NO_2 in atmosphere:

2.5.1. Reaction in Troposphere:

NOx is a primary pollutant in the troposphere as it is emitted directly (NO_2 in less fraction) During this stage NO is oxidized with the tropospheric Ozone in a few minutes minutes (Seinfeld & Pandis, 2016)

Eq.1

$$\mathbf{O_3 + NO \longrightarrow NO_2 + O_2}$$

The NO_2 produced in the above reaction is photolyzed by UV radiations. It is also dissociates by direct sun exposure in the noon time. Therefore under direct sun exposure the life of NO_2 is very short.

Eq.2

$$\mathbf{NO_2 + hv \longrightarrow NO + O\,(^3P)}$$

The net reaction is as following:

$$\begin{array}{lll} & NO + O_3 \longrightarrow & NO_2 + O_2 \\ & NO_2 \;\; hv \longrightarrow & NO + O_2 \\ \hline \text{Net} & O_3 - \;\; hv \longrightarrow & O_2 + O_2 \end{array}$$

2.5.2. Reaction in the Stratosphere:

Reaction.1

$$N_2O \longrightarrow N_2 + O(^1D)$$

Reaction.2

$$N_2O + O(^1D) \longrightarrow NO + NO$$

NO_x in the stratosphere mostly introduced by this reaction:

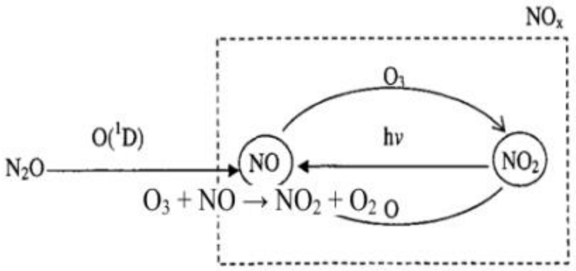


Figure 2.2. Reactions of NO_2 in stratosphere

The Chemical reactions in detail through which Nitrogen dioxide passed is:

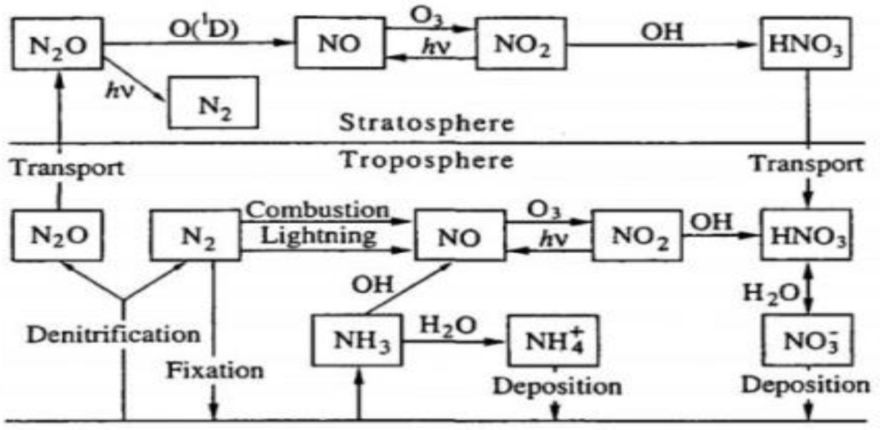


Figure 2.3. NO_2 Chemistry in atmosphere adopted from (Seinfeld & Pandis, 2016)

2.6. The techniques used for NO_2 measurement:

The optical detection of NO_2 with DOAS (Differential optical absorption spectroscopy) has been reported by a lot of articles (Rivera *et al.*, 2010), Nitrogen dioxide absorption spectrum in visible range which is usually suggested from the range of 405nm- 455nm (Shabbir *et al.*, 2016).

In Athens, for the first time by using spectral measurements from MAX-DOAS the nitrogen dioxide slant column densities have been retrieved (Gratsea *et al.*, 2016). The total column/tropospheric column of nitrogen dioxide from space by OMI usually have been experimented (Jin *et al.*, 2016). In china the ground-based MAX-DOAS for NO_2 have been compared with OMI (Jin *et al.*, 2016). In Shanghai NO_2 have also been measured by using MAX-DOAS during World Expo 2010 and compared the data with OMI satellite data (Chan *et al.*, 2015).

For the monitoring of NO_2 in ambient air the other applied techniques are as following:

The other applied techniques to monitor NO_2 in ambient air are as following:

1) Colorimetric Methods
2) Fourier Transform Infrared Spectrometry (FTIR)
3) Passive Analyzers
4) Spectroscopic Methods (DOAS)

5) Chemiluminescence Methods
6) Satellite Remote Sensing
7) Electrochemical Sensor

2.6.1. Colorimetric Methods

In this technique the reaction of organic dyes solutions with reactive NO_2 are performed, in a result a colored species are formed. But there is a problem about the applicability of this technique in a remote areas in a field because there is no analysis facilities are available. This technique are not representative isotopically for the direct emission sources.

There are number of analyzers formed for NO_2 monitoring and regulating in ambient air by using the mechanism principle of this device (Dahal & Hastings 2016).

2.6.2. Fourier Transform Infrared Spectrometry (FTIR)

For the ambient air quality monitoring analyzers one of the best known technique with a path lengths of 01 km or more is Fourier transform infrared spectrometry (FTIR). For the monitoring of NO_2 and other trace gases such as SO_2, O_3, NO and CO these analyzers are specially designed (Sosa et al,. 2016).

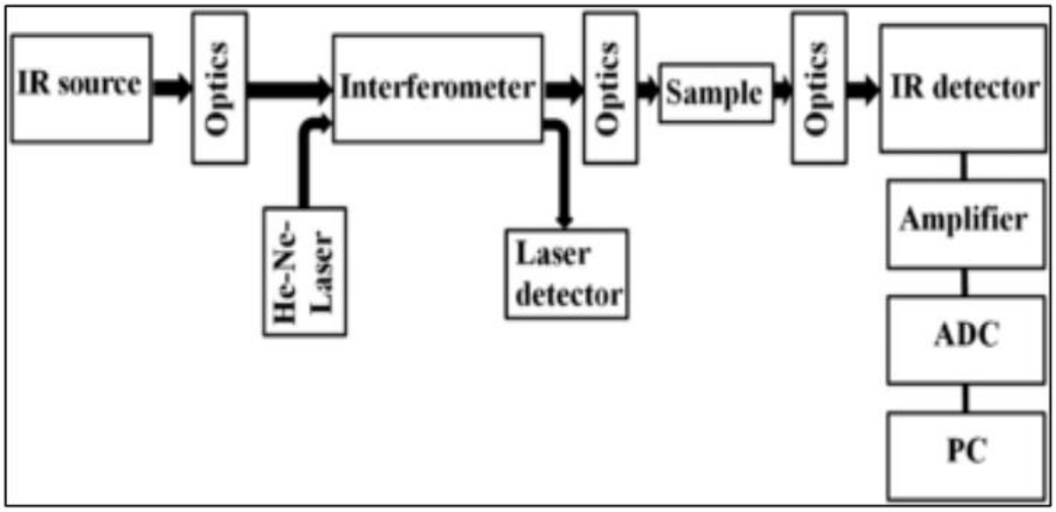


Figure 2.4. Components of FTIR adopted from (Sosa et al,. 2016).

Absorption of particular infrared radiation range is the basic principle of this method for NO_2 across long absorption paths. Along the path length very minute concentrations of NO_2 can be measured (up to ppbv) only by screening the magnitude of infrared light absorption. By using the computerized Fourier transformations NO_2 absorption signals are separated from the instrumental noise.

2.6.3. Passive Analyzers

Widely used devices for the nitrogen dioxide monitoring are the passive analyzers as they are simple in design and relatively low in cost. Over a large geographical area for the purpose of outdoor NO_2 monitoring the standard Ogawa passive diffusion samplers are widely used (Cyrys et al., 2012; Gillespie et al., 2017; Gillespie et al., 2016).

By this technique, the NO_2 samples are taken at a precise proportion from the atmosphere by the processes of natural diffusion of gas across a membrane known as passive sampling.

2.6.4. Spectroscopic Methods (DOAS)

For the identification of different trace gases concentration in the atmosphere DOAS is a widely used and very sensitive measurement technique (Piatt & Stutz, 2008) that was introduced by Platt et al., in 1979.

For the measurement of several trace gases in the atmosphere simultaneously DOAS is best known technique, because it allows the analysis of different chemical components in the observed air mass and also reduces the measurement time. DOAS can performed in a both way, passively and actively by using natural and artificial light sources respectively.

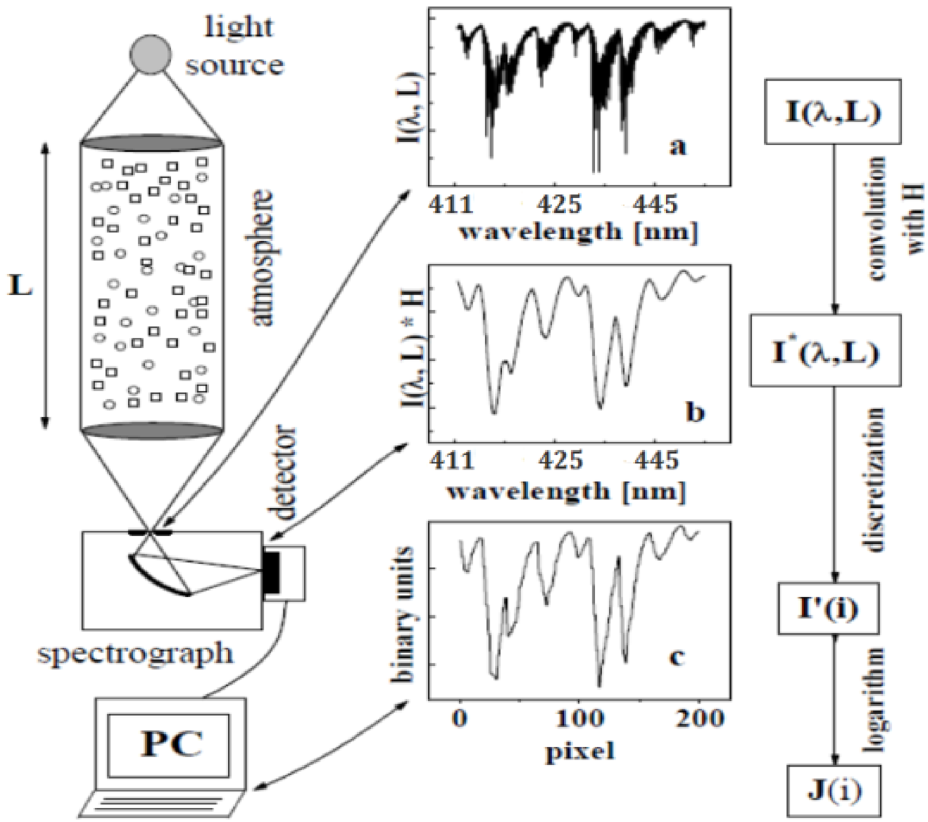


Figure 2.5. The Schematic diagram of DOAS setup adopted from Platt et al., in 1979.

Basically DOAS method based on “Lambert Beer Law” which shows the linear relationship between matter and light. It shows the relationship in incoming radiation (I0(λ)) to outgoing radiation (I(λ)) with the help of path length function of light, concentration (c) and absorption cross section (σ(λ)) of the species in the equation mentioned below:

$$\mathbf{I(\lambda) = Io(\lambda).e}^{-L\sigma(\lambda)c}$$

With the help of this relationship concentration of trace gas can be calculated just by keeping a sensor at some distance (L) and choosing a source of light of known spectral intensity.

2.8.5 Chemiluminescence Methods

The basic principle of cehmiluminescence method for the detection of NO_2 is the reduction to NO with the help of a heated catalytic converter and NO and NOx measurement are made by using the electric sensors. The nitrogen dioxide measurement are found by calculating the NOx and NO difference. For the monitoring of worldwide airborne NO_2 a number of such type analyzers are made by keeping the cehmiluminescence method as a reference (Riess, 1998). This is very significant as it has dual chamber system that have distinct chambers for the measurement of NO and NOx instantaneously. In the sample inlet NO is mixed into O_3 and the level of NO is measured.

All NO is oxidized into NO_2 in the mixing chamber and the remaining found as an excited NO_2 molecules. These excited NO_2 molecules release energy in the form of photons. With the help of thermal converter these NO_2 is reduced into NO.

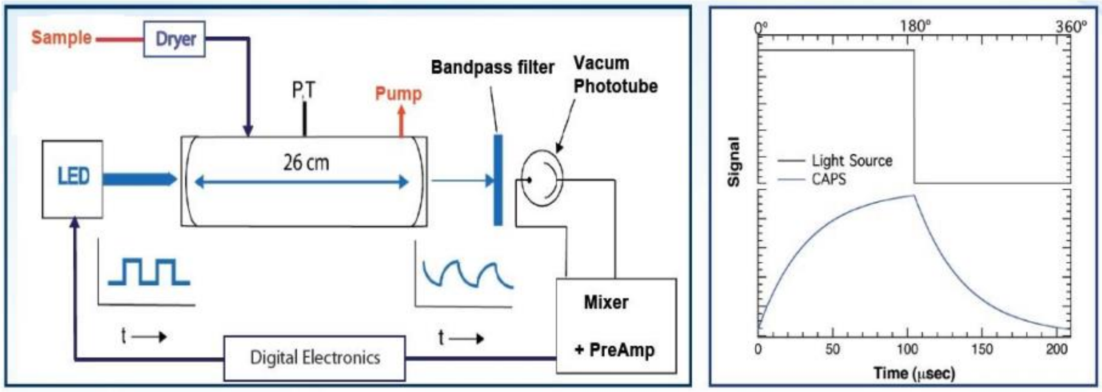


Figure 2.6. Chemiluminescence working principle adopted from (Riess, 1998)

2.6.6 Satellite Remote Sensing

For the NO_2 the Satellite remote sensing is generally based on DOAS technique. There are two possible modes of viewing in the satellite remote sensing, one is “**Nadir**” and the other is “**Limb**” in the Nadir viewing points down through the atmosphere measuring the reflected radiation from the Earth's surface, while in the “Limb mode”, satellite see through the atmosphere almost parallel to the surface of Earth (Rogers, 1990).

For the measurement of NO_2 the first satellite-borne capable spectroscope was the Global Ozone Monitoring Experiment (GOME), that covers a globe in every 3 days with viewing in a “Nadir mode” on the Earth's surface and pixel size of 320km – 40km. Next to GOME was the SCanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY) with a global coverage of 6-day in a Nadir mode and size of the pixel 30km – 60km (Richter *et al*., 2005 and Brinksma *et al*., 2008) after this in 2004 the Ozone Monitoring Instrument (OMI) was launched with every day global coverage viewing in a Nadir mode with a pixel size of 13km – 24km and has a best spatial and temporal resolution till date (Boersma *et al*., 2004).

2.6.7 Electrochemical Sensor

Electrochemical Sensors are designed for the detection of O_3 and NO_2 in a sample gas. For the ambient NO_2 pollution levels the electrochemical sensor technology based portable analyzers are radially available. These type of sensors are cheap than all other NO_2 samplers and provide good retention time and high sensitivity. It works on the principle of electrochemical reduction of NO_2 between two electrodes in an electrolytic solution. So the NO_2 present in a sample diffuses against a barrier towards the cell where the reduction takes place at the electrodes in a reaction cell. The electrons are generated by this reaction and current is produced which is proportional to the concentration of nitrogen dioxide. This sensors display the NO_2 pollution concentration on the connected display directly, from where average or continuous hourly data are estimated (Saffell et al,. 2003).

2.9. NO_2 Health Impacts:

NO_2 mainly impacted the respiratory system of living organisms. By breathing certain concentrations of nitrogen dioxide the risk of respiratory infection is enhanced or in severe conditions it may causes lungs dysfunction in elder ages mostly.

Human life is not only impacted by poor air quality but also animals and plants too. Approximately 0.9 million premature deaths occur in each year and disaster happens in Asia about ~60% by air pollution in cities (WHO, 2006).

In Lahore many causes of chronic obstructive pulmonary disease (COPD) were reported during the period of 1992-2002. Due to improper mass-transit management system in Lahore about 23-26% of excess carbon mono-oxide (CO) was observed (Aziz and Bajwa, 2008). A significant correlation would exist between urban air pollution and mass-transit system was also observed (Aziz and Bajwa, 2008).

2.8. Nitrogen Dioxide Environmental Impacts:

For sustaining the oxidizing capacity of the atmosphere NO_2 present in the atmosphere is very crucial. NO_2 photolysis is the main source of Ozone (O_3) in atmosphere during day time. The production of the hydroxyl groups (-OH) by the photolyzation of Ozone ($-O_3$) plays the purgative agent role in the atmosphere. So tropospheric ozone and NO_2 are toxic to the environment. The nitric-acid (HNO_3) is formed by the reaction of NO_2 and (-OH) which leads to the cause of acid rain. Over the industrial sectors NO_2 also contribute to radiative forcing in urban areas especially, as a greenhouse gas (Solomon *et al.*, 1999). Nitrogen deposition also leads to the cause of acidification and eutrophication of the water surfaces.

Conversely, NO_2 and tropospheric O_3 as well are toxic to the environment. NO_2 reacts with hydroxyl groups (-OH) to form nitric-acid (HNO_3) which is the main constituents of acid rain. NO_2 as a greenhouse gas, also contributes to radiative forcing in urban areas especially over the industrial sectors (Solomon *et al*., 1999). Acidification and eutrophication of the water surfaces is also caused by nitrogen deposition.

INSTRUMENTATION and METHODOLOGY

3.1. Mini MAX-DOAS-The Instrument

Mini MAX-DOAS (Multi Axis-Differential Optical Absorption Spectroscopy), can be used for the monitoring of trace gases in the atmosphere. It is a light weighted instrument and can be used for mobile as well as fixed ground monitoring of air pollutants. It is a specifically designed instrument for the measurement of backscattered sunlight (Bobrowski, Hönninger, Galle, & Platt, 2003).The sealed aluminum box contained certain electronics and fiber spectrograph, a stepper motor (precision=0.1 degree/step, frequency=784Hz) mounted outside the box rotate the instrument according to the modulated elevation viewing angles.

At the optics entrance a quartz lens with a focal length of 40mm exists. For the measurement of spectral range A **"Czerny Turner spectrometer (Ocean Optics Inc., USB-2000+)"** is used.

The spectrometer (used for continuous ground monitoring) with a range of 318-465 nm and spectral resolution of ~0.7nm was used. The instrument with a detector of 2048 pixels and Charged coupled device (1 dimensional-CCD) was used during the study. For regulating the instrument internal temperature there is a peltier (Thermoelectric cooling) a cooling device. A computer system with Xp operated Window and DOASIS software is continuously running for acquisition and storing the data.

3.2. Monitoring schedule:

Ground-based measurements were performed at "IESE (Institute of Environmental Science and Engineering), NUST (National University of Science and Technology)-Islamabad", from September 2017-September 2018 continuously however ground based data over IESE for the month of July 2018 was not monitored. The reason for not collecting data during the month of July are field campaigns, which were conducted from July 12 to July 25. The field Campaign were conducted in different sites of Northern areas (as shown in table below) with an automated and compact Mini MAX-DOAS instrument.

For field campaigns, the E.A were chosen as one 90 degree followed by four 30 degree angles (i.e., 30^0, 30^0, 30^0, 30^0, 90^0) with the integration time (Tini) of 60 seconds/scan. The high elevation angles were preferred to avoid the interferences in measurements from nearby obstacles and 30degree is preferred because AMF (air mass factor) is easy to calculate on this specified angle (Wagner *et al.,* 2010). In the other hand, for continuous Islamabad site monitoring (at NUST), these 2^0, 4^0, 5^0, 10^0, 15^0, 30^0, 45^0, 90^0 elevation angles were selected.

Table 3.1. Enlist the detailed schedule for fixed ground monitoring and Field campaigns

Activity Details	**Location**	**Dates**
**GM: Continuous Ground Monitoring	Islamabad	8th September 2017 – 30th September 2018
*FC-1: MAX-DOAS field campaign	Shinkiari(Sub-Tropical Chir-Pine Forest)	12th July 2018
*FC-2: MAX-DOAS field campaign	Shinkiari(Sub-Tropical Chir-Pine Forest)	13th July 2018
*FC-3: MAX-DOAS field campaign	National Tea Garden-Shinkiari	14th July 2018
*FC-4: MAX-DOAS field campaign	Pine Park Hotel, Shogran(Moist Temperate Forest)	16th July 2018

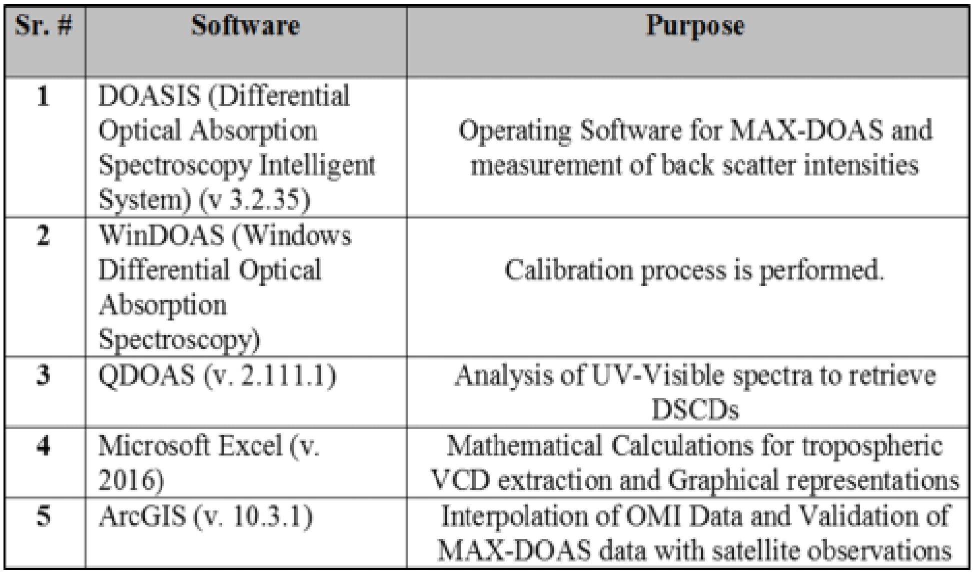
*FC-5: MAX-DOAS field campaign	Pine Park Hotel, Shogran(Moist Temperate Forest)	17th July 2018
*FC-5: MAX-DOAS field campaign	Pine Park Hotel, Shogran(Moist Temperate Forest)	18th July 2018
*FC-6: MAX-DOAS field campaign	Rama-Astore(Dry Temperate Forest)	21th July 2018
*FC-7: MAX-DOAS field campaign	Deosai National Park(Alpine Pasture)	22th July 2018
*FC-8: MAX-DOAS field campaign	Naran-Batakundi (Sub-Alpine Pasture)	25th July 2018

***FC**=Field campaigns, ****GM**=Ground Monitoring

3.3. Software's used in Research Work:

Different software's which were used during this research work to acquire-analyze and plot nitrogen dioxide are mentioned in the following table 3.2

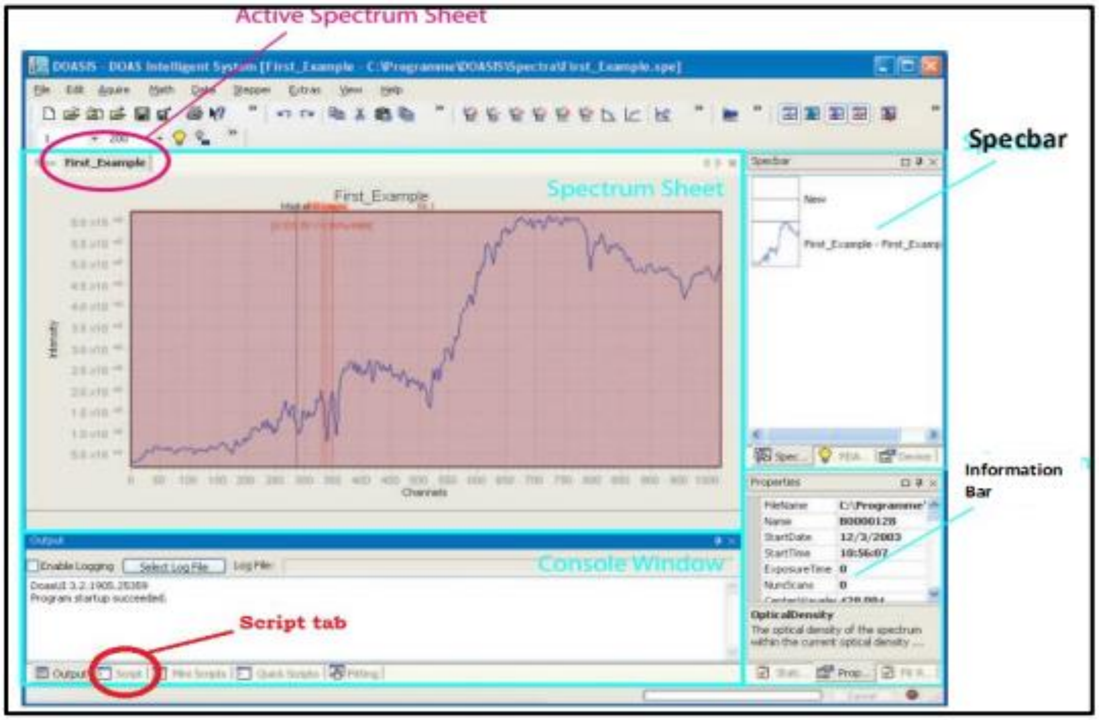
Table 3.2. Software's used in Research Work and their purpose



Sr. #	Software	Purpose
1	DOASIS (Differential Optical Absorption Spectroscopy Intelligent System) (v 3.2.35)	Operating Software for MAX-DOAS and measurement of back scatter intensities
2	WinDOAS (Windows Differential Optical Absorption Spectroscopy)	Calibration process is performed.
3	QDOAS (v. 2.111.1)	Analysis of UV-Visible spectra to retrieve DSCDs
4	Microsoft Excel (v. 2016)	Mathematical Calculations for tropospheric VCD extraction and Graphical representations
5	ArcGIS (v. 10.3.1)	Interpolation of OMI Data and Validation of MAX-DOAS data with satellite observations

3.4. DOASIS:

The DOASIS were used to operate "MAX-DOAS instrument" as it is used for acquisition of spectra. It also perform many other functions such as controlling the motor rotation, adjusting time of integration of each spectrum, controlling the peltier temperature etc. DOASIS software used to run Java script in which all the commands are adjusted accordingly. For the calculation of ring spectrum this software can also be used as ring is further used for fit analysis in QDOAS. As per commands in the script the instrument takes dark current and offset measurement automatically at night but we can measure offset and dark current of spectrometer manually by using this software. As they are used for zero correction of the MAX-DOAS Instrument. During the analysis in QDOAS the dark current and offset are further applied.



DoasIS 3.2.1905.25369
Program startup succeeded.

FileName	C:\Programme'
Name	B0000128
StartDate	12/3/2003
StartTime	10:56:07
ExposureTime	0
NumScans	0

OpticalDensity
The optical density of the spectrum within the current optical density ...

Figure 3.1: For acquisition of spectra Simple Interface of DOASIS

The large Tini (Exposure/integration time) and less number of scans are used for the measurement of dark current as dark current is the small electric current monitored in the photosensitive devices (Spectrometer) usually as enlisted in table 3.3.

Measurement of spectrum in “No photons” condition called Offset, it is measured in dark in other words. A smaller integration time and large number of scans are used for measuring Offset spectra as enlisted in table 3.3.

Table 3.3: For dark current and offset measurements usually used Values

Parameter	**Integration/Exposure time (milliseconds)**	**Scan numbers**
Offset Measurement	~10-100	~1000-10000
Dark current	~10000	1

3.5. NO_2 Analysis:

For the retrieval of NO_2 three major steps were carried out:

1) Wavelength calibration
2) Wavelength Convolution
3) NO_2 Analysis window

3.5.1. Wavelength calibration:

The WinDOAS (Windows Differential optical absorption spectroscopy) was used for calibration of wavelength. For calibration the spectrum (usually taken at 90o of noon time/with least SZA) taken at noon was used as it has high intensity. By applying the fit between a measured spectrum and a convoluted solar spectrum the calibration was executed. The solar spectrum wavelength was ascribed to the individual detector's pixels during this process. A high resolution solar spectrum measured by Kurucz is usually used as input that's why the calibration fit is also referred as "Kurucz-fit which is further convoluted according to the spatial resolution of the instrument (mini MAX-DOAS) used in the monitoring.

For performing and analyzing the fits in each sub-window {subwindows=6} the wavelength range was divided into several sub-windows. For the adjustment of any shift of spectrum between measured and convoluted spectra, the "shift and squeeze" was also applied during calibration. By using polynomial degree interpolation of the results of the individual sub-window were carried out which is specified by Slit Function parameter.

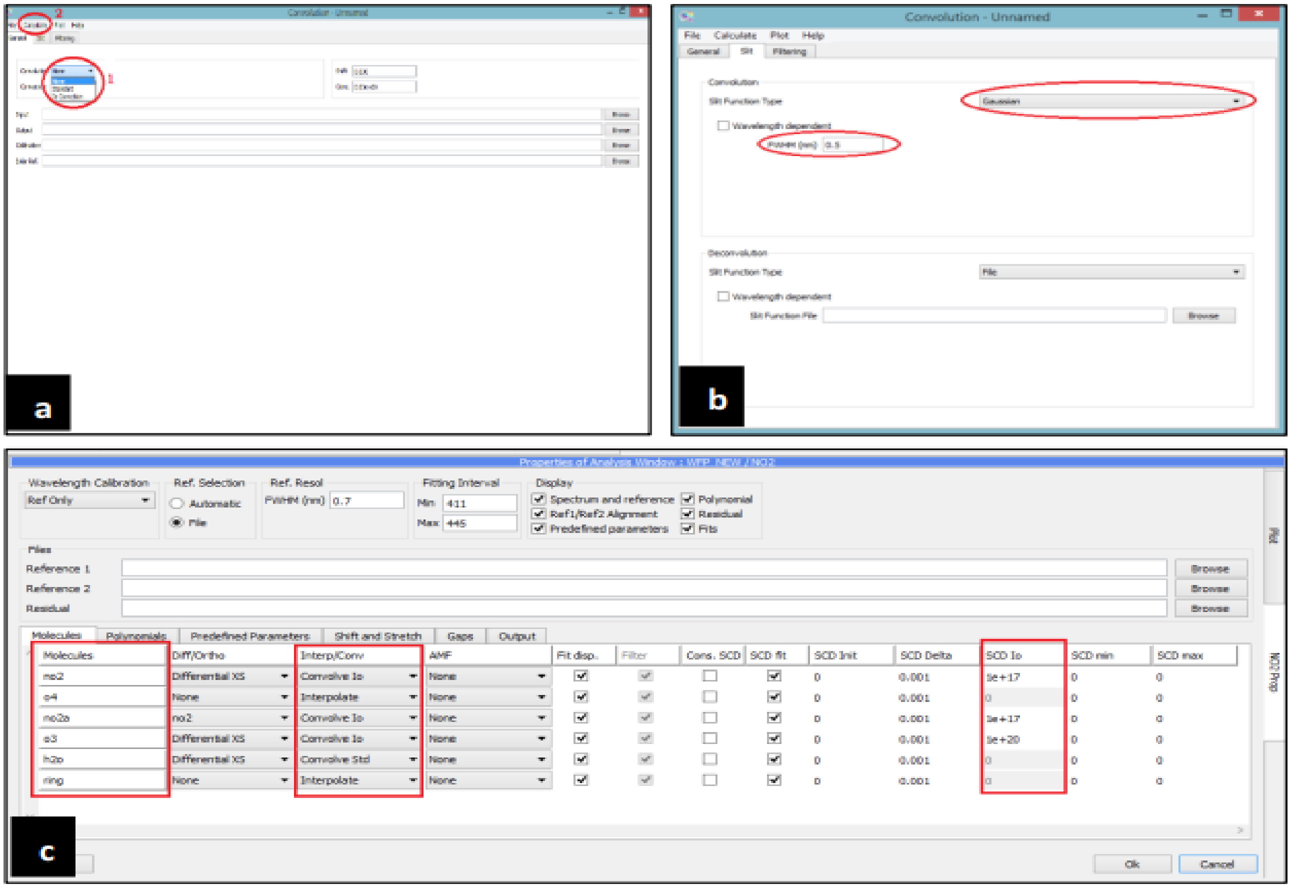
Calibration process repeated twice reduces the residual process. All measured spectra are evaluated by using the calibration file against a reference spectrum.

3.5.2. Wavelength convolution:

The convolution was performed in QDOAS software by using "Convolution tool", as Convolution is a mathematical process vital for wavelength processing operations. Convolutions are of two types:

1. Offline convolution

2. Online convolution



Convolution
Slit Function Type: Gaussian
☐ Wavelength dependent
FWHM (nm): 0.5

Deconvolution
Slit Function Type: File
☐ Wavelength dependent
Slit Function File:

Wavelength Calibration: Ref Only
Ref. Selection: ○ Automatic ● File
Ref. Resol FWHM (nm): 0.7
Fitting Interval Min: 411 Max: 445
Display: ☑ Spectrum and reference ☑ Polynomial ☑ Ref1/Ref2 Alignment ☑ Residual ☑ Predefined parameters ☑ Fits

Files
Reference 1
Reference 2
Residual

Molecules | Polynomials | Predefined Parameters | Shift and Stretch | Gaps | Output

Molecules	Diff/Ortho	Interp/Conv	AMF	Fit disp.	Filter	Cons. SCD	SCD fit	SCD Init	SCD Delta	SCD Io	SCD min	SCD max
no2	Differential XS	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+17	0	0
o4	None	Interpolate	None	☑	☑	☐	☑	0	0.001	0	0	0
no2a	no2	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+17	0	0
o3	Differential XS	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+20	0	0
h2o	Differential XS	Convolve Std	None	☑	☑	☐	☑	0	0.001	0	0	0
ring	None	Interpolate	None	☑	☑	☐	☑	0	0.001	0	0	0

Figure 3.2. Illustrates the convolution process; (a, b) offline convolution by QDOAS window (c) online convolution by QDOAS window

In the offline convolution the pre-convolved cross-sections are put into analysis window (Fayt *et al.*, 2013). Alternatively, in the online convolution, the cross-sections without any pre-convolution are directly put into analysis window of NO_2. In this automatically cross-sections are convolved. The method that is used during this study was online. The trace gas cross-sections that was used are mentioned in the table 3.4.

A high resolution cross-sections is convlve by using "Standard convolution" (Convolve Std) and with the help of calibration and slit function file already generated in a wavelength calibration process. Theoretical optical depth in convolution is calculated by "I0 correction" (Convolve I0)

Table 3.4: Details of cross-sections used with convolution specifications

Sr.#	Cross-sections	Convolution
1	NO_2 at 298K (Vandaele et al., 1996)	SDC I_0 correction (1e17 molecules/cm^2)
2	NO_2 at 220K (Vandaele et al., 1996)	SDC I_0 correction (1e17 molecules/cm^2)
3	O_3 at 223K (Serdyuchenko et al., 2014)	SDC I_0 correction (1e20 molecules/cm^2)
4	O_4 at 293K (Thalman and Volkamer, 2013)	Standard Convolution
5	H_2O (H_2O_HITEMP_2010_390-700_298K_1013mbar_air)	Standard Convolution
6	Ring (Ring_QDOAScalc_HighResSAO_Norm)	Ring Convolution

Option (Fayt *et al.*, 2013). Before starting the convolution, the FWHM (full width half Maximum is chosen as 0.7nm and slit function type is selected as Gaussian.

3.5.3. NO_2 Analysis:

QDOAS software was used for performing the NO_2 analysis. The analysis window range was 411nm to 450nm used. The wavelength range was selected to minimize the possible residual errors. Calibrated spectrum was used as reference spectrum for analysis. The cross-section which was used are given in "Molecules Tab" and polynomial of 4th degree for NO_2 analysis. According to requirement in the results some field/parameters were selected in the "Output Tab", Elevation viewing angle, RMS (root mean square/residue), Solar zenith Angle (SZA), and integration time etc. Then at the end, where the files wanted to be stored output file path was given. On all measured spectra the analysis were performed, NO_2DSCDs were obtained and finally in ASCII file the results were obtained.

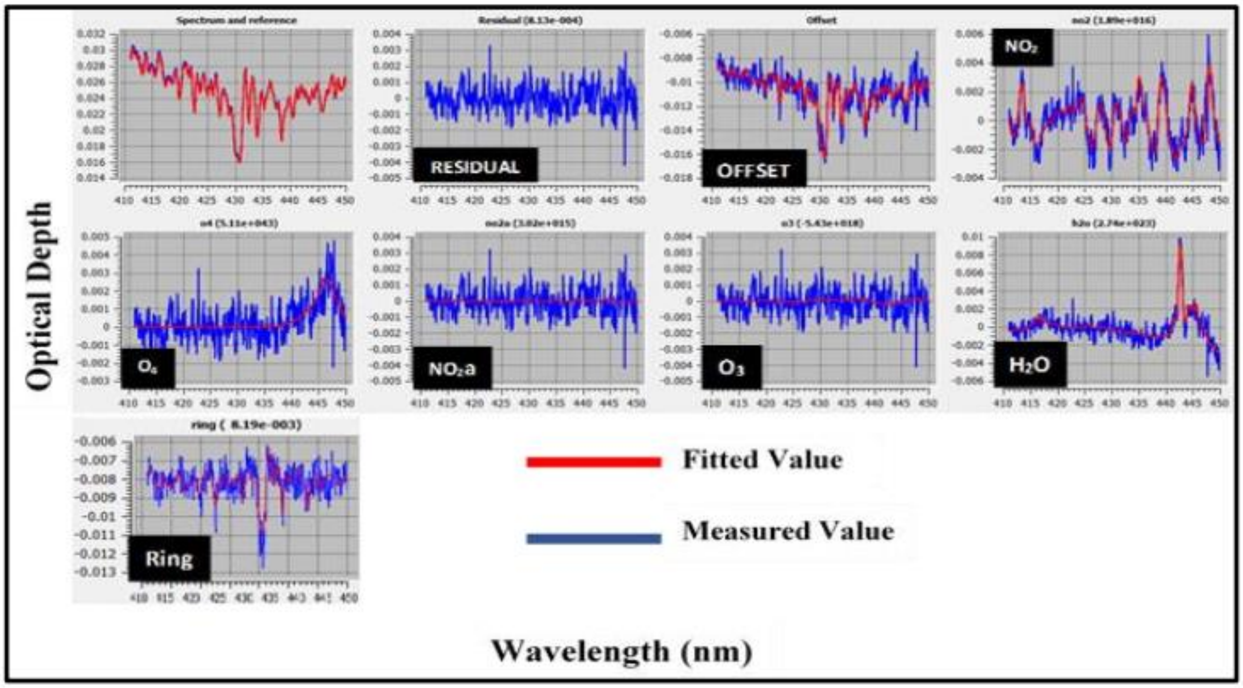
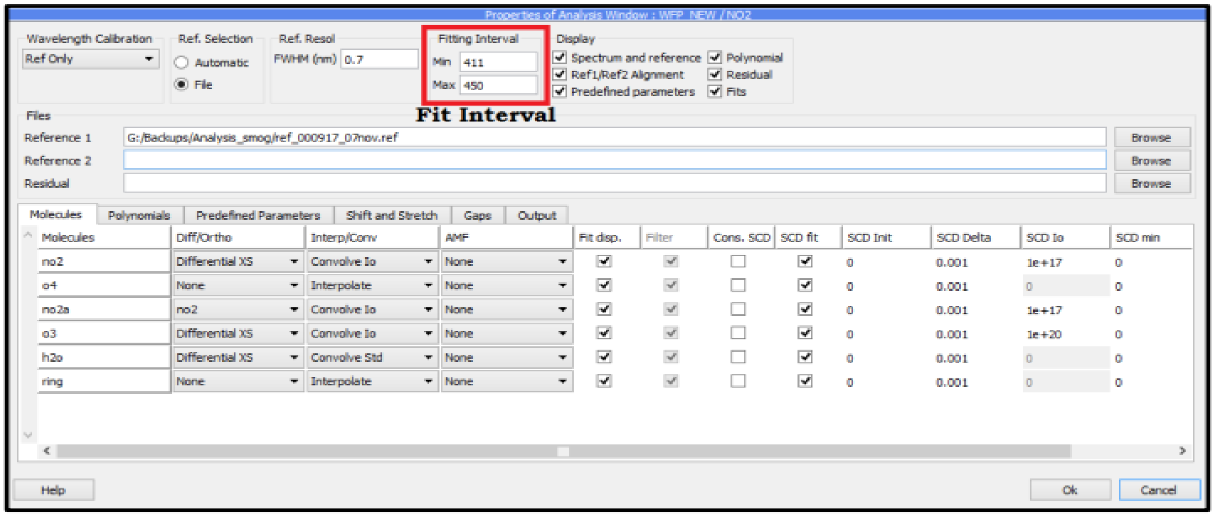


Figure 3.3. DOAS analysis in QDOAS for NO_2 analysis of ground monitoring data and field campaigns' data

In Microsoft excel ASCII files were further analysis. DSCDs respective errors and all selected parameters were obtained in final ASCII file as presented in the figure 3.6. The residue observed during analysis was $\leq 3\times10^{-3}$

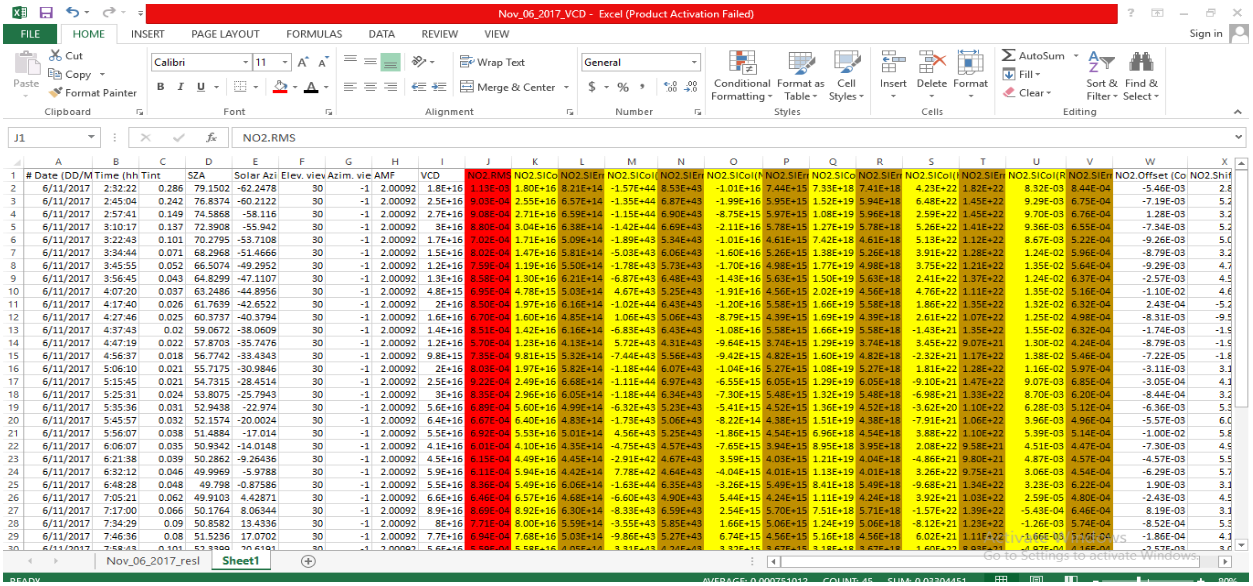


Wavelength Calibration: Ref Only
Ref. Selection: ○ Automatic ● File
Ref. Resol FWHM (nm): 0.7
Fitting Interval Min: 411
Fitting Interval Max: 450
Display: ☑ Spectrum and reference ☑ Polynomial ☑ Ref1/Ref2 Alignment ☑ Residual ☑ Predefined parameters ☑ Fits

Files
Reference 1: G:/Backups/Analysis_smog/ref_000917_07nov.ref
Reference 2:
Residual:

Molecules	Diff/Ortho	Interp/Conv	AMF	Fit disp.	Filter	Cons. SCD	SCD fit	SCD Init	SCD Delta	SCD Io	SCD min
no2	Differential XS	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+17	0
o4	None	Interpolate	None	☑	☑	☐	☑	0	0.001	0	0
no2a	no2	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+17	0
o3	Differential XS	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+20	0
h2o	Differential XS	Convolve Std	None	☑	☑	☐	☑	0	0.001	0	0
ring	None	Interpolate	None	☑	☑	☐	☑	0	0.001	0	0

Figure 3.4. *NO_2 Analysis window in QDOAS, showing fitting interval used for Nitrogen dioxide*



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X
1	# Date (DD/M	Time (hh	Tint	SZA	Solar Azi	Elev. viev	Azim. vie	AMF	VCD	NO2.RMS	NO2.SlCo	NO2.SlErr	NO2.SlCol(	NO2.SlErr	NO2.SlCol(N	NO2.SlErr	NO2.SlCo	NO2.SlErr	NO2.SlCol(	NO2.SlErr	NO2.SlCol(R	NO2.SlErr	NO2.Offset (Co	NO2.Shif
2	6/11/2017	2:32:22	0.286	79.1502	-62.2478	30	-1	2.00092	1.8E+16	1.13E-03	1.80E+16	8.21E+14	-1.57E+44	8.53E+43	-1.01E+16	7.44E+15	7.33E+18	7.41E+18	4.23E+22	1.82E+22	8.32E-03	8.44E-04	-5.46E-03	2.8
3	6/11/2017	2:45:04	0.242	76.8374	-60.2122	30	-1	2.00092	2.5E+16	9.03E-04	2.55E+16	6.57E+14	-1.35E+44	6.87E+43	-1.99E+16	5.95E+15	1.52E+19	5.94E+18	6.48E+22	1.45E+22	9.29E-03	6.75E-04	-7.19E-03	5.2
4	6/11/2017	2:57:41	0.149	74.5868	-58.116	30	-1	2.00092	2.7E+16	9.08E-04	2.71E+16	6.59E+14	-1.15E+44	6.90E+43	-8.75E+15	5.97E+15	1.08E+19	5.96E+18	2.59E+22	1.45E+22	9.70E-03	6.76E-04	1.28E-03	3.2
5	6/11/2017	3:10:17	0.137	72.3908	-55.942	30	-1	2.00092	3E+16	8.80E-04	3.04E+16	6.38E+14	-1.42E+44	6.69E+43	-2.11E+16	5.78E+15	1.27E+19	5.78E+18	5.26E+22	1.41E+22	9.36E-03	6.55E-04	-7.34E-03	5.2
6	6/11/2017	3:22:43	0.101	70.2795	-53.7108	30	-1	2.00092	1.7E+16	7.02E-04	1.71E+16	5.09E+14	-1.89E+43	5.34E+43	-1.01E+16	4.61E+15	7.42E+18	4.61E+18	5.13E+22	1.12E+22	8.67E-03	5.22E-04	-9.26E-03	5.0
7	6/11/2017	3:34:44	0.071	68.2968	-51.4666	30	-1	2.00092	1.5E+16	8.02E-04	1.47E+16	5.81E+14	-5.03E+43	6.06E+43	-1.60E+16	5.26E+15	1.38E+19	5.26E+18	3.91E+22	1.28E+22	1.24E-02	5.96E-04	-8.79E-03	3.2
8	6/11/2017	3:45:55	0.052	66.5074	-49.2952	30	-1	2.00092	1.2E+16	7.59E-04	1.19E+16	5.50E+14	-1.78E+43	5.73E+43	-1.70E+16	4.98E+15	1.77E+19	4.98E+18	3.75E+22	1.21E+22	1.35E-02	5.64E-04	-9.29E-03	4.7
9	6/11/2017	3:56:45	0.043	64.8299	-47.1107	30	-1	2.00092	1.3E+16	8.58E-04	1.30E+16	6.21E+14	-6.87E+43	6.48E+43	-1.43E+16	5.63E+15	1.50E+19	5.63E+18	2.41E+22	1.37E+22	1.24E-02	6.37E-04	-2.57E-03	4.5
10	6/11/2017	4:07:20	0.037	63.2486	-44.8956	30	-1	2.00092	4.8E+15	6.95E-04	4.78E+15	5.03E+14	4.67E+43	5.25E+43	-1.91E+16	4.56E+15	2.02E+19	4.56E+18	4.76E+22	1.11E+22	1.35E-02	5.16E-04	-1.10E-02	4.6
11	6/11/2017	4:17:40	0.026	61.7639	-42.6522	30	-1	2.00092	2E+16	8.50E-04	1.97E+16	6.16E+14	-1.02E+44	6.43E+43	-1.20E+16	5.58E+15	1.66E+19	5.58E+18	1.86E+22	1.35E+22	1.32E-02	6.32E-04	2.43E-04	-5.2
12	6/11/2017	4:27:46	0.025	60.3737	-40.3794	30	-1	2.00092	1.6E+16	6.70E-04	1.60E+16	4.85E+14	1.06E+43	5.06E+43	-8.79E+15	4.39E+15	1.69E+19	4.39E+18	2.61E+22	1.07E+22	1.25E-02	4.98E-04	-8.31E-03	-9.5
13	6/11/2017	4:37:43	0.02	59.0672	-38.0609	30	-1	2.00092	1.4E+16	8.51E-04	1.42E+16	6.16E+14	-6.83E+43	6.43E+43	-1.08E+16	5.58E+15	1.66E+19	5.58E+18	-1.43E+21	1.35E+22	1.55E-02	6.32E-04	-1.74E-03	-1.9
14	6/11/2017	4:47:19	0.022	57.8703	-35.7476	30	-1	2.00092	1.2E+16	5.70E-04	1.23E+16	4.13E+14	5.72E+43	4.31E+43	-9.64E+15	3.74E+15	1.29E+19	3.74E+18	3.45E+22	9.07E+21	1.30E-02	4.24E-04	-8.79E-03	-1.9
15	6/11/2017	4:56:37	0.018	56.7742	-33.4343	30	-1	2.00092	9.8E+15	7.35E-04	9.81E+15	5.32E+14	-7.44E+43	5.56E+43	-9.42E+15	4.82E+15	1.60E+19	4.82E+18	-2.32E+21	1.17E+22	1.38E-02	5.46E-04	-7.22E-05	-1.8
16	6/11/2017	5:06:10	0.021	55.7175	-30.9846	30	-1	2.00092	2E+16	8.03E-04	1.97E+16	5.82E+14	-1.18E+44	6.07E+43	-1.04E+16	5.27E+15	1.08E+19	5.27E+18	1.81E+22	1.28E+22	1.16E-02	5.97E-04	-3.11E-03	3.1
17	6/11/2017	5:15:45	0.021	54.7315	-28.4514	30	-1	2.00092	2.5E+16	9.22E-04	2.49E+16	6.68E+14	-1.11E+44	6.97E+43	-6.55E+15	6.05E+15	1.29E+19	6.05E+18	-9.10E+21	1.47E+22	9.07E-03	6.85E-04	-3.05E-04	4.1
18	6/11/2017	5:25:31	0.024	53.8075	-25.7943	30	-1	2.00092	3E+16	8.35E-04	2.96E+16	6.05E+14	-1.18E+44	6.34E+43	-7.30E+15	5.48E+15	1.32E+19	5.48E+18	-6.98E+21	1.33E+22	8.70E-03	6.20E-04	-8.44E-04	3.2
19	6/11/2017	5:35:36	0.031	52.9438	-22.974	30	-1	2.00092	5.6E+16	6.89E-04	5.60E+16	4.99E+14	-6.32E+43	5.23E+43	-5.41E+15	4.52E+15	1.36E+19	4.52E+18	-3.62E+20	1.10E+22	6.28E-03	5.12E-04	-6.36E-03	5.3
20	6/11/2017	5:45:57	0.032	52.1574	-20.0024	30	-1	2.00092	6.4E+16	6.67E-04	6.40E+16	4.83E+14	-1.73E+43	5.06E+43	-8.22E+14	4.38E+15	1.51E+19	4.38E+18	-7.91E+21	1.06E+22	3.96E-03	4.96E-04	-5.57E-03	6.0
21	6/11/2017	5:56:07	0.038	51.4884	-17.014	30	-1	2.00092	5.5E+16	6.92E-04	5.53E+16	5.01E+14	4.56E+43	5.25E+43	-1.86E+15	4.54E+15	6.96E+18	4.54E+18	3.88E+22	1.10E+22	5.39E-03	5.14E-04	-1.00E-02	5.8
22	6/11/2017	6:06:07	0.035	50.9342	-14.0148	30	-1	2.00092	4.1E+16	6.01E-04	4.10E+16	4.35E+14	-4.75E+43	4.57E+43	-7.65E+15	3.94E+15	8.95E+18	3.95E+18	2.08E+22	9.58E+21	4.51E-03	4.47E-04	-7.30E-03	4.9
23	6/11/2017	6:21:38	0.039	50.2862	-9.26436	30	-1	2.00092	4.5E+16	6.15E-04	4.49E+16	4.45E+14	-2.91E+42	4.67E+43	3.59E+15	4.03E+15	1.21E+19	4.04E+18	-4.86E+21	9.80E+21	4.87E-03	4.57E-04	-4.57E-03	5.5
24	6/11/2017	6:32:12	0.046	49.9969	-5.9788	30	-1	2.00092	5.9E+16	6.11E-04	5.94E+16	4.42E+14	7.78E+42	4.64E+43	-4.04E+15	4.01E+15	1.13E+19	4.01E+18	3.26E+22	9.75E+21	3.06E-03	4.54E-04	-6.29E-03	5.7
25	6/11/2017	6:48:28	0.048	49.798	-0.87586	30	-1	2.00092	5.5E+16	8.36E-04	5.49E+16	6.06E+14	-1.63E+44	6.35E+43	-3.26E+15	5.49E+15	8.41E+18	5.49E+18	-9.68E+21	1.34E+22	3.23E-03	6.22E-04	1.90E-03	3.1
26	6/11/2017	7:05:21	0.062	49.9103	4.42871	30	-1	2.00092	6.6E+16	6.46E-04	6.57E+16	4.68E+14	-6.60E+43	4.90E+43	5.44E+15	4.24E+15	1.11E+19	4.24E+18	3.92E+21	1.03E+22	2.59E-05	4.80E-04	-2.43E-03	4.5
27	6/11/2017	7:17:00	0.066	50.1764	8.06344	30	-1	2.00092	8.9E+16	8.69E-04	8.92E+16	6.30E+14	-8.33E+43	6.59E+43	2.54E+15	5.70E+15	7.51E+18	5.71E+18	-1.57E+22	1.39E+22	-5.43E-04	6.46E-04	8.19E-03	3.1
28	6/11/2017	7:34:29	0.09	50.8582	13.4336	30	-1	2.00092	8E+16	7.71E-04	8.00E+16	5.59E+14	-3.55E+43	5.85E+43	1.66E+15	5.06E+15	1.24E+19	5.06E+18	-8.12E+21	1.23E+22	-1.26E-03	5.74E-04	-8.52E-04	5.3
29	6/11/2017	7:46:36	0.08	51.5236	17.0702	30	-1	2.00092	7.7E+16	6.94E-04	7.68E+16	5.03E+14	-9.86E+43	5.27E+43	6.74E+15	4.56E+15	5.16E+18	4.56E+18	6.02E+21	1.11E+22	-1.66E-03	5.16E-04	-1.86E-04	4.1
30	6/11/2017	7:58:43	0.101	52.3399	20.6191	30	-1	2.00092	5.6E+16	5.59E-04	5.58E+16	4.05E+14	3.31E+43	4.24E+43	3.32E+15	3.67E+15	3.18E+18	3.67E+18	1.60E+22	8.93E+21	-4.97E-04	4.16E-04	-2.57E-03	3.0

Type equation here.

Figure 3.5. ASCII files obtained by QDOAS opened in Microsoft excel; red column represnting RMS, yellow columns showing DSCDs, brown columns illustrate slant column errors

3.6. Air Mass Factor (AMF) and SCDs Calculation:

Air Mass Factor is calculated in Microsoft excel as for deriving geometric expressions it is easy to use. The main purpose of it the derivation of NO_2 VCDs. Air Mass Factor is defined as the ratio of the actual path distance of solar radiation coming to atmosphere to the vertical path distance through atmosphere. For troposphere and stratosphere the AMF can be calculated as shown in figure 3.7.

Usually for the conversion of SCDs (Slant column densities) to VCDs (Vertical column densities) the AMF calculations are used.

The VCDs ($VCD_{trop)}$ in troposphere is equal to the ratio of SCDs and AMF as shown in the equation 1:

Equation 1

$$\mathrm{VCD}_{\mathrm{trop}} = \frac{\mathrm{SCD}_{\mathrm{trop}\ (\alpha)}}{\mathrm{AMF}_{\mathrm{trop}(\alpha)}}$$

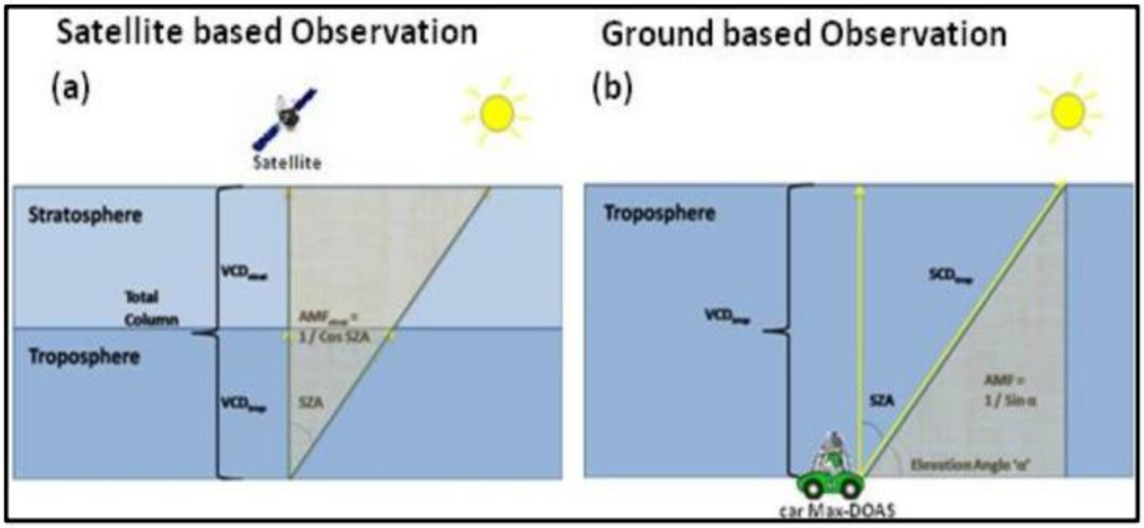


Figure 3.6. AMF calculations; (a) for satellite observations [Continuous ground monitoring] (b) For ground based observations [field campaigns' data] adopted from (Wagner et al., 2010)

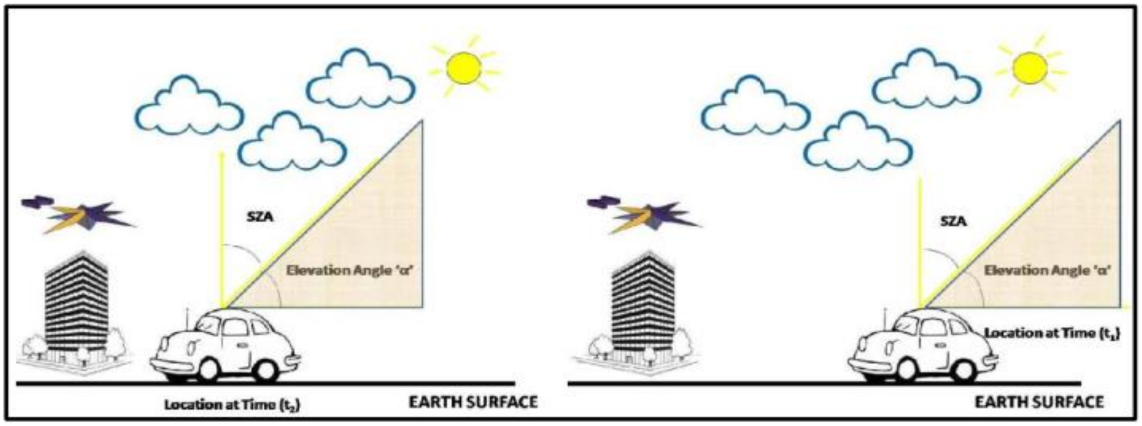


***Figure 3.7. Variability/complexity in AMF calculations for t1 and t2 adopted from* (Wagner et al., 2010)**

By using the geometric approximation the AMF can be assessed as shown in the equation 2:

Equation 2

$$\mathrm{AMF}_{\mathrm{trop}} = \frac{1}{\sin \alpha}$$

For the derivations of VCDs from field campaign data and ground monitoring data elevation angle of 30^{o} was selected.

For the ground monitoring, VCDs' extraction is much easier as in this case, after the calculation of AMF at elevation angle (α=30), the following equation is used to calculate NO2 VCDs:

Equation 3:

$$VCDS = \frac{DSCDs\ (\alpha = 30)}{(AMF - 1)}$$

3.7. Field Campaigns

ArcGIS software was used to map the field campaigns data. Field campaigns were conducted in different forest types of Northern area. An external GPS logger was used to record the coordinates during field campaigns as the instrument (MAX-DOAS) that was used in the field campaigns was not integrated with GPS logger. With respect to both "Universal Time Centre (UTC) and Pakistan Standard Time (PST)" GPS logger was used to record the coordinates. The time for GPS logger and MAX-DOAS was set to UTC to synchronize the readings of coordinates between MAX-DOAS and GPS logger. By using Microsoft Excel the Lat, Long of the respective measurements of MAX-DOAS were synchronized with each other and the resulting files were saved in CSV format (comma delimited). These saved CSV files were further opened in ArcGIS for mapping as shown in the Figure 3.8.

3.8. Validation of MAX-DOAS Observations by Satellite Data

For the validation of MAX-DOAS observations Ozone Monitoring Instrument (OMI) observations were used. The data used for this was OMNO2d v003 from TEMIS website (http://www.temis.nl/airpollution/no2.html). In ESRI grid format the data was downloaded and opened in Notepad++ for removing the negative values of-999 from the data. The file then opened in ENVI software and save it as ERDAS Imaging Tiff file as shown in figure 3.9.

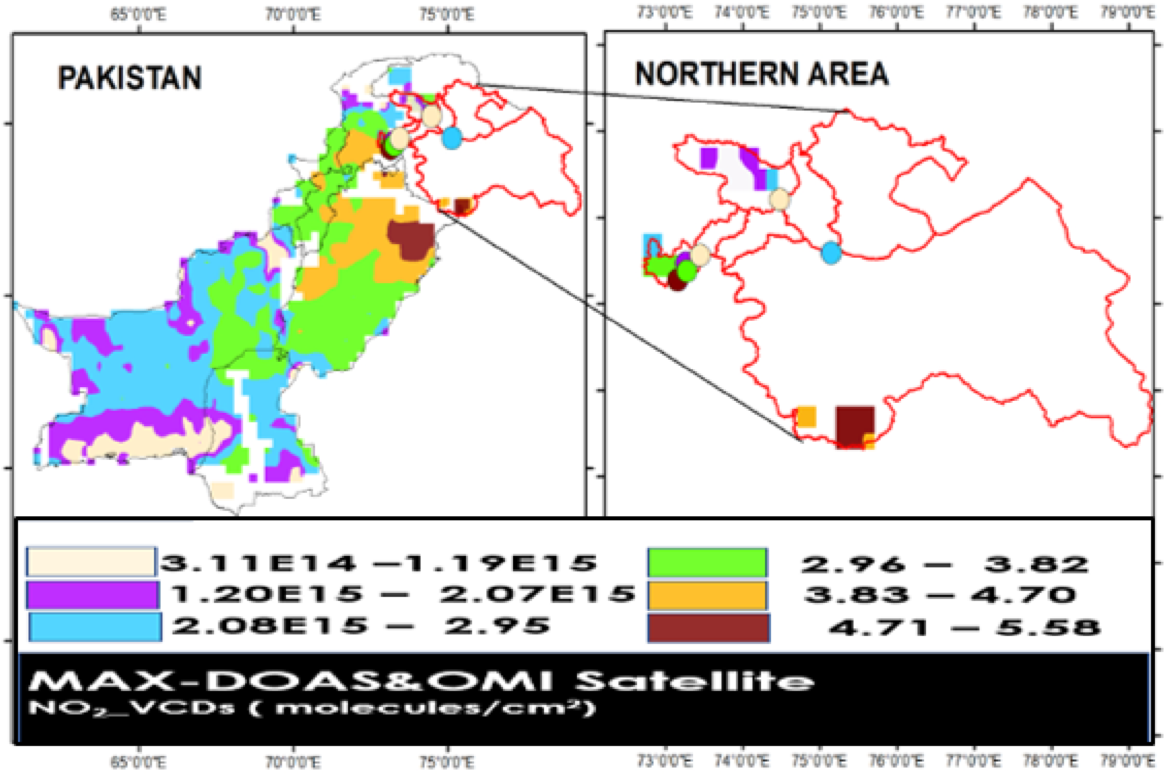
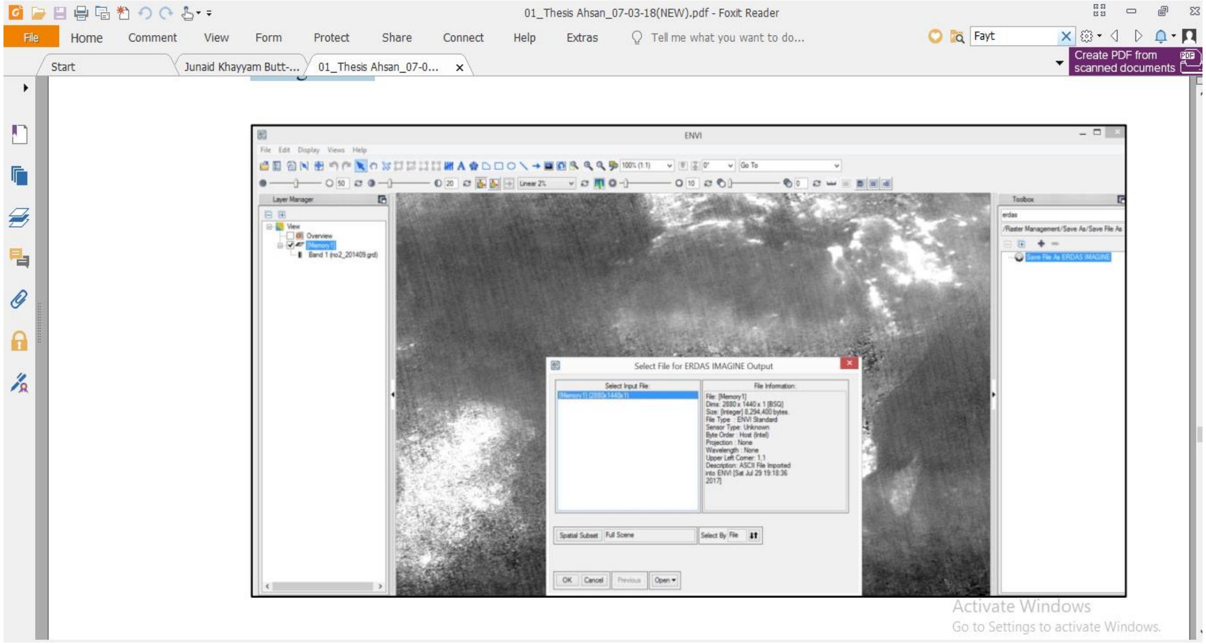


Figure 3.8. ArcGIS Mapping of NO_2 VCDs over different Forest types in Northern Areas of Pakistan



[Memory1] (2880x1440x1)

File: [Memory1]
Dims: 2880 x 1440 x 1 [BSQ]
Size: [Integer] 8,294,400 bytes.
File Type : ENVI Standard
Sensor Type: Unknown
Byte Order : Host (Intel)
Projection : None
Wavelength : None
Upper Left Corner: 1,1
Description: ASCII File Imported into ENVI [Sat Jul 29 19:18:36 2017]

Spatial Subset: Full Scene

Select By: File

Figure 3.9. Satellite Data Processing in ENVI

From ENVI the generated tiffs were opened and were further processed in ArcGIS for Map generation and extraction of values at the MAX-DOAS operated point. Then both the values from MAX-DOAS and satellite were compared for the validation of ground based MAX-DOAS results.

RESULTS AND DISCUSSION

4.1. Concentrations of NO_2 during Field Campaigns

MAX-DOAS measurements for NO_2 VCDs were performed from 12th July 2018 to 25th July 2018 periodically in the Northern Areas of Pakistan as shown in the table 4.1.

Table 4.1.: Maximum and average Concentrations of NO_2 observed during Field Campaigns

Location	Date	Avg._NO2 VCD (molec/cm2)	MAX_NO2 VCD (molec/cm2)	MAX_NO2 VCD (ppbv)
Shinkiari(Sub-Tropical Chir-Pine Forest)	7/12/2018	1.44E+15	1.9E+16	16.18
Shinkiari(Sub-Tropical Chir-Pine Forest)	7/13/2018	1.34E+15	3.69E+15	3.14
Tea Garden-Shinkiari	7/14/2018	5.59E+15	3.19E+16	27.18
Shogran(Moist Temperate Forest)	7/16/2018	8.19E+14	2.22E+15	1.89
Shogran(Moist Temperate Forest)	7/17/2018	9.87E+14	3.27E+15	2.78
Shogran(Moist Temperate Forest)	7/18/2018	7.15E+14	2.6E+15	2.21
Rama-Astore(Dry Temperate Forest)	7/21/2018	1.05E+15	6.04E+15	5.14
Deosai(Alpine Pasture)	7/12/2018	5.82E+14	1.22E+15	1.04
Naran-Batakundi(Sub-Alpine Pasture)	7/25/2018	9.32E+14	3.23E+15	2.75

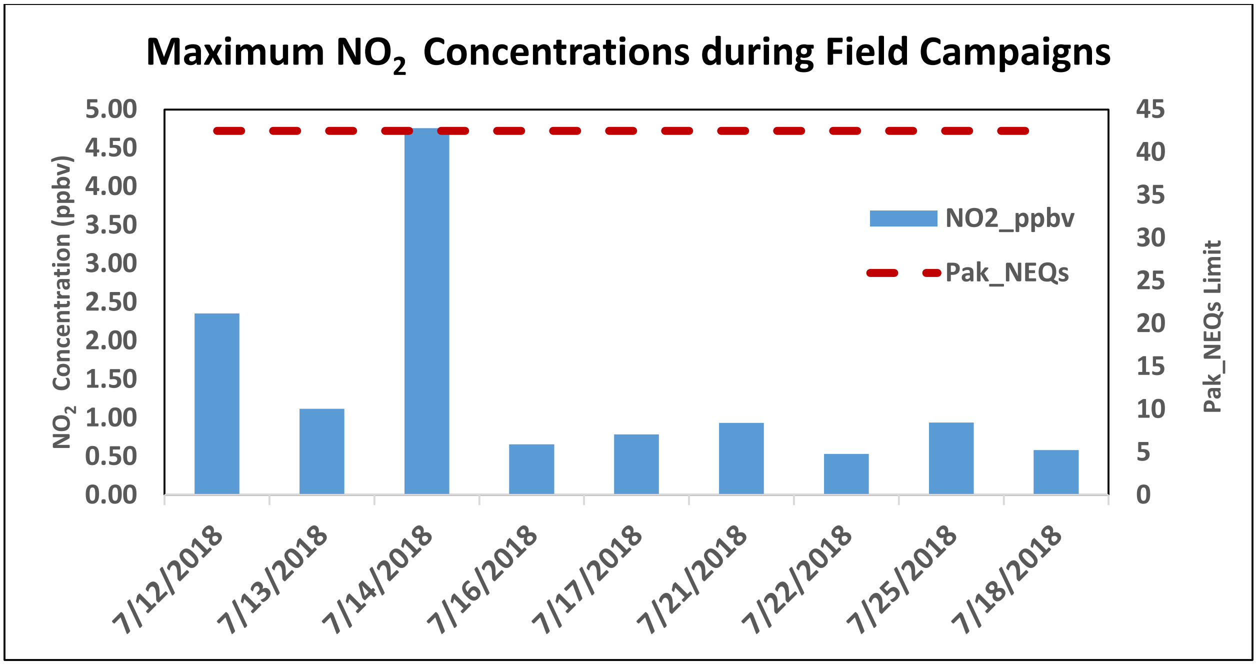


Figure 4.1. NO_2 conc. (ppbv.) for Field campaigns are within permissible limit of NEQs.

Figure 4.2 shows that the NO_2 concentration during the field campaigns of Northern Areas are within permissible limit of NEQ's during July 12th 2018 – 25 July 2018. The highest concentration at Tea Garden-Shinkiari (**lat 34.47243º, Long 73.26627º)** was observed as 5.59E+15 molecules/cm2 (4.79 ppb) along N35 Road on 14th July 2018, It may be due to the heavy traffic load on the road. In the other campaigns in Northern Areas NO_2 concentrations were below the NEQs limits as shown in the figure 4.1.

The Pak-NEQS standard for NO_2 is **42.5 ppbv (80µg/m3)** and the WHO conversion factor for NO2 is **1ppbv = 1.88 µg/m3**. From the campaigns data, it was observed that the NO_2 concentration was within limit.

4.2. Diurnal cycle of NO_2:

4.2.1. Diurnal cycle of NO_2 over Islamabad city

NO_2 diurnal cycle over Islamabad for the time period of almost 4 years (September 2014 - 2018) are shown in the figure 4.2. The diurnal cycle shows that the concentrations of NO_2 are higher initially with the start of the day as the sun rises and starts decreasing gradually up till noon and then starts increasing again after the mid-day passes. The most likely the reason for the higher concentrations of NO_2 during morning is due to the last night traffic, combustion activities and lack of photolysis process to degrade the nitrogen dioxide into nitrogen oxide. As soon as the sunlight increases the oxidation of NO_2 starts in the presence of OH radical which leads to the gradual decrease in atmospheric NO_2 concentration, with maximum degradation at noontime. But after the midday passes the sunlight decreases which leads toward the decrease in photolysis of NO_2, and hence NO_2 concentration reaches to maximum during evening.

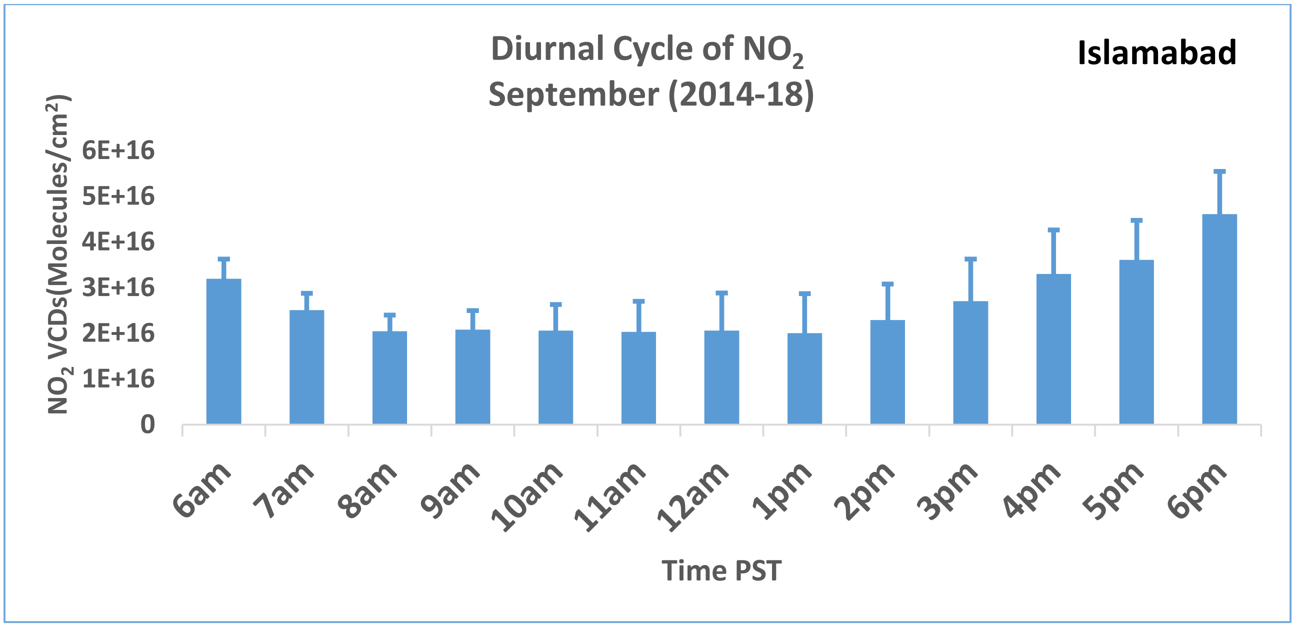


Figure 4.2. Averaged (6am to 6pm) Diurnal Cycle observed over NUST Islamabad by MAX-DOAS.

4.3. Monthly Cycle of NO_2

NO_2 from September 2014 to 2018 shows average annual decreasing trend in the summer and an increasing trend in the winter seasons (figure 4.3) (Kanaya *et al.*, 2014). During the summer NO_2 breaks down Due to photolysis effect, it is relatively higher in the summer than winter.

The slight increase during the month of April because most of the cloudy days during this month as photolysis rate is very low during cloudy days. But during the months of July and August because of moon soon season, as clouds cover the sky and decreases the sunlight for NO_2 photolysis, resulting in increased NO_2 concentrations during that period.

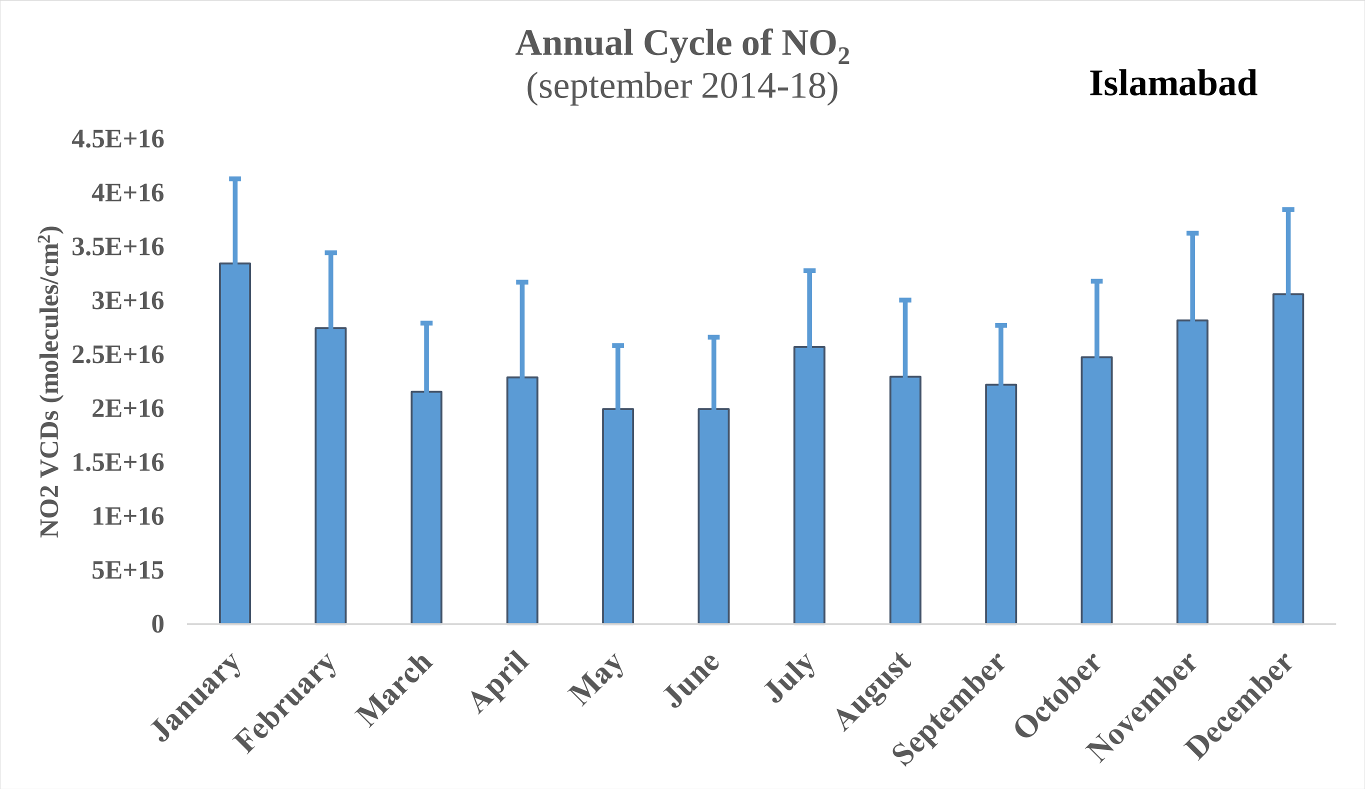


Figure 4.3. Nitrogen dioxide monthly averaged concentrations over Islamabad observed by MAX-DOAS

4.4. NO_2 Weekly Cycle

NO_2 weekly cycle shows almost similar trend throughout the week except Friday has low concentrations, due to business holiday on Friday.

On Saturday a rapid increase in NO_2 concentration may be due to resumption of business activities and heavy transportation, the movement of people who work in the offices or other organizations from Islamabad to their home town on Friday night or Saturday morning may also the cause of NO_2 peak.

The other possible reason of the peak the movement of people to Islamabad on weekend for the purpose of recreation, resulting in increased traffic on Saturday and Sunday, which may cause the increase in NO_2 concentrations on weekend.

The movement and activities of human beings are the main cause to increase tropospheric NO_2, the trends at weekends totally influenced by the traffic movement in Islamabad. Some related findings has already been studied by Kanaya et al., 2014.

4.5. Satellite Validation of MAX-DOAS Data

4.5.1. Field Campaigns:

The MAX-DOAS field campaigns observation in the Northern areas were validated with the respective satellite observations from the GIOVANNI website as shown in figure 4.6(a). The highest peaks for the campaigns for MAX-DOAS and OMI Satellite were observed in Pakistan Forest Institute and National Tea Garden, Shinkiari but within the NEQ's limits (42.5ppbv), where as in all other sites they are well below the permissible limit. But not a strong correlation (Pearson Value **r = 0.29**) was observed, as shown in the figure 4.6 (b)

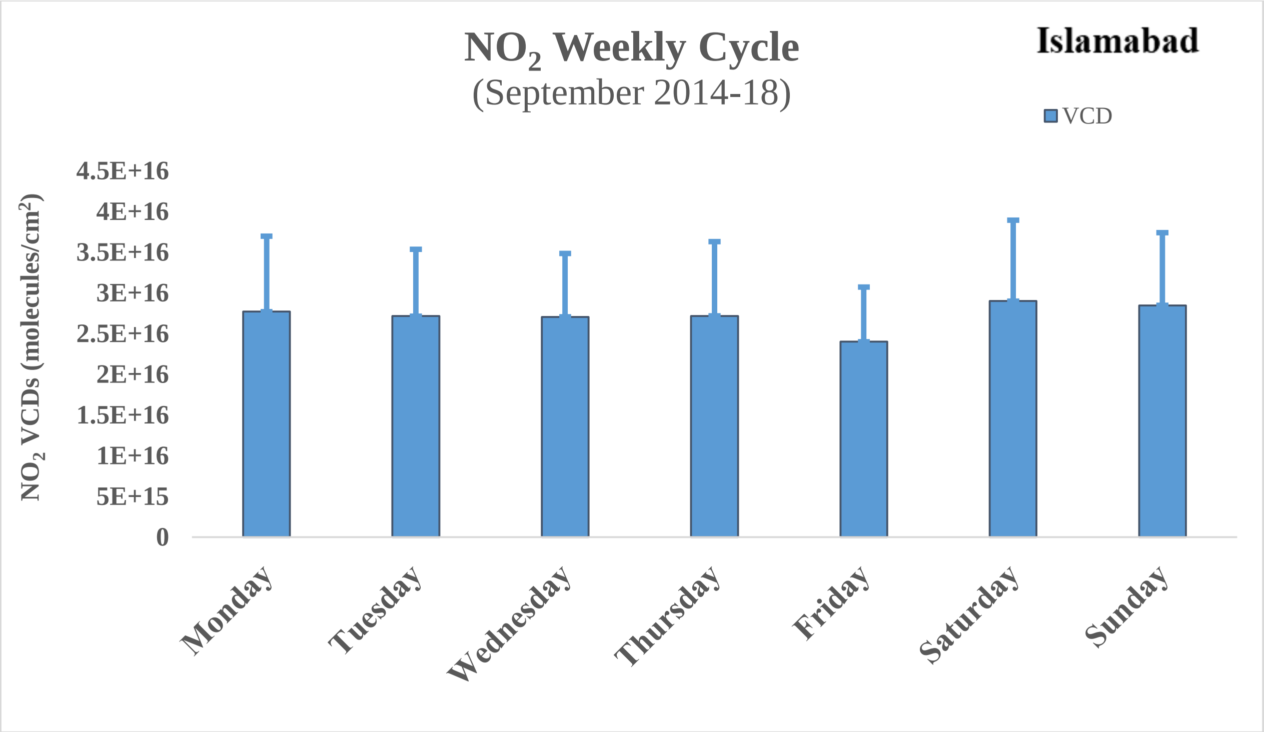


Figure 4.4. Weekly trend of nitrogen dioxide concentrations over Islamabad monitored by MAX-DOAS

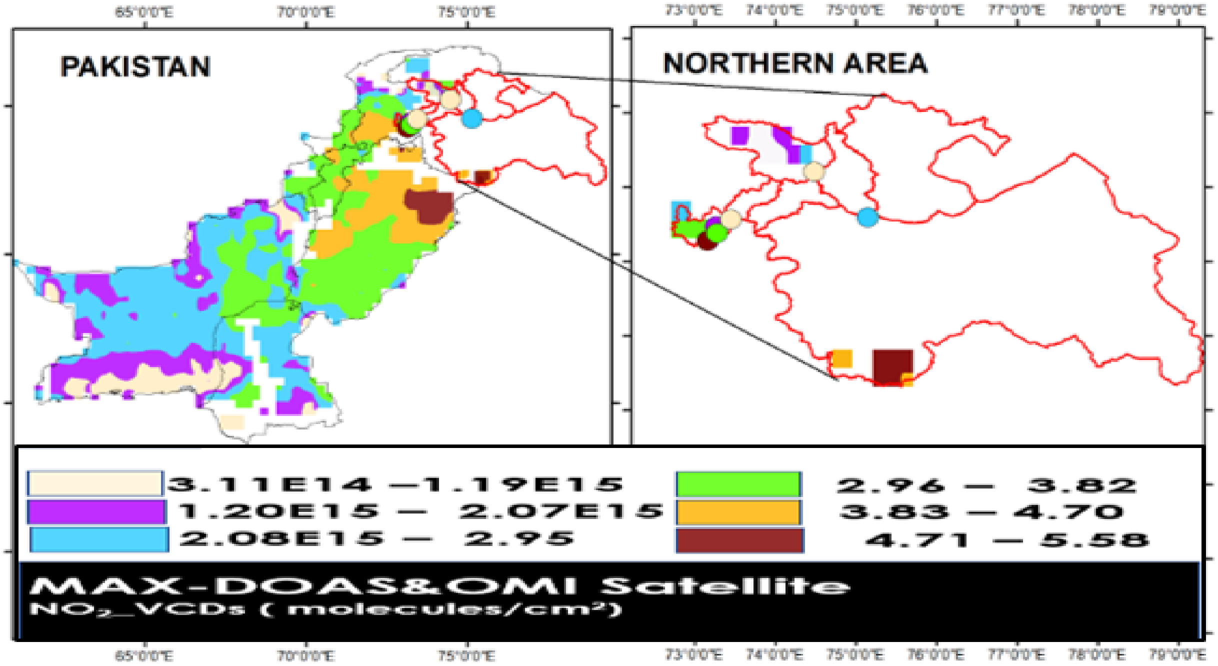


Figure 4.5. . NO_2 concentrations retrieved from MAX-DOAS and OMI satellite observations conducted in Northern Areas of Pakistan during the field campaigns

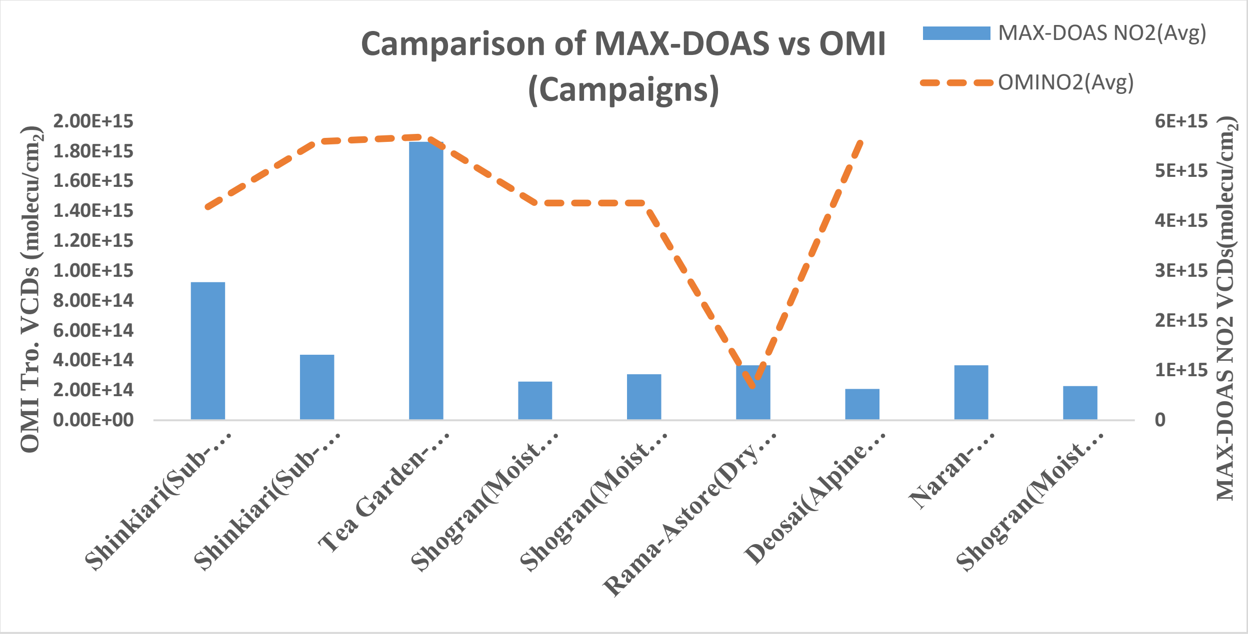


Figure 4.6. (a): Average NO_2 concentrations for MAX-DOAS vs OMI over different Forest types in Northern areas of Pakistan

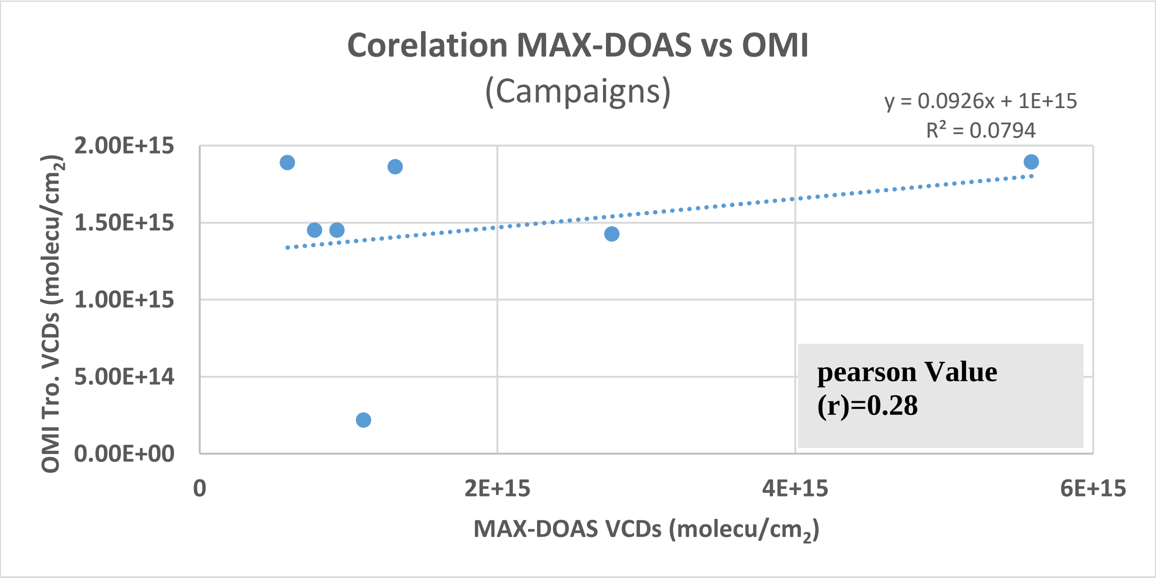


Figure 4.6. (b): Average NO_2 concentrations for MAX-DOAS vs OMI correlation over different Forest types in Northern areas of Pakistan

4.5.2. NO_2 Monthly Mean over Islamabad

The data from TEMIS website and OMI satellite (25ox 0.25o) was obtained as average of each month over Islamabad. During the months of December and January the peaks of Nitrogen dioxide

(NO_2) was observed. In the subsequent months the concentration is decreased gradually. For NO_2 OMI satellite values were underestimated (x 10^{15}) as they were much lesser than the MAX-DOAS values (x 10^{16}), it may be due to a multiple reasons such as cloud cover, aerosol shielding effect , and the less sensitivity of satellite observations towards the layers of surface. However OMI and MAX-DOAS concentrations trend were much more the same. MAX-DOAS and OMI satellite monthly average of NO_2 concentrations were compared.

MAX-DOAS monthly average were taken at three different time spans such as at 6:00am – 6:00pm (PST), 12:00pm – 2:00pm (PST), and 01:00pm – 02:00pm (PST) and were compared with OMI satellite data. Then correlation for all three times were calculated and pearson value “r” for the three times were .49, .52, and .85 respectively as shown in the figure 4.7,8,9 (b, b, & b). For the time span between 01:00pm – 02:00pm (PST) the best correlation was observed. The passing time of OMI over Pakistan is between 01:30pm 02:00pm (PST), so the correlation between MAX-DOAS and satellite was improved largely when the times for both observations were close to each other.

A scatter plot of the compared data is shown in Fig.4.9, together with a histogram of the frequency distribution of the differences. The histogram exhibits a close to normal distribution peaking at 80% with 95% of the data lying between 70% and 90%. The histogram for different season were also calculated but it is almost similar to the composite. As shown in Fig 4.9

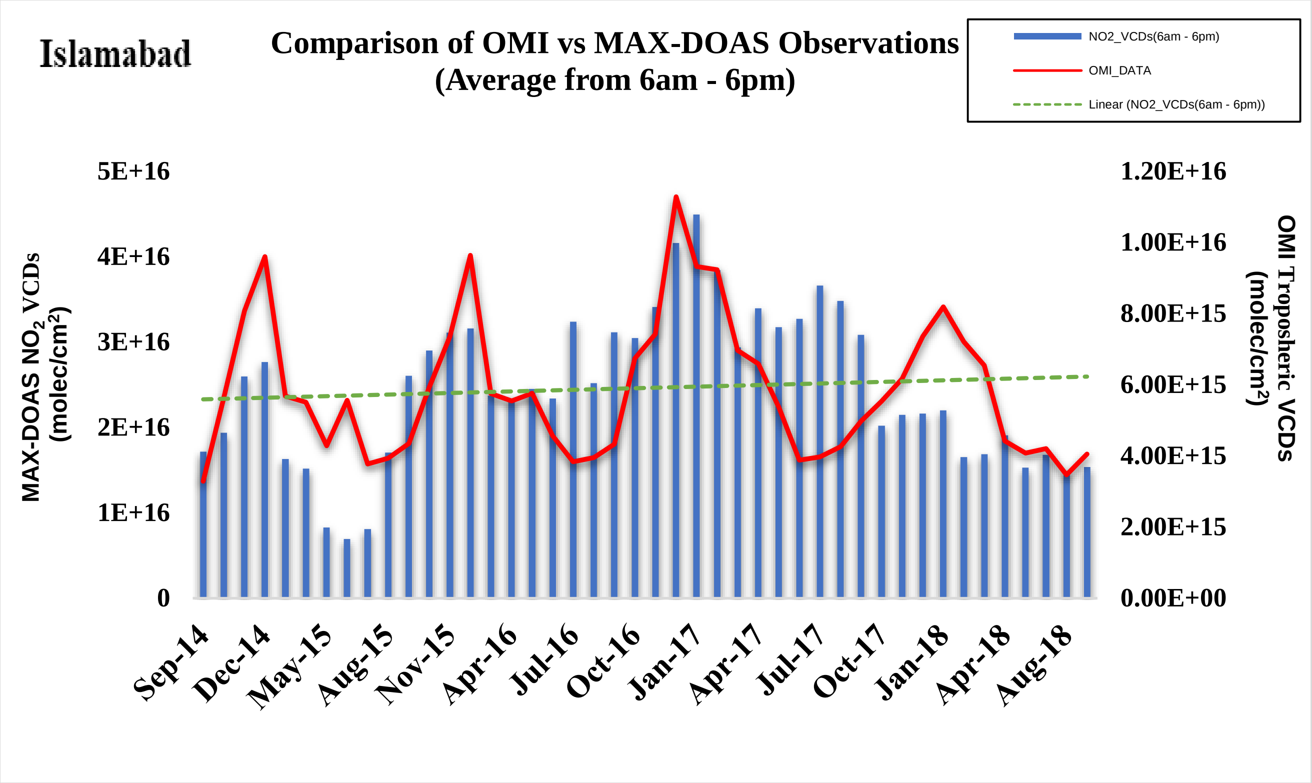


Figure 4.7.(a) NO₂ monthly average of MAX-DOAS (6am to 6pm) vs OMI over Islamabad

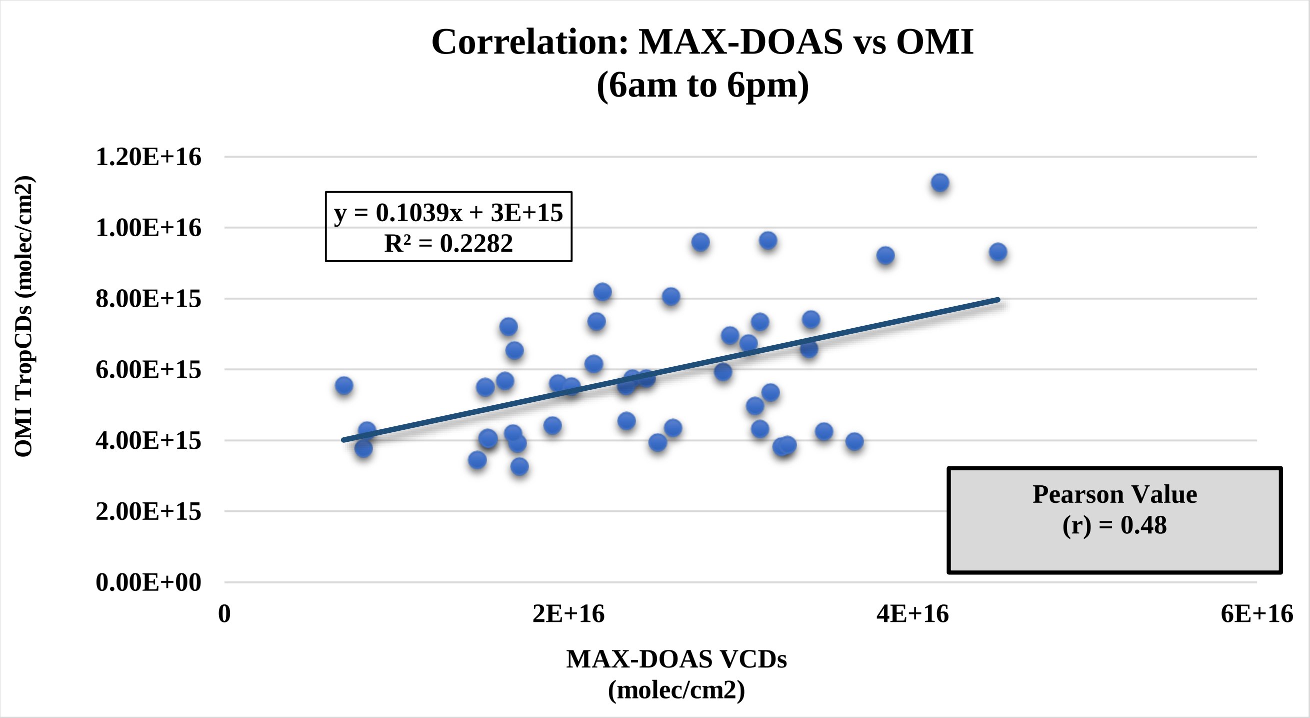


Figure 4.7. (b): MAX-DOAS (6am to 6pm) vs OMI correlation over Islamabad

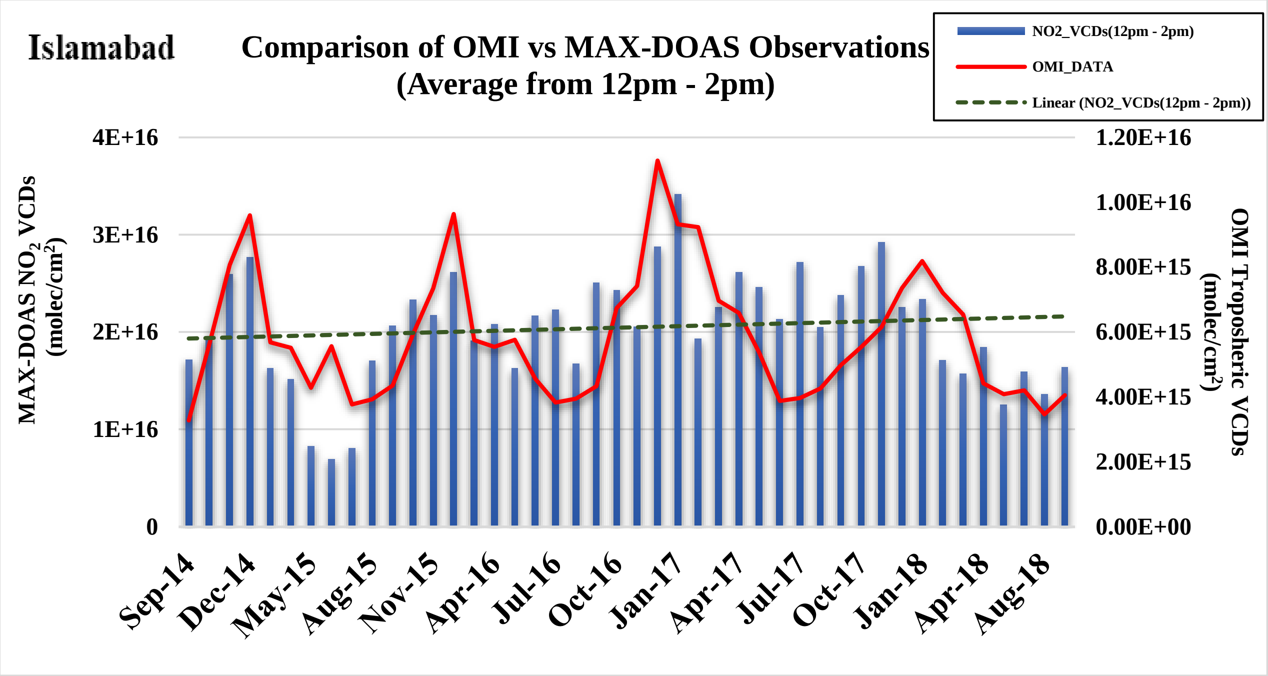


Figure 4.8. (a): NO_2 monthly average of MAX-DOAS (12pm to 2pm) vs OMI over Islamabad

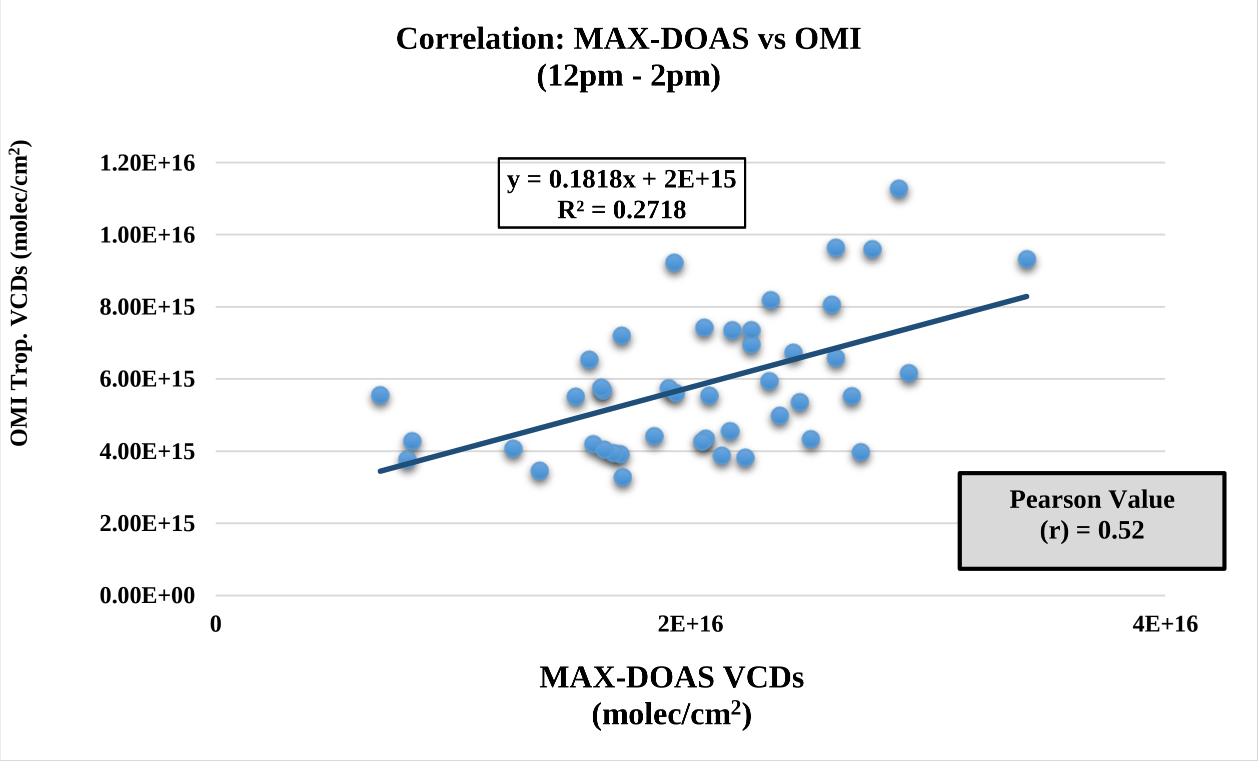


Figure 4.8. (b): MAX-DOAS (12pm to 2pm) vs OMI correlation over Islamabad

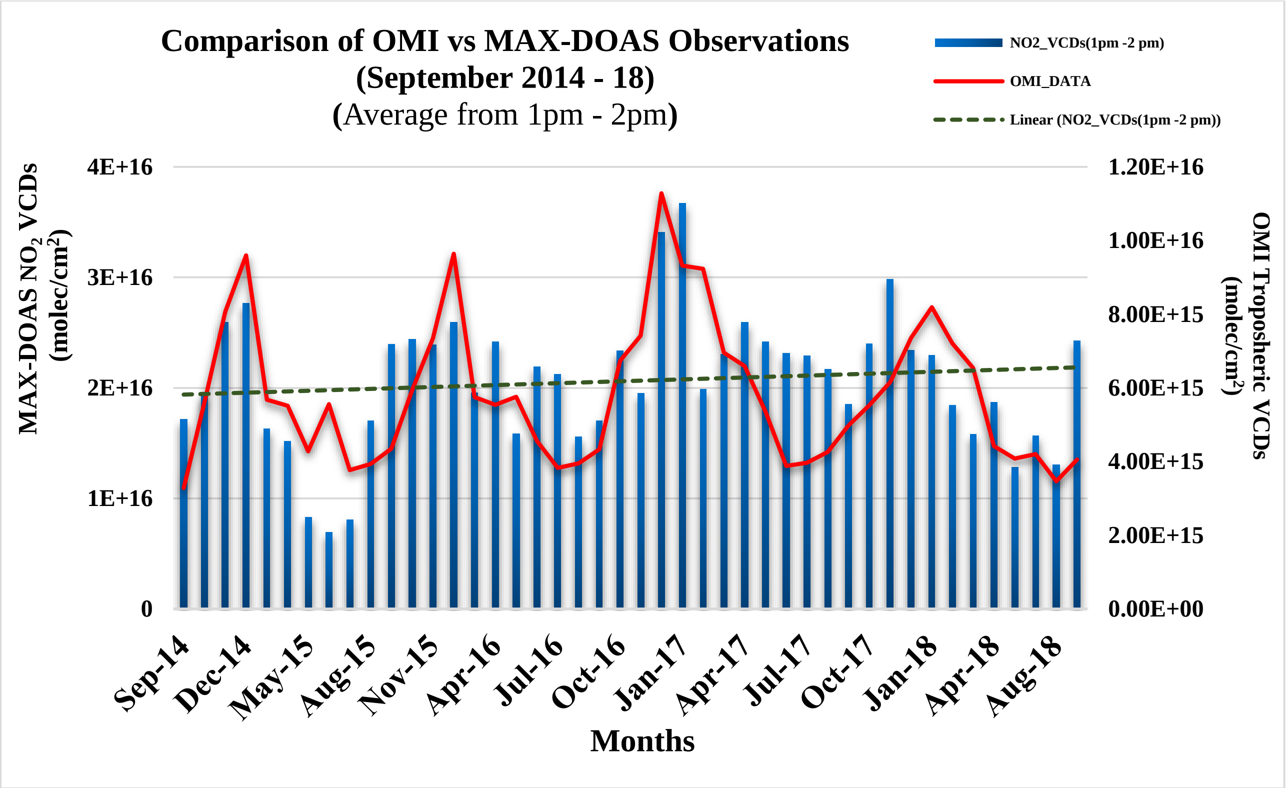


Figure 4.9. (a): NO_2 monthly average of MAX-DOAS (1pm to 2pm) vs OMI over Islamabad

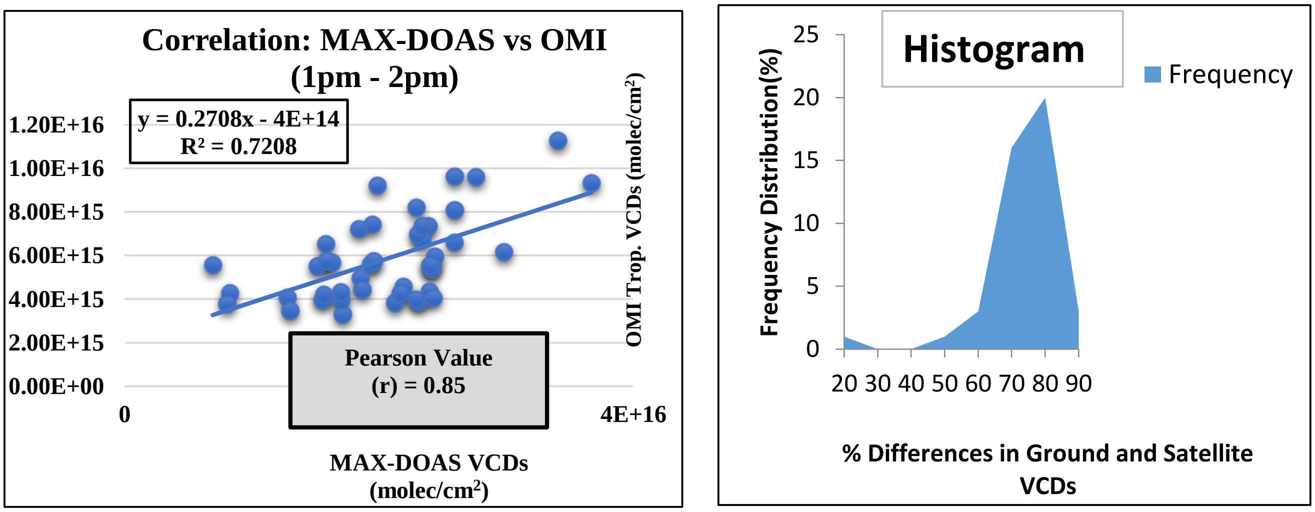


Figure 4.9. (b): MAX-DOAS (1pm to 2pm) vs OMI correlation over Islamabad (left) and Frequency distribution of VCDs differences between MAX-DOAS and Satellite.

4.5.3. Seasonal Frequency Histogram

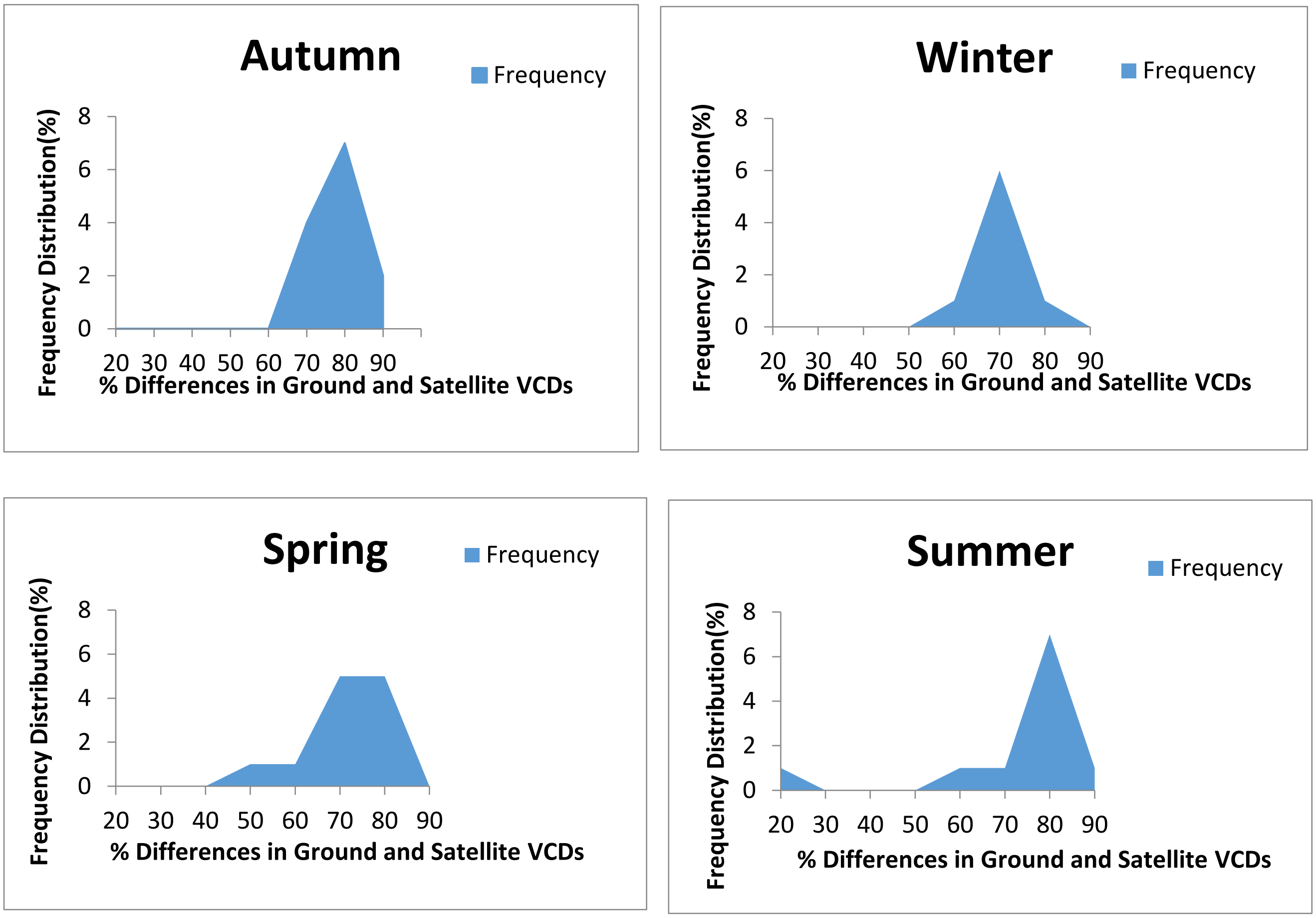


Fig.4.10. Seasonal Frequency distribution of VCDs differences between MAX-DOAS and Satellite.

CONCLUSION AND RECOMMENDATIONS

5.1. Conclusions

Fixed NO_2 monitoring was performed by using MAX-DOAS in the city of Islamabad (lat:33.7294° N, lon:73.0931° E) and different types of forest in Pakistan includes Pine Park Hotel (lat:34.3837° N, lon:73.2811° E) (Shogran, KPK), Shinkiari field station, Pakistan Forest Institute (lat:34.4724254° N, lon:73.2662724° E) and National tea garden (lat:34.28° N, lon:73.1629° E) (KPK),Rama (lat:35.2131° N, lon:74.4841° E), Bata kundi (lat:34.566° N, lon:73.4549° E), and deosai national park (lat:34.5934° N, lon:75.1513° E) (GB).

It was observed that the average concentration of NO_2 in the National tea Garden, Shinkiari is higher than the other sites. It may be due to the heavy traffic load on the nearby passing road (N15). Maximum NO_2 concentration at National Tea Garden was 3.19e16 molecules/cm^2 (27.18ppb), whereas for the other sites the NO_2 concentration was well below than that of Tea Garden Shinkiari.

NO_2 monitoring was performed in the city of Islamabad continuously for the period of 2014-2018, due to increase in the traffic load in the city, NO_2 concentration level showing an increasing trend within the city. From 2015-2016 there is 57% increase in the sale of local commercial vehicles and private cars according to Pakistan Automotive manufacturers Association (PAMA). One of the possible reason for the increase in NO_2 concentration level during the whole study period (2014-2018). Satellite comparison was also done using tropospheric OMI NO2 VCDs and MAX-DOAS observations. A good correlation was found in OMI and MAX-DOAS observation for Islamabad but not for field campaign data as satellite data is not available for all these days. Generally, similar NO2 spatial distributions are found in both data sets, although satellite observations are underestimated. The reason for this quantitative disagreement is mainly due to less sensitivity of satellite towards ground level pollutants. Also, satellite observations are representative over large ground area i.e. (swath path = 13 x 24 km2).

Field campaigns need to be done on regular basis, worldwide and under different atmospheric conditions for the improvement and better comparison of boundry level pollution with satellite observations.

5.2. Recommendations

Based on this study here are some of the recommendations, for the improvement of air quality and future improvements, techniques and practices related to air quality in the country**.**

The results of the present study shows that the concentrations of NO_2 is increasing with the passing years. It is because of increase in fossil fuel consumption both in transportation and industrial processes. The reduction in fossil fuel consumption by shifting towards renewable energy techniques can reduced the NO_2 level in atmosphere. Improvement in combustion technologies and catalytic converters in vehicles can also be reduce the NO_2 concentration.

On both provincial and federal level the air quality management plan should be introduced and implemented.

To avoid traffic load and congestions mass transit system should be introduced both in urban and rural areas.

Regular tuning and maintenance of the vehicles can also reduce the vehicular emissions.

On monthly and annual basis air quality improvement statistics should be shared publicly.

On regular basis air quality monitoring should be conducted and baseline should be prepared at least for the major cities of the country.

Awareness in school children, citizen groups etc. by sharing the causes and consequences of air pollution on state level.

To teach the public and other stakeholders effective media campaigns should be conducted.

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