

**NO₂ MONITORING ALONG NATIONAL HIGHWAY OF NORTHERN
PUNJAB USING CAR MAX-DOAS INSTRUMENT**



By

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It is certified that the contents and forms of the thesis entitled

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NORTHERN PUNJAB USING CAR MAX-DOAS
INSTRUMENT**

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For their endless affection, support and encouragement

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List of Abbreviation

$\mu\text{g}/\text{m}^3$	Microgram per meter
AMF	Air Mass Factor
ArcGIS	Arc Geographic Information System
C-CARGO	<u>C</u> limate <u>C</u> hange and <u>A</u> tmospheric <u>R</u> esearch <u>G</u> roup
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
GOME-2	Global Ozone Monitoring Equipment - 2
GOP	Government of Pakistan
HNO_3	Nitric Acid
IDW	Inverse Distance Weighting
IUCN	International Union for Conservation of Nature
JICA	Japan International Cooperation Agency
LTV	Light Transport Vehicle
Max-DOAS	Multi-axis Differential Optical Absorption Spectroscopy
N5-Highway	National Highway - 05
NDIR	Non Dispersive Infra-Red
NGO's	Non-Government Organizations
NH_3	Ammonia
NHA	National Highway Authority
NIOSH	National Institute for Occupational Safety and Health
NIPS	National Institute of Population Studies
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 Nitrate
PCTs	Pollution Control Techniques
PM	Particulate Matter
ppb	Parts per Billion
QGIS	Quantum Geographic Information System
RFO	Residual Fuel Oil
RMS	Root Mean Square
SFP	Slit function Parameter
USEPA	United States Environmental Protection Agency
UTC	Universal Time Centre
UV	Ultra Violet
VOCs	Volatile Organic Compounds
WHO	World Health Organization
WinDOAS	Windows Differential Optical Absorption Spectroscopy

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ABSTRACT

Air quality is an important environmental concern worldwide. National Environmental quality standards are implemented by regulatory authorities to improve the air quality on the bases of emission levels. US EPA defines 6 criteria air pollutants for the assessment of Air quality; Nitrogen Dioxide (NO₂) is one of them. The sources of NO₂ include emission from vehicles, power plants, lightning, soil emission etc. This study presents result of car MAX-DOAS field campaigns (2014-2015) conducted along national highways of Punjab. Main objectives of the field campaigns were to monitor NO₂ concentration level within and around major cities, and to identify the sources of NO₂ emissions. Result showed that the concentration of NO₂ varies in these cities e.g. 75×10^{15} molecules/cm² in Rawalpindi, 65×10^{15} molecules/cm² in Lahore and exceed the Pakistan National Environmental Quality Standards of 42.5 ppb. Furthermore, car MAX-DOAS results were compared with OMI observations. Result showed that OMI observations are largely underestimated especially over the urban centers of Punjab.

INTRODUCTION

1.1. Background

Recent economic growth in Pakistan has resulted in rapid urbanization, industrialization and vehicular growth. But it has also been responsible for releasing large amounts of different gaseous pollutants in the atmosphere. Also, the development is not quite uniform. A large amount of regional disparity exists in industrialization, population density, pattern of energy consumption, vehicular density and level of resource usage. Major industrial areas and major cities of Pakistan have been heavily polluted. To monitor the air quality is an essential step to characterize the air quality. WHO (World Health Organization), many regional and global environmental organizations used criteria pollutants to characterize the air quality of any place. Ozone, particulate matter, carbon monoxide, lead, nitrogen oxides and sulfur oxides are collectively termed as criteria pollutants (*US-EPA*). It was evaluated in 2010, greater than 51% of the world's population is living in the city limits, and it is not surprising to raise the number up to 61% by 2030 (*United Nations, 2009*). As a result of this hasty increase in the urban population, air quality requires a vital consideration in city areas, introducing new techniques and the developmental measures to reduce the air quality problems.

Introduction

Air pollution has become a potential threat to the environment and human health. All major cities of Pakistan are exposed to serious air pollution problems that need to be addressed so that its negative effects on human health and the environment are reduced. NO₂ is an important air pollutant. It is a strong oxidant and has been listed as a criteria pollutant by various environmental agencies (*US-EPA, 1990*). There has been a 5- fold increase in NO_x emissions since the pre-industrial era and the most rapid increase has been observed in Asia at the rate of 4-6% per year (*Garg et al., 2001; van Aardenne et al., 1999*). Sudden population increase and development in all aspects of life cause adverse impacts on environment and ultimately natural resources. (*Sheikh et al., 2007*).

Air pollution is the result of industrialization and population growth (*Aslam, 2012*). In major cities of Pakistan i.e. Islamabad, Rawalpindi, Gujranwala, Lahore and Karachi quality of air has deteriorated (*Lodhi-Pak-EPA, 2008*). Transport and industrial activities are the main causes of air pollution in urban areas of Pakistan, (*Ahmed et al., 2012; Jahangir et al., 2013; Ali et al., 2006; Khan et al., 2007, Hussain, 2010*). Level of NO₂ raised 25 times in Pakistan as

a result of increasing demand for energy, (*Khawaja et al., 2005*). Also, the air pollution causes the recurrent episodes of fog, mist and photochemical smog, (*Yasmeen et al., 2012, Muslehuddin et al., 2000*).

Vehicles and industrial plants are the major sources of air pollution in Pakistan, (*Ali et al., 2006; Zafar et al., 2012; Fenn et al., 2003*). Thus, it is necessary to monitor the air quality to identify the size and characteristics of pollutants into the atmosphere (*Shigeta, 2000*).

1.2. Pakistan National Environmental Air Quality Standards (Pak-NEQS) For Ambient Air

In Pakistan, the national environmental quality standards (Pak - NEQS) for individual air pollutants are given in the table 1.1.

Table 1.1: National Environmental Quality Standards for Ambient Air Quality

Pollutants units ($\mu\text{g}/\text{m}^3$)	Time-weighted average	Concentration in ambient air		Method of Measurement
		Effective from 1 st January 2009	Effective from 1 st January 2012	
Sulphur Dioxide (SO_2)	Annual Average	80	80	Ultraviolet Fluorescence Method
	24 hour Average	120	120	
Oxides of Nitrogen as (NO)	Annual Average	40	40	Gas Phase Chemiluminescence
	24 hour Average	40	40	
Oxides of Nitrogen as (NO_2)	Annual Average	40	40	Gas Phase Chemiluminescence
	24 hour Average	80 *(42.5 ppbv)	80 *(42.5 ppbv)	
Ozone (O_3)	1 hour	180	130	Non Dispersive UV Absorption Method
Suspended Particulate Matter (SPM)	Annual Average	400	360	High Volume Sampling (Average Flow rate not less than $1.1 \text{ m}^3/\text{minute}$)
	24 hour Average	550	500	
Respirable Particulate Matter (PM_{10})	Annual Average	200	120	B Ray Absorption Method
	24 hour Average	250	150	
Respirable Particulate Matter ($\text{PM}_{2.5}$)	Annual Average	25	15	B Ray Absorption Method
	24 hour Average	40	35	
	1 hour Average	25	15	
Lead (Pb)	Annual Average	1.5	1	AAS Method after sampling using EPM 2000 or Equivalent Filter Paper
	24 hour Average	2	1.5	
Carbon Monoxide (CO)	8 hours Average	5	5	Non Dispersive Infra Red (NDIR) Method
	1 hour Average	10	10	

GOP, Revised National Environmental Quality Standards for Ambient Air, S.R.O. 1062(I)/2010.

*Conversion is based on WHO conversion factor for Nitrogen Dioxide (NO_2) $1 \text{ ppbv} = 1.88 \mu\text{g}/\text{m}^3$

It is necessary to monitor these substances regularly, to assess the Pakistan's ambient air quality and to cope with rapidly growing problem of air pollution.

1.3. Study Area

The study area comprises of major cities along National Highways of Punjab and continuous point observation over IESE (Institute of Environmental Sciences and Engineering) National University of Sciences and Technology (NUST) Islamabad. The topography of this area greatly varies from the mountainous region to plain areas. Population density, movement and number of vehicles, industrial and development pattern also varied in the study area.

1.4. The Present Study

This research mainly focuses on monitoring NO₂ column densities along the National Highways of Punjab and continuous monitoring at IESE-NUST site in Islamabad. MAX-DOAS (Multi -Axis differential optical absorption spectroscopy) instrument is used in this research study. The device was set at IESE, H-12 Sector, Islamabad for continuous observations. Field campaigns were carried out along the national highways of northern Punjab. Subsequent analysis was performed using winDOAS, results of satellite and ground based observations were compared. This is discussed in detail in chapter 4. The ultimate objectives of this study were:

1. Nitrogen Dioxide (NO₂) concentration monitoring along National Highway of Northern Punjab.
2. To identify the potential sources of NO₂ emissions along the National Highway of Northern Punjab.
3. To compare the satellite observation for NO₂ concentration with Car-Max-DOAS measurements.

1.5. Expected Benefits from the Study

The results of this study will act as a guidance for further research in the field of air pollution monitoring. The results of this research study may guide to understand the contribution of various sources that effect the concentration of trace gases in the study area. The outcomes of this research work can be useful for other research institutions, non-governmental organizations (NGOs) and environmental agencies that are working on other aspects of air pollution such as health impacts, climate change mitigations as well as adaptations. It can provide guidance to policy-makers, decision-makers and regulatory authorities, to comply with the effective execution of current standards. Comparison of satellite observations with car MAX - DOAS results over study area will allow to contain the sources of emissions of NO₂ over the selected area as well as cross-border sharing regions. Once potential sources of air

pollution identified, effective methods of pollution control (PCTs) may be suggested to overcome the problems of air pollution in Pakistan.

LITERATURE REVIEW

This section provides an overview of all work associated with atmospheric NO₂ required to frame this research project. It includes NO₂ cycle, impacts of NO₂ and its chemistry in the atmosphere. The local, regional, and global transport emissions as well as fate of NO₂ in the atmosphere is also presented in this chapter along with in situ and remote monitoring techniques of NO₂.

2.1. Atmosphere

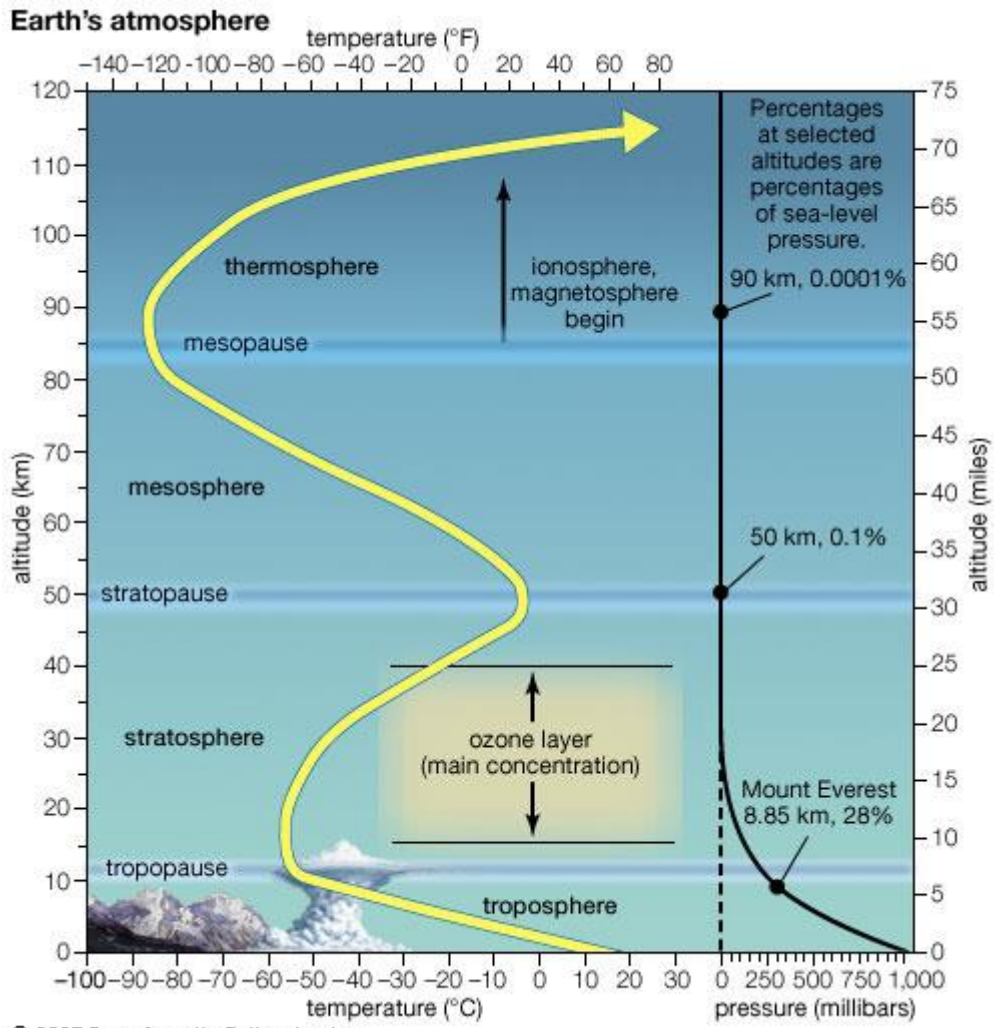
Atmosphere is composed of a thin layer of various gases surrounding the Earth. As altitude increases, the density decreases. The boundary between the atmospheric layers and outer space is not well defined, but atmospheric thickness is around 100 km. (Seinfeld and Pandis, 2006). Vertically, these layers are formed by variation of temperature with altitude. The first layer nearest to the surface of the Earth is the troposphere. Its thickness is about 10-15 kilometers. Weather patterns on earth are determined by the conditions present in this layer. The name is derived from the Greek word “tropes” which means “mixture “. This layer is important in air quality analysis as the contaminant dispersion occurs in this layer. This layer may benefits in dilution of different pollutants as the adverse effects could be reduced to local level. While on the other hand, this may also lead to air pollution problems because air pollutants move from an area of high concentration to an area of low concentration. The stratosphere is the second layer and extends to 50 km. Both layers make up 99% of air mass and are of great importance from the environmental point of view. (Khokhar, 2006).

The atmosphere consists mainly of nitrogen and oxygen along with certain other gases mainly argon. These three species make up more than 99.9% of the atmosphere. The rest of the 0.1% consists of water vapors, carbon dioxide (CO₂), methane (CH₄), noble gases and other trace constituents (Seinfeld and Pandis, 2006).

2.2. Pressure and Temperature Vertical Profiles

Figure 2.1 represents temperature profile along with pressure curve. In the troposphere, the temperature decreases with altitude and tropopause (at the top of the troposphere) is the point where the air stops cooling with altitude.

Above the troposphere is the stratosphere containing the ozone layer, which extends up to nearly 20 kilometers. The temperature increases with altitude in the stratosphere. Stratopause is the boundary between stratosphere and mesosphere. It is the region where maximum temperature occurs. Above stratopause the mesosphere occurs where again the temperature decreases with altitude. It extends up to 85 kilometers where mesopause occurs above which is the thermosphere. In the thermosphere, temperature increases with altitude due to absorption of ultraviolet (UV) solar radiation by species such as N_2 and O_2 .



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Figure 2.1: Atmospheric Layers of the Earth. Yellow curve indicating a usual vertical trend of temperature, while the black curve indicating the pressure profile

2.3. Atmospheric Trace Gases

Atmospheric trace gases are low in concentration, but play a very significant role in air quality issues. Today's major environmental concerns such as climate change, acid precipitation, ozone depletion and smog formation in developed areas are because of trace gases. Man-made activities have altered the atmospheric composition in recent years especially increased levels of greenhouse gases.

Tropospheric ozone (O_3) is mainly produced by photochemical oxidation of NM-VOCs (methane and non-methane volatile organic compounds) that occurs in the presence of NO_x and CO. Greenhouse effect is also triggered by the presence of tropospheric O_3 . The process of chemical ozone depletion is caused by the species possessing longer lifetime like CH_4 , N_2O , halocarbons and their breakdown products that even diffuse in the stratosphere.

Air quality and climate are interconnected. Any change in atmospheric chemistry can affect the weather and vice versa. Atmospheric changes can modify the impact of radiative forcing and lifetime of greenhouse gases and the ozone layer distribution. (*Forster et al. IPCC, 2007*).

VOCs other than methane plays a vital role in ozone production, and significantly effects the troposphere's oxidizing capacity. NMVOCs plays a vital role in SOA (secondary organic aerosols) formation (*Kanakidou et al., 2005*). Hence they have significant impact on tropospheric composition (*Houweling et al., 1998*).

2.4. A Key Criteria Pollutant: Nitrogen dioxide (NO_2)

Nitrogen dioxide (NO_2) is reddish brown in color with pungent odor and also absorbs lights. The most common contamination due to Nitrogen dioxide is photochemical smog Nitrogen dioxide is produced from various sources like burning of fossil fuel, coal, fuel burning in automobiles, industrial process and lightning. The major cause of NO_2 (air pollution) is tremendous increase in vehicular number throughout the world. (*Lundy et al., 2011, Han et al., 2006*)

The most prominent trace gas in atmosphere is nitrogen dioxide. The natural source of nitrogen dioxide is lightening in the troposphere and sometimes stratosphere. Nitrogen dioxide plays a vital role in the tropospheric and stratospheric chemistry of the atmosphere and has significant role in ozone depletion. (*Lamarque et al., 1996*).

2.4.1 Sources of Nitrogen Dioxide

The atmosphere is mainly composed of 78% of nitrogen gas followed by oxygen which is 21%. This 78% of nitrogen gas cannot be used by plants as it is present in inert/unreactive form, to use this nitrogen gas, it has to transform into different inorganic forms mainly nitrites (NO_2), nitrates (NO_3) and ammonia (NH_3). Nitrogen dioxide is produced from both natural and anthropogenic sources. Natural sources are biological growth, forest fire, lightening and decay. The most common anthropogenic sources are industrial activities, vehicular exhaust and coal burning. Figure 2.2.

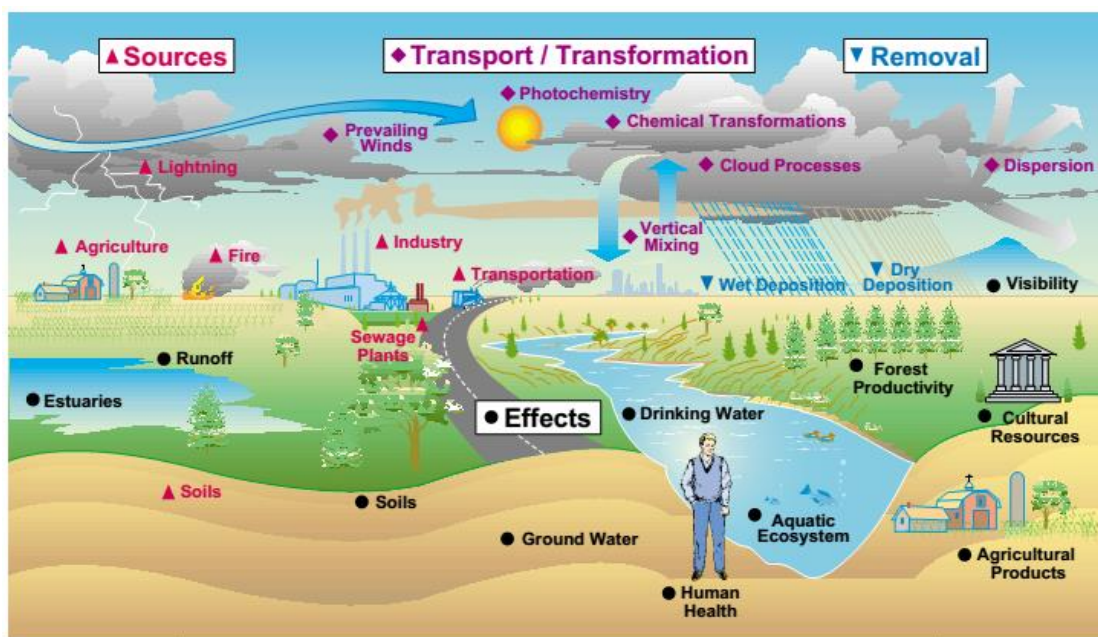


Figure 2.2: Tropospheric Nitrogen Cycle

*Source (National Science and Technology Council Committee on Environment and Natural Resources, Air Quality Research Subcommittee, 1999).

NO_x exists in various forms which include (even less than 9%) nitrous oxide, nitric oxide and nitrogen dioxide. Nitrogen dioxide production is directly proportional to temperature as with the increase in temperature nitrogen dioxide production also increases. Agriculture activities also play a vital role in nitrogen dioxide emissions especially fertilizers that convert nitrogen dioxide to nitrous oxide. The life time of NO_2 ranges from hours to few days. (Seinfeld and Pandis, 2006; Jaeglé et al., 1997) (Crutzen et al., 1979; Takegawa et al., 2003).

2.4.2. NO_x Cycle

The rapid cycling between NO and NO₂ due to oxidation and photo catalytic reactions is the basic part of NO_x cycle. This conversion takes place in few minutes and these species (NO+NO₂) are together known as NO_x. This step is also known as the null cycle.



Net Reaction:



The sink for NO_x is its conversion into HNO₃ by oxidant OH:



The NO_x is lost at night by oxidation of NO₂ by Ozone and consequent change of the NO₃ to N₂O₅:



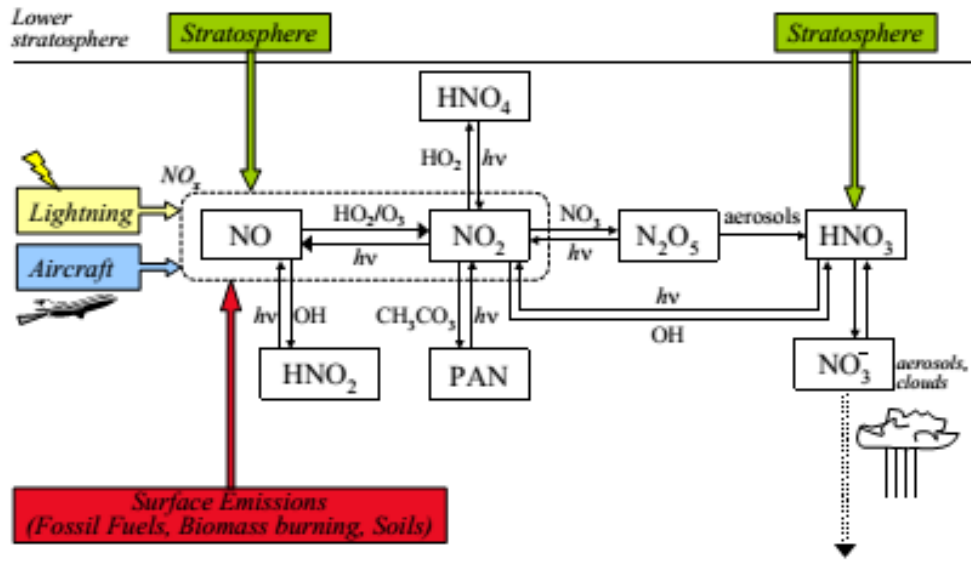


Figure 2.3: The NO_x Cycle

N₂O₅ is formed only at night, because NO₃ and NO₂ are available during night time whereas during day time NO₃ is photolyzed to NO₂.



NO_x oxidation, results in N₂O₅ and HNO₃, both have long retention times in the atmosphere. During daytime, these species are ultimately transformed back to NO_x.



Nitrous Oxide (N₂O) is produced both from natural as well as anthropogenic sources. Its retention time is long which allows it to be transported to the stratosphere. Therefore, HNO₃ and N₂O₅ serve as reservoirs for NO_x. The final removal of NO_x takes place in the troposphere in the form of HNO₃ by acid deposition.

2.4.3. Impacts of Nitrogen Dioxide

Nitric oxide is the most abundantly emitted oxide of Nitrogen in the atmosphere, it is harmless, but changes into NO₂ in the air. Mostly higher concentration of NO₂ is poisonous to plants, it can harm the leaves and reduce the growth of plants and performance. Nitrogen Dioxide may also cause adverse effects even at lower concentrations but in the presence of ozone and SO₂. Being a component of photochemical smog, NO₂ also act as a precursor in the production of photo chemically produced O₃.

2.4.3.1. Health Impacts

Nitrogen dioxide affects respiratory system of living organisms. The risk of respiratory disease such as malfunctioning increases at old age by inhaling specific amount of nitrogen dioxide. Hospital admissions and high mortality rate due to respiratory diseases are associated with nitrogen dioxide pollution.

Many experimental studies reported that the dose of NO₂ concentration equal/greater to 100 ppbv can cause significant health impacts on humans and animals due to its poisonous nature. Exposure to NO₂ levels greater than its current levels of air pollution have larger effects on health. (*WHO, 2003*).

2.4.3.2. Environmental Impacts

Environmental impacts of Nitrogen oxide family are discussed below:

2.4.3.2.1. Ozone at Ground Level and Photochemical Smog

Ground level or "bad" ozone is not released directly into the air, but it is produced by chemical reactions between nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the presence of sunlight. Tropospheric ozone reacts with particulate matter (PM) and produces photochemical smog. Nitrogen dioxide produces secondary particles called nitrates which result in haze and also reduce visibility. The brown haze of urban cities is due to the accumulation of NO₂ on cities.

2.4.3.2.2. Acid Rain

NO₂ reacts with hydroxyl ions and produces HNO₃/HNO₂. Acid rain acts as a sink for nitrogen oxides. It has adverse effects on human health, environment and infrastructure, around 60 ppbv of nitrogen dioxide disallows the development of plants. NO₂ produces acids and their high destructive for construction material.

2.5. Remote Sensing and DOAS

Both in situ techniques (sampling) and remote sensing techniques can be used for the measurement of atmospheric parameters and elements. Remote sensing is a native to investigation and exploration for military purposes.

With the passage of time it has been embraced for science issues, initially with the monitoring of the ozone layer (*Dobson and Harrison, 1926*), then its expansion to understand the different aspects of environmental issues.

Trace gases can be monitored from both satellite platforms and from the ground based spectroscopic observations. Different spectroscopic approaches can be applied to observe the quality of ambient air. All these procedures have varied to some extent, but they are built on the “The Lambert Beer Law” which illustrates the link between matter and light. Diverse trace gases have been observed by Differential Optical Absorption Spectrometry (DOAS) (*Platt and Perner 1979; Cheng and Chan, 2004; Kim and Kim, 2001*)

2.5.1 Active and Passive DOAS

MAX - DOAS is a Passive DOAS technique that is used to monitor the different tropospheric trace gases (*Sinreich et al., 2005*). In fact it has been applied for tracking various trace gases, such as BrO, HCHO, NO₂, SO₂ and CHOCHO (*Wagner et al., 2011*). Both active and passive techniques are utilized for spectroscopic observations but these are expensive and complicated as compared to other techniques that are used to monitor the NO₂.

2.5.2. DOAS

DOAS is a type of remote sensing equipment that observes trace gases that occur in the UV visible region. It is widely used in in the field of atmospheric science. It can be used to observe various molecules such as NO₂, O₃, HCHO, H₂O, O₄, and SO₂.

The basic principle of absorption measurements is the Lambert-Beer law: the reduction of electromagnetic radiation is correlated to the amount of absorbing particles in the optical path,

$$I(\lambda) = I_o(\lambda) e^{-\alpha L C} \quad (\text{Eq.2.1})$$

Where

“I_o” = incident flux,

“I” = the measured flux,

“α” = absorption cross section of the targeted species,

“L” = distance over which the absorption takes place,

“C” = concentration of the absorbing species (or density).

The existence of different gases, aerosols and scattering processes limit the use of Lambert Beer law. DOAS allows us partly, to overcome the limitations particularly the scattering process. DOAS Principle is shown in Figure. (For details see *Platt, 1994*)

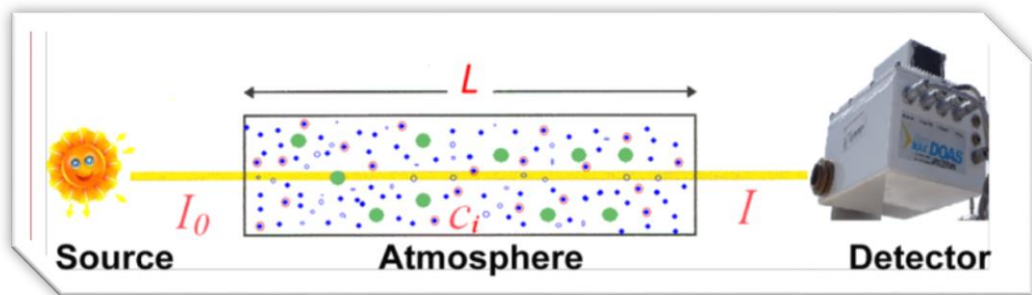


Figure 2.4: Illustration of DOAS Principle

Keeping the scattering processes in considerations the DOAS equation becomes:

$$I(\lambda) = I_o(\lambda) \cdot \exp\left(-\int_0^L \left(\epsilon_R(\lambda, l) + \epsilon_M(\lambda, l) + \sum_i \sigma_i(\lambda, p, T) \cdot c_i(l)\right) dl\right) \quad (\text{Eq.2.2})$$

$I(\lambda)$: Intensity of light after absorption through the atmosphere

$I_o(\lambda)$: Intensity of the light source

λ :	Wavelength
$\varepsilon_R(\lambda, l)$:	Coefficient of Rayleigh scattering
$\varepsilon_M(\lambda, l)$:	Coefficient of Mie scattering
$\sigma_i(\lambda, p, T)$:	Absorption cross-section of the absorber i
$c_i(l)$:	Concentration of the absorber i
p :	Pressure
T :	Temperature
L :	Light path length

The DOAS technique divides the trace gas absorption cross-sections into two parts.

$$\sigma(\lambda) = \sigma_b(\lambda) + \sigma'(\lambda) \quad (\text{Eq.2.3})$$

σ_b = broadband scattering and absorption,

σ' = differential absorption cross-section,

The exponent in the Beer-Lambert Law is split into two parts; one changing “slowly” with wavelength and scattering, and other giving a strong dependence on the wavelength due to narrow-band trace gas absorption. The Beer-Lambert Law can now be written as:

$$I(\lambda) = I_0(\lambda) \cdot \exp\left(-\int_0^L \left(\varepsilon_R(\lambda, l) + \varepsilon_M(\lambda, l) + \sum_i \sigma_{b,i}(\lambda) \cdot c_i(l)\right) dl\right) \cdot \exp\left(-\int_0^L \left(\sum_i \sigma'_i(\lambda) \cdot c_i(l)\right) dl\right) \quad (\text{Eq.2.4})$$

Figure 2.5 shows the contribution of scattering processes to the attenuation of radiation in the atmosphere. Aerosol scattering and Rayleigh scattering show broadband extinction only, while trace gas absorption causes narrow and broadband extinction.

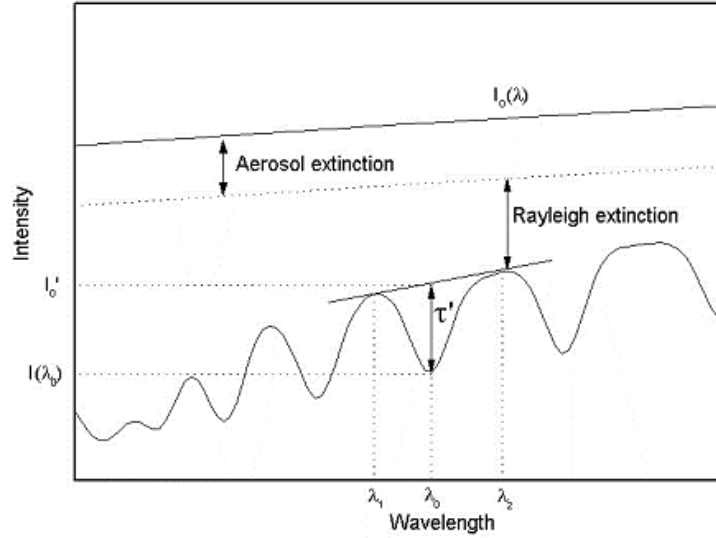


Figure 2.5: Attenuation of radiation in the atmosphere

The broadband part of Eq. 2.4 is then merged with the initial light intensity I_0 to form the differential baseline intensity I_0' .

$$I_0' = I_0(\lambda) \cdot \exp\left(-\int_0^L \left(\varepsilon_R(\lambda, l) + \varepsilon_M(\lambda, l) + \sum_i \sigma_{b,i}(\lambda) \cdot c_i(l)\right) dl\right) \quad (Eq.2.5)$$

Now, the Beer-Lambert Law can be formulated in differential form applied by the DOAS technique.

$$\tau'(\lambda) = \ln\left(\frac{I_0'(\lambda)}{I(\lambda)}\right) = \int_0^L \left(\sum_i \sigma_i'(\lambda) \cdot c_i(l)\right) dl \quad (Eq.2.6)$$

$\tau'(\lambda)$ is referred to as the differential optical density, and can be considered as a result of DOAS measurement.

Lambert Beer law is the basic principle for the absorption measurements, “the reduction of electromagnetic radiation is correlated to the amount of absorbing particles into the optical path”

2.6. Recent Studies on NO₂ Pollution using Car-MAX-DOAS

Wagner et al., 2010, retrieved NO₂ VCD by using MAX-DOAS observations from Brussels to Heidelberg in September, 2006. Elevation angles of 22°, 40°, and 90° were adjusted for observation. OMI satellite data was used for the validation of car Max-DOAS observations which showed, “The comparison with OMI satellite observations yields fair agreement i.e. satellite observations are 25 to 100% larger than the Auto-MAX-DOAS observations”.

Shaiganfar et al., 2011, retrieved NO₂ VCD's by using car MAX-DOAS in two months (April 2010 and January 2011) in the capital of India (New Delhi). The concentration of NO₂ was linked to traffic crowding and other sources present in the study area. Max DOAS results for NO₂ emissions were validated with satellite observations.

Constantin et al., 2011, monitored Nitrogen Dioxide in the southeastern area of Romania, for two consecutive months of July and August in 2011. Industrial areas and busy roads were selected in this study. According to this study iron and steel industries were the main sources of higher NO₂ emissions in cities, high traffic was the main cause for high NO₂ concentration along the ring roads and within cities around South East cities of Romania.

Kanya et al., 2014, retrieved NO₂ VCD by Max-DOAS at seven sites, in China, Japan, Korea and Russia. In this study it was observed that “Mean diurnal variation of nitrogen dioxide trend decrease during daytime and during weekends.

2.6.1. Recent Studies on NO₂ Pollution Monitoring in Pakistan

Transportation, Power plants and industries contributed almost 70% of NO₂ pollution in Pakistan (*GOP/IUCN, 1992*). Vehicles rate of growth had evaluated 33.61% per annum in Pakistan from 1995 to 2005 (*Ilyas et al., 2007*), which has deteriorated the quality of ambient air.

Pak-NEQS executed but monitoring of air quality has been ignored in Pakistan. NO₂ is also included in the list of criteria Pollutants. A research study was conducted in 2000 by Pakistan Environmental Protection Agency (Pak-EPA) and Japan International Cooperation Agency (JICA) to evaluate the condition of ambient in three cities of Pakistan, (Lahore, Rawalpindi, and Islamabad). In this study Sulphur Dioxide, Carbon Monoxide, Ozone, Nitrogen Oxides, Particulate Matter and Hydrocarbons (collectively termed as criteria pollutants) were monitored. Traffic jam was the main reason for higher concentration of NO_x in these cities.

Research shows that Lahore is the most polluted city of Pakistan with respect to air quality. (JICA, 2000).

Ali et al., 2006, observed the quality of ambient air beside different divisions of N-5 highway. Diverse sampling methods were applied to observe the criteria pollutants and Noise Level. Highest NO_x level was found along Lahore – Gujranwala Section of N-5 Highway.

Zafar et al., 2012 observed NO₂ concentration at different sites of Islamabad and Rawalpindi. This study was completed in two phases, in first phase observations were taken in the winter whereas during second phase observations were taken in the spring season. The concentrations of NO₂ were linked or associated with traffic jamming and industrial processes within twin cities.

Jahangir et al., 2013 observed NO₂ level close to the public and private sector hospitals in twin cities (Rawalpindi and Islamabad). Concentrations of NO₂ were found higher in those hospitals which are situated along the busy roads as a result of regular traffic jamming.

C-CARGO has taken initiative as a pioneer group for air quality monitoring at National University of Sciences and Technology (NUST) using Mini MAX-DOAS. *Mehdi et al., 2013* observed NO₂ concentration within twin cities (Rawalpindi/Islamabad) by using Car MAX-DOAS. *Nisar et al., 2013*, observed NO₂ and Formaldehyde (HCHO) concentration with MAX-DOAS at Institute of Environmental Sciences and Engineering (IESE), NUST. *Shabbir et al., 2013*, observed concentration of NO₂ along N-5 Highway. *Fatima et al., 2013*, developed database for NO₂ concentration from satellite observation using SCIAMACHY (2002 – 2012) OMI (2004 – Present) and GOME-2 (2007 – Present) to check spatial and temporal trend of NO₂ pollution over Pakistan. In this study concentration of NO₂ was observed highest in winter and over urban areas of Pakistan.

INSTRUMENTATION AND METHODOLOGY

Mini MAX-DOAS Instrument:

The instrument Mini - MAX - DOAS is used on a mobile platform (named car MAX- DOAS) (Bobrowski *et al.*, 2003). The dimensions are 13cm x 14cm x 19cm, because it is light weighted and fully automated spectrometer. The entrance optics is controlled by a closed aluminium box which contains a fiber joined spectrograph. A stepper motor control the elevation of the viewing angle by rotating the entire instrument. A quartz lens 40mm focal length is present at the optical input. A spectrometer (USB2000+, Ocean Optics Inc.) is used to disperse light. The spectral range of instrument is from 320–460 nm with a resolution of 0.7 nm. DOASIS software installed on a laptop with Windows XP operating system was used for field measurements (Kraus, 2006).

3.1. Measurements at IESE NUST Site:

Point based observations of NO₂ concentrations were started from April 2014 to July 2015 on a daily basis from dawn to dusk over IESE (Institute of Environmental Sciences and Engineering), National University of Sciences and Technology, Islamabad. Elevation angles of 2°, 4°, 5°, 6°, 10°, 15°, 30°, 45° and 90° were used to take solar irradiance spectra. The time period of nine minutes for a cycle of viewing angles was chosen as one minute per measure/spectrum. The internal temperature for MAX-DOAS was set at 15°C to take observations. Wind speed and wind direction are considered as an essential parameters for the quantification of different air pollutants. So, wind data was collected from Air Resources Laboratory (ARL), (NASA's freely available meteorological data) during entire study. <http://ready.arl.noaa.gov/READYamet.php>.

3.2. Field Campaigns along National Highways of Punjab:

The Mini-MAX-DOAS was fixed on the roof a van and field campaigns were conducted to monitor the NO₂ concentrations along National Highways of Punjab. Field campaigns were completed in three phases. In first phase field campaigns were conducted within twin cities (Islamabad/Rawalpindi). The first field campaign was conducted on November 12, 2014 from IESE (Institute of Environmental Sciences and Engineering) NUST, Islamabad to Rawalpindi (Faizabad). In this field campaign some major points of Islamabad, such as Margalla Railway

Station, Zero point and Karachi Company were covered. On next day November 13, 2014 field campaign was conducted from IESE (Institute of Environmental Sciences and Engineering) NUST, Islamabad to Rawalpindi (Faizabad). In this campaign high traffic areas within Rawalpindi city were covered such as N-5 Highway, Gulistan colony (near Attock oil refinery), Airport choke and Faizabad.

A second phase was done from February 17, 2015 to February 19, 2015. On first day of 2nd phase (February 17, 2015), field Campaign was conducted from Islamabad to Kamoke (Gujranwala). In this field campaign major cities along National Highway such as Rawalpindi, Gujar Khan, Sohawa, Dina, Sarai Alamgir, Kharian, Gujrat and Wazirabad were also covered. On February 18, 2015, field campaign was conducted from Lahore to Jaranwala (Faisalabad). In this field campaign major points within Lahore city and other cities along National Highway like Sheikhpura, Shahkot and Sangla Hill were observed. On the third day of the 2nd phase, field campaign was conducted from Faisalabad to Nowshera virkan (Gujranwala). In this field campaign major points within Faisalabad city and other cities along National Highway like Jaranwala, Sangla Hill, Shahkot, Sheikhpura and Nowshera virkan were observed.

The third phase was completed from February 23, 2015 to February 28, 2015. On the 23rd February, field campaign was conducted along Motorway from Islamabad to Kot Momin (Sargodha). On February 24, 2015 field Campaign was conducted along National Highway from Faisalabad to Shorkot via Jhang. On February 25, 2015 field campaign was conducted from Multan to Muzaffargarh. At the start Multan city was encircled, then Muzaffargarh along the National Highway was covered. On the 26th February, field campaign was conducted from Dera Ghazi Khan to Kot Adu via Taunsa Sharif along the National Highway. On February 27, 2015 field campaign was conducted from Taunsa Sharif to Khanewal, covering other cities along National Highway i.e. Kot Addu, Muzaffar Garh, Multan and Kabirwala. On February 28, 2015 field campaign was conducted from Okara to Lahore covering other cities along National Highway i.e. Renala Khurd and Pattoki. The instrument was adjusted in a position at which its lens was observing in backward direction. Most of the field campaigns were conducted in sunny days. For Field campaigns elevation angles were selected as 30°,30°,30°,30°,30°,30°, and 90°. Angles of higher elevation were selected to overcome the influence of buildings and trees in Car MAX-DOAS measurements. To calculate the tropospheric AMF, angles of 30° are preferred due to their effectiveness. (*Wagner et al. 2010*). The integration time of one minute for each spectrum was chosen. Car MAX-DOAS set up was connected to a laptop and a power of 12 volts was supplied to the motor of MAX-DOAS by a

lead battery. The source of continuous power supply for laptop and instrument was also arranged for every field campaign.

3.3. Differential Optical Absorption Spectroscopy Intelligent System (DOASIS)

DOASIS is an essential software that is utilized to run the mini MAX-DOAS instrument and to record the observed spectra as displayed in figure 3.1. There is a list of functions that are controlled by DOASIS i.e. integration time of spectrum, movement of stepper motor, the internal temperature of the spectrometer and calculation of Ring Spectrum.

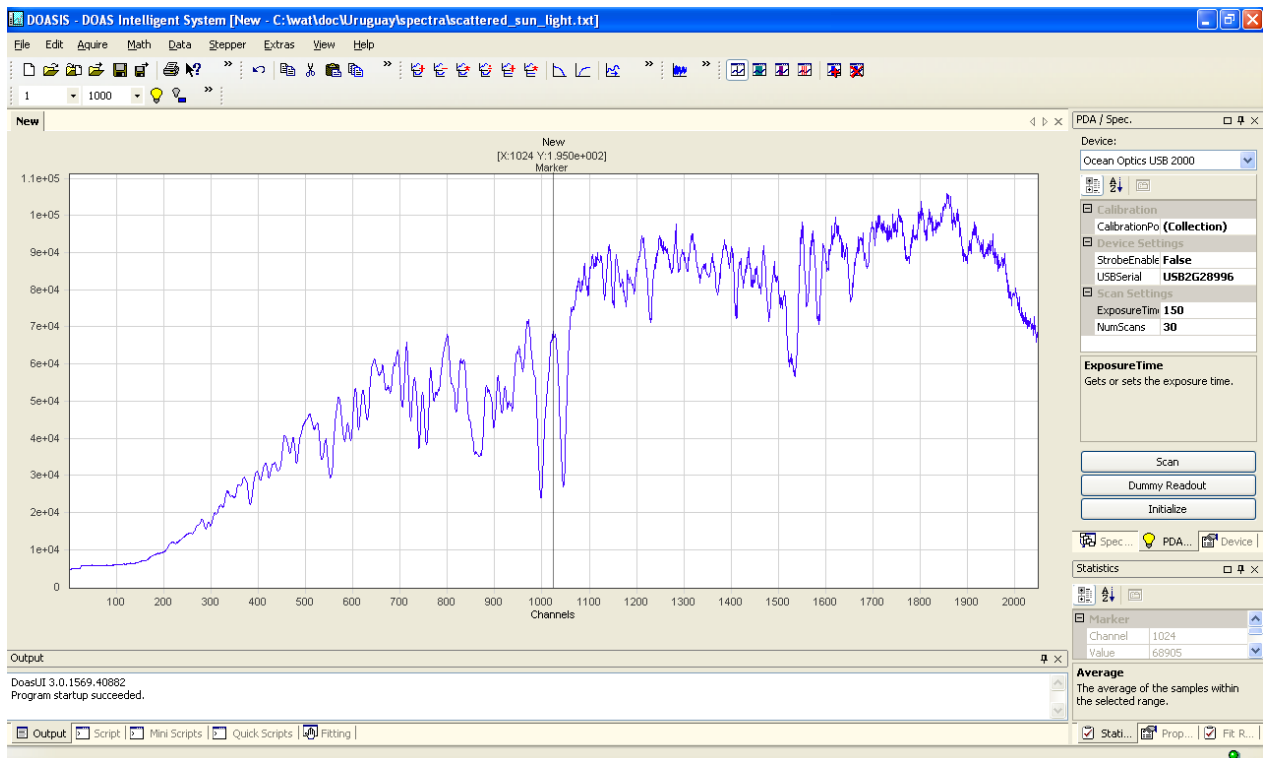


Figure 3.1: A DOASIS Window

Dark current and offset for Spectrometer are also measured by DOASIS which are used as a zero correction for the recorded spectra. Dark current and offset are the measurements of spectrometer, which are taken in the absence of sunlight or in the dark.

3.4. Windows Differential Optical Absorption Spectroscopy (WinDOAS)

WinDOAS (Windows Differential Optical Absorption Spectroscopy) software was used to analyze the recorded spectra for the retrieval of differential slant column densities. (*Platt and Stutz, 2008, Fayt and van Roozendael, 2001*). For the calibration of wavelength, a high resolution solar spectrum was used (*Kurucz et al., 1984*). In this research study 411-450 nm

fitting interval was chosen for NO₂. List of cross sections of trace gases, which are used for DOAS fit was; NO₂ at 298K (*Vandaele et al., 1996*), NO₂ at 220K (*Vandaele et al., 1996*), H₂O Hitran (*Rothman et al., 2005*), O₃ at 223K (*Bogumil et al., 2003*), O₄ Hermans (*Hermans et al., 1999*). In WinDOAS analysis, a Reference Spectrum recorded at noon, a polynomial of fifth order and a Ring Spectrum calculated by using DOASIS were also included.

Some major steps for NO₂ analysis, in which WinDOAS is utilized are following:

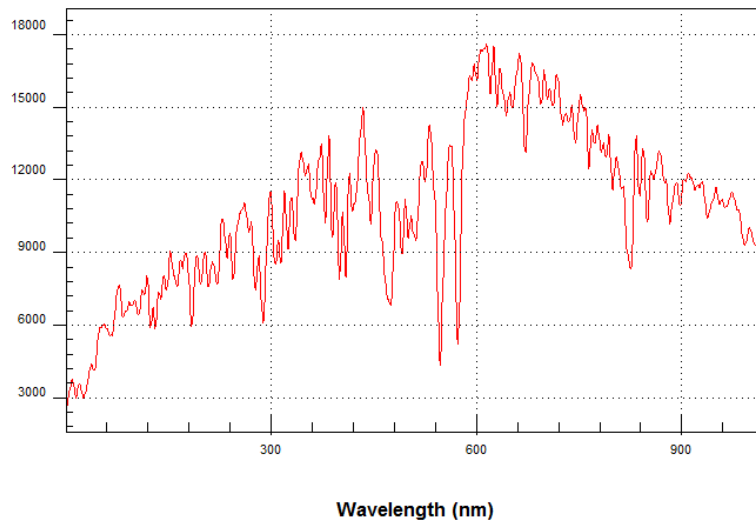
1. Pre-Calibration
2. Wavelength Calibration
3. Wavelength Convolution
4. NO₂ Analysis Window

Pre-Calibration:

First a measured spectrum, which was used for calibration, was selected (e.g. a zenith spectrum during noon). This spectrum was used later as Fraunhofer reference spectrum.

The selected spectrum was corrected for offset and dark current and it was saved as ASCII file. Then, it was displayed (e.g. in EXCEL) as a function of pixel number (for Mini MAX-DOAS measurements: 2048 pixels). The ASCII file can easily be created with WINDOAS: just browse the selected spectrum; then use the right mouse button and chose the option: save as ASCII'. By this procedure the spectrum is also corrected for offset and dark current (if the dark current and offset spectra were correctly selected in WINDOAS before (section 'instrumental')).

No calibration file was selected in WINDOAS before browsing the spectrum (menu: ‘instrumental’). Then the first column directly contains the pixel number.



Example for a measured spectrum (at 90° elevation around noon) displayed as function of the pixel number. (The axis label with ‘wavelength’, but actually pixel number is displayed).

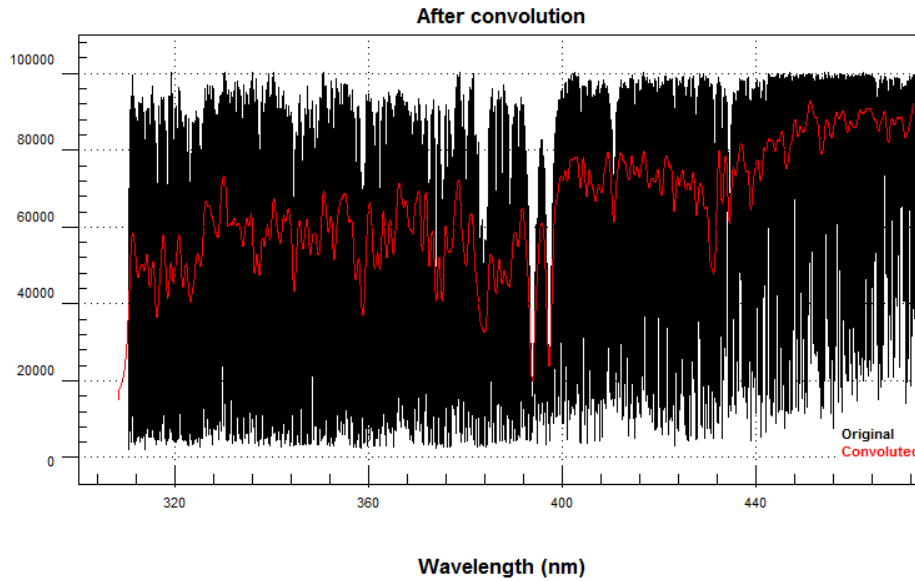
Note: (Special case if the signal to noise ratio of the measured spectrum is poor, then the features of the Fraunhofer lines are masked by noise. In such cases the precalibration is difficult. Thus the spectrum should be smoothed before the precalibration is done. The smoothing can be done by using the convolution tool. In such case reference spectrum should be convoluted by selecting the reference spectrum as input file as well as a calib file).

Then a high resolution solar spectrum was convoluted using an approximate FWHM corresponding to the own measurements. (For Mini-MAX-DOAS measurements typical values of the FWHM are between 0.5 and 2 nm). The convolution was done with WINDOAS. For this purpose a calibration file was created. It covers the approximate wavelength range of the own measurements. For Mini MAX-DOAS measurements in the UV and blue spectral range, the spectral range of the calibration file was chosen between about 300 nm and 470 nm. The calibration file contains only one column: the wavelength in steps of about 0.05 nm.

The calibration file was used to convolute the high resolution solar spectrum in WINDOAS. As slit function a Gaussian function the FWHM was about 0.7 nm.

	A	B
1	300	
2	300.05	
3	300.1	
4	300.15	
5	300.2	
6	300.25	
7	300.3	
8	300.35	
9	300.4	
10	300.45	
11	300.5	
12	300.55	
13	300.6	
14	300.65	
15	300.7	
16	300.75	
17	300.8	
18	300.85	
19	300.9	
20	300.95	
21	301	
22	301.05	
23	301.1	
24	301.15	
25	301.2	
26	301.25	
27	301.3	
28	301.35	

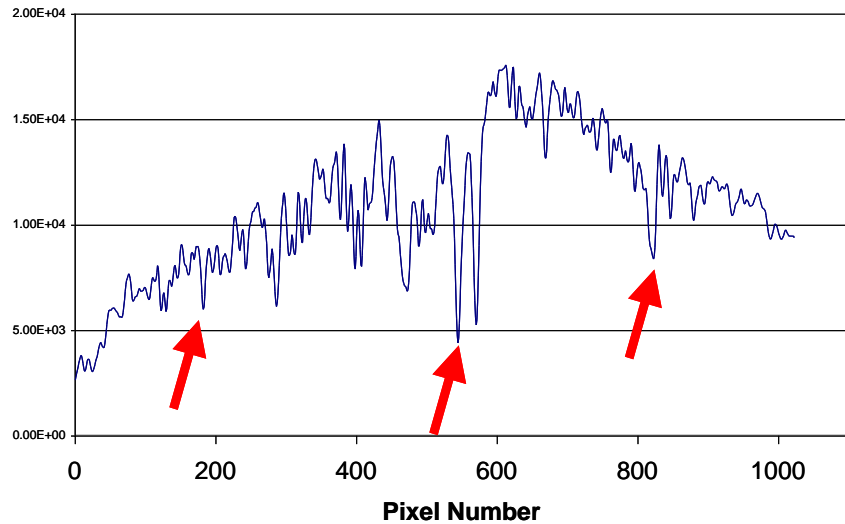
This figure shows the first lines of a calibration file (starting with 300 nm and ending at 472 nm (not shown here))



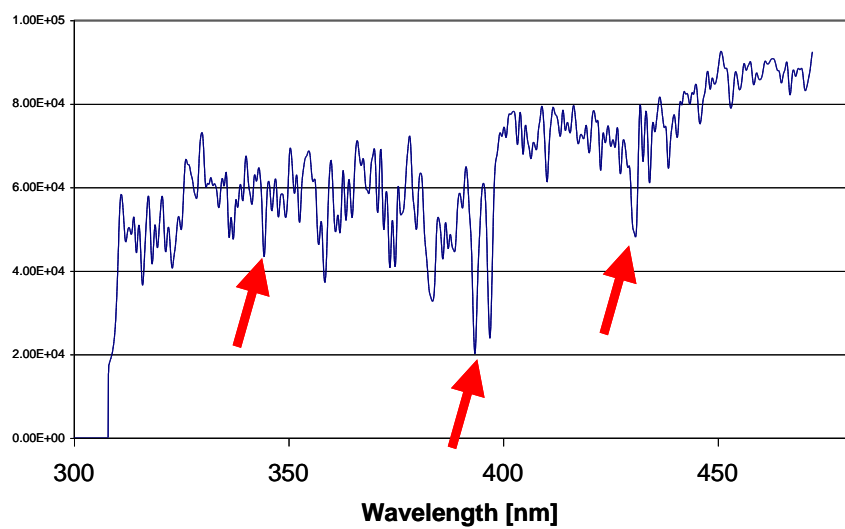
Example of a convoluted high resolution solar spectrum (FWHM was chosen as 0.7 nm).

Display the measured spectrum (as function of pixel number) and the convoluted sun spectrum (as function of wavelength). (Make sure that the wavelength is displayed in the following format: 329.85, but not as 3.29e3). For each Fraunhofer line, a pixel number was selected from the measured spectrum, and the wavelength from the convoluted solar spectrum. (See example below on the next page)

Measured spectrum



Convolved solar spectrum

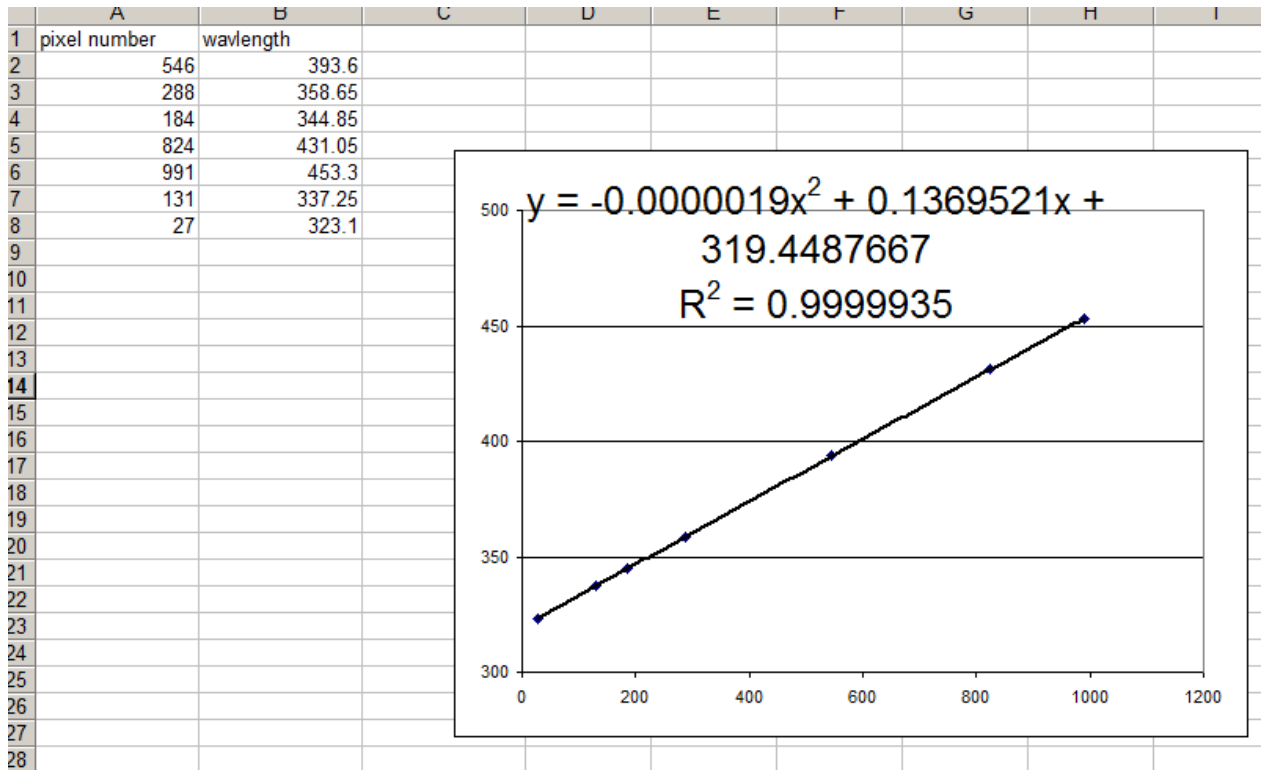


Then a table was created having two columns:

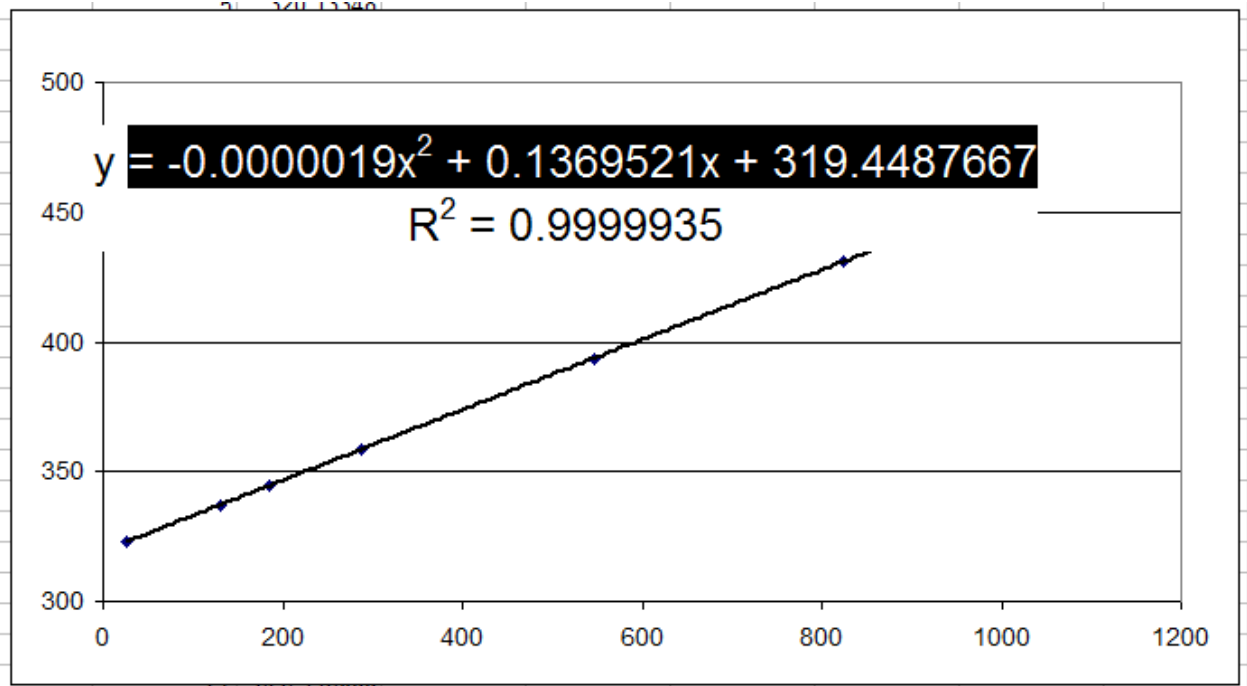
First column: pixel number of a selected Fraunhofer line

Second column: wavelength of the selected Fraunhofer line

Two digits were written after the decimal point for wavelength.



Whole wavelength range of instrument was covered, that means data points at small pixel numbers (e.g. around 100) as well as at high pixel numbers (e.g. 1900) and in between. Then the wavelength was plotted versus the pixel number, and a second order polynomial is fitted to the data points. The EXCEL option was chosen to display the polynomial formula in the diagram. It was confirmed that all points lie exactly on the curve of the fitted polynomial, and that R^2 value was very close to one (0.999). Then a new ECXEL sheet was opened, pixel numbers were taken in the first column (for Mini-MAX-DOAS in the range from 1 to 2048). Polynomial formula was copied into the second column of the EXCEL sheet. Polynomial formula was displayed in ‘scientific format’ with 6 digits after the decimal point. Then polynomial formula was marked with the cursor like in the figure below. (Formula was copied **without** the ‘y’ on the left side).



‘Control-c’ command was used to copy the polynomial formula and ‘control-v’ command to insert the polynomial formula in the second column of the EXCEL-sheet. (see figure below)

	A	B	C	D	E
1	1	= -0.0000019x ² + 0.1369521x + 319.4487667			
2	2				
3	3				
4	4				
5	5				
6	6				
7	7				
8	8				
9	9				
10	10				
11	11				

Then the formula was changed in the following way:

-replace the ‘x2’ with ‘*a1^2’

-replace the ‘x’ with ‘*a1’

The EXCEL sheet should look like:

	A	B	C	D	E	F
1	1	319.585717				
2	2					
3	3					
4	4					
5	5					
6	6					
7	7					
8	8					
9	9					
10	10					

Then it was insert in to the whole column B as given below.

	A	B	C	D
1	1	319.585717		
2	2	319.722663		
3	3	319.859606		
4	4	319.996545		
5	5	320.13348		
6	6	320.270411		
7	7	320.407338		
8	8	320.544262		
9	9	320.681182		
10	10	320.818098		
11	11	320.95501		
12	12	321.091918		
13	13	321.228823		
14	14	321.365724		
15	15	321.502621		
16	16	321.639514		
17	17	321.776403		
18	18	321.913289		
19	19	322.050171		
20	20	322.187049		

Then the second column (column B) was saved as ASCII file. This file is the pre-calibration file.

The easiest way to save it with only one column is to copy the second column in the first column of a new EXCEL sheet using the right mouse button, 'paste special', then select

'values'. Then, save the file as ASCII file (text file with space). (It was confirmed that the format of the column is acceptable (see example below) :

-format of column: 'number' with 3 digits after the decimal point

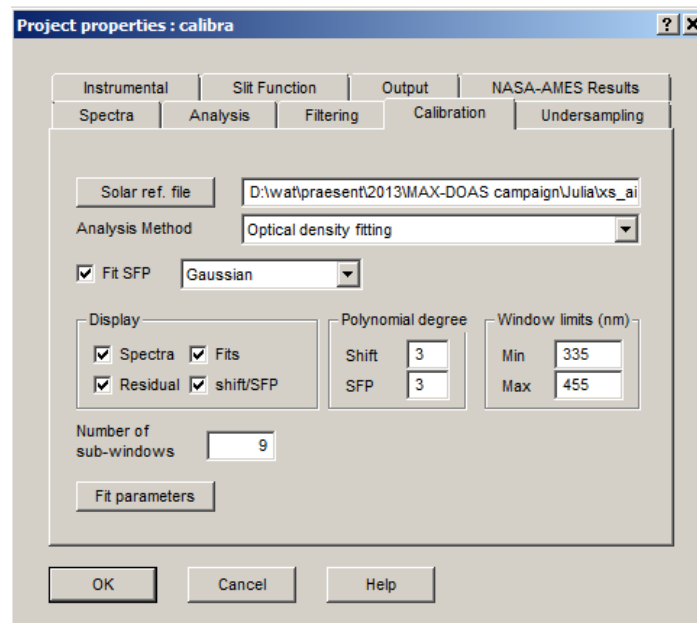
	A
1	275.229
2	275.387
3	275.546
4	275.705
5	275.864
6	276.022
7	276.181
8	276.339
9	276.498
10	276.656
11	276.814
12	276.972
13	277.130
14	277.288
15	277.446

This file can be used as ASCII file. The pre-calibration is now completed.

Wavelength Calibration:

WINDOAS was used. The precalibration file was loaded in 'instrumental'.

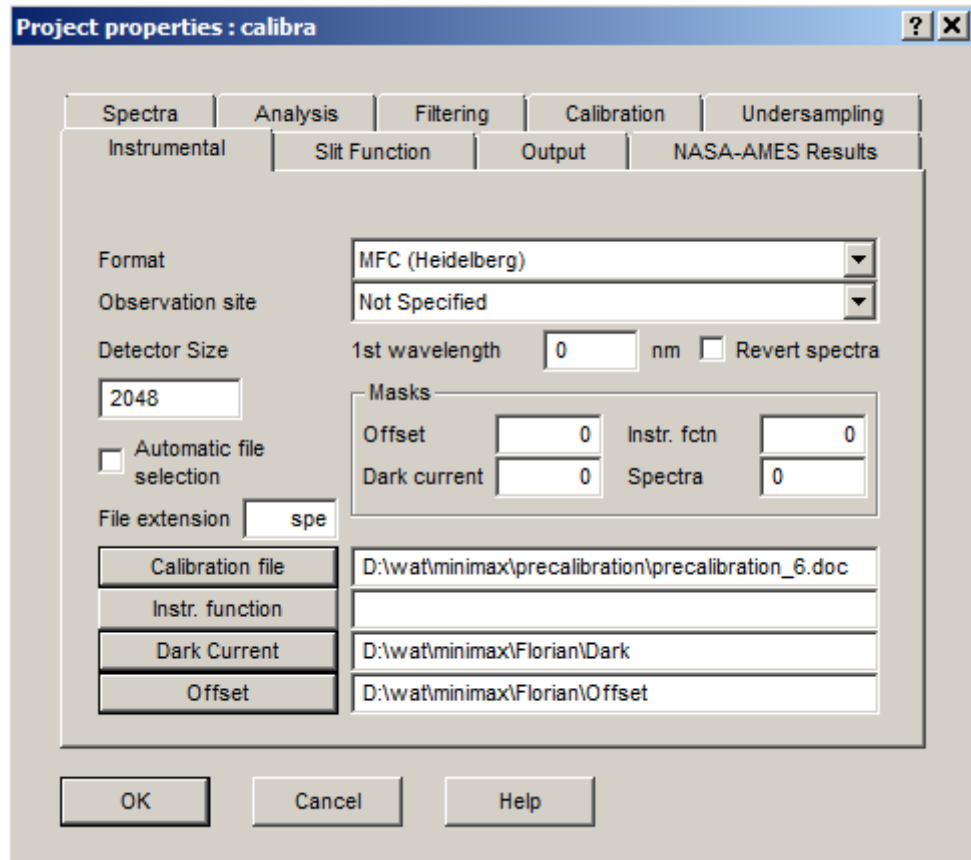
Then menu 'calibration' was opened:



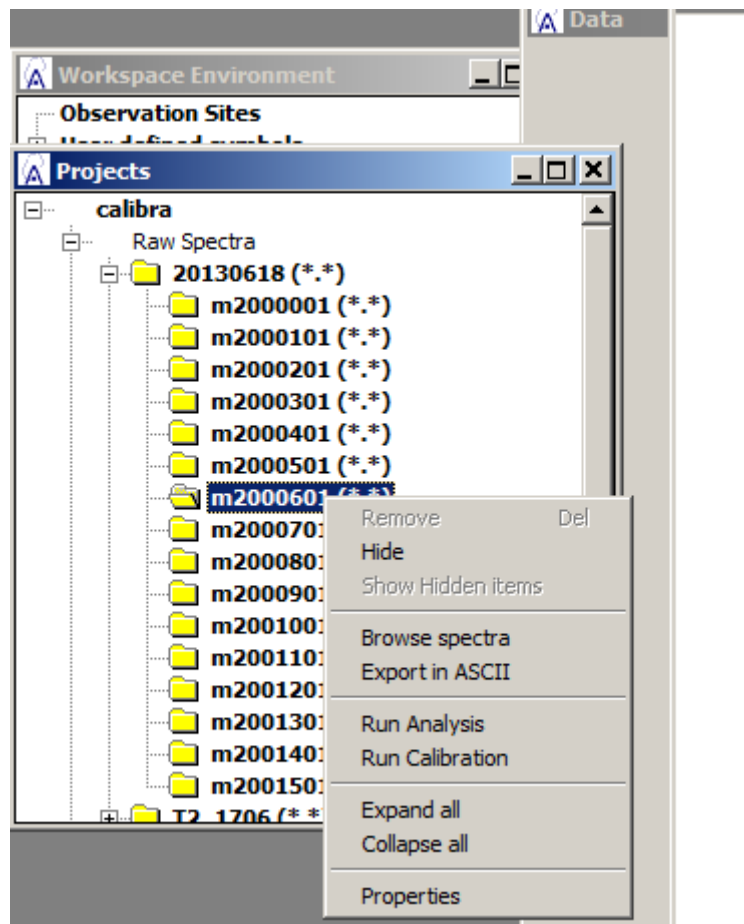
'Solar ref. file': SOLARFLVAC05_air_wavelength.DAT was chosed.

(This file contains a high resolution solar spectrum; the first column contains the wavelengths in air). Then wavelength range for the calibration was chosen. This wavelength range was smaller than that of instruments' spectrometer. The number "7" was chosen in number of sub-windows.

The format 'mfc heidelberg' was selected in the menu 'instrumental':

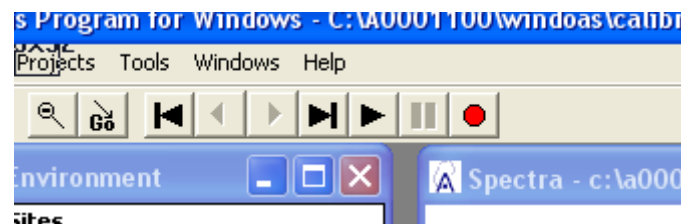


Then Fraunhofer reference spectrum was selected in the list of spectra and by using right mouse button this option was selected, 'run calibration'. See window on next page.

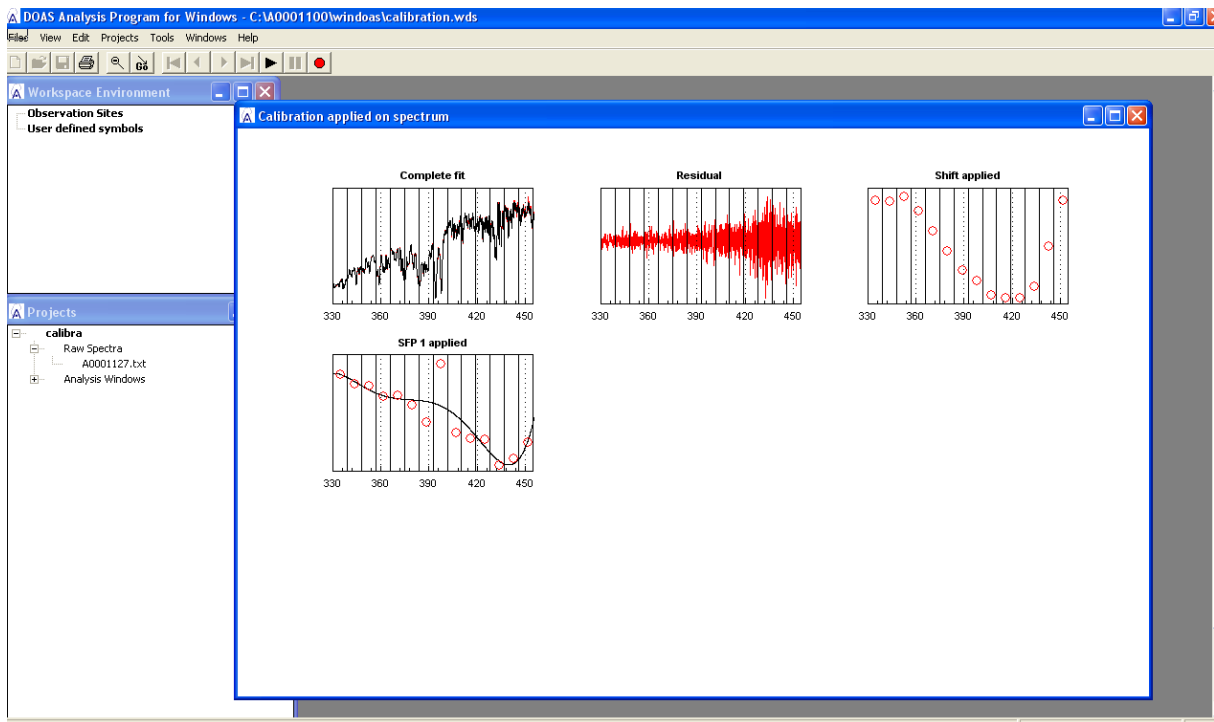


Now the spectrum appears.

Then by clicking at the arrow button in the menu line



As result, the following graph appears:



The first window shows the result of the fit (in red the measured spectrum; in black the convoluted solar spectrum)

The second window shows the residual of the fit (the difference between the measured spectrum and the fit result)

The third window shows the determined shift (individual points for the different sub-windows) with respect to the pre-calibration.

The fourth window shows the determined spectral resolution (FWHM) for the different sub-windows.

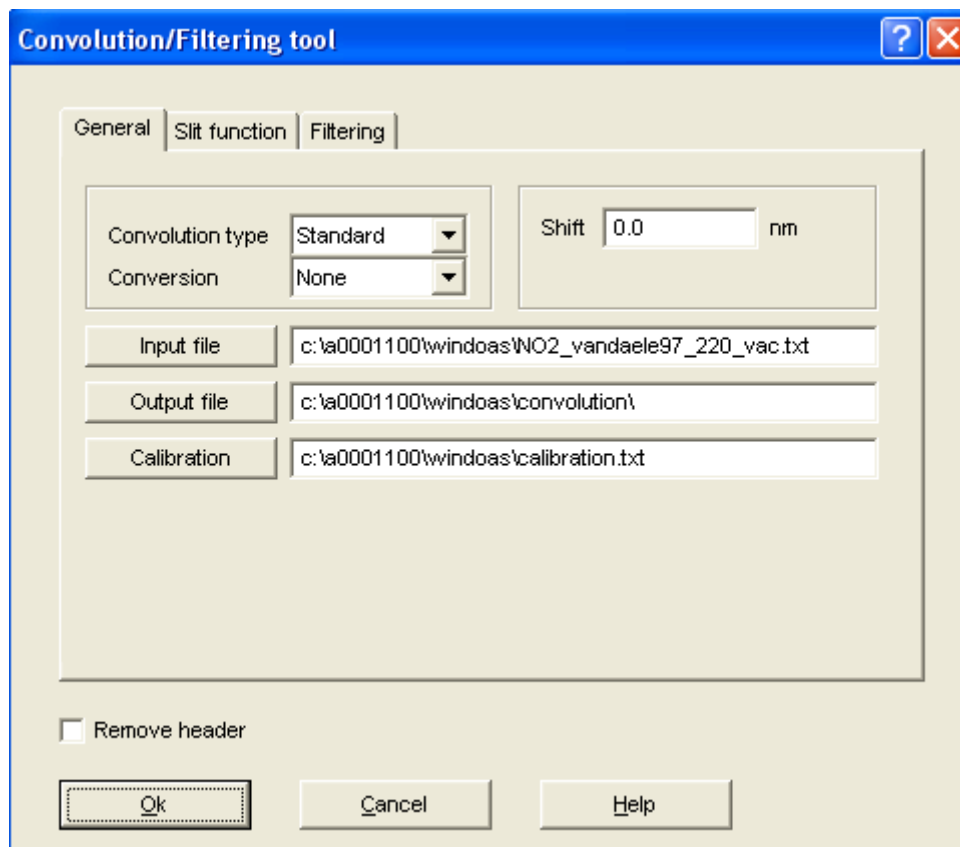
All small figures can be enlarged by clicking on them. Then, they can be saved as figures or as asci files. If the fit does not work, and an error message appears, you have to modify the fit settings (minimum wavelength, maximum wavelength, and number of fit windows).The general recommendation is to make the wavelength range narrower (larger minimum and smaller maximum wavelengths) and to reduce the number of sub-windows. The process of calibration was repeated two times for the accuracy of this procedure. When 'Complete fit' was looking good, by clicking on the sub plot the figure was got enlarged. Then by using the right mouse button, this was saved as ASCII file. It was the final calibration file for this project.

Then by clicking on the sub-plot ‘SFP 1 applied’, the figure was got enlarged. Then by using the right mouse button, it was saved by clicking on the option ‘save as ASCII file’. The file contains the FWHM of the slit function. It was used for the convolution of the cross sections.

Wavelength Convolution

This process was started by clicking on the top menu ‘tools’, then ‘convolution/filtering’ was selected.

The following menu was appeared:



Here, three paths were specified and calibration file was used that was derived in previous step

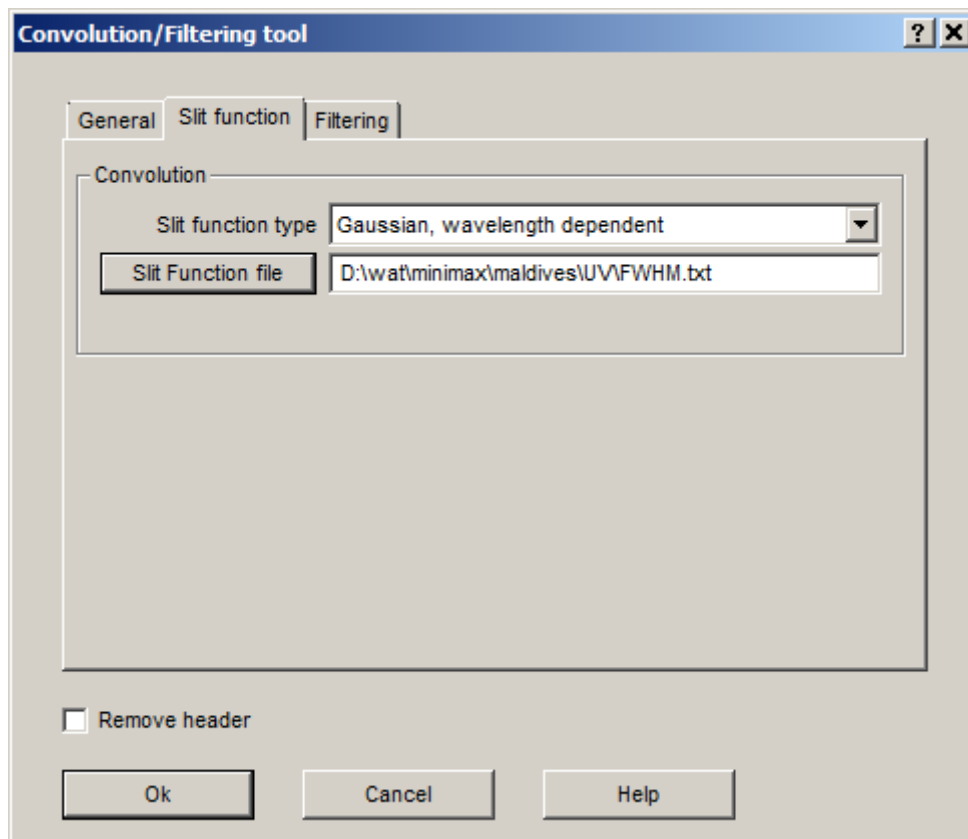
The output path directory was specified in which the convoluted cross sections were stored

The input path describes the file with the high-resolution cross section to be convoluted, convolution type has to be ‘standard’ (for convolution) or ‘none’ (for interpolation), and a second menu appears when ‘slit function’ was selected:

In the simplest case, just select ‘Gaussian’ and specify a value for the FWHM.

For the normal case, ‘Gaussian, wavelength dependent’ was selected.

For the 'slit function file' select the FWHM file that was created in calibration step.



The result of the spectral convolution is displayed and saved in the folder you had specified. In this step following trace gases cross sections were convoluted:

1. H₂O_hitran.xs_std
2. no2_298K_vanDaele.xs_std
3. no2a_220K_vanDaele.xs_std
4. o3_223K_Bogumil.xs_std
5. o4_Hermans_web.xs_std &
6. Ring spectrum calculated by DOASIS from the given spectrum.

NO₂ Analysis Window:

The NO₂ analysis window was selected as 411 nm to 450 nm (Wagner *et al.*, 2010). This wavelength range was selected after various run and based on lowest possible residual (fit errors). The calibrated spectrum is used as the reference spectrum for the analysis window. The paths of all the cross section are given in the Cross Sections Tab. The polynomial order of 5th degree was used for our NO₂ fitting analysis window. At the end the output file path is given to WinDOAS. The analysis is 'RUN' on all the measured spectra and the resulting NO₂ DSCDs are obtained as ascii files.

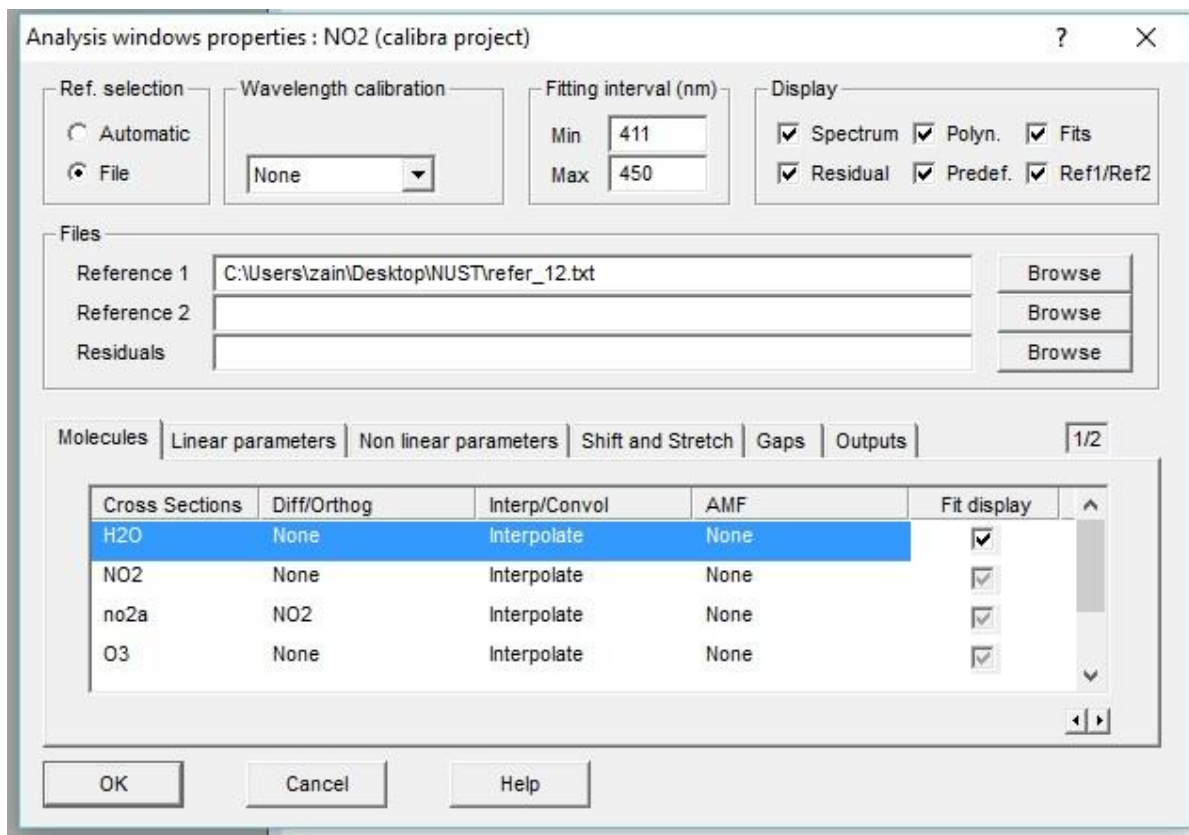


Figure 3.2: WinDOAS NO₂ Analysis Window

An example of NO₂ DOAS fit is presented below in figure 3.3.

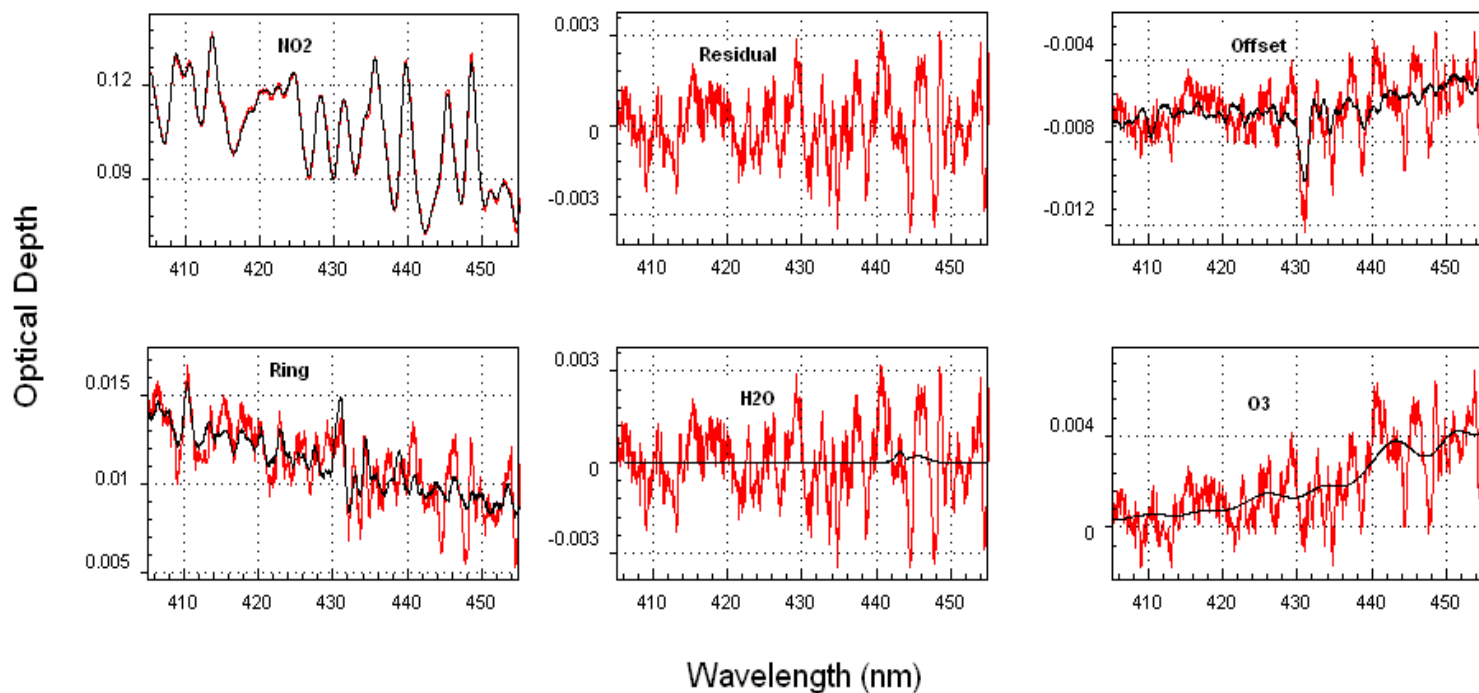


Figure 3.3: Typical Win-DOAS analysis window showing DOAS fit for field campaign Data

The residual (fit error) is below 0.3% (3 per mill). The residual DSCDs are stored in a text (ascii) file along with other parameters like time (UTC), date, elevation angle, SZA etc. as presented in figure 3.4.

The results acquired using WinDOAS can be opened in MS Excel as:

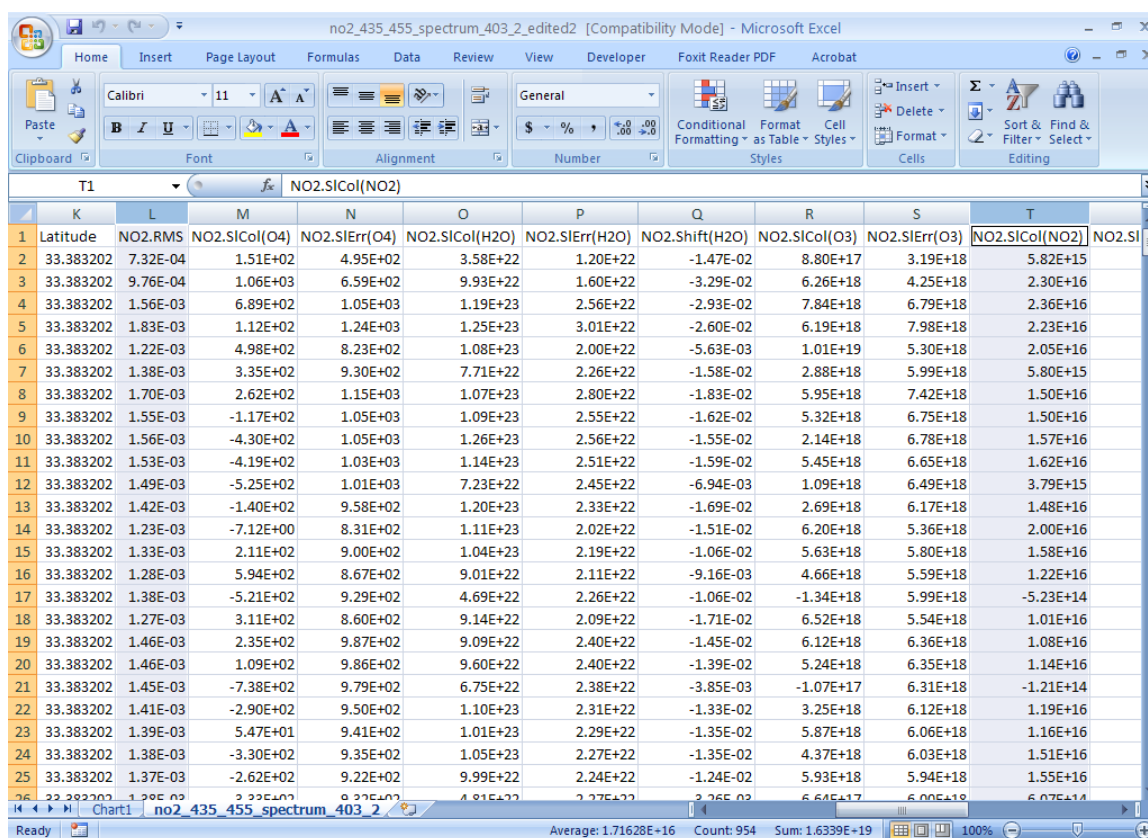


Figure 3.4: Microsoft Excel Window showing NO₂ Root Mean Squares (RMS) and NO₂ (DSCD) values

3.4.1 Air Mass Factor and NO₂ VCD Extraction Calculation using MS Excel

The Air Mass Factor is defined as the ratio between the path length of the solar radiation through the atmosphere and the perpendicular path length through the atmosphere. The AMF can be calculated both for troposphere and stratosphere as shown in figure 3.5.

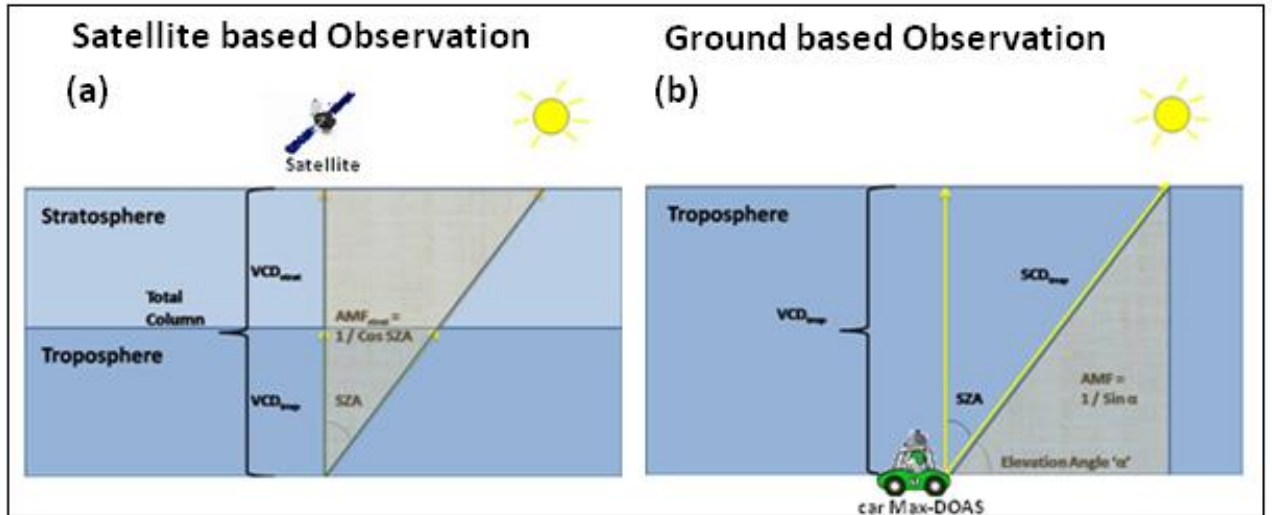


Figure 3.5: Air Mass Factor (AMF) for Troposphere and Stratosphere

Air mass factor (AMF) is mandatory for the conversion of slant column densities (SCDs) into vertical column densities (VCDs) given by the formula in equation 4.2. In case of car MAX-DOAS, the AMF calculation is very complicated and tricky as well (Wagner *et al.*, 2010). Because SCDs are column densities integrated along the light path, but in case of car MAX-DOAS the AMF changes every instant and in order to calculate the AMF we followed the method as prescribed in Wagner *et al.* 2010

DSCD_{ref} and Stratospheric SCD were used for the extraction of tropospheric VCDs. The DSCD_{offset}(SZA); differential slant column densities (DSCDs) as function of solar zenith angle (SZA), method was used for determination of the DSCD_{ref} and the stratospheric background. We used only DSCDs that had RMS of residuals smaller than 4.0×10^{-3} and 3.5×10^{-3} for 13th and 14th November respectively as shown in figure 3.9. The offset could be measured according to the following equation (Wagner *et al.*, 2010).

$$DSCD_{\text{offset}}(SZA) = \frac{AMF_{90^\circ} \cdot DSCD_{\alpha} - AMF_{\alpha} \cdot DSCD_{90^\circ}}{AMF_{\alpha} - AMF_{90^\circ}} \quad \text{Eq. 3.1}$$

The tropospheric VCD (VCD_{trop}) is the ratio of the SCD and the AMF (Wagner *et al.* 2010; Ibrahim *et al.*, 2010).

$$VCD_{\text{trop}} = \frac{SCD_{\text{trop}}(\alpha)}{AMF_{\text{trop}}(\alpha)} \quad \text{Eq. 3.2}$$

The air mass factor can be estimated using the geometric approximation (*Brinkma et al., 2008; Celarier et al., 2008*).

$$\text{AMF}_{\text{trop}} = \frac{1}{\sin \alpha} \quad \text{Eq. 3.3}$$

The elevation angle of 30° was selected for the NO₂ DSCD measurements. The reason to choose sequence of 30° elevation angle was that the AMF value by geometric approximation is 2, which makes our calculations much easier.

The tropospheric SCD at elevation angle α can be estimated using the equation using DSCD_{ref} (*Wagner et al., 2010*).

$$\text{SCD}_{\alpha} = \text{DSCD}_{\alpha} + \text{DSCD}_{\text{ref}} - \text{SCD}_{\text{strat}} \quad \text{Eq. 3.4}$$

Knowing the AMF_{trop} for the elevation angle α and SCD _{α} , VCD_{trop} can be extracted for our measurements.

MS Excel is used for simple mathematical calculation during AMF analysis and to represent the data in graphical figures. The NO₂ DSCD in the results acquired using WinDOAS are used for extraction of NO₂ VCD. The Air Mass Factor (AMF) is calculated in MS Excel using Geometric Approximation Method. Whereas NO₂ VCD are extracted using Offset Method.

For this purpose threshold limit was decided for each individual day. The threshold was fixed at 5 x 10⁻³.

NO₂ VCD extraction was done using Offset Method via MS Excel using all the 30° angles for NO₂ DSCD (*Wagner et al., 2010*). The result obtained gave a clear picture of NO₂ pollution over the project area.

3.4.2 Plotting of NO₂ VCDs over Project Area

To plot the NO₂ VCD, the measured VCDs needed to be plotted according to their coordinate of measurements. As the geographic coordinates were taken using a Global positioning System (GPS) logger because the instrument didn't had any geographic coordinates logging setup. The GPS system used in this study kept the record of time in both Universal Time Centre (UTC) and Pakistan Standard Time (PST) along with other parameters like longitude, latitude, altitude etc.

The time UTC was used to create link between instrument measurements and coordinates recorded in GPS. SQL queries were applied to our dataset in this regard. By applying these queries the NO₂ VCDs were mapped using Arc-GIS according to their coordinates.

The NO₂ measurements were converted to shape-files to be mapped. The plotted values were then used for source identification within the study area.

3.4.3. Satellite Validation of MAX-DOAS Observations Using ArcGIS

Tropospheric NO₂VCDs from ozone monitoring instrument (OMI) (*Boersma et al., 2007*) was compared with ground-based mini MAX-DOAS measurements performed at IESE-NUST site

OMI onboard NASA Earth Observation Satellite Aura is in space since 2004. It is nadir viewing spectrograph that can measure the sunlight. It covers the range from 270 nm to 500 nm with a resolution of 0.5 nm (*Boersma et al., 2007*). Local equator crossing time is between 13:40 and 13:50. Its spatial resolution is 24×13 km² in nadir. In this study, OMI NO₂ tropospheric VCD level-2 product from NASA Goddard Earth Sciences Data and Information Services Center (GES DISC) website (<http://disc.sci.gsfc.nasa.gov/Aura>) were used. For detailed description of OMI products please refer to Levelt et al., (2006).

RESULTS AND DISCUSSION

4.1. Field Campaigns

Several field campaigns were performed along National Highways of Punjab and the results of these campaigns are shown below.

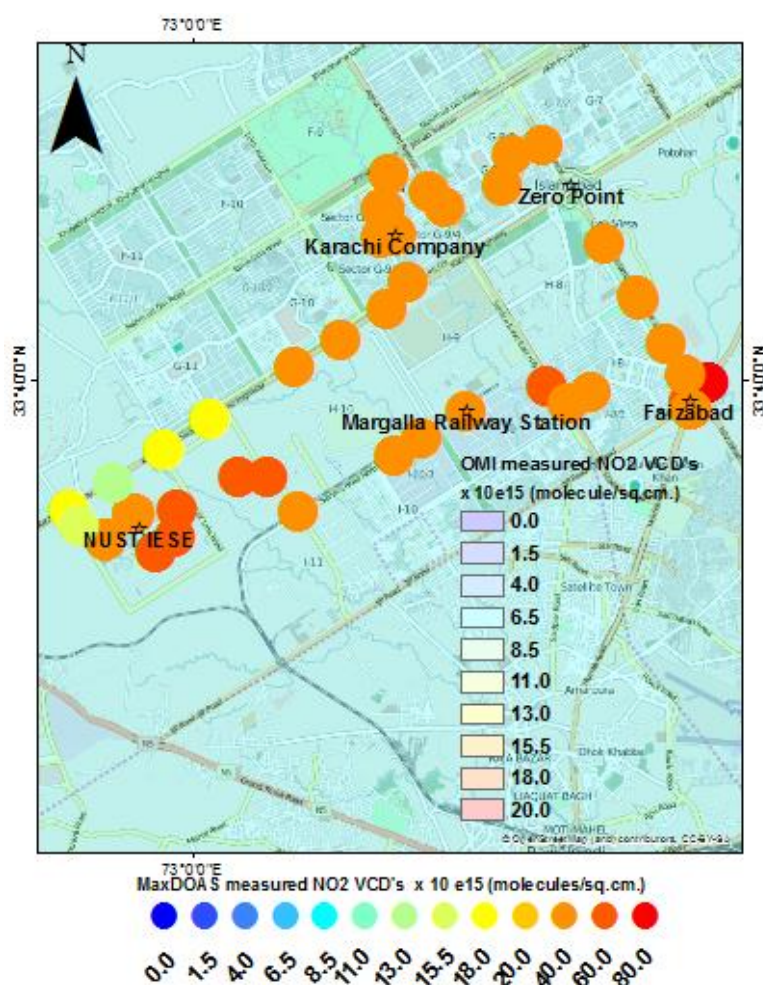


Figure 4.1: NO₂ VCDs measured by car MAX DOAS on 12th November, 2014 and OMI Observations

First field campaign was conducted on November 12, 2014 within twin cities (Rawalpindi, Islamabad). In this field campaign area around 36.14 km was covered. Background pixels are showing satellite observations and MAX-DOAS observations are at the front. Satellite

observations are underestimated as compare to ground based MAX-DOAS observations due to their lower sensitivity. Highest value for NO₂ VCDs was observed near Faizabad that was 6.26E+16 (molecules/cm²) (53.3 ppb) because of higher traffic density at Faizabad.

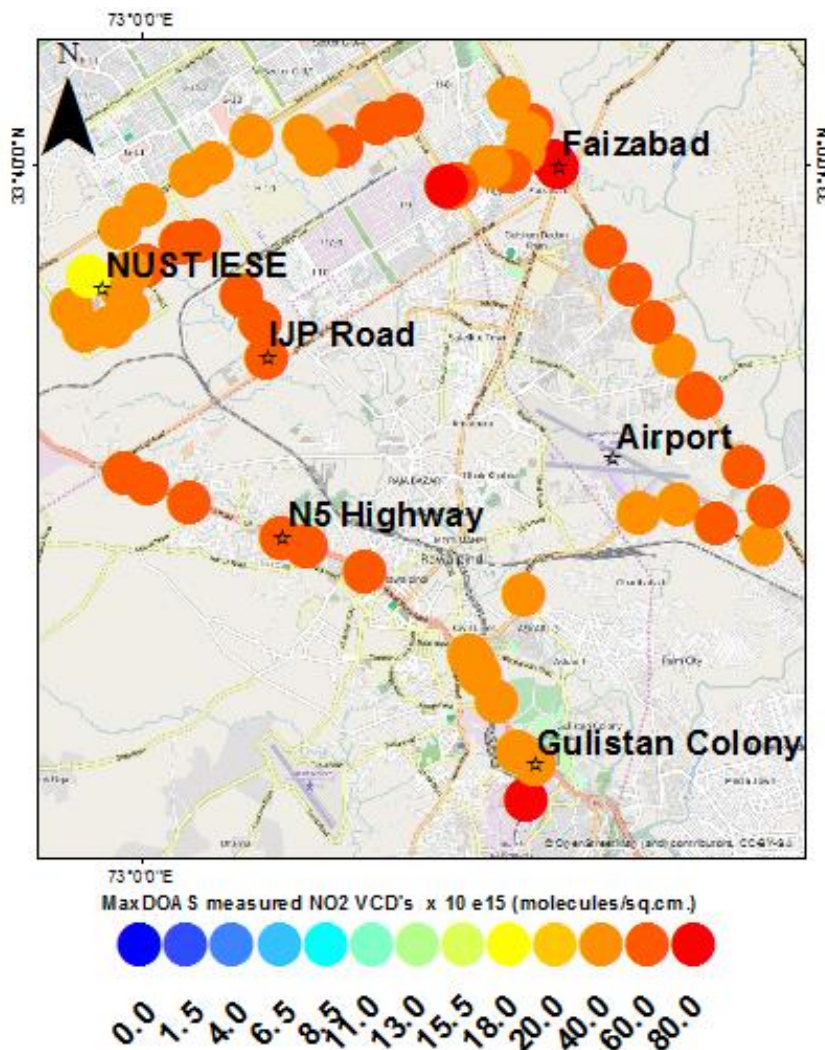


Figure 4.2: NO₂ VCDs measured by car MAX DOAS on 13th November 2014.

Second field campaign was conducted on November 13, 2014 within twin cities. In this field campaign area around 62.45 km was covered. Unfortunately the OMI satellite data over the study area was missing on that day. Highest value for NO₂ VCDs was observed by MAX-DOAS near Faizabad that was 7.54E+16 (molecules/cm²) (64.20 ppb) because of higher traffic density at Faizabad.

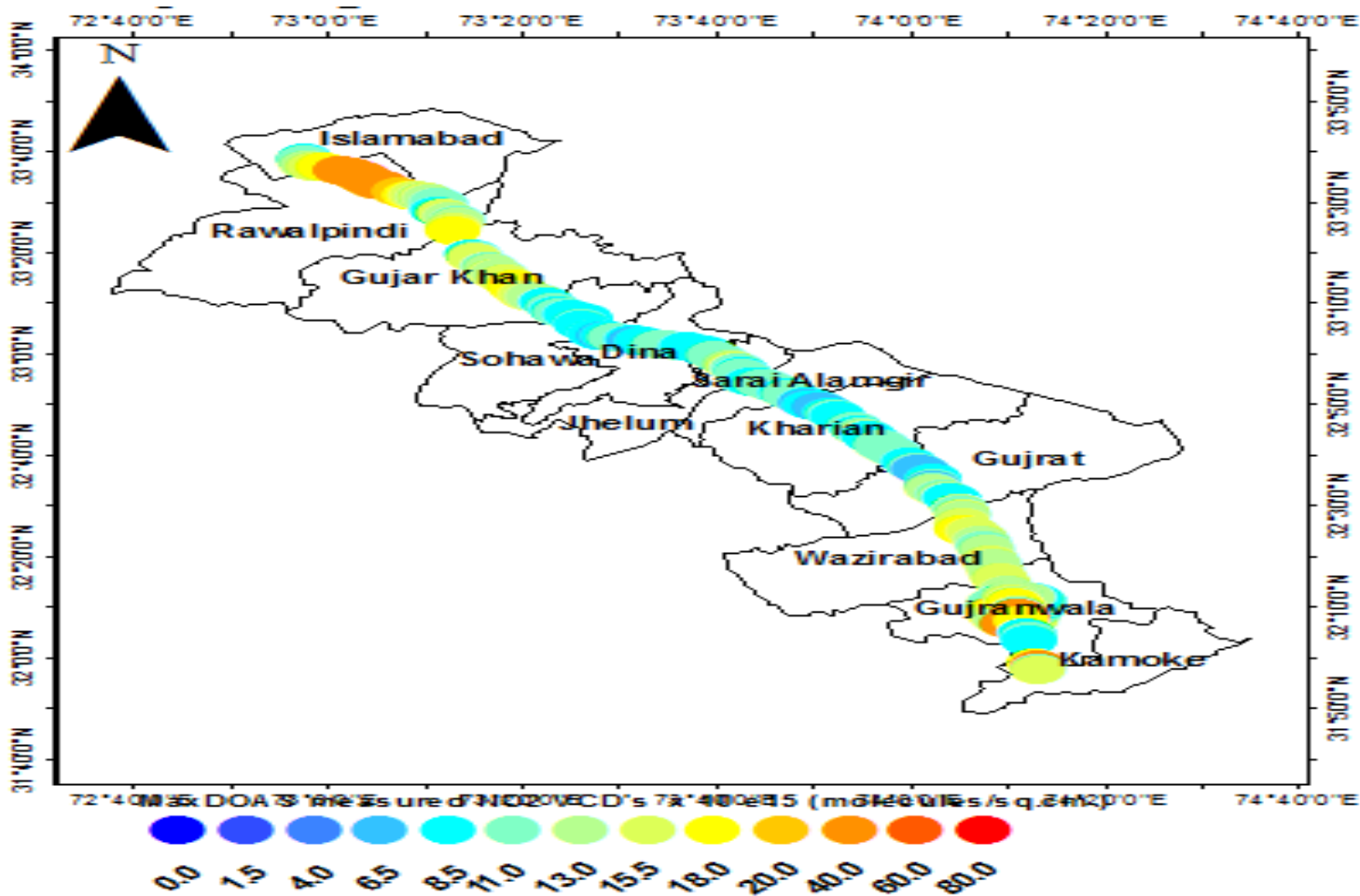


Figure 4.3: NO₂ VCDs measured by car MAX-DOAS on 17th February 2015

This field campaign was conducted from Islamabad to Kamoke along National Highway on February 17, 2015. In this field campaign area around 322.116 km was covered. In this field campaign higher values of NO₂ concentration were found in Rawalpindi and Gujranwala. The other cities along National Highway such as Gujar Khan, Jhelum, Kharian and Gujrat are less polluted as these are less populated and clean as compared to Gujranwala. Highest value for NO₂ VCDs was observed in Gujranwala that was around 3.72×10^{16} (molecules/cm²) (31.67 ppb) as Gujranwala is highly populated and industrial city.

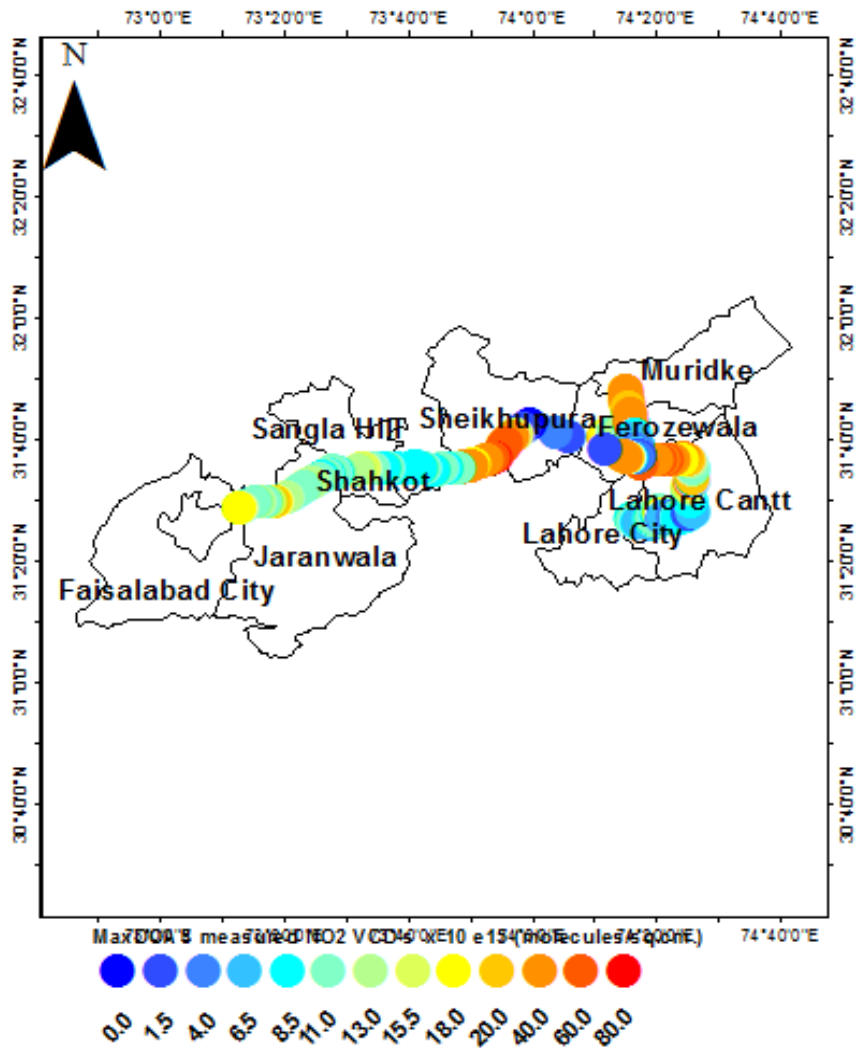


Figure 4.4: NO₂ VCDs measured by car MAX DOAS on 18th February 2015.

This field campaign was conducted from Lahore to Jaranwala along National Highway on February 18, 2015. In this field campaign area around 257.9 km was covered. In this field campaign higher values were observed in Lahore and Sheikhupura. Highest value for NO₂ VCDs was observed in Sheikhupura that was around 6.51E+16 (molecules/cm²) (55.43 ppb) as Sheikhupura is an industrial city.

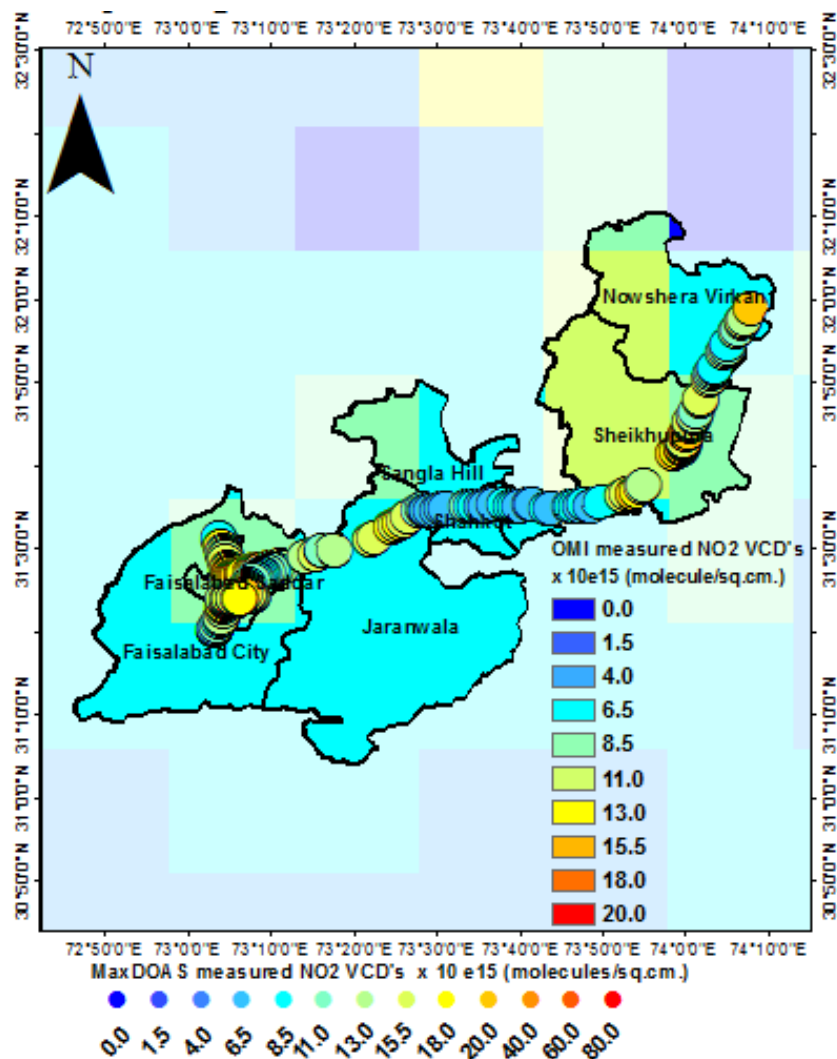


Figure 4.5: NO₂ VCDs measured by car MAX DOAS on 19th February, 2015 and OMI Observations

This field campaign was conducted from Faisalabad to Nowshera wirkan along National Highway on February 19, 2015. In this field campaign area around 228.3 km was covered. Highest value for NO₂ VCDs was found in Faisalabad that was around 2.44E+16 (molecules/cm²) (20.78 ppb) because February 19, 2015 was a cloudy day that may be the main reason for low concentration of NO₂ over Faisalabad.

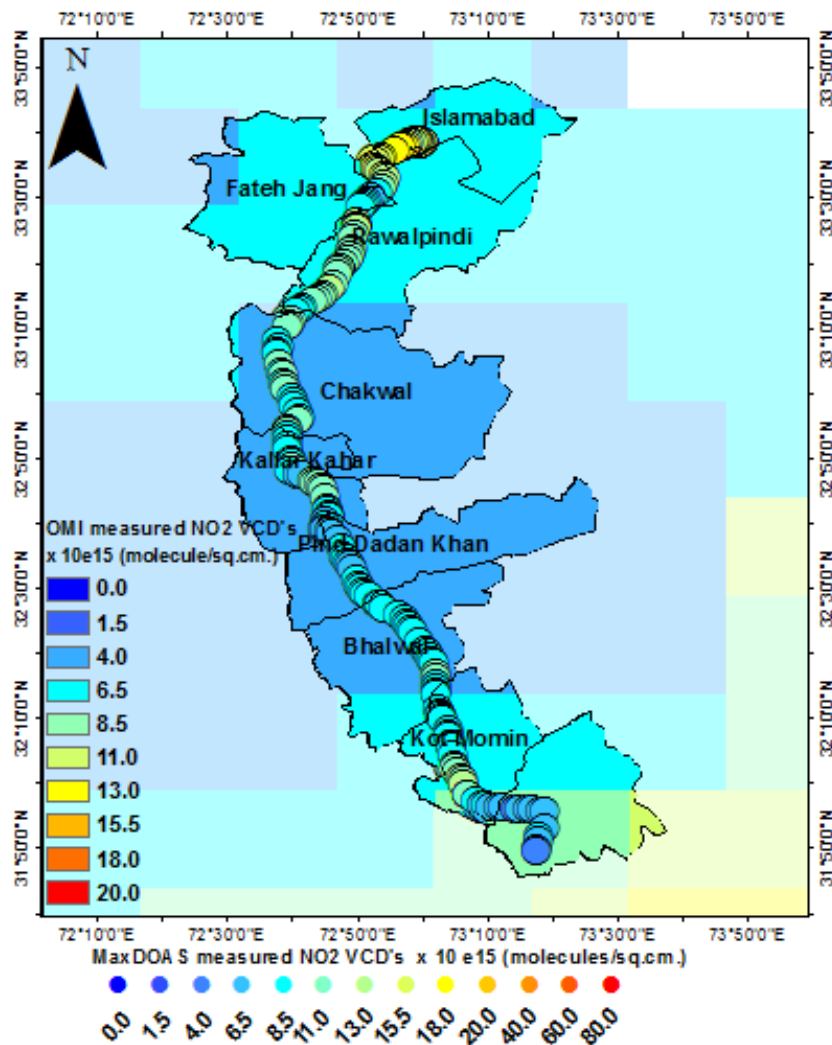


Figure 4.6: NO₂ VCDs measured by car MAX DOAS on 23rd February 2015 and OMI observations.

This field campaign was conducted from Islamabad to Kot Momin along Motorway on February 23, 2015. In this field campaign area around 309.4 km was covered. Highest value for NO₂ VCDs was observed by MAX-DOAS in Islamabad that was around 2.16E+16 (molecules/cm²) (18.39 ppb) and was within the Pak. NEQS limit. Motorway is less polluted as compared to National Highway because of low traffic as compared to National Highway.

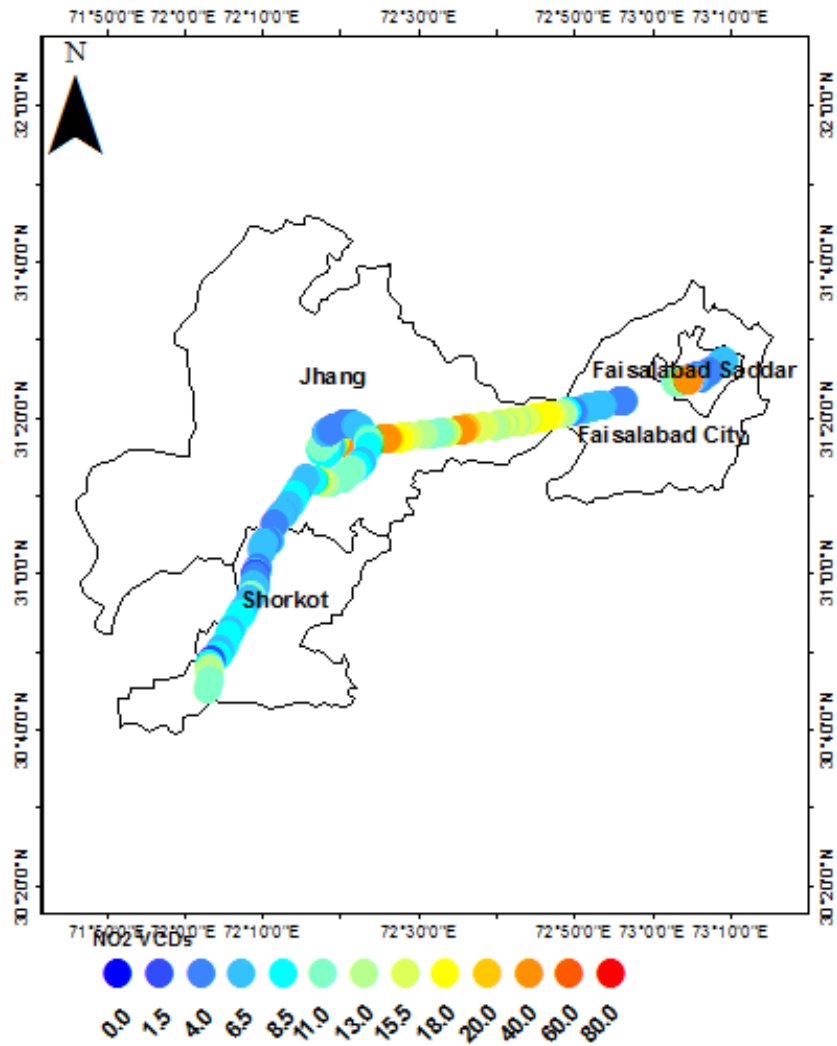


Figure 4.7: NO₂ VCDs measured by car MAX DOAS on 24th February 2015.

This field campaign was conducted from Faisalabad to Shor Kot along National Highway on February 24, 2015. In this field campaign area around 213.9 km was covered and the highest observed value was 2.79×10^{16} (molecules/cm²) (23.76 ppb) in Faisalabad. Jhang and Shor kot are less polluted because these are agricultural areas and Faisalabad is an industrial city.

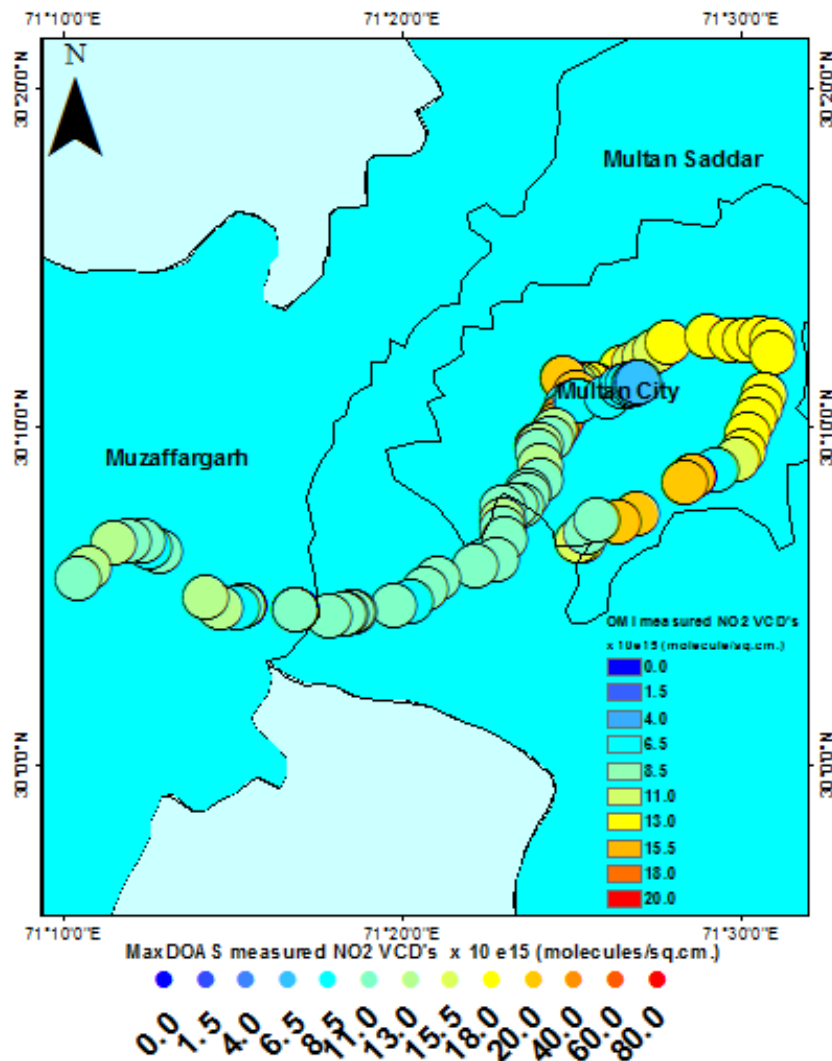


Figure 4.8: NO₂ VCDs measured by car MAX DOAS on 25th February, 2015 and OMI Observations

This field campaign was conducted within Multan and Muzaffargarh along National Highway on February 25, 2015. In this field campaign area around 95.35 km was covered and the highest value was 2.32×10^{16} (molecules/cm²) 19.75 ppb that was observed in Multan.

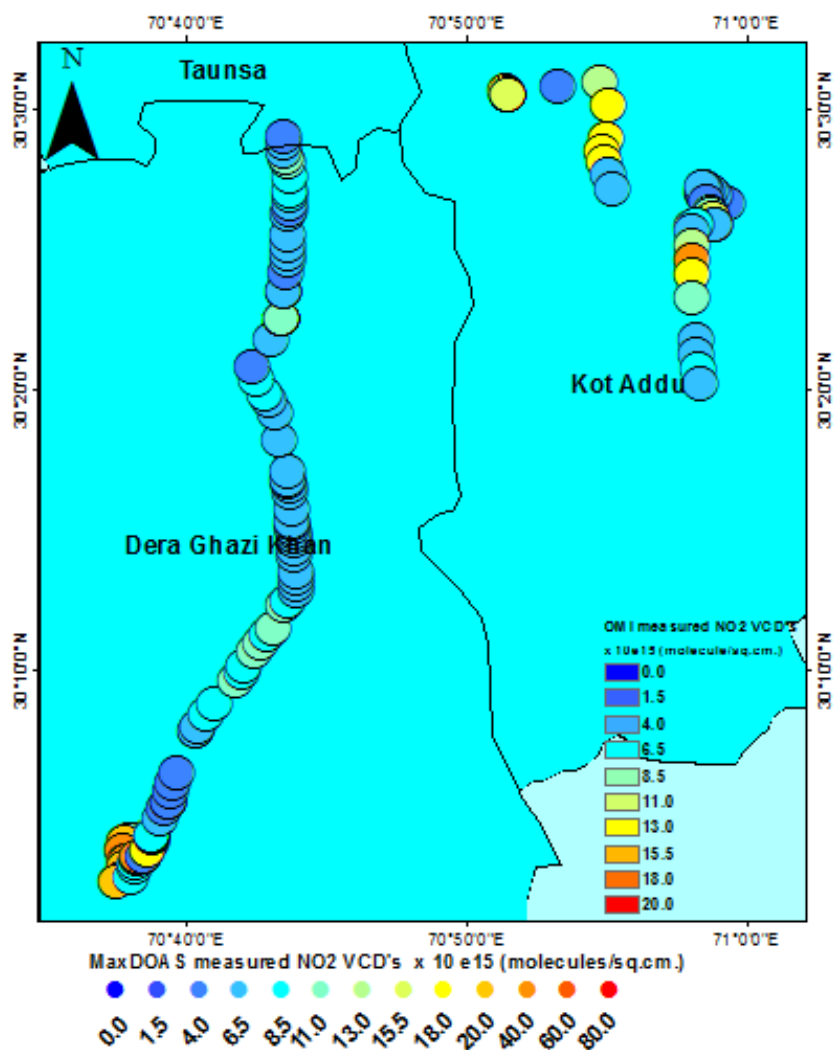


Figure 4.9: NO₂ VCDs measured by car MAX DOAS on 26th February, 2015 and OMI Observations

This field campaign was conducted from Kot adu to Dera Ghazi Khan along National Highway on February 26, 2015. In this field campaign area around 127.3 km was covered and the highest value was observed by MAX-DOAS in Dera Ghazi Khan that was around $2.17\text{E}+16$ (molecules/cm²) (18.48 ppb).

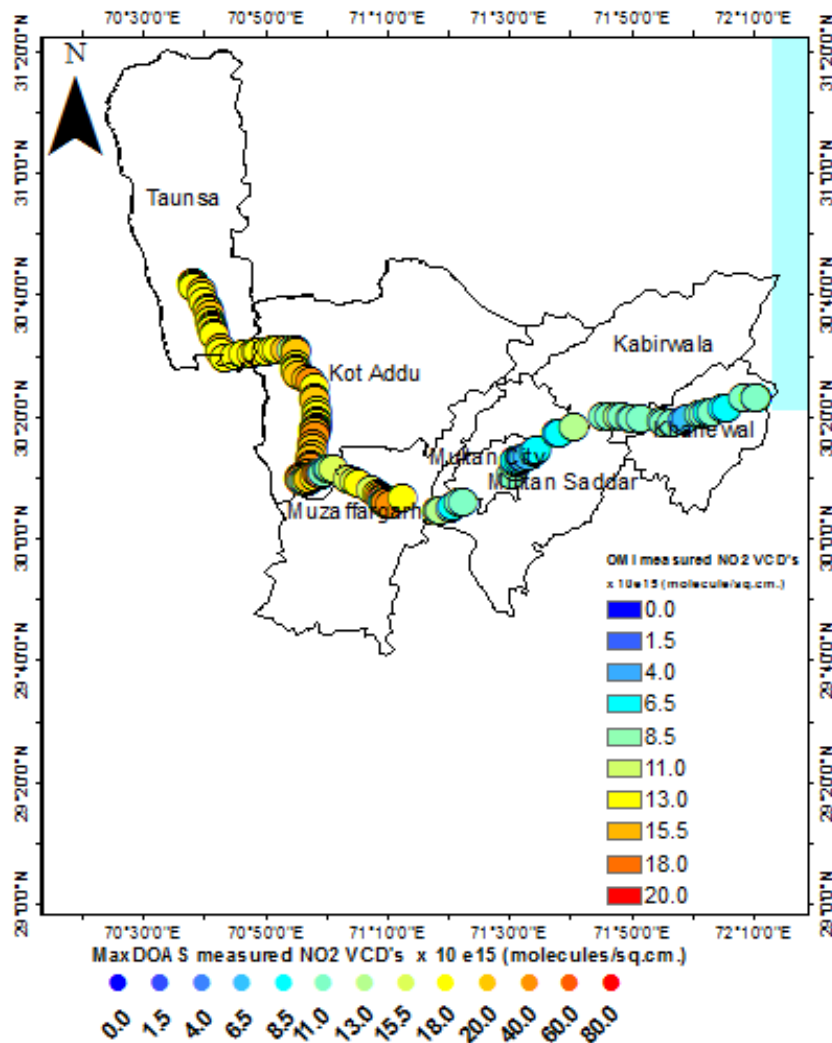


Figure 4.10: NO₂ VCDs measured by car MAX DOAS on 27th February 2015.

This field campaign was conducted from Taunsa sharif to Khanewal along National Highway on February 27, 2015. In this field campaign area around 271.9 km was covered and the highest value was observed by MAX-DOAS in Muzafar Garh that was around 3.56E+16 (molecules/cm²) (30.31 ppb).

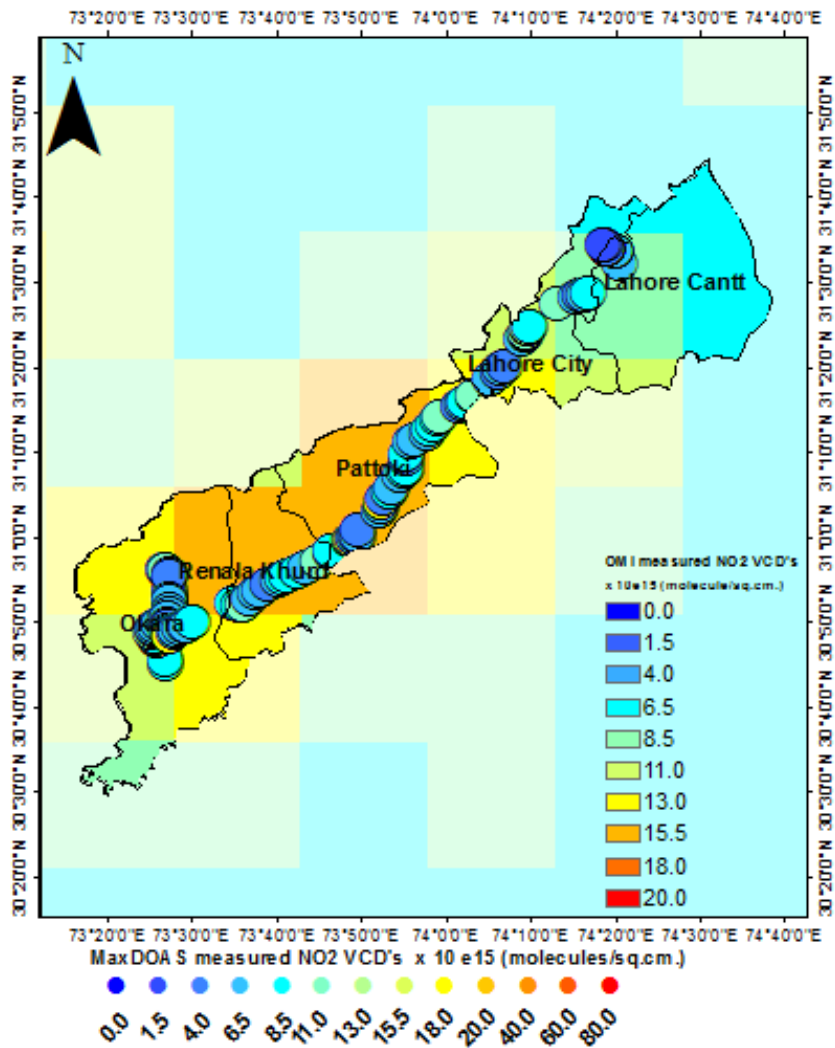


Figure 4.11: NO₂ VCDs measured by car MAX DOAS on 28th February, 2015 and OMI Observations

This field campaign was conducted from Lahore to Okara along National Highway on February 28, 2015. In this field campaign area around 195.4 km was covered and the highest value was observed by MAX-DOAS in Okara that was around 2.66×10^{16} (molecules/cm²) (22.65 ppb).

4.2. Temporal Analysis

Tropospheric NO₂ VCDs, retrieved from mini MAX-DOAS observations from April, 2014 till July, 2015 are presented in Figure 4.12. NO₂ Show higher peaks in winter as the photolysis rate is reduced in winter and burning of fossil fuels increases for indoor space heating. NO₂ VCDs shows minimal peaks in summer due to high photolysis rate.

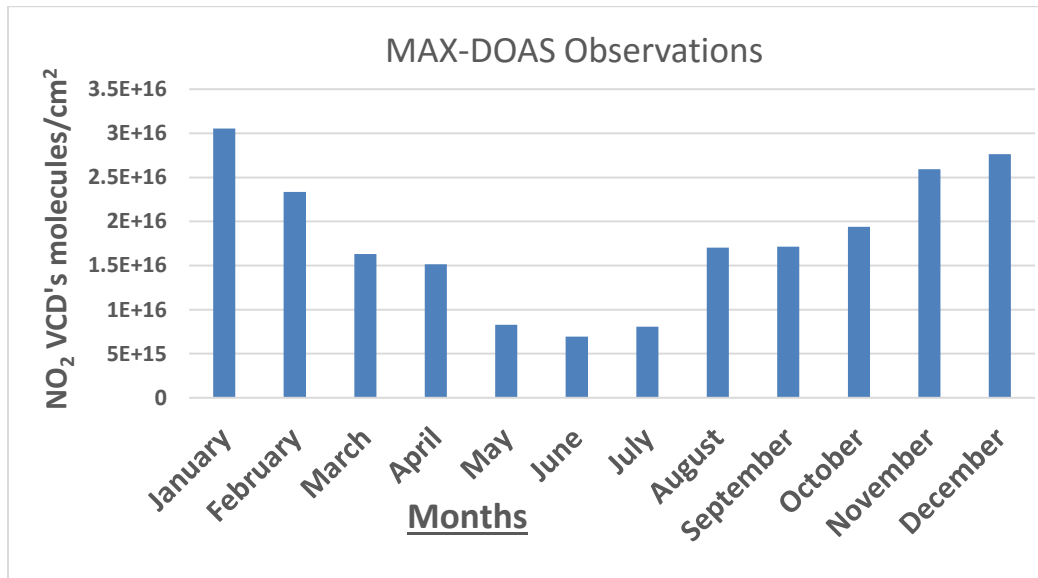


Figure 4.12: Seasonal variation of tropospheric Mean NO₂ Conc. Molecules/cm² from 2014-2015 measured from MAX DOAS

Then NO₂ VCDs observed by MAX DOAS were changed into number density by dividing them with supposed vertical height

$$\text{“NO}_2 \text{ Number Density (molec./cm}^3\text{) = NO}_2 \text{ VCD (molec./cm}^2\text{) / 30000 cm} \text{”}$$

The calculated NO₂ number density can be directly converted into NO₂ mixing ratios according to the following formula:

$$\text{NO}_2 \text{ mixing ratio (ppbv) = NO}_2 \text{ Number Density (molec./cm}^3\text{) / } 2.503 \times 10^{10} \text{ (molec./cm}^3\text{)”}$$

The observed concentration of NO₂ exceeded WHO limits at some occasions.

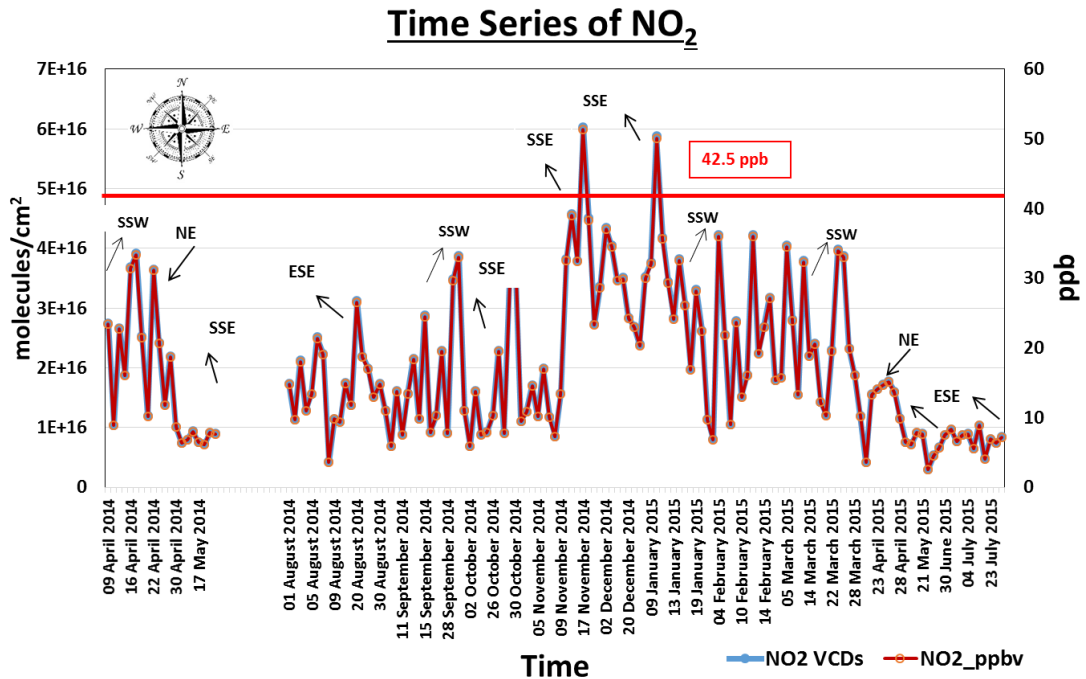


Figure 4.13: Time series and Mixing Ratios of Tropospheric Mean NO₂ concentration Molecules/cm² from 2014-2015

This graph shows the time series of NO₂ VCDs in blue and mixing ratios in red for a time period of April, 2014 to July, 2015 measured at IESE-NUST monitoring site.

This graph shows NO₂ peaks in April and dips in May. During the months of June and July of 2014, no observations were recorded due to malfunctioning of the instrument. However, increase in NO₂ VCDs were observed in October, November of 2014 and January of 2015. Then once again a decrease is observed from May to July 2015.

Black arrows are indicating the wind direction on that respective day. It is worth to mention that NUST is relatively a clean Area but showing high concentration predominantly during the wind movement from SSW or SSE. Which indicates that the NO₂ pollution sources exist in SSW and SSE of the IESE monitoring site. In fact NO₂ VCDs exceeding the NEQS limit over IESE Site when air masses were transported from nearby regions of Rawalpindi and I-10 industrial sector of Islamabad.

4.3. Diurnal Profile of Nitrogen Dioxide

The Diurnal cycle of NO₂ VCDs was observed by MAX-DOAS from April, 2014 to July, 2015. The diurnal sketch is shown in figure 4.14. The values of NO₂ concentration was found maximum in the morning and evening as a result of higher movements of vehicles in the morning and evening and lower intensity of sunlight as compared to day time. The level of NO₂ concentration was lowest at noon because of high photolysis.

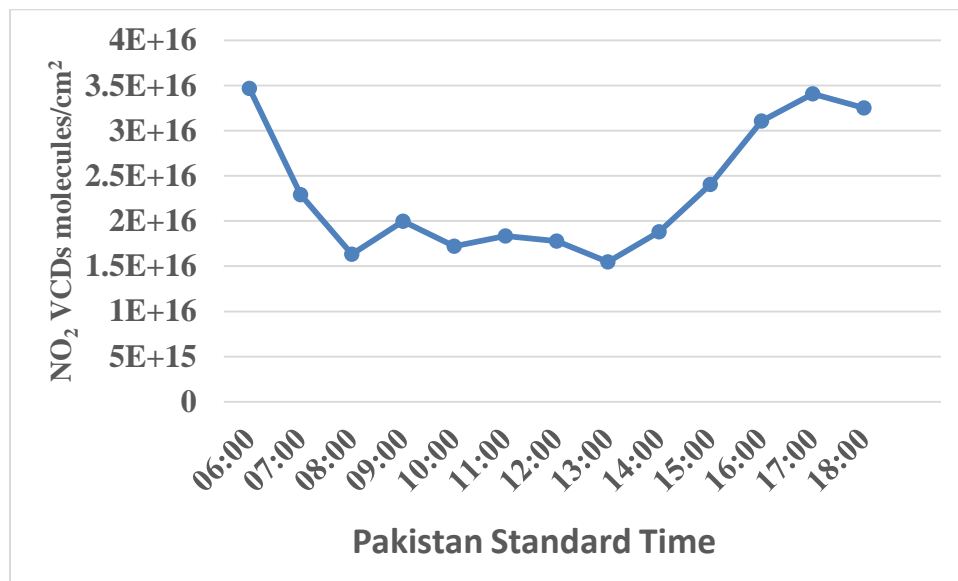


Figure 4.14: Diurnal Cycle of NO₂ VCDs Molecules/cm² from April 2014-July 2015

4.4. Weekly cycle of Nitrogen Dioxide Concentration

The weekly cycle of NO₂ concentration over a period of April, 2014 to July, 2015 is shown in fig. 4.15 on next page. This figure shows a peak in working days and decrease at weekends as a result of less traffic. Availability of CNG for a few days also reduces the concentration of NO₂.

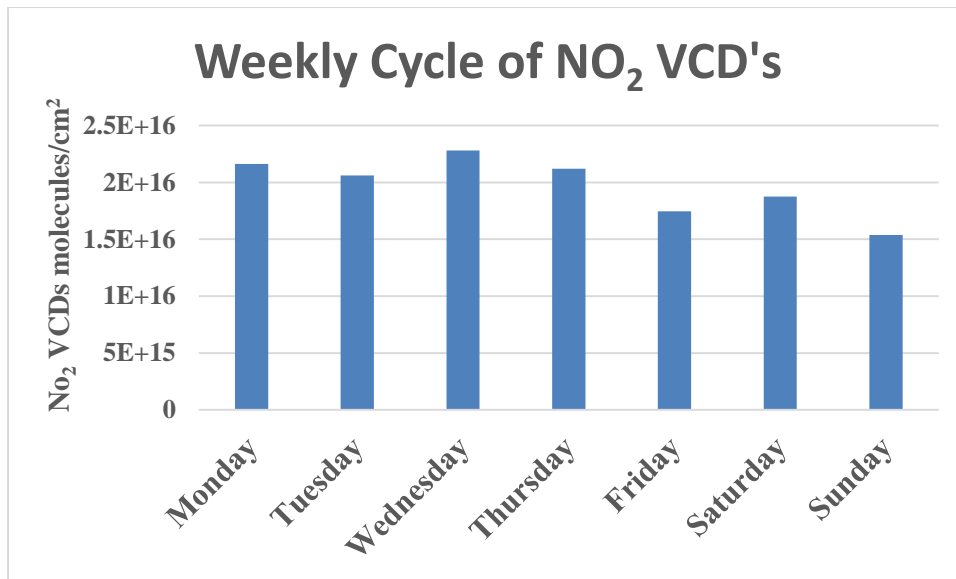


Figure 4.15: weekly Cycle of NO₂ VCDs Molecules/cm² from April 2014-July 2015

4.5. Comparison of Ground based monitoring and Satellite Observations (OMI)

Results of Ground based monitoring by using MAX DOAS and results of Satellite observations (OMI) are shown in fig. 4.16. From April, 2014 to July, 2015.

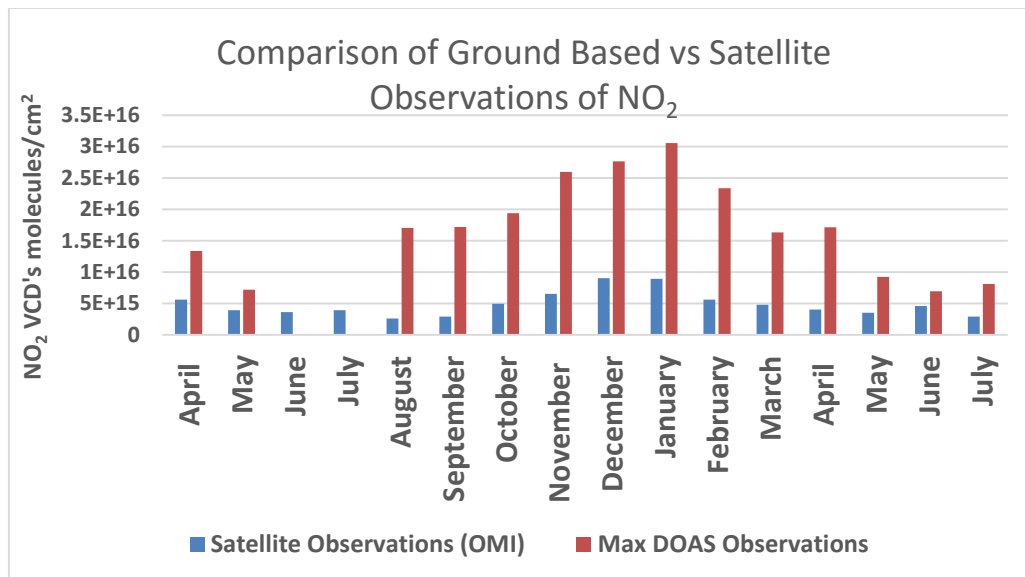


Figure 4.16: MAX DOAS measurements VS OMI Satellite Observations from April 2014-July 2015

Unfortunately, MAX DOAS data for two months (June and July 2014) is missing. Otherwise, Satellite data and OMI observations show a similar decreasing trend in summer and increasing

in winter. Both showed the highest concentrations of NO₂ in the month of January. Though both Satellite observations and MAX DOAS monitoring show similar trend, but Satellite observations are underestimated because of their lower sensitivity and in addition Satellite shows mean values but MAX DOAS observations are point based direct measurements.

4.6. Spatial Analysis

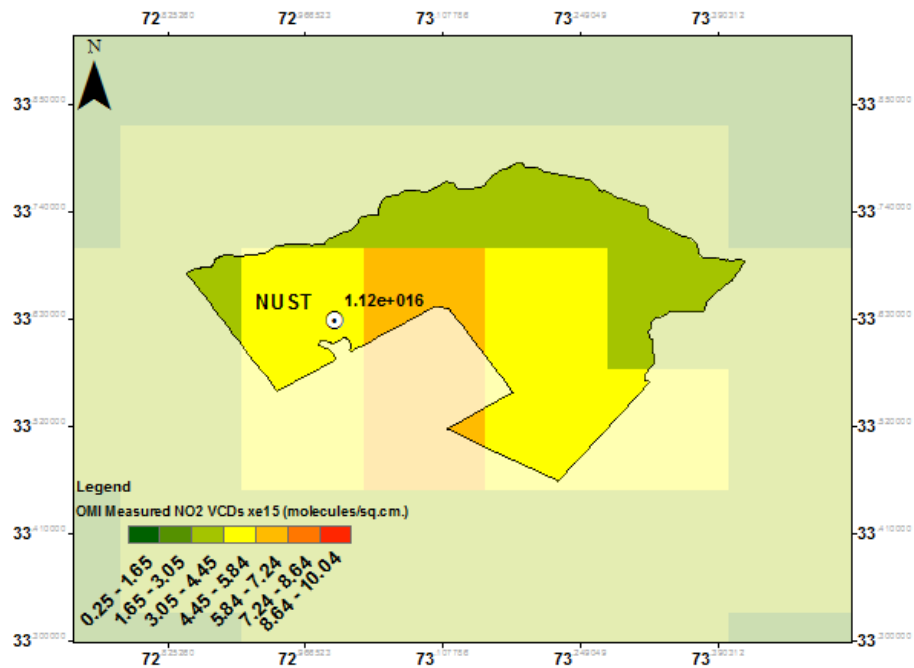


Figure 4.17: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for April 2014

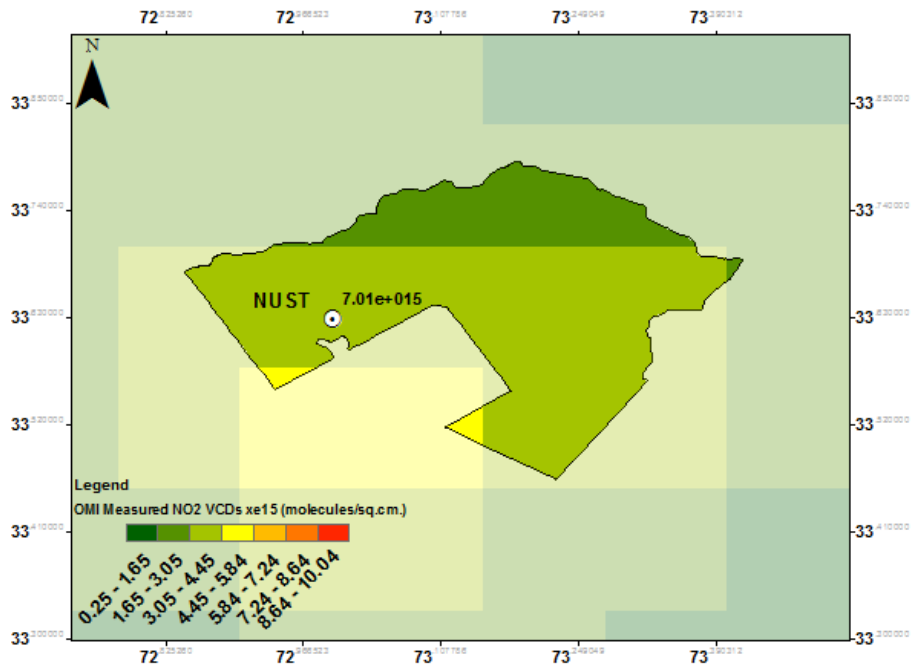


Figure 4.18: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for May 2014

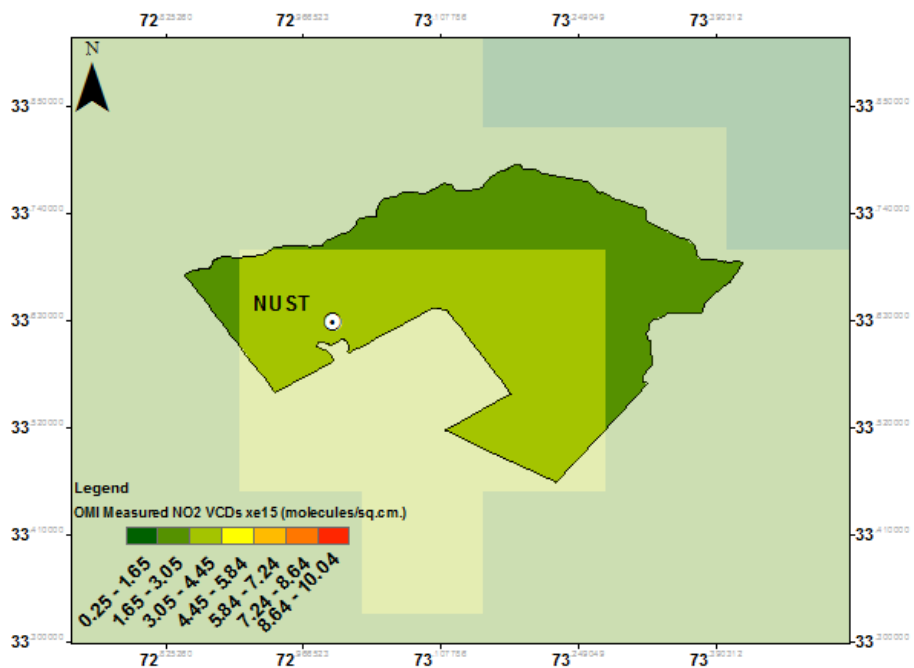


Figure 4.19: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for June 2014

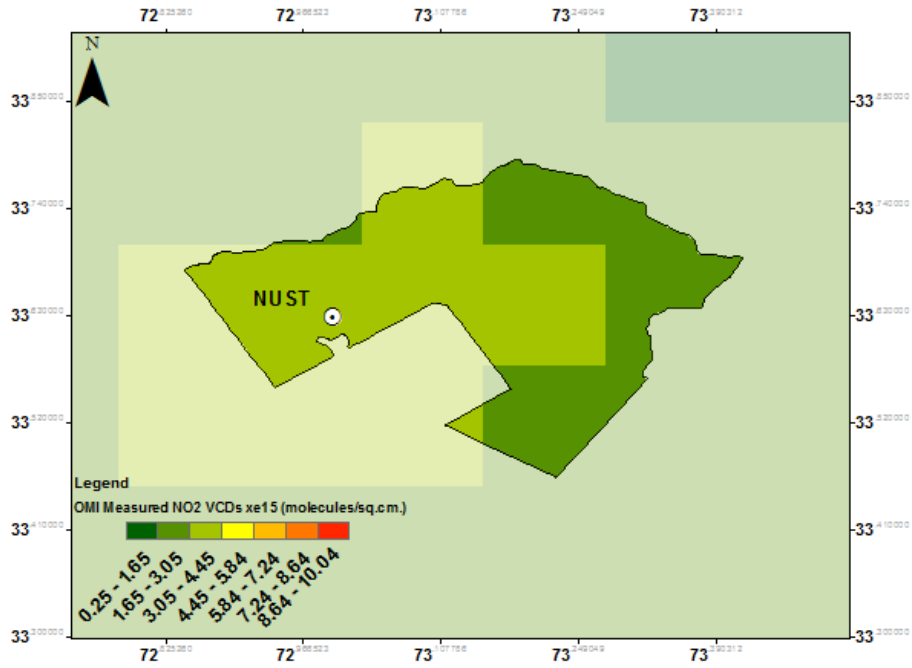


Figure 4.20: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for July 2014

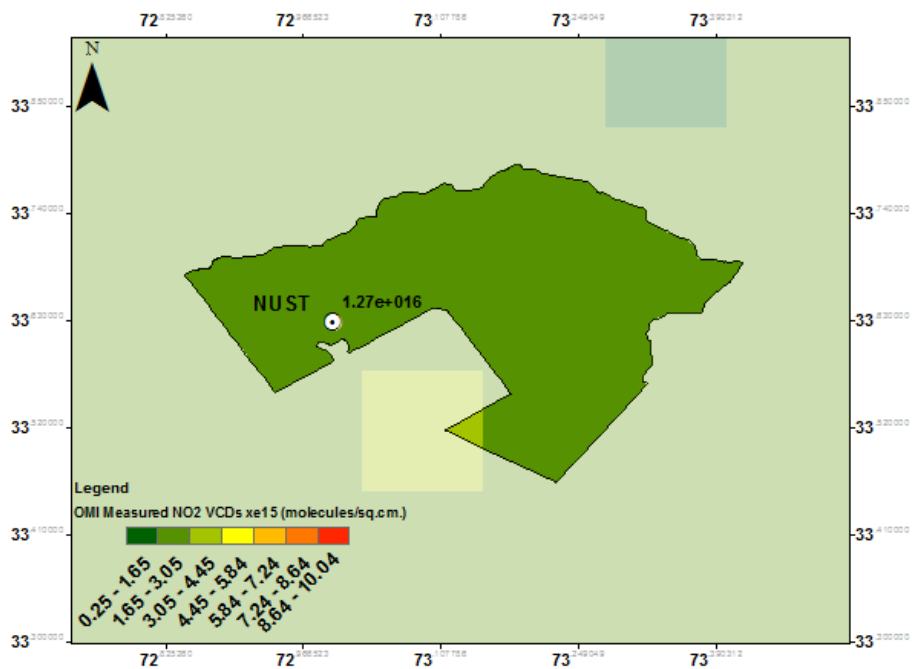


Figure 4.21: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for August 2014

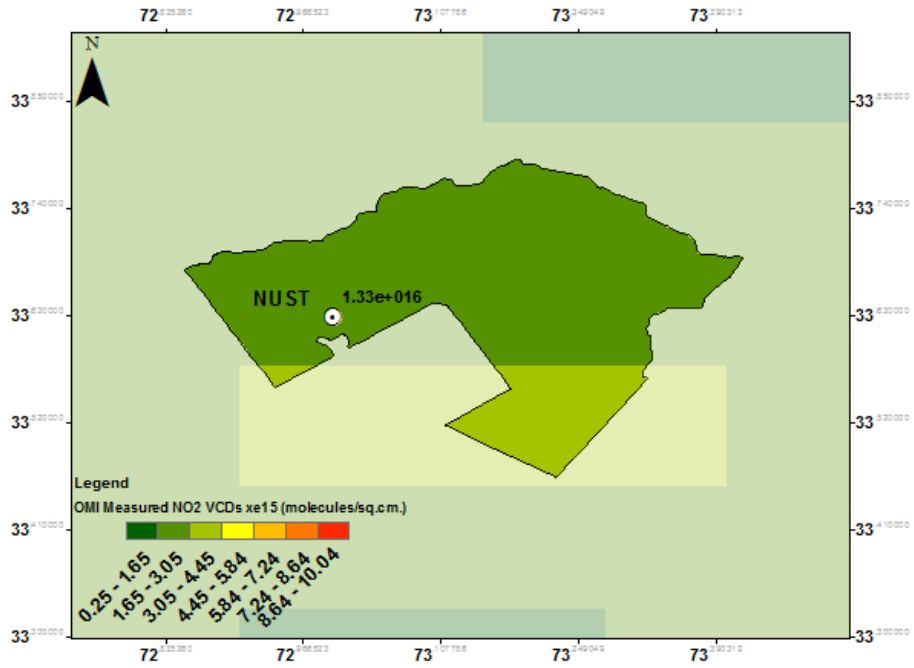


Figure 4.22: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for September 2014

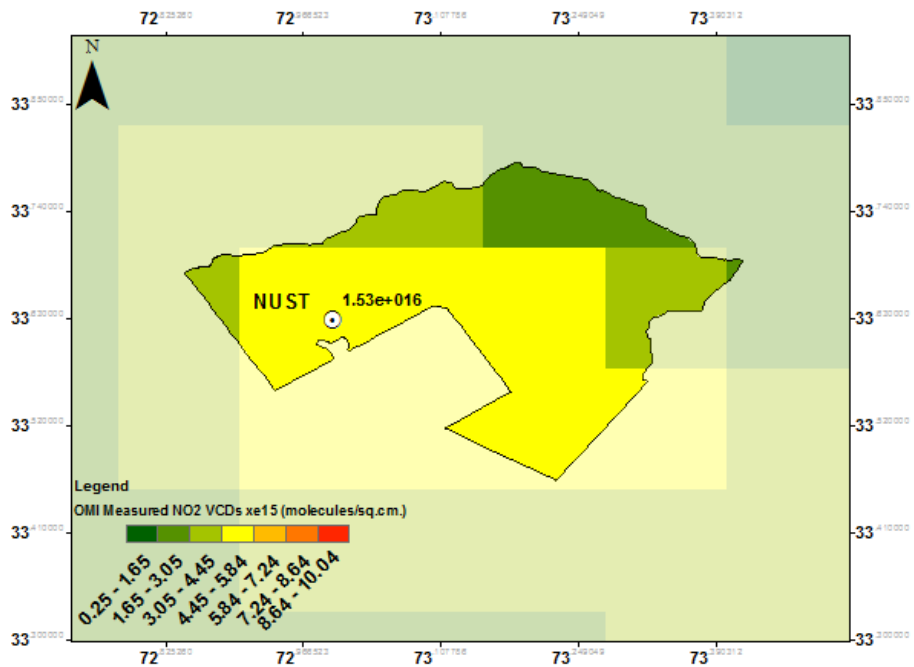


Figure 4.23: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for October 2014

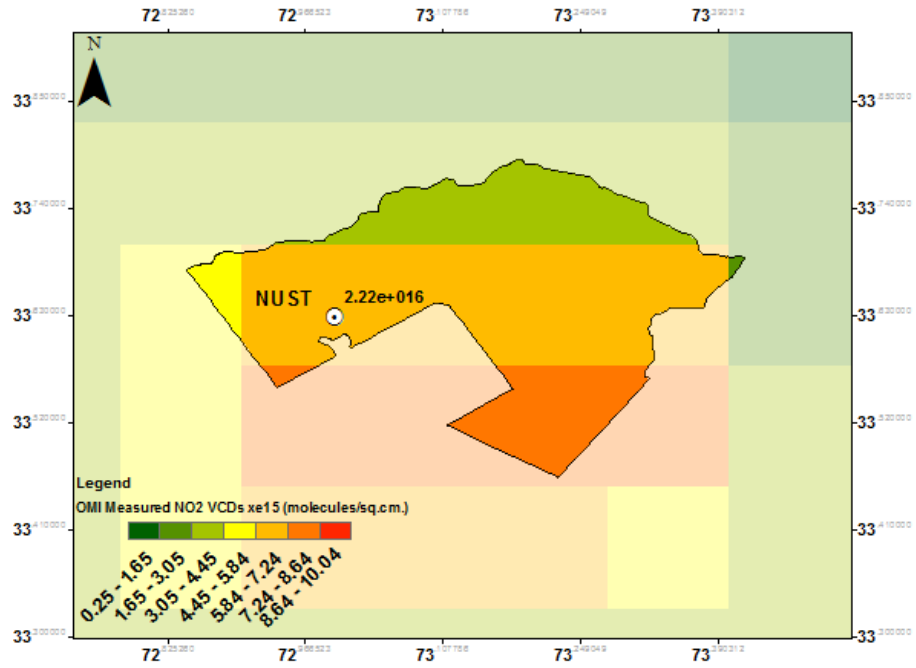


Figure 4.24: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for November 2014

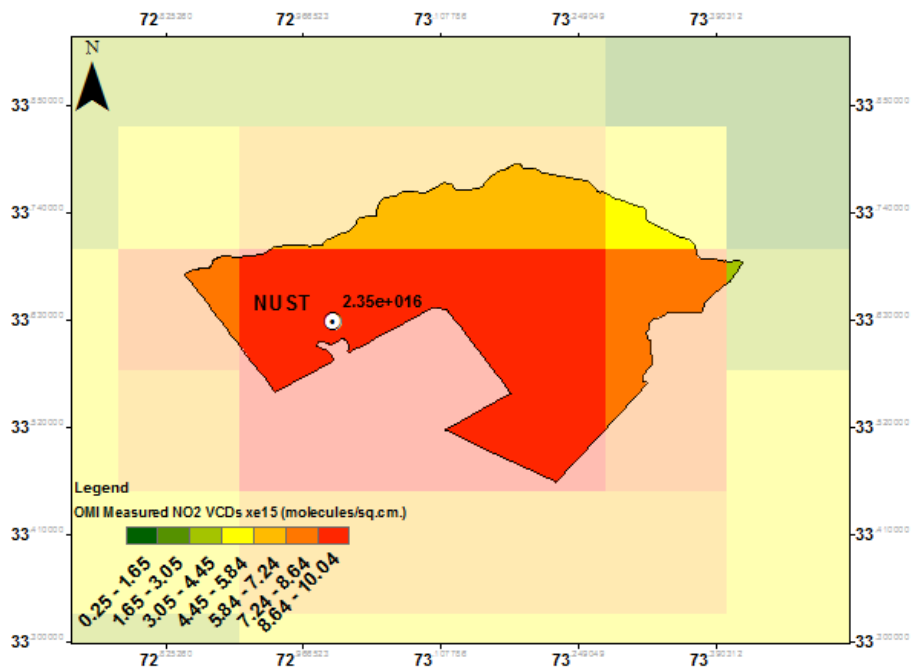


Figure 4.25: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for December 2014

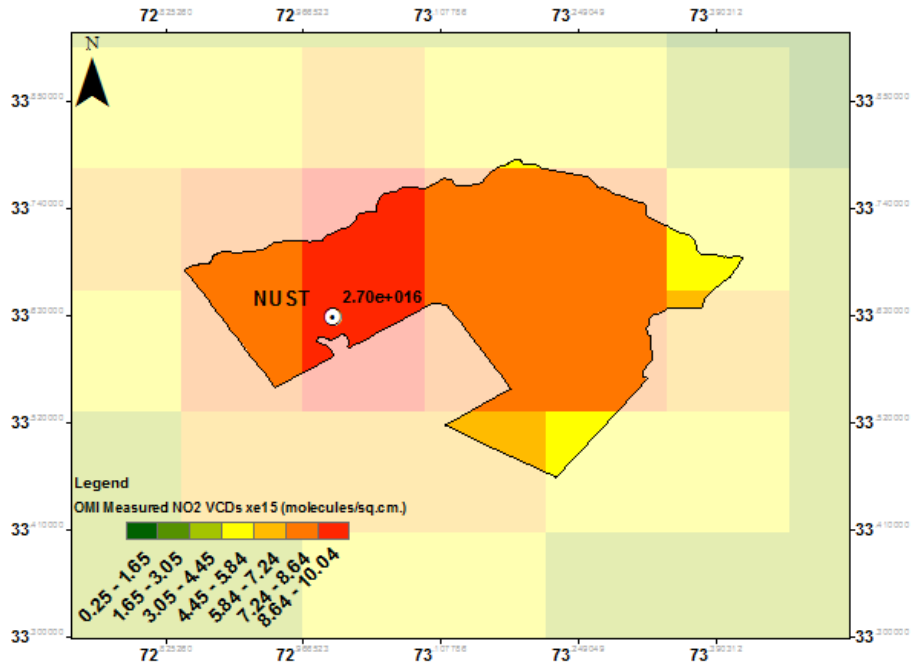


Figure 4.26: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for January 2015

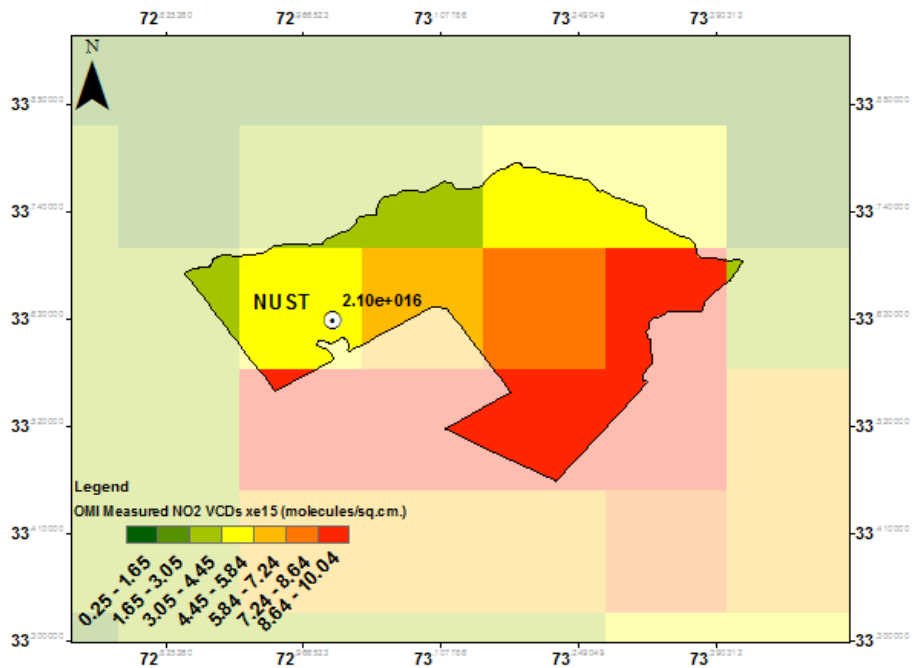


Figure 4.27: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for February 2015

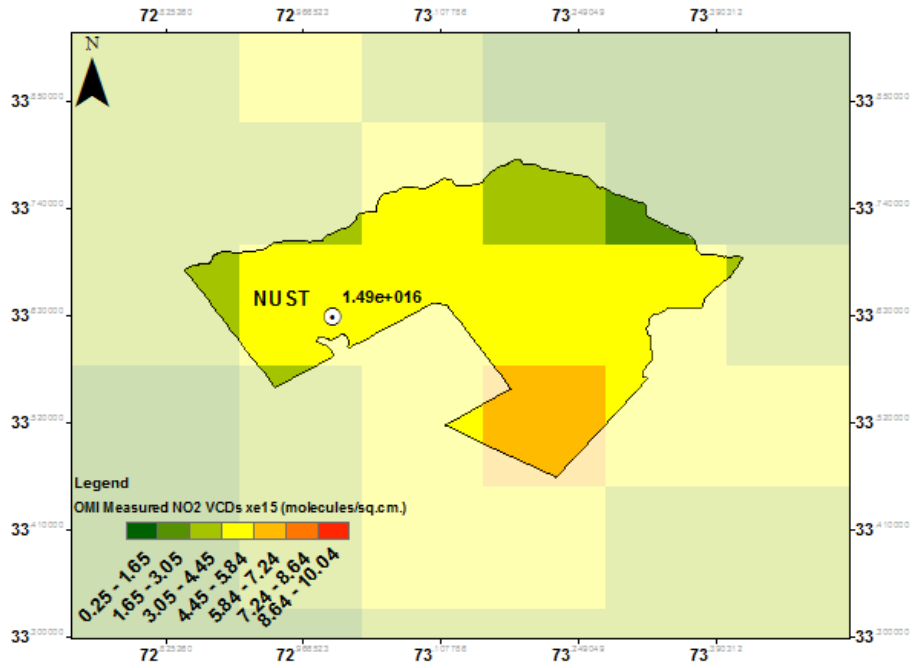


Figure 4.28: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for March 2015

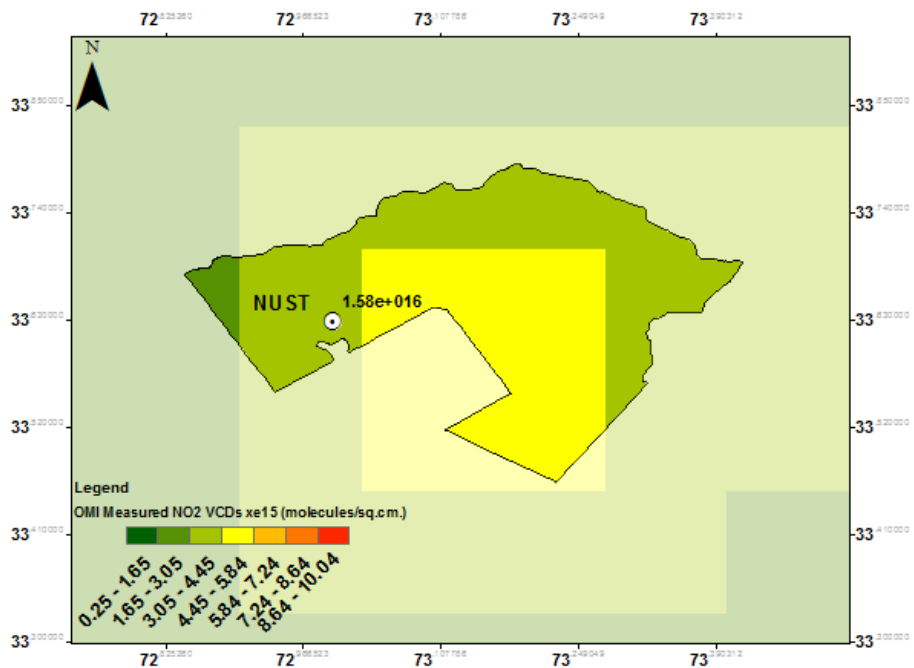


Figure 4.29: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for April 2015

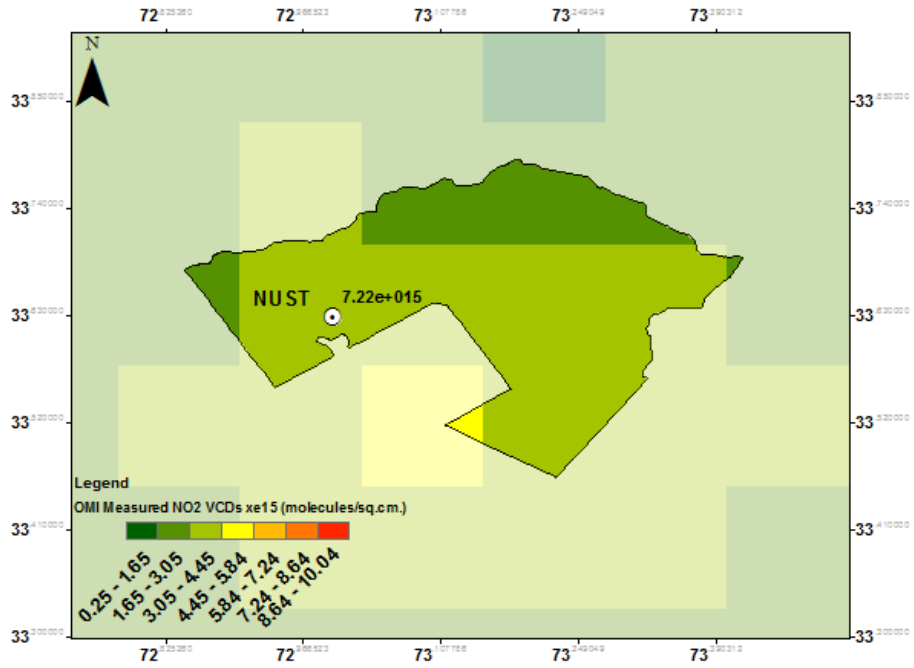


Figure 4.30: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for May 2015

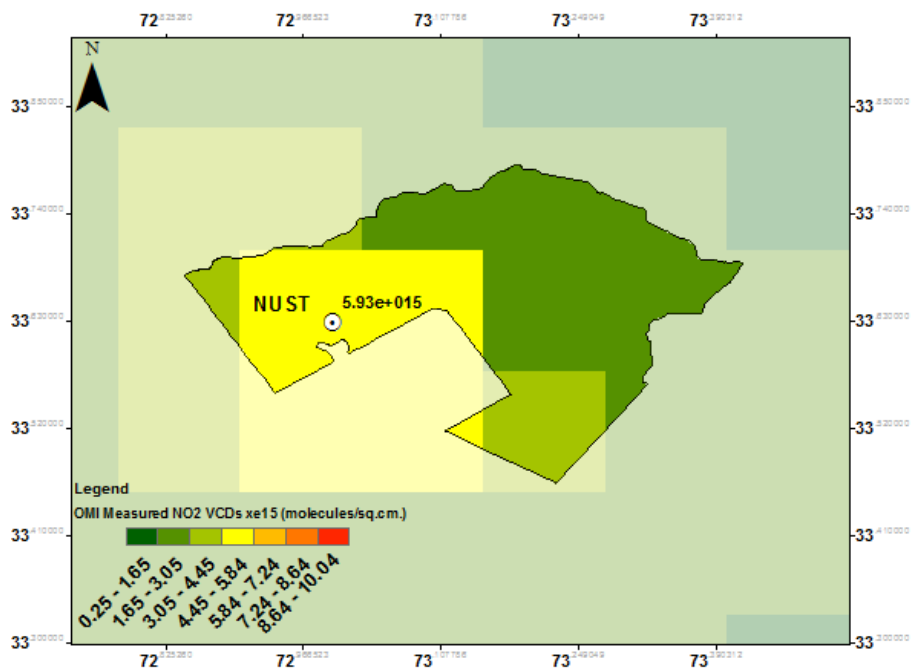


Figure 4.31: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for June 2015

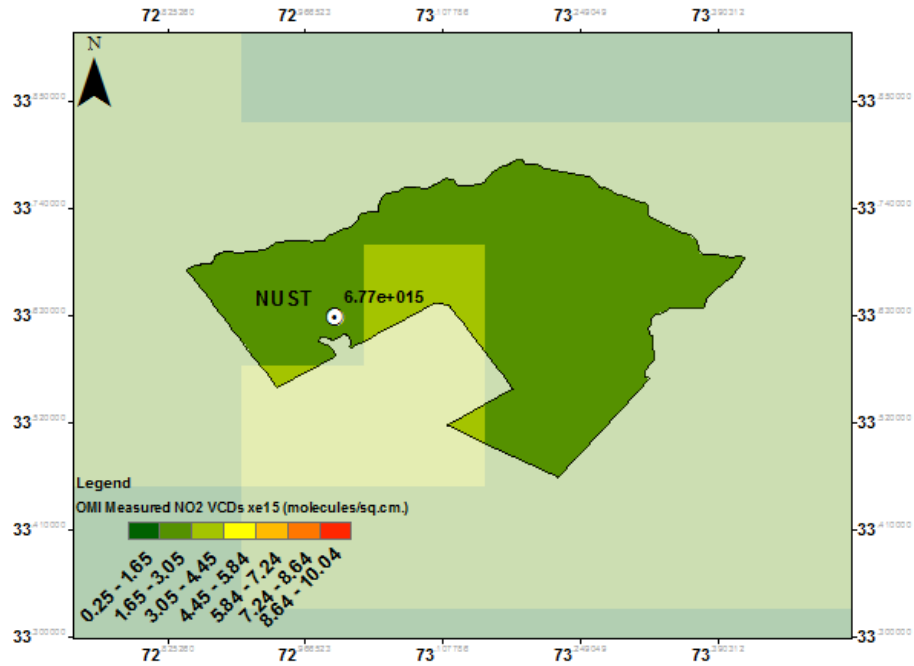


Figure 4.31: Showing Monthly mean Values of NO₂ concentrations (molecules/cm²) over Islamabad for July 2015

Fig. These are the maps showing monthly average values of NO₂ concentration over the capital city (Islamabad) of Pakistan from April, 2014 to July, 2015. The white circle with black spot specifies the monthly observed average values of NO₂ by Max-DOAS at IESE, NUST. Variations in temperature and the availability of OH ions cause the monthly variations of NO₂ concentration as presented above in Maps

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- Tropospheric column observations by MAX-DOAS were used to prepare the data base and keep the record of temporal evolution of NO₂ concentration at IESE. Highest values of NO₂ concentrations were observed along busy roads and near industrial areas, but most of the time the observed values were within WHO limits except for few locations.
- Results showed that road segments in northern Punjab are more polluted as compared to that in southern Punjab because of higher traffic density, population density and industrialization.
- Motorway (M-2) is less polluted as compared to National Highway because of less and controlled traffic volume.
- Continuous observations of NO₂ at a fix site were analyzed over IESE, NUST during the time period of April, 2014 to July, 2015. There is no specific pollution source within NUST premises but the observed NO₂ concentration was found higher on some occasion. Analysis shows that wind speed and direction in addition to other meteorological parameters play a significant role in determining the NO₂ pollution levels at IESE-NUST site. Kashmir Highway and Golra Moar are high traffic areas close to the NUST that are expected to be the primary source of air pollutants in NUST.
- The Higher NO₂ concentration were observed at the time of sun rise and sun set, but lower at noon because of higher photolysis rate. Comparison of MAX-DOAS observations with Ozone Monitoring Instrument showed similar trends but MAX-DOAS observed values were than OMI observations. This can be explained by the fact that MAX-DOAS observations are representative for point based observations as compared to OMI observations which are averaged over a pixel size of 13x24 km².

5.2 Recommendations

Some following suggestions are recommended on the basis of this research study to address the air quality issues and for future studies in this field.

1. More field campaigns may be conducted frequently over the same area to identify the possible major sources of pollution in that area.
2. Pollution Control Techniques (PCTs) may be adopted to reduce NO₂ levels like use of alternative fuels, improved combustion technology, energy saving strategy and the use of catalytic converter technology in vehicles.
3. Excessive traffic jams and vehicular emissions may be reduced by introducing Mass Transit System and better traffic management plan.
4. Public and Private sector awareness may also be raised by data sharing, awareness campaigns and media involvement.
5. There is a dire need to devise effective Air quality management plans at both regional and National levels with updated NEQS. Such studies should be performed in more numbers as they may help to provide an idea about updated Air quality situation.

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