INVESTIGATING THE IMPACTS OF EXTENSIVE USE OF CNG ON NO_2 COLUMN DENSITY OVER ISLAMABAD-RAWALPINDI USING SATELLITE AND GROUND BASED OBSERVATIONS

By

Zeeshan Javed

(NUST201261070MSCEE65212F)

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST)
Islamabad, Pakistan

(2015)

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

Investigating the Impacts of Extensive Use of CNG on NO_2 Column Density over Islamabad-Rawalpindi Using Satellite and Ground Based Observations

Submitted by

Zeeshan Javed

Has been found satisfactory for the requirements of the degree of
Master of Science in Environmental Science

Supervisor: _____
Dr. Muhammad Fahim Khokhar
Assistant Professor
IESE, SCEE, NUST

Member: _____
Dr. Imran Hashmi
Professor
IESE, SCEE, NUST

Member: _____
Dr. Muhammad Arshad
Associate Professor
IESE, SCEE, NUST

External Member:_____
Dr. Rizwan Bulbul
Assistant Professor
Department of Space Sciences
Institute of Space and Technology,
Islamabad

This thesis is dedicated to my Mother & Father

For their endless affection, support and encouragement

ACKNOWLEDGEMENTS

All praise to Allah Almighty for giving us the blessing of Wisdom.

This dissertation would not have been possible without the guidance and the help of several individuals who, in one way or another, contributed in the preparation and completion of this study.

First and foremost, I would like to express my gratitude to my supervisor ***Dr. Fahim Khokhar*** *for the useful comments, remarks and engagement through the learning process of this master thesis. Furthermore, many thanks also go to Dr.* ***Imran Hashmi*** *and* ***Dr. Muhammad Arshad*** *who had always been very considerate and supportive in my research work.*

I am also thankful to ***Dr. Rizwan Bulbul*** *(IST) for the technical support during my research work.*

I am grateful to the staff of the Air & Noise Pollution Lab for being very helpful during the field work.

I would also like to extend my thanks to all of my friends, well-wishers and love ones who gave me support, without whose support and understanding it would have taken a much longer time to finish this work.

Zeeshan Javed

Table of Contents

List of Abbreviation

$\mu g/m^3$	Microgram per Cubic meter
AMF	Air Mass Factor
ArcGIS	Arc Geographic Information System
C-CARGO	Climate Change and Atmospheric Research GrOup
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 Nitrile
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

List of Tables

List of Figures

Abstract

Air pollution is a major environmental concern worldwide. In Pakistan, urbanization and traffic is increasing at a faster rate and consequently the air pollution. Compressed Natural Gas (CNG) is an inexpensive, indigenous energy resource which currently accounts for the majority of automobile and domestic energy consumption. This extensive CNG usage, heavily influences the atmospheric composition and hence air quality. This study is designed to monitor the NO_2 concentrations over Islamabad-Rawalpindi, Pakistan. Mini MAX-DOAS (Multi Axis – Differential Optical Absorption Spectroscopy) instrument was used to perform ground-based measurements. The spectra were acquired for a period of six months i.e. October 2013-march 2014 at IESE, NUST and field campaigns were conducted in different scenarios when CNG was and was not available. Analysis was performed to retrieve NO_2 Differential Slant Column Densities (DSCD). It was observed that CNG availability significantly reduced the NO_2 Levels. Satellite observations from Ozone Monitoring Instrument (OMI) were compared with the ground-based observations from Mini MAX-DOAS. Tropospheric NO_2 VCDs derived from ground-based mini MAX-DOAS measurement at IESE-NUST monitoring site showed a reasonable agreement with satellite observations over Islamabad-Rawalpindi, Pakistan. The wind data was also used to identify the possible pollution pathways at NUST. High traffic densities on IJP Road, Kashmir Highway and N-5 Highway are the main sources of air pollution being transported to IESE-NUST monitoring site

Chapter 1

INTRODUCTION

1.1. Background

Fast advancement and modern development has prompted the issue of air pollution in the developing countries, including Pakistan, bringing about serious health consequences. Air quality monitoring is the first stride to recognize the extent and characteristics of air pollution. World Health Organization (WHO) and numerous national and global environmental organizations characterize air quality on the basis of certain criteria pollutants. Criteria pollutants include, ozone, particulate matter, carbon monoxide, lead, nitrogen oxides, and sulfur oxides (*US-EPA*). It was assessed in 2010, that more than 51% of population of the world exist in urban ranges, and this is unsurprising to ascend to 61% by till 2030 (*United Nations, 2009*). Because of this hurried development in the urban populace, the urban environment contamination is an issue that now requires vital consideration, presenting new advances and developing measures ought to be considered to move toward feasible and incorporated arrangement.

1.2. Compressed Natural Gas (CNG)

World largest CNG user is Pakistan, declared in earlier 2010. Currently, more than 3,000 CNG stations are operating in 99 towns and villages, and over 1,000 would be installed in the next two years. These stations have provided employment to over 50,000 people in Pakistan (Khan et al., 2014)

A surge in the number of CNG-fuelled vehicles aggravated the winter Compressed Natural Gas (CNG) shortage in Pakistan. During last five years almost 80% of vehicles are using Compressed Natural Gas (CNG). CNG consumption has

increased in Pakistan. CNG is a mixture of hydrocarbons, mainly methane. Oxidation of methane results in the formation of formaldehyde in the atmosphere and troposphere especially in those regions where CNG is used on larger extent.

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

According to Pakistan National Environmental Quality Standards (Pak-NEQS) limits for certain pollutants are given for the ambient air.

Table 1.1: National Environmental Quality Standards for Ambient Air Quality

Pollutants units (µg/m^3)	Time-weighted average	Concentration in ambient air Effective from 1st January 2009	Effective from 1st January 2012	Method of Measurement
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 m^3/ 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 ($PM_{2.5}$)	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 ppbv = 1.88 µg/m^3

Monitoring of these pollutants ought to be done regularly to asses' ambient air quality over Pakistan to cope with the growing issue of air contamination. The Pak-NEQS for ambient air quality are presented in table 1.1.

1.4. Study Area

Islamabad and Rawalpindi are seen as a component. The two cities are 15 km away and can be considered as a single mega-city. Islamabad is the capital city. Islamabad and Rawalpindi are both in the Pothwar plateau in northwest Pakistan. Twin Cities are at 33 ° 40N 73 ° 10E. The total population of over 4.5 million. The climate of Islamabad has a typical humid subtropical climate version. Rapid population growth and progress in all aspects has always been growing tensions over natural resources and causing adverse effects on the environment (Sheikh et al., 2007).

Population growth and industrialization are major causes of increase in atmospheric pollution (Aslam, 2012). Air quality has worsened, especially in the major cities of Karachi, Lahore, Rawalpindi, Islamabad, Gujranwala and Faisalabad (Lodhi-Pak-EPA, 2008). The main sources of air pollution in urban centers in Pakistan are transport and industrial activities (Ahmed et al., 2012; Jahangir et al., 2013; Ali et al., 2006; Khan et al., 2007, Hussain, 2010). Due to increased demand for energy, NO2 levels increased 25-fold in the power sector in Pakistan (Khawaja et al., 2005). Therefore, air pollution results in photochemical smog, fog and mist (Yasmeen et al., 2012, Muslehuddin et al., 2000). Air quality monitoring is mandatory in order to know the size and characteristics of air pollutants (Shigeta, 2000).

Due to flexible packages of loans provided by the government / banks and growth of car rental agencies in the past decade, the number of cars have increased and air quality has worsened.

1.5. The Present Study

Rapid development and rise in vehicular density in Pakistan has created severe socioeconomic, environmental, health, and welfare impacts.

This study principally focusses on the monitoring of NO_2 column densities over the twin cities of Rawalpindi and Islamabad. This measurement is done using Max-Doas (Multi-Axis Differential Optical Absorption Spectroscopy). The instrument was mounted on IESE, sector H-12, Islamabad for continuous point observations. Field campaigns were conducted in different regions of Rawalpindi-Islamabad. Further analysis was performed by using DOASIS, and the results were compared with satellite observation of NO_2 over study region. This study was structured around two major objectives i.e.

- To estimate the concentration of NO_2 over the cities of Rawalpindi-Islamabad
- To evaluate the impact of extensive use of CNG on NO_2 concentration

1.6.Expected Benefits From The Study:

Outcomes of this research will provide baseline for advance research in air pollution monitoring. The study will help us to know the contribution of several sources (traffic congestion, industrial activities and meteorological parameters etc.) on trace gas concentrations. By assessing the contamination profile over the urban areas, one can better constrain the emission from each city. The information can be utilized as a gauge by other organizations and Non-Government Organizations (NGO's)

Chapter 2

LITERATURE REVIEW

2.1. Atmospheric Composition

The air is a dynamic framework in which different gasses, fluids and solids collaborate with one another constantly; making it an extremely troublesome framework to understand it. However the air is separated into four parts. (Wallace et al., 2006) as illustrated in figure 2.1.

1. Troposphere
2. Stratosphere
3. Mesosphere
4. Thermosphere

2.1.1. Troposphere:

The troposphere is the lower most part of Earth's air. It contains more or less 75% of the atmosphere's mass and 99% of its water vapor and aerosols. The normal profundity of the troposphere is 17 km (11 mi) in the middle latitudes. It is deeper in the tropics, up to 20 km (12 mi), and shallower close to the polar areas, nearly 7 km (4.3 mi) in winter. The most reduced piece of the troposphere, where contact with the Earth's surface impacts wind stream, is the planetary limit layer. This layer is normally a couple of hundred meters to 2 km (1.2 mi) deep relying upon the landform and time of day. Nitrogen -78%, Argon - 1% , Oxygen - 21%, with variable concentration of H_2O, CO, CH_4, NO_2, CO_2, O_3, and N_2O. The ozone level in the troposphere is low; nearly 8% of the aggregate ozone exists in the troposphere. (Encyclopedia of Science & Technology, 1984)

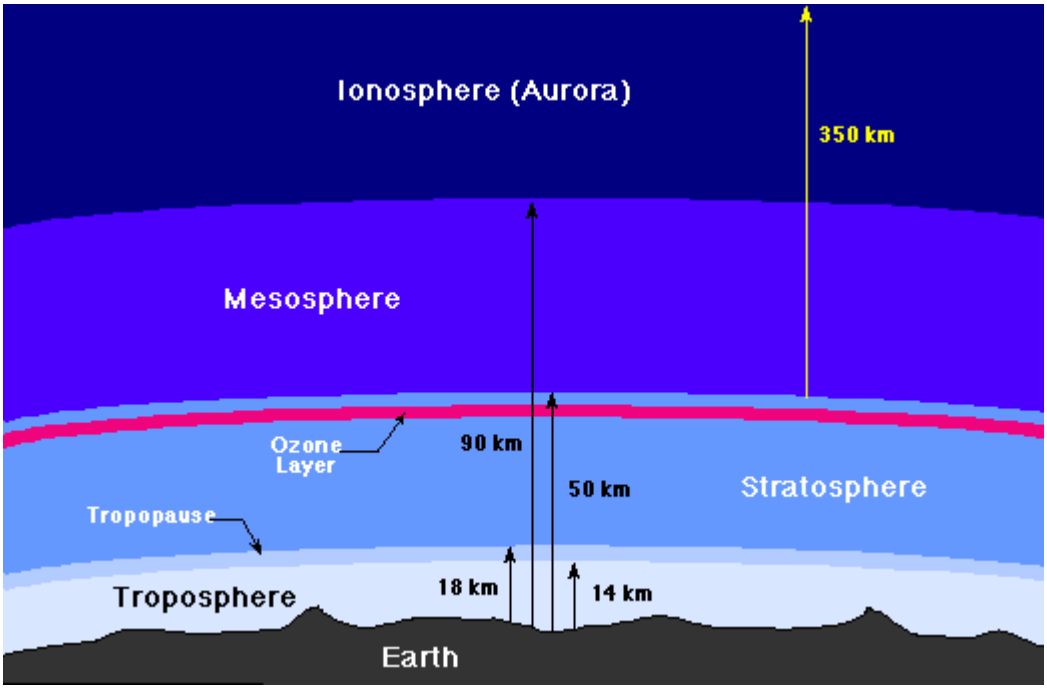


Figure 1.1: Atmospheric composition of Earth

2.1.2. Stratosphere

The layer of the atmosphere right over the troposphere is the stratosphere. The border between the troposphere and the stratosphere is known as the tropopause. The stratosphere goes nearly till 50 km over the surface of the earth. It is categorized by occurrence of Ozone (O3) as it retains destructive ultra-violet beams and keeps it from getting to the world's surface.

2.1.3. Mesosphere

The term mesosphere is derived from two Greek words, "*mesos"* meaning "middle" and "*sphaira"* meaning "ball". This layer of the atmosphere occur between stratosphere and thermosphere. It extends up to 90 km above the earth's surface. The mesosphere is difficult to study and researchers have not sufficient data of mesosphere due to confinement of abundance of excess of weather balloons and jet planes in the mesosphere. The directions of satellites are also over the mesosphere.

2.1.4 Thermosphere

The thermosphere is present in the middle of the mesosphere and the exosphere. It extends from about 90 km to 1,000 km, above the earth surface. The atoms in the thermosphere are broken by high vitality UV and X-beam photons present in the daylight. In the upper thermosphere, nuclear oxygen (O), nuclear nitrogen (N), and helium (He) are the fundamental constituents.

2.2. Atmospheric Trace Gases

Atmospheric trace gases are of great importance because they play a significant role in environmental issues of earth in spite of their low concentration. The processes like stratospheric ozone depletion, climate change, acid deposition and photochemical smog in urban areas are occurring due to atmospheric trace gases. Human and anthropogenic actions have altered the composition of atmosphere for the past few years.

Anthropogenic activities have increased the greenhouse gas concentration. Man-made halocarbons has increased the greenhouse effect. Photochemical oxidation of Methane and non-methane volatile Organic Compounds (NMVOCs) occurring in the presence of oxides of nitrogen and carbon monoxide produce tropospheric ozone (O_3) which also results in greenhouse effect. The long-lived species CH_4, halocarbon, and N_2O reach the stratosphere and their degradation products cause ozone chemical depletion.

Atmospheric species interact through physical and chemical processes and are connected in a non-linear and very complicated way producing feedbacks that can increase or reduce the disturbance. According to scientific evidence Climate and air

quality are strongly connected. Any alteration in climate can affect the chemical atmospheric composition, for example by changing emissions or atmospheric chemical processes. Impact on radiative forcing and lifetime of greenhouses gases is caused by changes in atmosphere and distribution of ozone (Forster et al. IPCC, 2007).

Non-methane volatile organic compounds (NMVOCs) play a role in production of ozone therefore they have a significant impact on the oxidizing capacity of global troposphere. NMVOCs have significant impact on composition of troposphere (Houweling et al., 1998). They also play important part as precursors of secondary organic aerosols (SOA) (Kanakidou et al., 2005).

2.3. Nitrogen Dioxide (NO_2): A Major Criteria Pollutant

Nitrogen dioxide (NO_2) gas is reddish-brown in color with an irritating pungent odor. The light is absorbed by NO_2 and results in the mist of yellow-brown color seen regularly over the metropolitan cities. It is one of the major constituents of photochemical smog. NO_2 is only the pollutant that has not been in control from the start the air quality standards. The reason is that the sources of NO_2 includes vehicles and power plants which are increasing in number, resulting in increase of NO_2. (Lundy et al., 2011, Han et al., 2006)

NO_2 is a significant atmospheric trace gas in the atmosphere of Earth. It is present in the troposphere (due to lightning) and in the stratosphere naturally. It is a main species in both tropospheric and stratospheric chemistry. In the stratosphere, this plays an important part in the destruction of ozone and transformation of halogen oxides in species which are less active. The main sources of NOx in the troposphere (family of nitrogen oxides NO + NO2) are soil emissions, the combustion processes of

automobiles, industrial processes, the burning of biomass and lightning (Lamarque et al., 1996).

2.3.1. Sources of Nitrogen Dioxide

Atmosphere contains a large amount of nitrogen in the form Nitrogen gas (N_2) which form 78% of the atmosphere. This nitrogen gas is inactive and it cannot be used by plants. It is then transformed into various secondary products which are used by plants and animals e.g. Nitrates $(NO_3)^-$, Nitrites $(NO_2)^-$, Ammonia (NH_3) etc. Oxides of nitrogen occur naturally and also are formed by human activities. Their natural sources include lightning, bacterial processes, biological growth, decay and forest fires. Anthropogenic source is from the burning of fossil fuels i.e. from vehicular emissions and industrial activities as represented in figure 2.3.

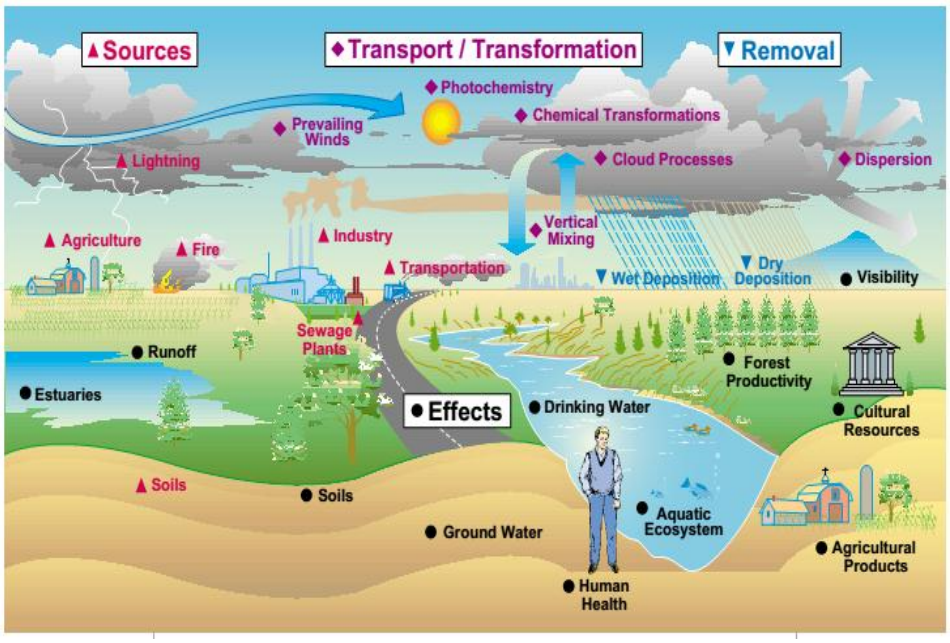


Figure 2.2: Atmospheric nitrogen pathways.

**Source: Adapted from National Science and Technology Council Committee on Environment and Natural Resources, Air Quality Research Subcommittee, 1999.*

Nitrogen oxides occur in the form of nitric oxide, some is nitrous oxide and less than 10 percent is nitrogen dioxide. The measure of nitrogen dioxide created changes

with the temperature of combustion; as temperature raises, the amount of nitrogen dioxide produced also increases. Agriculture also plays a role in nitrogen oxide emissions with the usage of fertilizers contributing nitrous oxide to the atmosphere. Whereas, NO_2 lifetime ranges from few hours to some days (Seinfeld and Pandis, 2006; Jaeglé et al., 1997) (Crutzen et al., 1979; Takegawa et al., 2003). The sinks of nitrogen oxides involve dry and wet deposition in the form of acid rain.

2.3.2. NOx Cycle

Its basic part is rapid cycling among NO and NO_2 due to oxidation and photo catalytic reactions. This conversion take place in few minutes and these species ($NO+NO_2$) are together known as NO_x. This step is also called as the null cycle.

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad \text{(Eq.1)}$$

$$NO_2 + h\nu\ (+O_2) \longrightarrow NO + O_3 \qquad \text{(Eq.2)}$$

Net Reaction:

$$O_3 + h\nu \longrightarrow O_3 \qquad \text{(Eq.3)}$$

The sink for NO_x is its conversion into HNO_3 by oxidant OH:

$$NO_2 + OH + M \longrightarrow HNO_3 + M \qquad \text{(Eq.4)}$$

The NO_x is lost at night by oxidation of NO_2 by Ozone and consequent change of the NO_3 to N_2O_5:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad \text{(Eq.5)}$$

$$NO_3 + NO_2 + M \longrightarrow N_2O_5 + M \qquad \text{(Eq.6)}$$

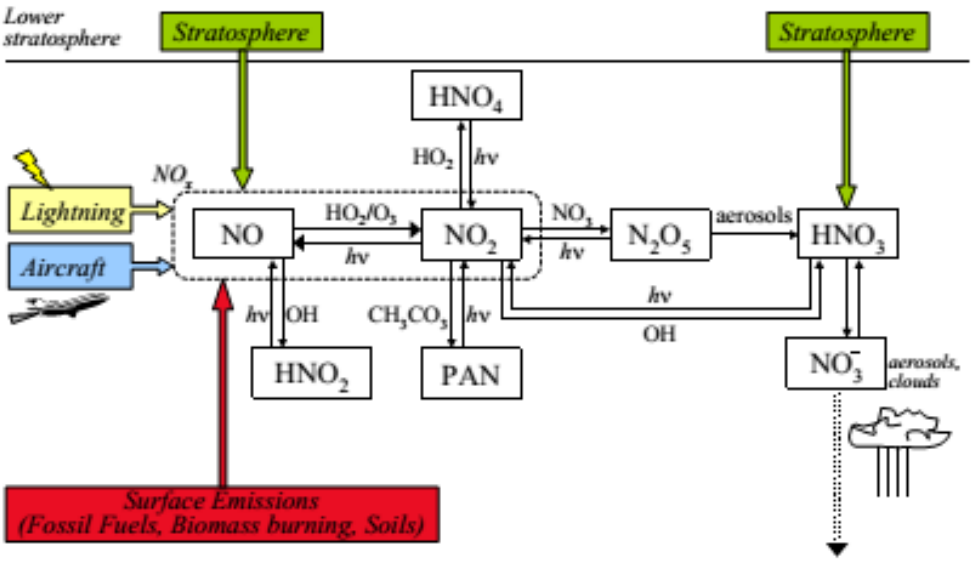


Figure 2.3: The NOx Cycle

N_2O_5 is formed only at night, because NO_3 is photolyzed to NO_2 during daytime:

$$NO_3 + h\nu \longrightarrow NO_2 + O \qquad \text{(Eq.7)}$$

NOx oxidation, results in N_2O_5 and HNO_3, both have long retention times in the atmosphere. During daytime, these species are ultimately transformed back to NO_x.

$$HNO_3 + h\nu \longrightarrow NO_2 + OH \qquad \text{(Eq.8)}$$

$$HNO_3 + OH \longrightarrow NO_3 + H_2O \qquad \text{(Eq.9)}$$

$$NO_3 + h\nu \longrightarrow NO_2 + O \qquad \text{(Eq.10)}$$

$$N_2O_5 + h\nu \longrightarrow NO_3 + NO_2 \qquad \text{(Eq.11)}$$

Nitrous Oxide (N_2O) is produced both through natural as well as anthropogenic activities. Its retention time is long which allow it to be transported in the stratosphere.

Therefore, HNO_3 and N_2O_5 serve as reservoirs for NO_x. The final removal of NO_x takes place in the troposphere in the form of HNO_3 by acid deposition.

2.3.3. Impacts of Nitrogen Dioxide

Nitrogen oxides are released primarily in the form of nitric acid (NO) oxide, is non-toxic, but it converts into NO_2 in air.

At high levels of pollution, primarily NO_2 is toxic to plants, can damage the leaves and cut the growth and performance. In combination with ozone (O_3) or sulfur dioxide (SO_2), nitrogen dioxide can cause harmful effects at even lower levels of pollution. As a constituent of photochemical smog, nitrogen dioxide is precursor of photochemical production O_3

2.3.3.1.Health Impacts

The respiratory system of living organisms is affected by nitrogen dioxide. The danger of respiratory disease is increased by breathing certain concentration of nitrogen dioxide and it can results in malfunctioning of lungs in old age. There is additionally a relationship between nitrogen dioxide contamination levels and rise in death rates and hospital admissions because of respiratory diseases.

Experimental studies on humans and animals shows that severe dose of NO_2 up to or above 100 ppbv concentrations – because of its toxic nature can cause significant health impacts. NO_2 exposure at levels above current ambient pollution levels has hostile health impacts (WHO, 2003).

2.3.3.2.Environmental Impacts

NO_2 brings about a broad variability of environmental effects on account of different species, compounds and derivatives in the group of nitrogen oxides. These effects are examined in the following section:

Ozone at Ground Level and Photochemical Smog: Ground level or "bad" ozone is formed when volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) reacts in the presence of sunlight. The ozone and the particulate matter (PM) formed cause the formation of photochemical smog.

Acid Rain: HNO_3 and HNO_2 are secondary pollutants of NO_2. For oxides of nitrogen major sink is the Acid rain; acid rain has numerous harsh effects on ecosystems, human health and infrastructure (buildings, bridges etc.). Nitrogen dioxide concentration of 60 ppbv is toxic to plants. It declines plant development. NO_2 forms acids and these can be corrosive to building materials at higher concentrations.

2.4. Remote Sensing and DOAS

Atmospheric elements and parameters can be measured by in situ techniques (taking samples) or by remote sensing. Remote sensing originates from military surveillance and investigation purposes, which is still key feature of this technique.

Over time, remote sensing was espoused for scientific issues, starting with the monitoring of the ozone layer (Dobson and Harrison, 1926), extending our understanding about nature and has turn into a significant tool in environmental science. Spectroscopic observations can be performed from ground-based instruments on several locations and a global view of trace gas can be observed from satellite-based platforms. Ambient air quality can be monitored by using different spectroscopic

methods. These methods have few differences but normally they are based on the "The Lambert Beer Law" which shows the relation among light and matter. Different trace gases have been measured by Differential Optical Absorption Spectrometry (DOAS) (Platt and Perner 1979; Cheng and Chan, 2004; Kim and Kim, 2001)

.

2.4.1.Active and Passive DOAS:

MAX-DOAS technique which falls in the passive DOAS category is used for monitoring of trace gases in the troposphere (Sinreich et al., 2005). The MAX-DOAS technique has been effectively used for the monitoring of different trace gases e.g. BrO, HCHO, NO_2, SO_2 and CHOCHO (Wagner et al., 2011). Both active (using artificial lighting sources) and passive (using sunlight) techniques are used in spectroscopic measurements. But these techniques are comparatively complicated and significantly more costly than the other NO_2 measurement techniques.

2.4.2.DOAS

DOAS is a technology of remote sensing allowing the monitoring of atmospheric trace gases through the use of structured absorption bands in the ultraviolet and visible spectral regions. It is one of spectroscopic methods and applied on a large scale in atmospheric research. The relevant molecules include NO_2, O_3, HCHO, H_2O, O_4, and SO_2

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,

$$I(\lambda) = I_o(\lambda)\, e^{-\alpha LC} \qquad \textit{(Eq.2.1)}$$

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*)

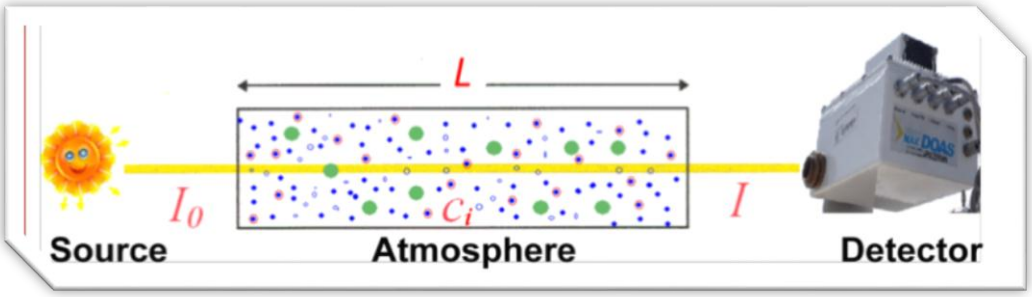


Figure 2.4: Illustration of DOAS Principle

Keeping the scattering processes in considerations the DOAS equation becomes:

$$I(\lambda) = I_0(\lambda)\cdot\exp\left(-\int_0^L\left(\varepsilon_R(\lambda,l)+\varepsilon_M(\lambda,l)+\sum_i\sigma_i(\lambda,p,T)\cdot c_i(l)\right)dl\right) \quad \textit{(Eq.2.2)}$$

$I\ (\lambda)$: 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.

$$\sigma(\lambda) = \sigma_b(\lambda) + \sigma'(\lambda) \qquad \textit{(Eq.2.3)}$$

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 one giving a strong dependence on the wavelength due to narrow-band trace gas absorption. The Beer-Lambert Law can now be written as:

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

$$\cdot\exp\left(-\int_0^L\left(\sum_i\sigma_i'(\lambda)\cdot c_i(l)\right)dl\right) \qquad \textit{(Eq.2.4)}$$

Scattering processes contributes 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.

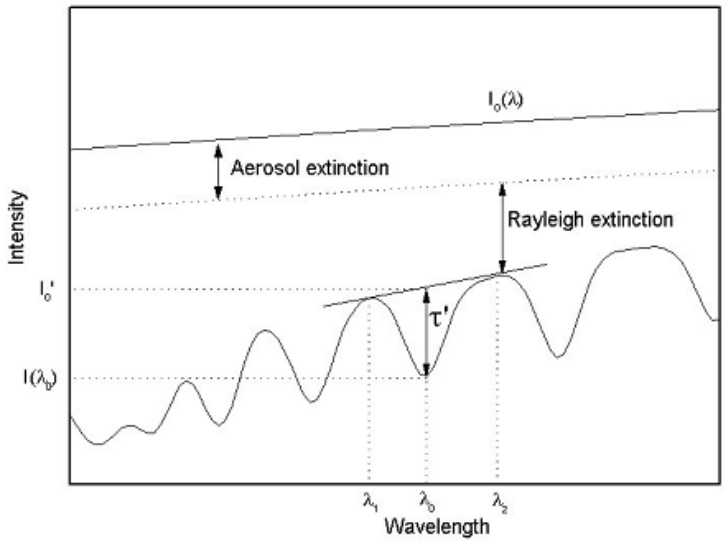


Figure 2.5: Attenuation of radiation in the atmosphere

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'.

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

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

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

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

2.5. Recent Studies on NO_2 Pollution using Car-Max-DOAS

Wagner et al., 2010, retrieved NO_2 VCD with MAX-DOAS observations by car drive from Brussels to Heidelberg in September, 2006 (Wagner et al., 2010). Three elevation angles 22°, 40°, and 90° were used for measurements. Ground based observations were validated using Ozone Monitoring Instrument (OMI) satellite data

which showed, fair agreement i.e. as compared to Auto-MAX-DOAS observations, satellite observations were 25 to 100% larger (Wagner et al., 2010).

Shaiganfar et al., 2011, retrieved NO_2 VCD's in New Delhi (INDIA) by using Car-MAXDOAS in April 2010 and January 2011. The NO_2 concentrations were related to traffic congestion and other sources present in the study area. Furthermore these NO_2 emissions were validated with satellite data.

Constantin et al., 2011, measured Nitrogen Dioxide during the month of July and August 2011, in the South-Eastern part of Romania. The experiment focused on areas with emissions of nitrogen dioxide from industrial areas or busy roads. It was observed that nitrogen dioxide concentrations were due to iron and steel industry away from cities, heavy traffic within the cities and ring roads around South East cities of Romania.

Kanya et al., 2014, conducted observations of NO_2 VCD at seven sites, in Korea Japan, Russia, and China using Max-DOAS. The average general diurnal variation of NO_2 showed daytime decrease and weekend reductions

2.6. RECENT STUDIES ON EFFECT OF CNG ON AIR QUALITY

Suthawaree et al., 2012, studied influence of extensive CNG usage on air quality of Dhaka it was observed trace gases concentrations were significantly reduced when CNG fuelled vehicles were increased

Goyal et al., 2013, studied scenario of air quality in Dehli after CNG implementation and they found out that NO_X emissions were reduced by 6 % after CNG implementation

Recent Studies on NO_2 Pollution Monitoring in Pakistan

70% of NO_2 pollution in Pakistan is being emitted from industries, transportation and power plants (*GOP/IUCN, 1992*). The growth rate of vehicles from 1995 to 2005 in Pakistan has been 33.61% annually (Ilyas et al., 2007), which has worsened the ambient air quality.

After the implementation of Pak-NEQS, nothing has been done for air quality monitoring in Pakistan. Nitrogen Dioxide is one of the criteria pollutant. To assess the situation of ambient air quality in Pakistan, Pakistan Environmental Protection Agency (Pak-EPA) and Japan International Cooperation Agency (JICA) conducted air sampling in Lahore, Rawalpindi, and Islamabad in 2000. The criteria pollutants i.e. Sulphur Dioxide, Carbon Monoxide, Ozone, Nitrogen Oxides, Particulate Matter and Hydrocarbons were monitored during the study. In the cities NO_x levels were high mainly due to traffic jamming. Lahore was found to be the most polluted city in terms of air quality (JICA, 2000).

Ali et al., 2006, monitored ambient air quality along different sections of N5 highway. Different sampling techniques were used to monitor different criteria pollutants i.e. i.e. Sulphur Dioxide, Carbon Monoxide, Ozone, Nitrogen Oxides and Noise Level. Lahore – Gujranwala Section of the highway was found to be polluted with NOX.

Zafar et al., 2012 monitored NO_2 pollution at different locations of the Islamabad and Rawalpindi city. The study was divided in two phases, in first phase measurements were done in winter season while the second phase measurements were done in spring season. The NO_2 pollution was correlated with traffic jamming and industrial activities of the twin cities.

Jahangir et al., 2013 monitoring NO_2 concentration near private and public sector hospitals in the cities of Rawalpindi and Islamabad. NO_2 concentration was higher near hospitals located on the busy roads due to frequent traffic jamming.

Many initiatives have been taken to monitor air quality at National university of Sciences and Technology (NUST) using Mini Max-DOAS instrument.

Mehdi et al., 2013 monitored NO_2 within the cities of Rawalpindi and Islamabad with mobile monitoring.

Nisar et al., 2013, monitored NO_2, Formaldehyde (HCHO) and Ozone (O_3) with Max-DOAS mounted on roof top of Institute of Environmental Sciences and Engineering (IESE), NUST.

Shabbir et al., 2013, monitored NO_2 concentration along N-5 Highway. *Fatima et al., 2013*, prepared database for NO_2 Vertical column densities (VCDs) from satellites observation using SCIAMACHY (2002 – 2012) OMI (2004 – Present) and Global Ozone Monitoring Experiment-2 (GOME-2) (2007 – Present) to study spatial and temporal trends of NO_2 pollution over Pakistan. According to the study the NO_2 levels are highest near the urban centers of Pakistan with NO_2 levels highest during the winter season.

Chapter 3

INSTRUMENTION AND METHODOLOGY

3.1 Mini Max-DOAS Instrument:

The Mini-MAX-DOAS instrument is used on a mobile platform (termed as Car Max-DOAS) (Bobrowski et al., 2003). The dimensions are 13cm × 19cm × 14cm, as it is light weighted and fully automated spectrometer. The entrance optics is controlled by a closed aluminum box which contains a fiber joined spectrograph. A stepper motor controls the elevation of the viewing angle by rotating the whole instrument. A 40mm focal length quartz lens is present at the entrance optics. 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).

3.2 Measurements at IESE NUST SITE:

The measurements started from October 2013 to March 2014 and the measurements were taken on continuous basis from dawn to dusk. Solar irradiance spectra were recorded at the 1°, 2°, 4°, 5,6,, 8°, 10°, 15°, 20°, 30°, 45° and 90° elevation viewing angles. The interval of an individual measurement was one minute resulting in a total of around ten minutes per complete cycle of viewing angles. Temperature of the mini MAX-DOAS instrument was set at 15C for all the measurements. In the month of January 2014 CNG was closed, while in rest of the months it was available. For accurately quantifying emissions of various air pollutants, information about wind speed, wind direction are mandatory parameters. Therefore the wind data was collected

during the entire study period from NASAs freely available meteorological data from Air Resources laboratory (ARL). http://ready.arl.noaa.gov/READYamet.php.

3.3 Field Campaigns within twin cities:

The Mini-MaxDOAS was mounted on a van and field campaigns were conducted in twin cities of Rawalpindi-Islamabad. Field campaigns were done in two phases. In first phase campaign was conducted in Rawalpindi and Islamabad on 30th December 2013 when CNG was banned. During the 2nd phase field campaigns were conducted when CNG was available from 4th of March to 8th of March 2014, in different areas of Rawalpindi-Islamabad. The viewing direction of the lens of the instrument was adjusted to view in backward direction. The monitoring days were fairly sunny. The elevation angles were chosen as one 90° angle followed by 4 angle of 30° (i.e. 1x90°, 4x30°). To avoid interference in measurements from nearby buildings or trees sequence of higher angles were chosen. The 30° angles are preferred due to their ease in calculation for tropospheric Air mass Factor (AMF) (Wagner et al., 2010). The integration time for an individual spectrum was approximately 60 seconds. The whole setup was connected to the laptop and 12 volts battery was used as a power source. A power backup for laptop and instrument was also available for the complete filed campaigns.

3.4 Software used for Research Work

The estimation and plotting of Nitrogen Dioxide VCD required use of various software as presented in table 3.1.

Table 3.1: Software and their Purpose for use in Research Work

Sr. No.	Software	Purpose

1.	Differential Optical Absorption Spectroscopy Intelligent System (DOASIS)	Operating Software for MaxDOAS and measurement of back scatter intensities
2.	Windows Differential Optical Absorption Spectroscopy (WinDOAS)	Analysis of UV-Visible Spectra by DOAS to retrieve DSCDs
3.	Microsoft Excel	Mathematical Calculations for tropospheric VCD extraction and Graphical representations
4.	SQL Database	Time Linkage between coordinates and extracted NO_2 VCD
5.	Arc Geographic Information System (ArcGIS)	Plotting and representation of measured NO_2 VCD over maps

3.4.1 Differential Optical Absorption Spectroscopy Intelligent System (DOASIS)

DOASIS is used to operate the car Max-DOAS instrument during its recording of measured spectra as shown in figure 3.2. It has various functions as to control stepper motor, integration time of spectrum and internal temperature of the spectrometer. DOASIS is also used for Ring spectrum calculation which is later used in the DOAS fit analysis.

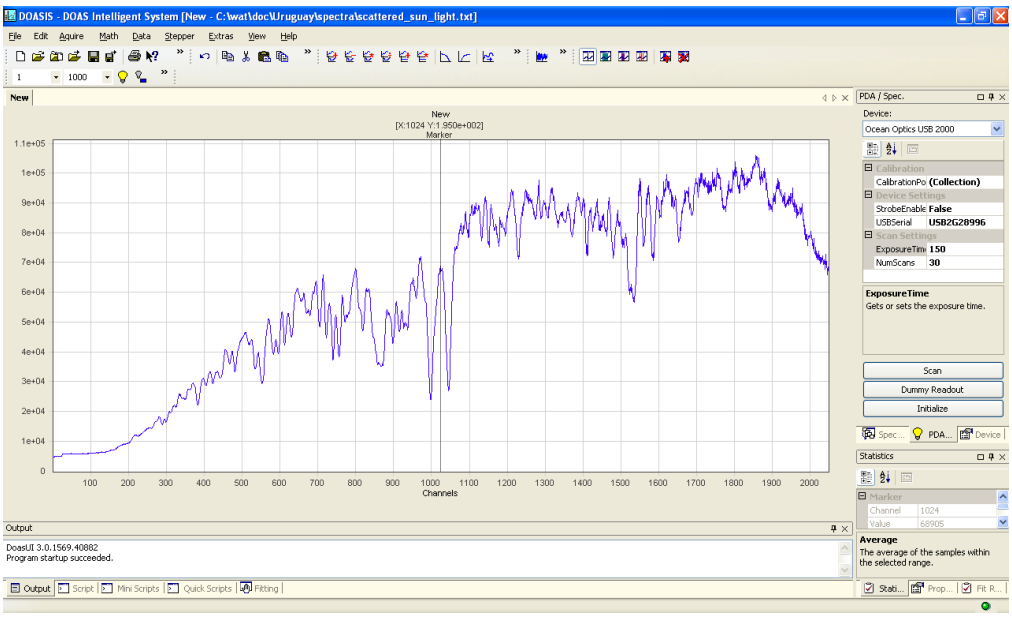


Figure 3.1: A DOASIS Window

DOASIS is also used to measure dark current and offset for the spectrometer. These are used as zero correction for the measured spectra. Offset is the spectrometer

measurement of spectrum in dark. For offset spectra, a smaller integration time (per scan), e.g. 3 milliseconds and a high scan number, e.g. 1000 is used. Dark current is the small current Which flows through the spectrometer. For dark current spectra, a moderate integration time (per scan), e.g. 10000 milliseconds and a small scan number, e.g. 1, is used (for details refer to *Khokhar, 2006* available at IESE library).

3.4.2 Windows Differential Optical Absorption Spectroscopy (WinDOAS)

The measured spectra were analyzed using WinDOAS (Windows Differential Optical Absorption Spectroscopy) software for retrieval of differential slant column densities (Platt and Stutz, 2008, Fayt and van Roozendael, 2001). A high resolution solar spectrum was used for wavelength calibration (Kurucz et al., 1984). A wavelength analysis window chosen for NO_2 was 411–445 nm. The trace gas absorption cross sections used for the DOAS fit were; NO_2 at 298K (Vandaele et al., 1996), NO_2 at 220K (Vandaele et al., 1996), H_2O at 290K (Rothman et al., 2005), O_3 at 241K (Bogumil et al., 2003), O_4 at 296K (Hermans et al., 1999). Also a polynomial of fifth order, a Reference Spectrum and a Ring Spectrum calculated from by using DOASIS were also included in the analysis to minimize the residual.

For NO_2 analysis WinDOAS is used in three major steps:

1. Wavelength Calibration
2. Wavelength Convolution
3. NO_2 Analysis Window

Wavelength Calibration: The high intensity noon spectrum is used for calibration process. The spectral calibration is done by fitting a spectrum to a convoluted spectrum. During the fitting process, the wavelength from the solar spectrum will be assigned to the individual detector pixels of the own measurements. In addition, also the spectral resolution of the own measurement is determined (intensity as function of wavelength).

Often the calibration fit is referred to as “Kurucz-fit” because usually a high resolution spectrum from the Kurucz solar atlas is used as input and convoluted according to spatial resolution of the used mini Max-DOAS instrument.

Number of sub-windows is used to divide the whole wavelength range into several sub-windows. The actual fit is performed separately in each of these sub-windows. Shift and squeeze option is available in order to adjust if there is any spectral shift between measured and convoluted spectra. “Shift/Slit Function Parameter (SFP)” indicates the polynomial degree used for interpolating the results of the individual sub-windows.

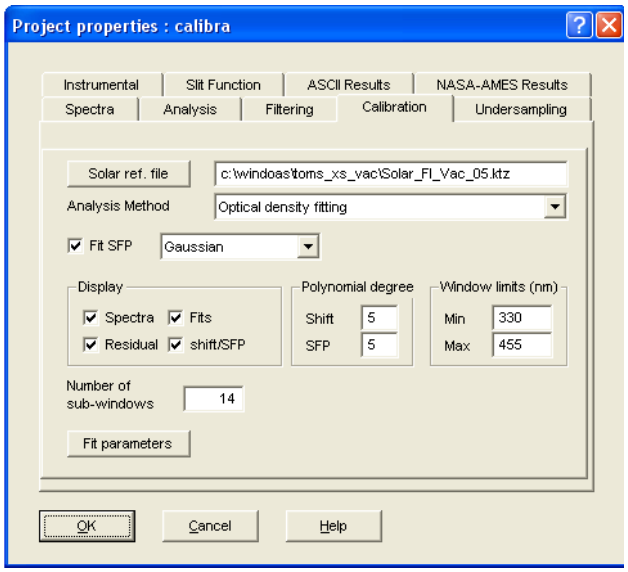


Figure 3.2: WinDOAS Calibration Window

The calibration process is repeated twice to minimize the residual error of the calibration process. The entire measured spectra are analyzed using the calibrated spectrum referred as reference spectrum.

Wavelength Convolution: Convolution is a simple mathematical operation which is fundamental to wavelength processing operations..

We used the slit function type as Gaussian shape. In the case of NO_2, which is analyzed around 440nm, Full Width Half Maximum (FWHM) of 0.5 nm is chosen, as slit function parameter (SFP).

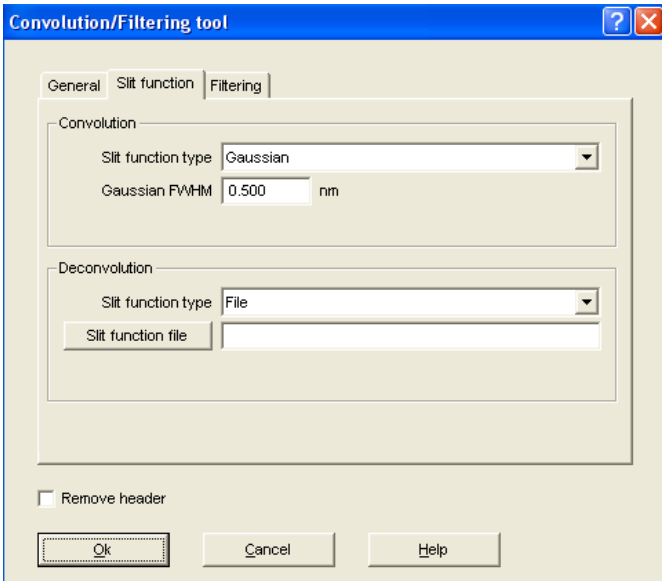


Figure 3.3: WinDAOS Convolution Window

NO_2 Analysis Window: The NO_2 analysis window was selected as 411 nm to 445 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 5^{th} degree was used for our NO_2 fitting analysis window. In the end the output file path is given to WinDOAS. The analysis is 'RUN' on all the measured spectra and NO_2 DSCDs are obtained as a result in .ascii file.

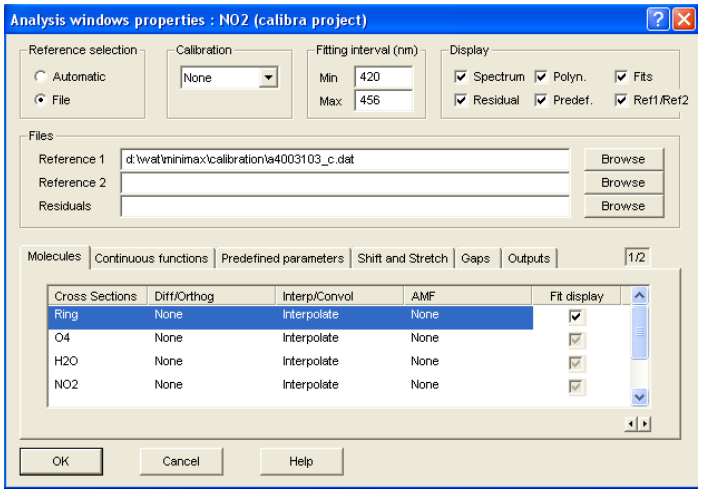


Figure 3.4: WinDAOS NO_2 Analysis Window

An example of NO_2 DOAS fit is presented below in figure 3.6.

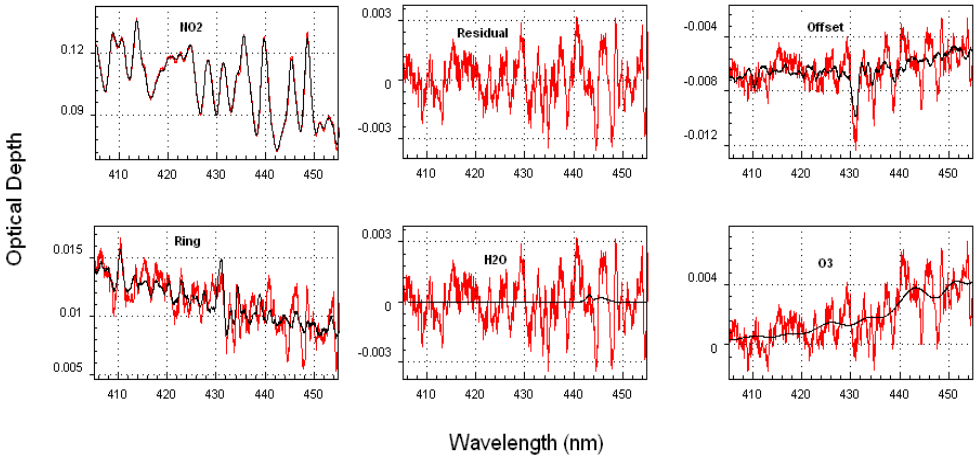
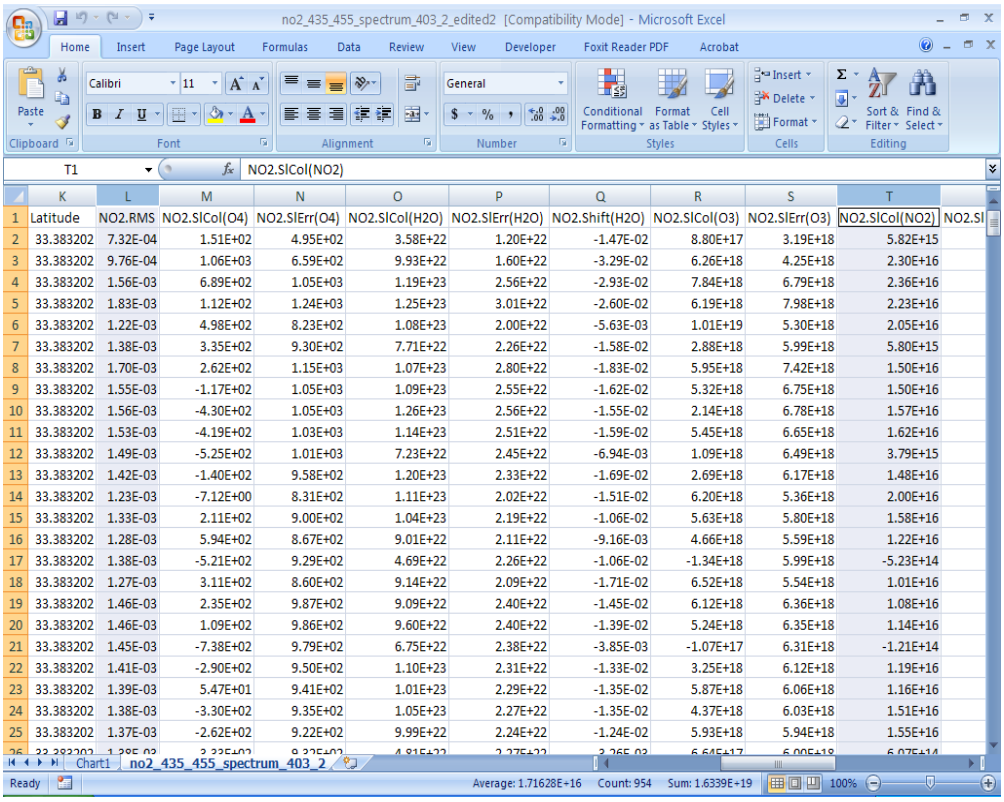


Figure 3.5: Typical Win-DOAS analysis window showing DOAS fit for field campaign Data

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 3.7.

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



no2_435_455_spectrum_403_2_edited2 [Compatibility Mode] - Microsoft Excel

	K	L	M	N	O	P	Q	R	S	T	
1	Latitude	NO2.RMS	NO2.SlCol(O4)	NO2.SlErr(O4)	NO2.SlCol(H2O)	NO2.SlErr(H2O)	NO2.Shift(H2O)	NO2.SlCol(O3)	NO2.SlErr(O3)	NO2.SlCol(NO2)	NO2.Sl
2	33.383202	7.32E-04	1.51E+02	4.95E+02	3.58E+22	1.20E+22	-1.47E-02	8.80E+17	3.19E+18	5.82E+15	
3	33.383202	9.76E-04	1.06E+03	6.59E+02	9.93E+22	1.60E+22	-3.29E-02	6.26E+18	4.25E+18	2.30E+16	
4	33.383202	1.56E-03	6.89E+02	1.05E+03	1.19E+23	2.56E+22	-2.93E-02	7.84E+18	6.79E+18	2.36E+16	
5	33.383202	1.83E-03	1.12E+02	1.24E+03	1.25E+23	3.01E+22	-2.60E-02	6.19E+18	7.98E+18	2.23E+16	
6	33.383202	1.22E-03	4.98E+02	8.23E+02	1.08E+23	2.00E+22	-5.63E-03	1.01E+19	5.30E+18	2.05E+16	
7	33.383202	1.38E-03	3.35E+02	9.30E+02	7.71E+22	2.26E+22	-1.58E-02	2.88E+18	5.99E+18	5.80E+15	
8	33.383202	1.70E-03	2.62E+02	1.15E+03	1.07E+23	2.80E+22	-1.83E-02	5.95E+18	7.42E+18	1.50E+16	
9	33.383202	1.55E-03	-1.17E+02	1.05E+03	1.09E+23	2.55E+22	-1.62E-02	5.32E+18	6.75E+18	1.50E+16	
10	33.383202	1.56E-03	-4.30E+02	1.05E+03	1.26E+23	2.56E+22	-1.55E-02	2.14E+18	6.78E+18	1.57E+16	
11	33.383202	1.53E-03	-4.19E+02	1.03E+03	1.14E+23	2.51E+22	-1.59E-02	5.45E+18	6.65E+18	1.62E+16	
12	33.383202	1.49E-03	-5.25E+02	1.01E+03	7.23E+22	2.45E+22	-6.94E-03	1.09E+18	6.49E+18	3.79E+15	
13	33.383202	1.42E-03	-1.40E+02	9.58E+02	1.20E+23	2.33E+22	-1.69E-02	2.69E+18	6.17E+18	1.48E+16	
14	33.383202	1.23E-03	-7.12E+00	8.31E+02	1.11E+23	2.02E+22	-1.51E-02	6.20E+18	5.36E+18	2.00E+16	
15	33.383202	1.33E-03	2.11E+02	9.00E+02	1.04E+23	2.19E+22	-1.06E-02	5.63E+18	5.80E+18	1.58E+16	
16	33.383202	1.28E-03	5.94E+02	8.67E+02	9.01E+22	2.11E+22	-9.16E-03	4.66E+18	5.59E+18	1.22E+16	
17	33.383202	1.38E-03	-5.21E+02	9.29E+02	4.69E+22	2.26E+22	-1.06E-02	-1.34E+18	5.99E+18	-5.23E+14	
18	33.383202	1.27E-03	3.11E+02	8.60E+02	9.14E+22	2.09E+22	-1.71E-02	6.52E+18	5.54E+18	1.01E+16	
19	33.383202	1.46E-03	2.35E+02	9.87E+02	9.09E+22	2.40E+22	-1.45E-02	6.12E+18	6.36E+18	1.08E+16	
20	33.383202	1.46E-03	1.09E+02	9.86E+02	9.60E+22	2.40E+22	-1.39E-02	5.24E+18	6.35E+18	1.14E+16	
21	33.383202	1.45E-03	-7.38E+02	9.79E+02	6.75E+22	2.38E+22	-3.85E-03	-1.07E+17	6.31E+18	-1.21E+14	
22	33.383202	1.41E-03	-2.90E+02	9.50E+02	1.10E+23	2.31E+22	-1.33E-02	3.25E+18	6.12E+18	1.19E+16	
23	33.383202	1.39E-03	5.47E+01	9.41E+02	1.01E+23	2.29E+22	-1.35E-02	5.87E+18	6.06E+18	1.16E+16	
24	33.383202	1.38E-03	-3.30E+02	9.35E+02	1.05E+23	2.27E+22	-1.35E-02	4.37E+18	6.03E+18	1.51E+16	
25	33.383202	1.37E-03	-2.62E+02	9.22E+02	9.99E+22	2.24E+22	-1.24E-02	5.93E+18	5.94E+18	1.55E+16	

Chart1 | no2_435_455_spectrum_403_2

Ready | Average: 1.71628E+16 | Count: 954 | Sum: 1.6339E+19 | 100%

Figure 3.6: Microsoft Excel Window showing NO_2 Root Mean Squares (RMS)

3.4.3 Air Mass Factor and NO_2 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 3.8.

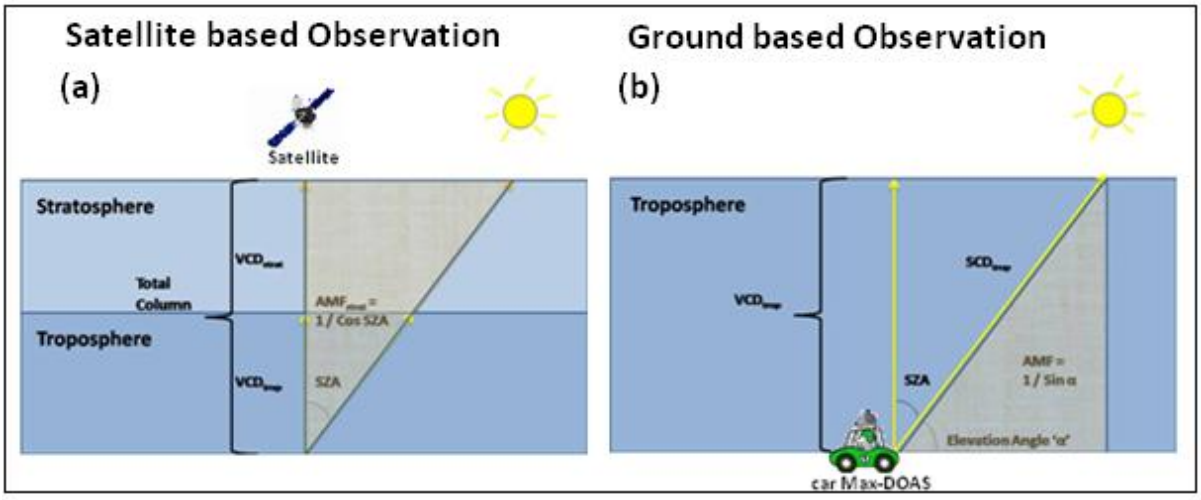


Figure 3.7: Air Mass Factor (AMF) for Troposphere and Stratosphere

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 as In order to calculate 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. The offset could be measured according to the following equation (Wagner et al., 2010).

$$\mathrm{DSCD}_{\mathrm{offset}}(SZA) = \frac{\mathrm{AMF}_{90^\circ}.\mathrm{DSCD}_{\alpha} - \mathrm{AMF}_{\alpha}.\mathrm{DSCD}_{90^\circ}}{\mathrm{AMF}_{\alpha} - \mathrm{AMF}_{90^\circ}} \qquad \textit{Eq. 3.1}$$

The tropospheric VCD (VCDtrop) is the ratio of the SCD and the AMF (Wagner et al. 2010; Ibrahim et al., 2010).

$$\mathrm{VCD}_{\mathrm{trop}} = \frac{\mathrm{SCD}_{\mathrm{trop}\,(\alpha)}}{\mathrm{AMF}_{\mathrm{trop}(\alpha)}} \qquad \textit{Eq. 3.2}$$

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

$$\mathrm{AMF}_{\mathrm{trop}} = \frac{1}{\sin\alpha} \qquad \textit{Eq. 3.3}$$

The elevation angle of 30° was selected for the NO_2 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).

$$SCD_{\alpha} = DSCD_{\alpha} + DSCD_{ref} - SCD_{strat} \qquad Eq.\ 3.4$$

Knowing the AMF_{trop} for the elevation angle α and SCD_{α}, VCDtrop 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 NO_2 DSCD in the results acquired using WinDOAS are used for extraction of NO_2 VCD. The Air Mass Factor (AMF) is calculated in MS Excel using Geometric Approximation Method. Whereas NO_2 VCD are extracted using Offset Method.

For this purpose threshold limit was decided for each individual day. The threshold was fixed at 5×10^{-3}.

NO_2 VCD extraction was done using Offset Method via MS Excel using all the 30° angles for NO_2 DSCD (Wagner et al., 2010). The result obtained gave a clear picture of NO_2 pollution over the project area.

3.4.4 Plotting of NO_2 VCD over Project Area

To plot the NO_2 VCD, the measured VCD needed to be plotted according to their coordinate of measurements. Geographic coordinates were taken using a Global positioning System (GPS) logger because the instrument didn't had any geographic coordinates logging setup. Our GPS system 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 NO_2 VCD were mapped using Arc-GIS according to their coordinates.

The NO_2 measurements were converted to shape-files to be mapped. The plotted values were then used for source identification within the study area.

3.4.5 Satellite Validation of Max-DOAS Observations Using ArcGIS

Tropospheric NO_2VCD from ozone monitoring experiment (OMI) (Boersma et la., 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. This is done in 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 NO_2 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) and Boersma et al., (2007).

Chapter 4

RESULTS AND DISCUSSION

4.1 Temporal Analysis:

Tropospheric NO_2 VCD, retrieved from mini Max-DOAS measurements, performed from October 2013 till March 2014 are converted into mixing ratio. It was assumed that the NO_2 is located close to the ground surface near to the emission sources. Assuming that NO_2 is confined in a box profile between the surface and 300m. The observed NO_2 VCDs were converted into number density by dividing the assumed vertical height:

Firstly the observed NO_2 VCD were converted into number density by dividing with assumed vertical height

NO_2 Number Density (molec. /cm^3) = NO2 VCD (molec./cm^2) / 30000 cm

The calculated **NO_2** number density can be directly converted into **NO_2** mixing ratios according to the following formula:

NO_2 mixing ratio (ppbv) = NO_2 Number Density (molec./cm^3) / 2.503 10^{10} (molec./cm^3)

The concentration of observed **NO_2** was higher than the limits prescribed by WHO.

Time series presented, is daily mean **NO_2** mixing ratio and green vectors are indicating the mean wind direction for that particular day. Peaks in **NO_2** indicated very interesting behavior and role of meteorological parameters especially wind direction. These high peaks were mainly induced by favorable wind direction and speed causing the polluted air masses being transported to IESE-NUST site. The peaks in **NO_2** columns were observed when the wind direction was WSW, SSW. It can be clearly seen from the figure that these high peaks are a result of NO_2 pollution being transported from the IJP road and N-5 Highway.

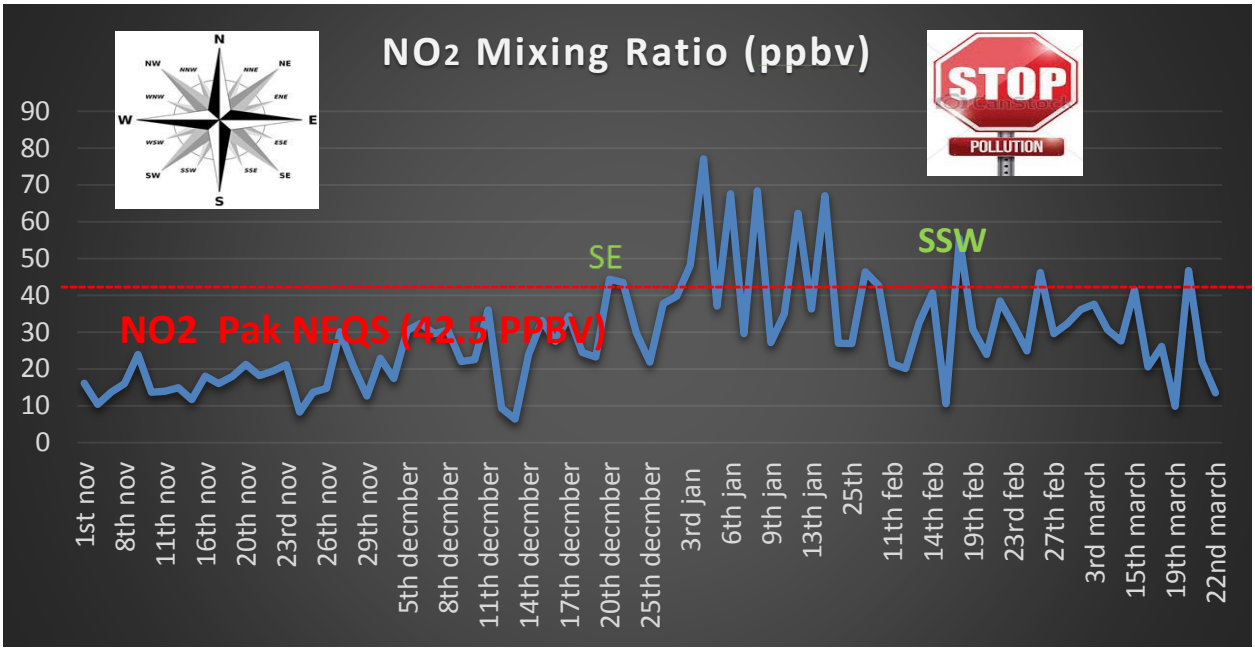


Fig 4.1. Temporal Variation of NO_2 mixing ratio over Islamabad (November 2013-March 2014)

Figure 4.1. Shows the daily averaged temporal variation of NO_2 mixing ratios over IESE NUST (October 2013-March 2014) and comparison of NO_2 levels with existing WHO standards (WHO-limit-doted red line).

4.2 DIURNAL PROFILE OF NO2

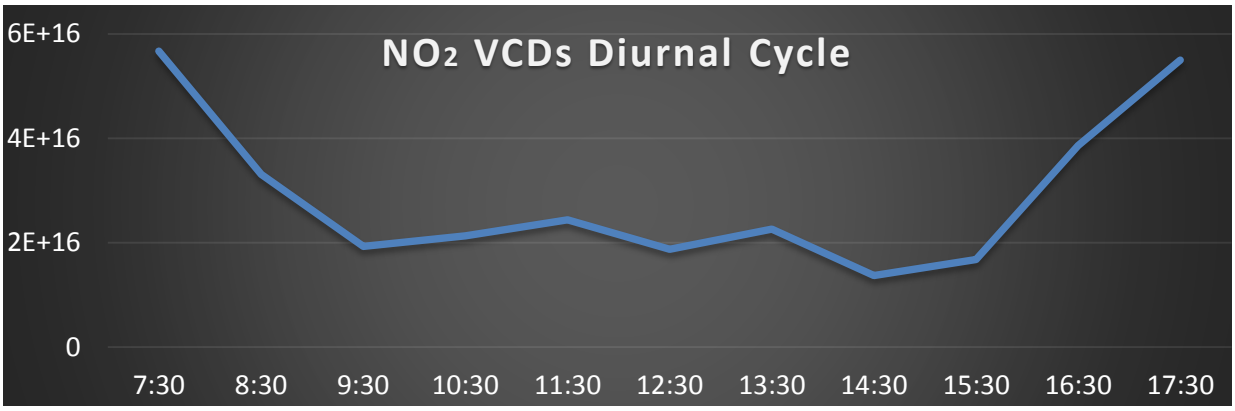


Fig 4.2. NO_2 VCDs Diurnal Profile

The diurnal profile was obtained for all different angles. The concentration of NO_2 was higher in the morning and evening time due to high traffic density and rush

hours and low intensity of sunlight. The concentration is low during the noon time due to high photolysis rate. Another trend can be seen from the figure below that the concentration of NO_2 is higher for smaller angles and decrease at higher angles. This is due to the reason that the lower angles are closer to the emission sources close to the ground and hence we get higher concentrations and as we move away from the emission sources the concentration of NO_2 decreases with higher elevation angles.

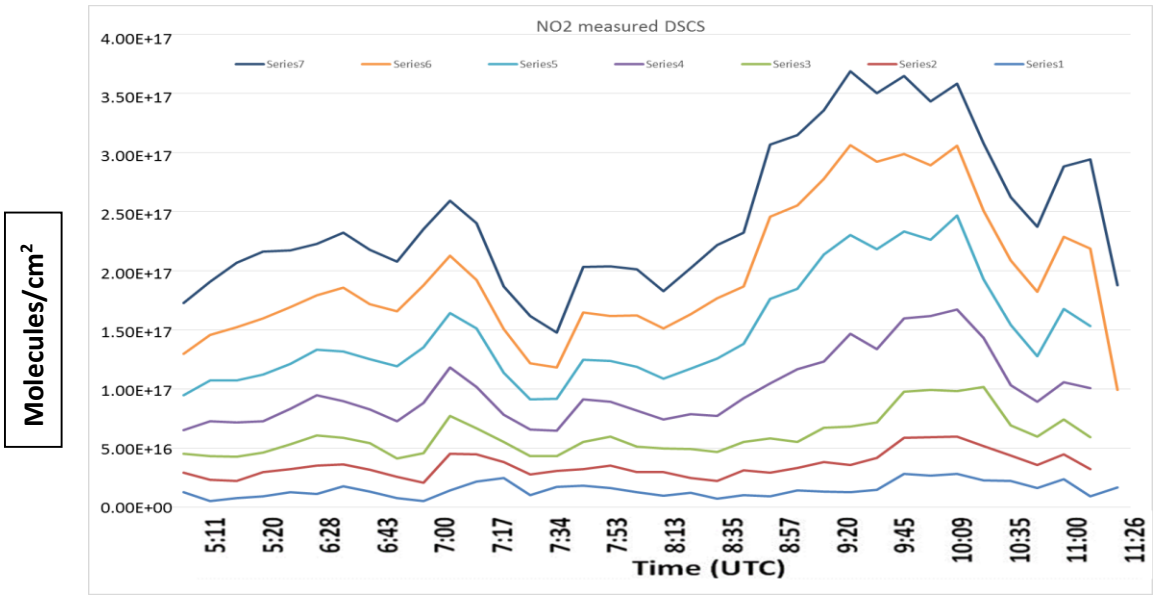


Fig 4.3. NO_2 Concentration at different viewing angles

4.3 CNG availability and NO_2:

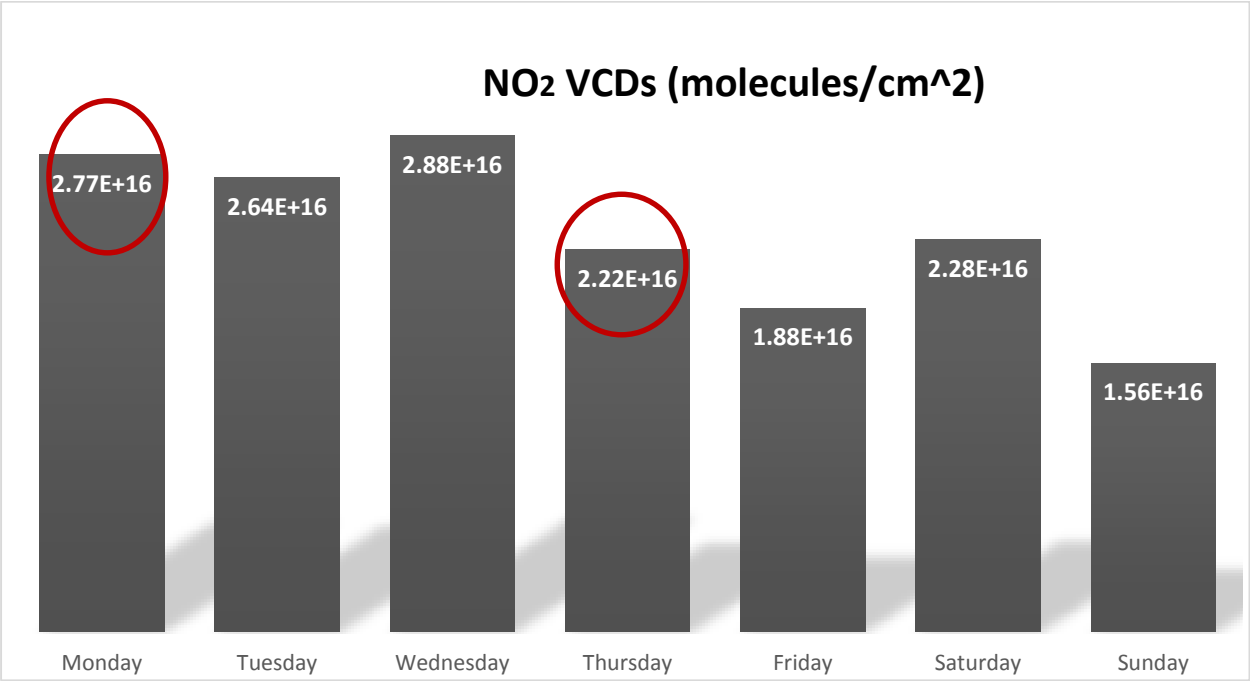


Fig 4.4. Weekly trend of NO_2 column density over Islamabad (October 2013-Marxh 2014). Bars represent the standard deviation.

Figure 4.4. Displays the weekly cycle of NO_2 concentration over Islamabad for the time period September 2013-March 2014.

.

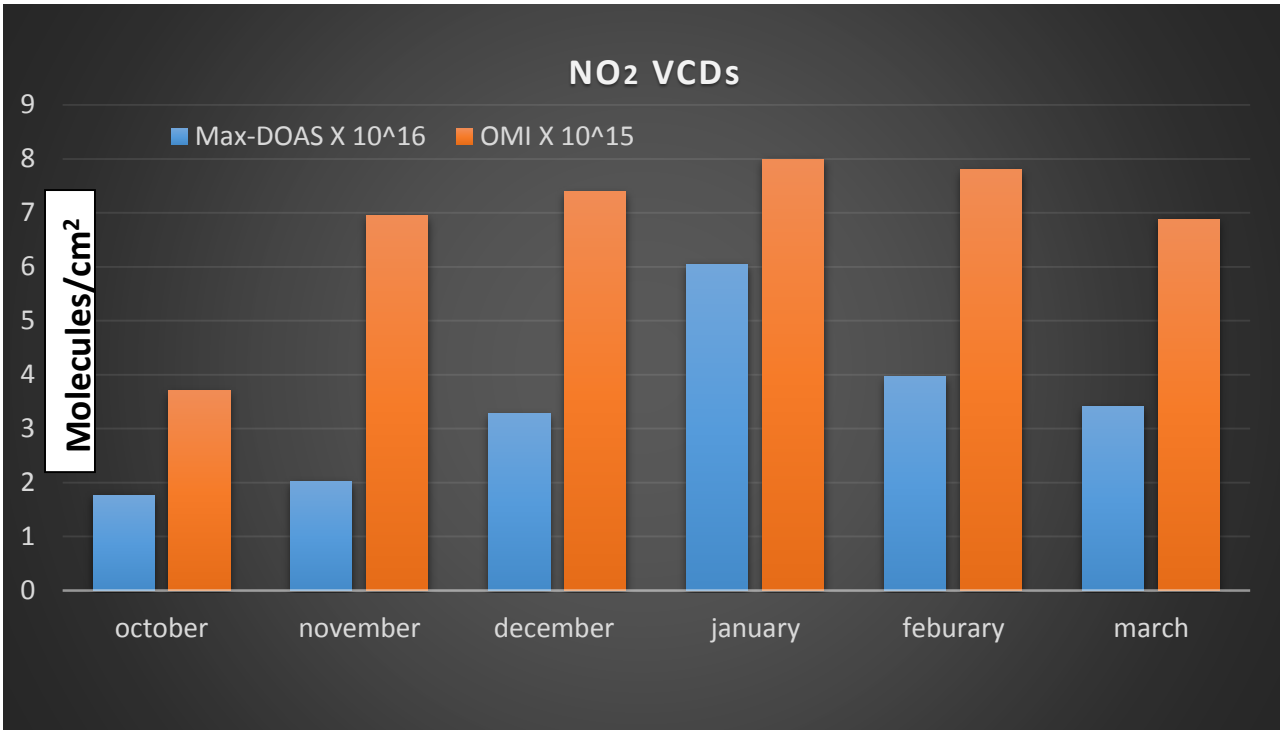


Fig 4.5. Monthly trend of no2 column density over Islamabad (October 2013-march 2014). Bars represent the standard deviation.

Figure 4.5. Displays the monthly cycle of NO_2 concentration over Islamabad for the time period September 2013-March 2014.

NO_2 Concentration was found to be highest in the month of January 2014 because CNG was completely closed in this month and other reason can be rate of photolysis is slow in the winter season. Both Max-DOAS and OMI data sets showed similar trends

4.4 Spatial analysis

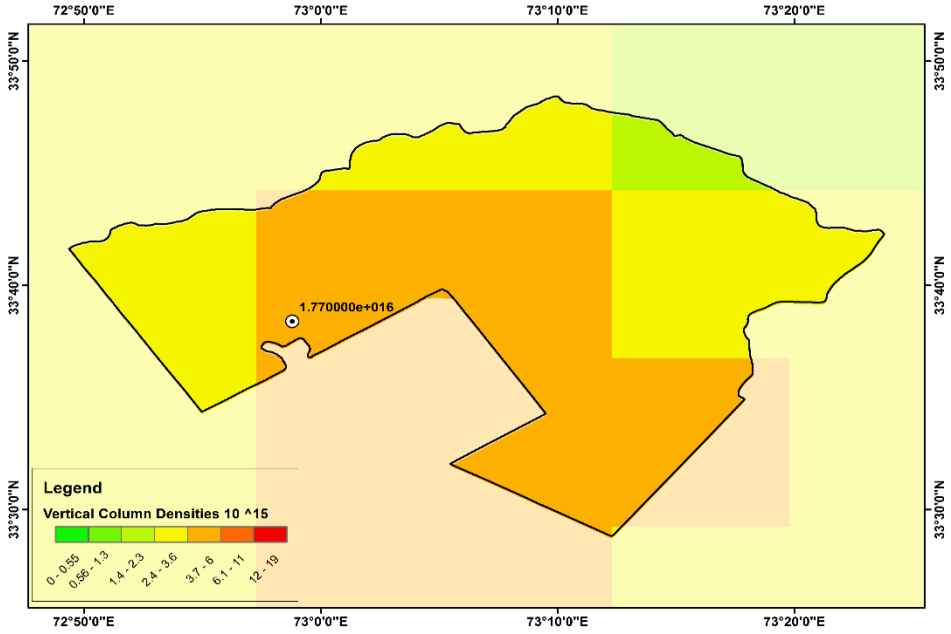


Fig 4.6. NO_2 concentration (molecules/cm^2) over Islamabad Monthly average map for October 2013

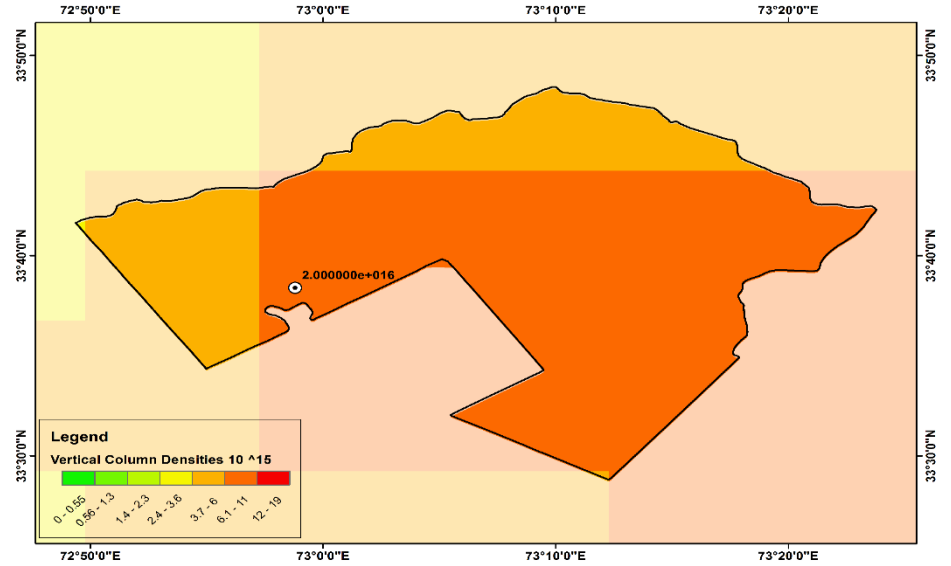


Fig 4.7. NO_2 concentration (molecules/cm^2) over Islamabad Monthly average map for November 2013

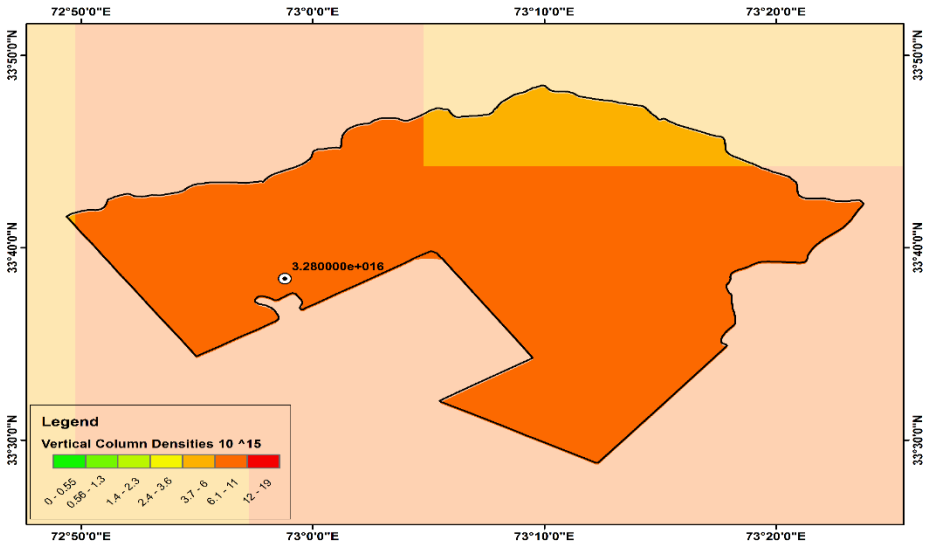


Fig 4.8. NO_2 concentration (molecules/cm^2) over Islamabad Monthly average map for December 2013

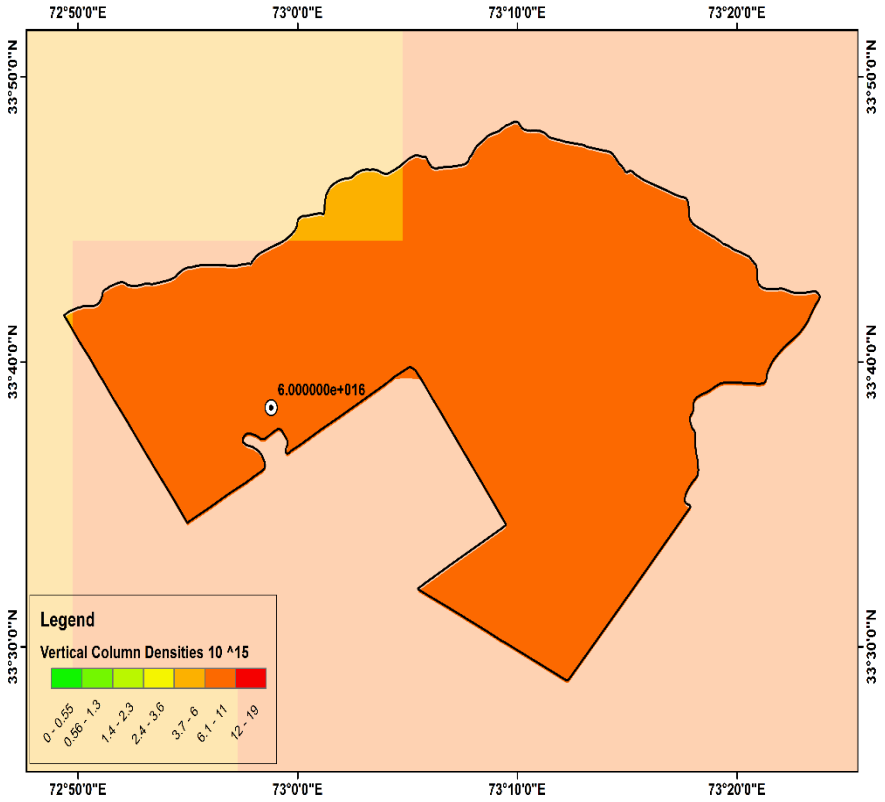


Fig 4.9. NO_2 concentration (molecules/cm^2) over Islamabad Monthly average map for January 2014

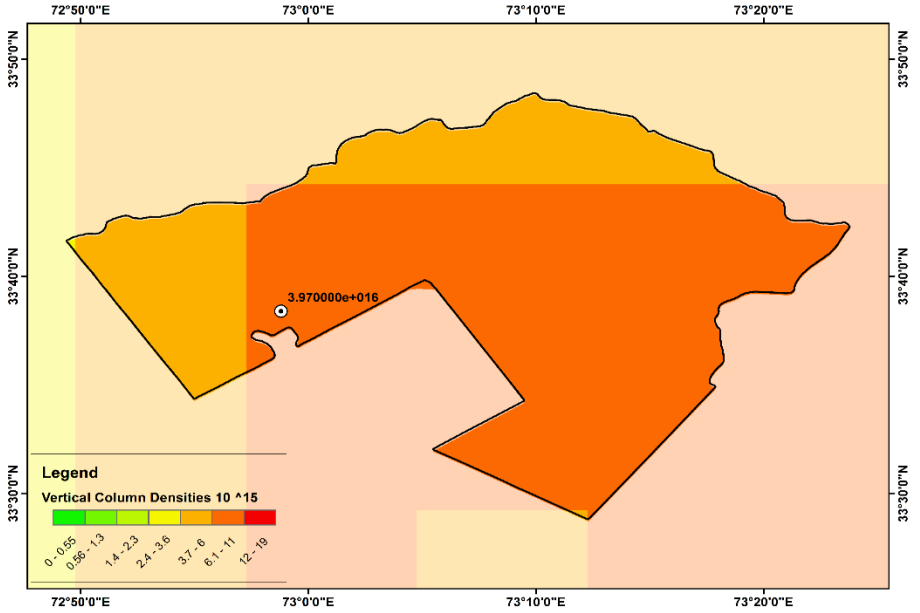


Fig 4.10. NO_2 concentration (molecules/cm^2) over Islamabad Monthly average map for February 2014

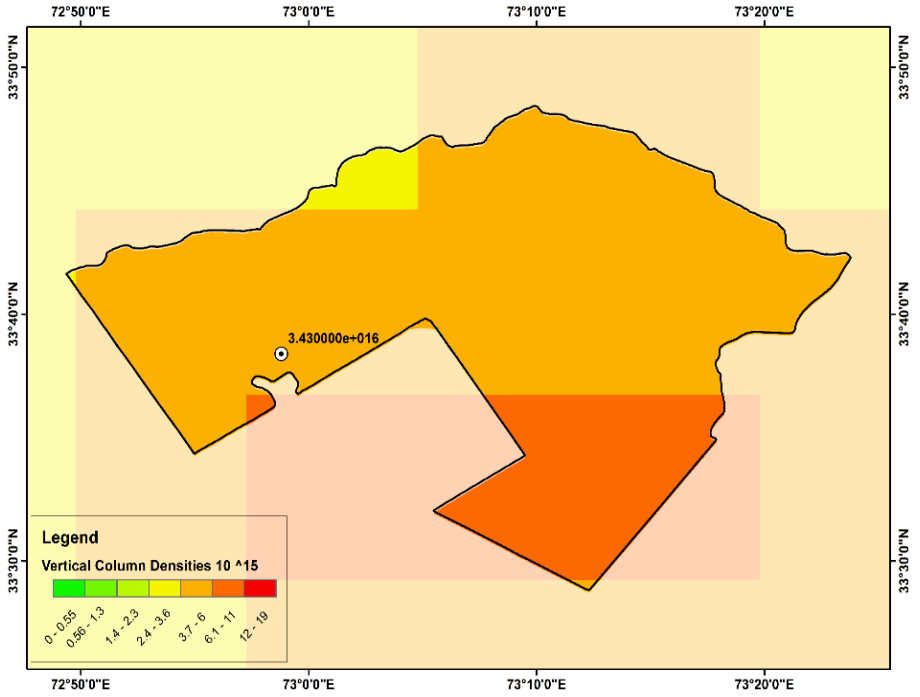


Fig 4.11. NO_2 concentration (molecules/cm^2) over Islamabad Monthly average map for March 2014

Figures 4.6.-4.11. Shows spatial distribution of monthly mean NO_2 concentration in molecules/cm^2 over Islamabad during the time period of October 2013-march 2014. The black circle indicates the concentration at IESE, NUST. The monthly maps are prepared by taking the daily concentration of NO_2.

The above maps show the monthly averaged concentration of NO_2 for the study period of October 2013-March 2014. The concentration over IESE-NUST is represented by the black circle. The maps shows the ICT region Islamabad. These maps were generated by taking the daily concentrations of NO_2 over Islamabad region and then taking the monthly mean of these values. The variation in NO_2 concentration can be seen from the maps. For detailed information the legend is provided.

4.5 Field Campaigns

Field campaigns comprised of two phases of monitoring, first when CNG was closed on 30th December 2013 and other group of campaigns were conducted from 4TH of March 2014 to 7th of March 2014 when CNG was available. Satellite observations for these days were needed. But unfortunately the satellite overpass was not over our project area on 7th March, 2014.

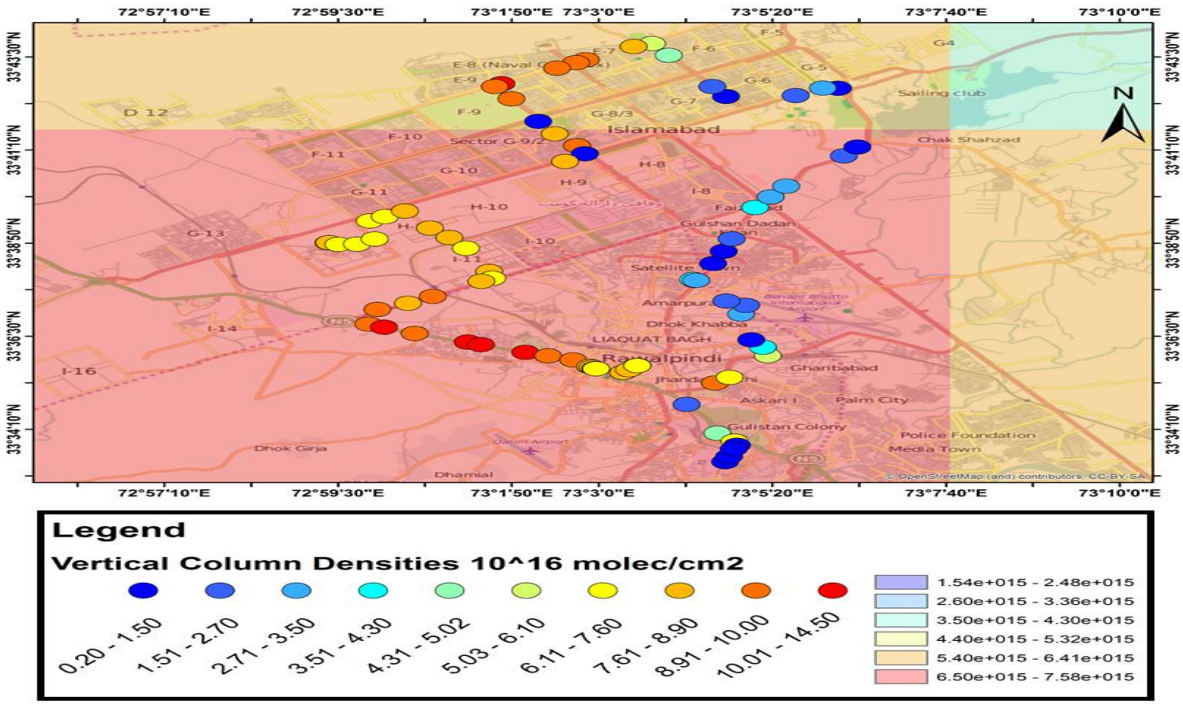


Figure 4.12. Comparison of the tropospheric NO_2 VCDs on 30th December, 2013 measured from OMI and car MAX-DOAS

Figure 4.12. Shows the comparison of the tropospheric NO_2 VCDs on 30th December, 2013 from car MAX-DOAS and OMI observations when CNG was closed. In both observations the same general trend of NO_2 is observed: highest values of NO_2 are found around busy road the N-5 highway of Rawalpindi. The maximum VCDs for NO_2 over Rawalpindi-Islamabad when CNG was closed found to be in the range of 12 x 10^{16} molecules/cm^2.

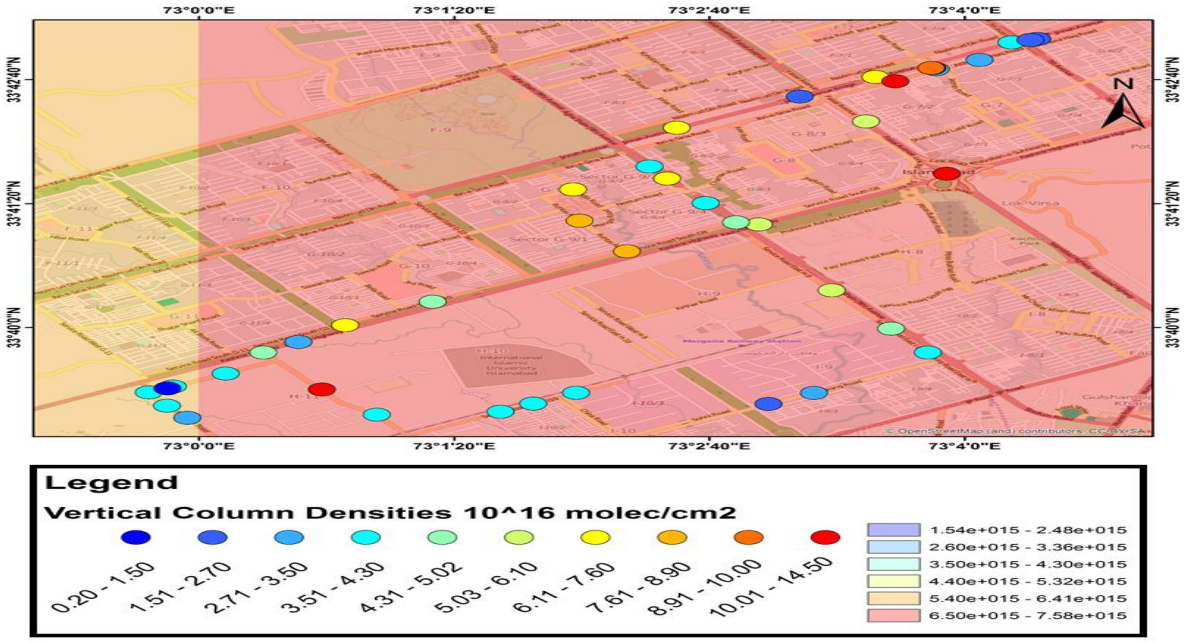


Figure 4.13. Comparison of the tropospheric NO_2 VCDs on 4th March, 2014 measured from OMI and car MAX-DOAS

Figure 4.13. Shows the comparison of the tropospheric NO_2 VCDs on 4th of March 2014, car MAX-DOAS and OMI observations when CNG was open. In both observations the same general trend of NO_2 is observed: highest values of NO_2 are

found around busy road near Zero point and blue area. VCDs for NO_2 over Rawalpindi-Islamabad, when CNG was open were found to be in the lower range.

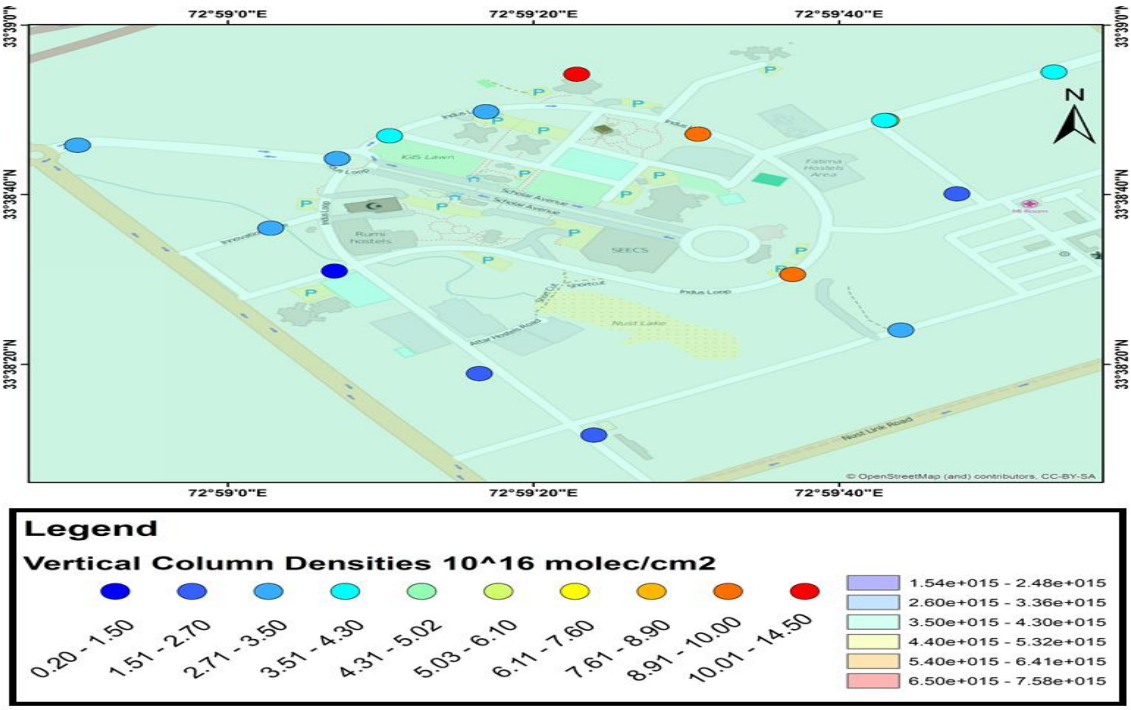


Figure 4.14. Comparison of the tropospheric NO_2 VCDs on 5th March, 2014 measured from OMI and car MAX-DOAS over NUST

Figure 4.14. Shows the comparison of the tropospheric NO_2 VCDs on 5th of March 2014, car MAX-DOAS and OMI observations over NUST H-12 Islamabad. In both observations the same general trend of NO_2 is observed: this area is relatively less pollutes as compared to other areas.

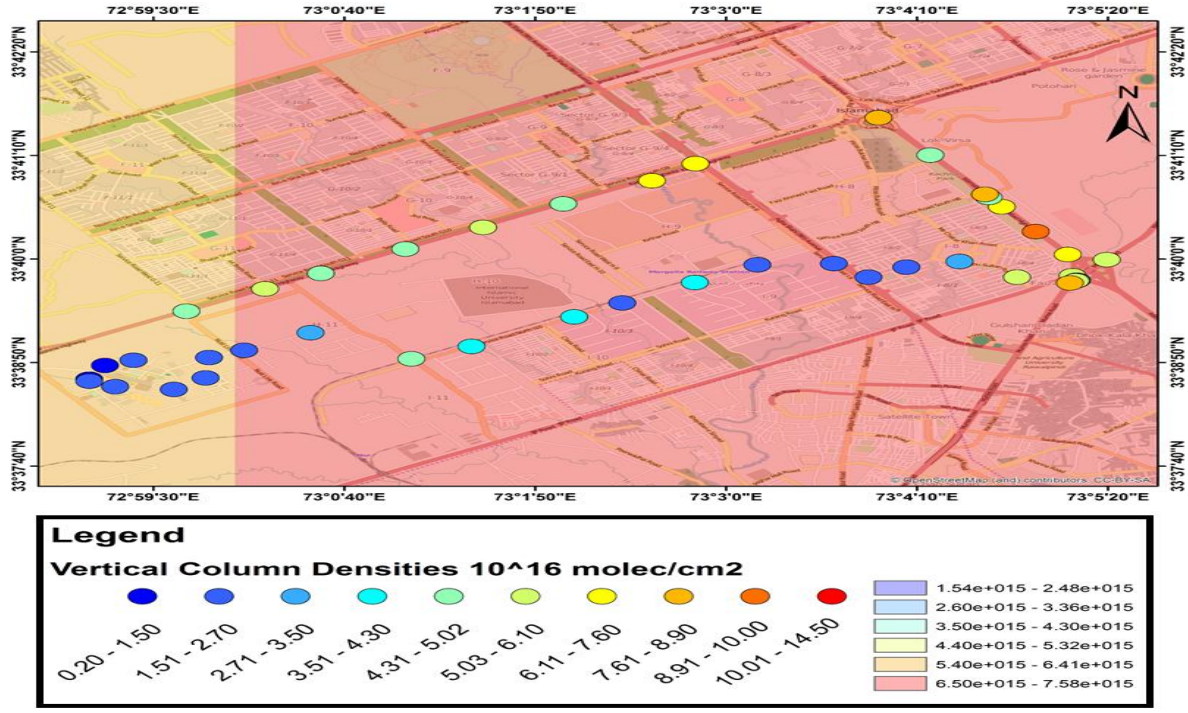


Figure 4.15. Comparison of the tropospheric NO_2 VCDs on 6th March, 2014 measured from OMI and car MAX-DOAS

Figure 4.15. Shows the comparison of the tropospheric NO_2 VCDs on 5th of March 2014, car MAX-DOAS and OMI observations over NUST H-12 Islamabad CNG was open, highest values of NO_2 are found around busy road near Zero point and Express Highway. VCDs for NO_2 over Rawalpindi-Islamabad, when CNG was open were found to be in the lower range.

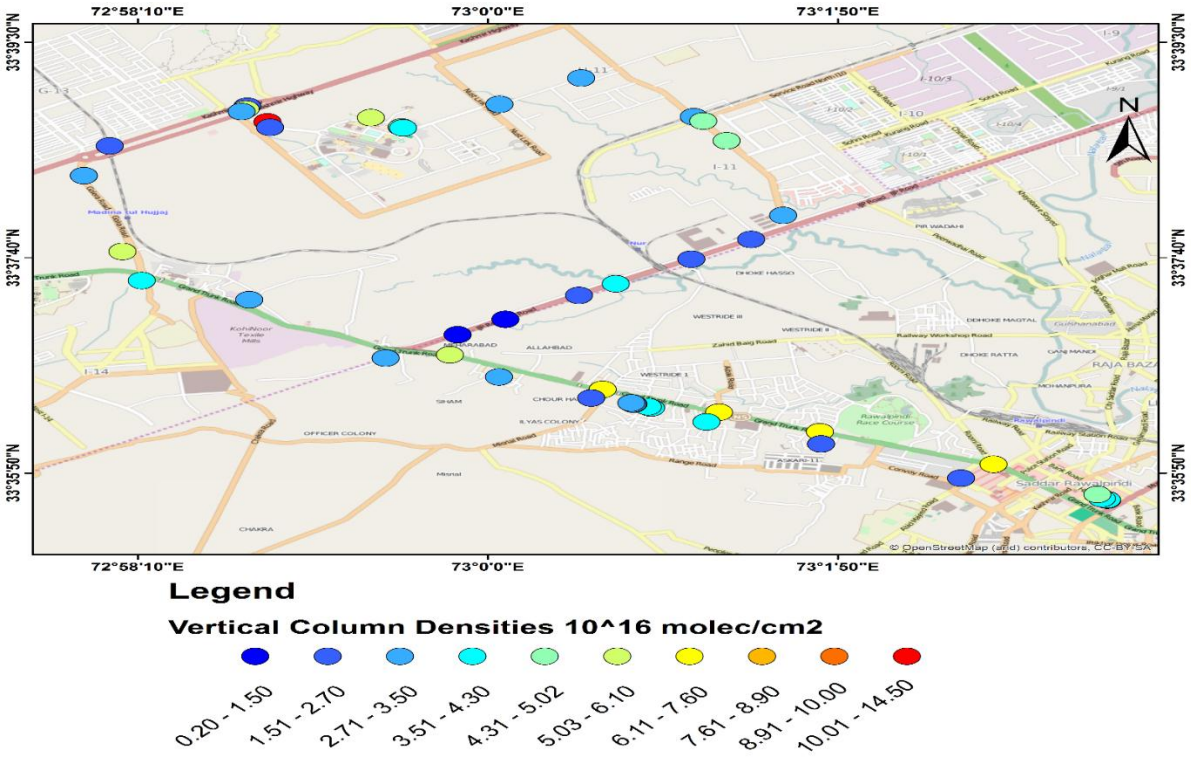


Figure 4.16. Tropospheric NO_2 VCDs on 7th March, 2014 measured from car MAX-DOAS

Figure 4.16. Shows the tropospheric NO_2 VCDs on 6th of March 2014, measured from car MAX-DOAS, pollution levels were low on this day because of morning showers.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Tropospheric columns measurements from Mini MAX-DOAS instrument was used to prepare data base of NO_2 concentrations during the time period October 2013- March 2014. The concentration of NO_2 was higher as compared to the guidelines provided by WHO.

Wind direction/speed plays an important role in transporting the pollutants away from the emission sources. NUST is considered as a clear site as there are no particular sources of pollution. The high concentrations over NUST were due to the wind direction that helped the transfer of pollutants from the nearby areas towards NUST.

High traffic densities on IJP Road and N-5 Highway are the main source of pollution being transferred to NUST. NO_2 levels were higher on busy roads (12 x 10^16 molec/cm^2). NO_2 pollution levels exceeding Pak – NEQS limits (maximum 79.5 PPBV)

NO_2 levels were higher in the morning and evening but lower in day time due to photolysis. CNG availability significantly reduced the NO_2 Levels. Similar spatial trends were found when compared with the Ozone Monitoring Instrument (OMI). Differences are mainly due to the reason that MAX-DOAS gives the point observations whereas OMI gives us the average observations.

5.2 Recommendations

Following recommendations based on our findings from this study are suggested in order to combat air quality related issues and to further improve the air quality monitoring in the country.

1. The outcomes of this study helped to identify, a relationship between air pollutants and sources of pollution, therefore, Pollution Control Techniques (PCTs) could be proposed for the abatement of pollution. As use of fossil fuels in both industry and vehicles is the main reason of NO_2 emissions, therefore, NO_2 pollution levels can be reduced by energy saving strategy, alternative fuels, improved combustion technology, use of catalytic converter technology in vehicles.
2. On State level, Mass transit system should be introduced in larger urban areas in order to avoid unnecessary traffic jams and consequently to abate traffic emissions
3. To run effective media campaigns to teach the public and other stakeholders will improve the understanding and will raise the concern for air quality. Educating school children, citizen groups etc. by sharing the results of such field campaigns.
4. Furthermore, at State, Provincial and City government level, Air quality management planning should be done and models should be used for assessment of the air quality, besides incorporating legislations in Environmental Laws on emission reductions of NO_2 and other criteria pollutants.

REFERENCES

Adukpo, D. C. (2002). Characterisation of a Max-Doas Instrument and Application to Satellite Validation, Msc. Environmental Physics Thesis, Institute Of Environmental Physics and Remote Sensing, University Of Bremen,.

Ahmad, S. S., Aziz, N., Ejaz, M., And Shah, M. T. A. (2012). Integration Of GIS And Artificial Neural Network for Prediction of Ozone Concentration in Semi-Rural Areas of Rawalpindi and Islamabad, International Journal Of Computational Engineering Research, Vol. 2.

Ali M., A. M. (2008). Air Pollution due to Traffic, Air Quality Monitoring along Three Sections of National Highway N-5, Pakistan, Environ Monit Assess 136:219–226.

Ashraf, N., Mushtaq, M., Sultana, B., Iqbal, M., Inam, M. and Shahid, S.A. (2013). Preliminary monitoring of tropospheric air quality of Lahore City in Pakistan; International Journal of Chemical and Biochemical Sciences, IJCBS, 3(2013):19-28.

Brohede, S. (2002). Differential Optical Absorption Spectroscopy -How Does it Work and What can it Measure?

Cede, A., Herman, J., Richter,A., Krotkov, N., And Burrows, J. (2006) Measurements of Nitrogen Dioxide Total Column Amounts a Brewer Double Spectrophotometer in Direct Sun Mode, Journal Of Geophysical Research, Vol. 111, D05304.

Chan, K. L., Pöhler, D., Kuhlmann, G., Hartl, A., Platt, U., And Wenig, M.O. (2012). NO_2 Measurements in Hong Kong Using Led Based Long Path Differential Optical Absorption Spectroscopy, Atmospheric Measurement Techniques.

Constantin, D. E., Merlaud, A., Fayt, C., Voiculescu, M., Roozendael, M. Van, Balin I., and Georgescu, L. P. (2011). Measurements of Tropospheric NO_2 in a Romanian Region Using a Mobile DOAS System, Workshop on Optoelectronic Techniques for Environmental Monitoring.

Crawford, E., And, Williams, T. (2006) Smog and Population Health, Library Of Parliament, Canada.

Crutzen, P. J. (1970). The Influence of Nitrogen Oxides on the Atmospheric Ozone Content, Clarendon Laboratory, Oxford University, Quart. J. R. Met. Soc. (1970), 96, pp. 320-325.

Edner, H., Ragnarson, P., Spannare, S., and Svanberg, S. (1991). Differential Optical Absorption Spectroscopy (DOAS) System for Urban Atmospheric Pollution Monitoring, Optical Society of America, Vol. 32, No. 3.

Fenn, M. E., Haeuber, R., Tonnesen, G. S., Baron, J. S., Clarke S. G., Hope, D., Jaffe, D. A., Copeland, S., Geiser, L., Rueth, H. M., and Sickman, J. O. (2003). Nitrogen Emissions, Deposition, and Monitoring in The Western United States, University of California Press, Vol. 53, No. 4, Pp. 391-403.

Government of Pakistan, EPA. (2010). National Environmental Quality Standards For Ambient Air.

Government of Pakistan, E. P. A., And J.I.C.A. (2000). Measurement Of NO_2 Concentration in Different Cities of Pakistan Using Diffusion Samplers (Karachi, Islamabad, Peshawar, Lahore and Quetta), Pak-EPA/JICA.

Government of Pakistan (GOP), National Institute of Population Studies (NIPS). (2010). District Population Profiles (Rawalpindi, Jhelum, Gujrat, Gujranwala and Lahore).

Government of Pakistan (GOP), National Highway Authority (NHA). (2010). Daily Traffic Averages.

Halla, J. D., Wagner, T., Beirle, S., Brook, J. R., Hayden, K. L., O'brien, J. M.,Ng, A., Majonis, D., Wenig, M. O., And Mclaren, R. (2011). Determination of Tropospheric Vertical Columns of NO_2 and Aerosol Optical Properties in A Rural Setting Using Max-Doas, Atmospheric Chemistry And Physics.

Han, X., Naeher L. P. (2006).A Review Of Traffic-Related Air Pollution Exposure Assessment Studies in the Developing World, Science Direct, Environment International 32 (2006) 106 – 120.

Hönninger, G., Friedeburg, C. Von, And Platt, U. (2004). Multi Axis Differential Optical Absorption Spectroscopy (Max-DOAS), Atmospheric Chemistry and Physics, Atmos. Chem. Phys., 4, 231–254.

Hussain, T.: Pakistan's Energy Sector Issues. (2010). Energy Efficiency And Energy Environmental Links The Lahore Journal Of Economics, 15: Se (September 2010), Pp. 33-59.

Ilyas, S. Z. (2007). A Review of Transport and Urban Air Pollution in Pakistan, Journal of Applied Science Environmental Management, Vol. 11 (2) 113 - 121.

J.F., D. H. (2003). Accounting For Raman Scattering In DOAS, The Royal Dutch Meteorological Institute, Sn-OMIE-KNMI-409.

Jahangir, S., Ahmad, S. S., Aziz, N., Shah, M. T. A. (2013). Spatial Variation of Nitrogen Dioxide Concentration in Private and Public Hospitals of Rawalpindi and Islamabad, Pakistan, Journal Of International Environmental Application & Science, Vol. 8 (1): 16-24.

Jameel, A., Shah, N., & Khan, Z.F. (2008). Weather in Pakistan Postmonsoon Season (October - December 2006) Pakistan Journal Of Meteorology, Vol:4.

Jensen, J. R. (2007). Remote Sensing of The Environmet, An Earth Resource Perespective, Edition 2, pp. 10-50.

Johansson, M., Rivera, C., De Foy, B., Lei, W., Song, J., Zhang, Y., Galle, B., and Molina L. (2009). Mobile Mini-DOAS Measurement of The Emission Of NO_2 and HCHO from Mexico City, Atmospheric Chemistry and Physics Discussions.

Khan, M., Khan, A. R., Aslam, M. T., Anwar, T., Shah, J. (2008). Study of Atmospheric Pollution due to Vehicular Exhaust at the Busy Cross Roads in Peshawar City (Pakistan) and its Minimizing Measures, Journal Of Chemical Society, Pakistan, Vol. 30, No. 1.

Khwaja M. A., A. K., S. R. (2005). Air Pollution: Key Environmental Issues in Pakistan, Sustainable Development Policy Institute.

Lodhi. Z. H., Pakistan Environmental Protection Agency. (2008). Article on Ambient Air Quality in Pakistan.

Martin, R. V. (2003). Global Inventory of Nitrogen Oxide Emissions Constrained by Space-Based Observations of NO_2 columns, Journal of Geophysical Research, Vol. 108.

Mazhar, F. and Jamal, T. (2009). Temporal Population Growth of Lahore, Journal of Scientific Research, Vol. XXXIX No. 1.

Muslehuddin, M., Mir, H., & Faisal., N. (2004). Recent Occurrence of Fog over Pakistan (1997 To 2000), Pakistan Journal of Meteorology, Vol. 1.

Onursal, B., Gautam, S.P. (1997). Vehicular Air Pollution, Experiences From Seven Latin American Urban Centers, The World Bank, Latin American And The Caribbean Region, Technical Department, pp.36, 123-265.

Raducon, G., Stefan, S.. (2009). Characterization Of Traffic Generated Pollutants In Bucharest, Atmosfera 22(1), 99-110.

Richter, A., Burrows, J. P., Nüß, H., Granier, C. & Niemeier, U. (2005). Increase in Tropospheric Nitrogen Dioxide Over China Observed from Space, Nature, Vol 437.

Rozanov, V. V., And Rozanov, A. V. (2010). Differential Optical Absorption Spectroscopy (DOAS) and Air Mass Factor Concept for a Multiply Scattering Vertically Inhomogeneous Medium: Theoretical Consideration, Atmospheric Measurement Techniques, Atmos. Meas. Tech., 3, 751–780.

Shaiganfar, R., Beirle, S., Sharma, M., Chauhan, A., Singh, R. P., and Wagner T. (2011). Estimation of NOx Emissions from Delhi Using Car Max-DOAS Observations and Comparison with OMI Satellite Data, Atmospheric Chemistry and Physics.

Tomczak, M. (1998). Spatial Interpolation and its Uncertainty Using Automated Anisotropic Inverse Distance Weighting (IDW) - Cross-Validation/Jackknife Approach, Journal of Geographic Information and Decision Analysis, Vol. 2, No. 2, pp. 18-30.

United States, EPA. (1998). NOx, How Nitrogen Oxides affect the Way We Live and Breathe, Office of Air Quality Planning and Standards Research Triangle Park, Nc 27711.

Wagner T., Shaiganfar R., And Platt U. (2010). Mobile Max-DOAS Observations of Tropospheric Trace Gases, Atmospheric Measurement Techniques, Atmos. Meas. Tech., 3, 129–140.

Wallace, John M. and Peter V. Hobbs. (2006). Atmospheric Science; An Introductory Survey.Elsevier. Second Edition,. ISBN 13:978-0-12-732951-2. Chapter 1.

Working Group on Nitrogen Dioxide, European Commision, Directorate, XI, (1997). Position Paper On Air Quality: Nitrogen Dioxide.

World Health Organization (WHO). (2003). Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide, pp. 48-58.

World Health Organization. (2005). WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide And Sulfur Dioxide (Summary of Risk Assessment), Global Update.

Yasmeen, Z., Rasul, G., Zahid., M. (2012). Impact of Aerosols on Winter Fog of Pakistan, Pakistan Journal of Meteorology Vol. 8.

Zafar, L., Ahmad, S. S., Syed, W. A. A., & Ali, S. S. (2012). Temporal Variations in Nitrogen Dioxide Concentration due to Vehicular Emmissions in Islamabad Capital Territory (ICT) & Rawalpindi, Science International (Lahore), 24(3),265-268.