MONITORING NITROGEN DIOXIDE CONCENTRATIONS OVER ISLAMABAD AND RAWALPINDI USING CAR MAX-DOAS

By

Syeda Hadiqa Mehdi

(2011-NUST-MSPhD-EnvS-03)

A thesis submitted in partial fulfillment of requirements for the degree of

Master of Science

in

Environmental Science

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
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It is certified that the contents and forms of the thesis entitled

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

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I dedicate this thesis to my family
for their endless support and
encouragement

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SYEDA HADIQA MEHDI

Table of Contents

LIST OF ABBREVIATIONS

NO_2	Nitrogen dioxide
OH	Hydroxyl
NTRC	National Transport Research Center
WHO	World Health Organization
OMI	Ozone Monitoring Instrument
VCDs	Vertical Column Densities
IPCC	Intergovernmental Panel on Climate Change
DOAS	Differential Optical Absorption Spectroscopy
SCDs	Slant Column Densities
AMF	Air Mass Factor
MAX-DOAS	Multi Axis – Differential Optical Absorption Spectroscopy
Pak-NEQS	Pakistan National Environmental Quality Standards

LIST OF TABLES

LIST OF FIGURES

Abstract

Air quality is one of the major environmental concerns worldwide. Air quality standards are implemented by regulatory authorities to maintain the air quality based on criteria pollutants; Nitrogen dioxide (NO_2) is one of them. It is a reddish-brown gas with a pungent, irritating odour. It absorbs light, precursor for tropospheric ozone formation and leads to the yellow-brown haze sometimes seen over cities - photochemical smog. NO_2 is only the criteria pollutant that has not been in control since the advent of air quality standards (US-EPA, 1990). The reason behind is the variety of NO_2 sources like vehicles, power plants, lightening, soil emission, solid waste burning, oil refineries etc. Rapid increase in vehicles on roads is the most contributing source of air pollution in Pakistan (Khawaja and Khan, 2005) and worldwide. (Lundy et al. 2011, Han et al. 2006)

This thesis presents tropospheric nitrogen dioxide (NO_2) measurements made by car Max-DOAS (Multi Axis-Differential Optical Absorption Spectroscopy) instrument. The measurements were performed during various field campaigns within H-12 main Campus NUST and within the cities of Islamabad and Rawalpindi. The device was mounted on the roof top of a van with lens pointing backward. Retrieved NO_2 column densities exhibited spatial variances within Islamabad and Rawalpindi with large amount were measured on the road segments of Inter Junction Principle (IJP) road and around the Attock Oil Refinery (ARL) area. These high column densities are attributed mainly to traffic, stack emissions, congestion and solid waste dumping site along IJP road. Correlation of NO_2 mixing ratios with population and number of registered vehicles were also made was found significant. Furthermore, the results were validated with OMI satellite observation for respective days.

The comparison gave similar NO_2 spatial trends, although satellite observations are found to be under estimated.

Chapter 1

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 mega cities of Pakistan have been heavily polluted. The temporal and spatial measurements NO_x (Nitrogen oxides) are quite limited in Pakistan. Hence there is dire need of continuous observations of NO_2 (Nitrogen dioxide) pollution in the major cities of Pakistan.

1.2. Introduction

Air pollution has emerged as a potential threat for the environment and human health. All major cities of Pakistan are exposed to severe problem of air pollution which should be addressed so that its negative consequences on the health of humans and environment are reduced. NO_2 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).

Globally, NO_2 is released through combustion of fossil fuel, biomass burning, lightning and the microbiological processes in soil (Lee *et al*., 1997). Around 50% is released from industry and traffic and around 20% from biomass burning. Out of natural, approx. 10% emissions are through lightning while 15% from soil due to the activity of microbes (Lee *et al.*, 1997). Subject to the different meteorological conditions, the photolysis ratio and the amount of OH (hydroxyl) radicals, the lifetime of NO_2 ranges from a few hours to 1 day (Crutzen, 1979). It has a big role to play in the chemistry of atmosphere, and is noted for the formation of secondary air pollutants and the acidification of environment. NO_2 has the ability to affect ozone (O_3) which is an important gas in the atmosphere, and OH (Logan *et al.*, 1981; Thompson, 1992).

Road transport has increased at a very faster pace in Pakistan during the last decade. According to the National Transport Research Center (NTRC), total number of registered vehicle were increased to 52 % from 1991‐ 1992 to 2006‐2007 as related to road infrastructure in last 16 years (Sindhu, 2008). This continuous increase is leading to severe problems like traffic jams and consequently increased air pollution. A study carried out by Ahmed et al. in 2011 showed that the NO_2 concentration was above the standards set by World Health Organization (WHO) at all the sampling points within Islamabad and Rawalpindi.

Therefore, the levels of NO_2 should be comprehensively assessed for the purpose of making effective policies in controlling air pollution. Pak-NEQs have been formulated in order to keep the air quality in check.

According to Pakistan National Environmental Quality Standards (Pak-NEQS) limits for certain pollutants are given for the ambient air. Therefore monitoring of these pollutants should be done periodically to observe and check the air quality. Pakistan National Environmental Quality Standards (Pak-NEQS) by the Ministry of Environment are devised to cope with the increasing problem of ambient air pollution. The Pak-NEQS for NO_2 are as follows

Table 1.1: National Environmental Quality Standards for NO_2

Pollutants	**Time-weighted average**	**Concentration in ambient air**		**Method of Measurement**
		Effective from 1st January 2009	**Effective from 1st January 2012**	
Oxides of Nitrogen as (NO_2)	Annual Average	40 µg/m^3	40 µg/m^3	Gas Phase Chemiluminiscence
	24 hour Average	80 µg/m^3 *(42.5 ppbv)	80 µg/m^3 *(42.5 ppbv)	

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

1.3. The Present Study

In the current study nitrogen dioxide (NO_2) column densities are quantified in the cities of Islamabad and Rawalpindi by using car MAX-DOAS observations. The spectra were observed using Mini Max-DOAS device mounted on the car. The measured spectra were analyzed to retrieve differential slant column densities. After the analysis time linkages were created for latitude and longitude of the column densities calculated by using a GPS data logger. Then the results were plotted over Q-GIS and in the end results were validated with the available satellite data.

Chapter 1 deals with the introduction of this study. Starting from the background and then highlighting the NO_2 pollution globally and in Pakistan, aims and objectives of the present study. Chapter 2 gives the literature review. Different literature has been cited starting from Earth's atmosphere to NO_2 trends observed globally. Chapter 3 describes the methodology, the data collection and how the results were analysed. The results and discussion is given in Chapter 4 and in the end conclusions and recommendations are presented in Chapter 5.

1.4. Aims and Objectives

The objectives of this study were:

- To determine nitrogen dioxide concentrations within the cities of Islamabad and Rawalpindi.

- To validate it with other available measurements such as satellite measurements.

Chapter 2

LITERATURE REVIEW

2.1. Atmospheric Chemistry

The earth's atmosphere mainly consists of 78 % nitrogen, 20 % oxygen and low percentage of argon and other gases. The trace gases represent less than 1 % of the atmosphere. Many of the existing trace gases in the atmosphere can be observed by spectroscopic methods, while these gases absorb and scatter the sun light. A known technique to evaluate the atmospheric trace gases is DOAS.

Chemical species are emitted to the atmosphere by a variety of sources. Some of these sources, such as fossil fuel combustion, originate from human activity and are called anthropogenic. Others originate from natural processes of biological organisms and are called biogenic. Still others, such as volcanoes, originate from non-biogenic natural processes (Jacob, 1999).

Nitrogen dioxide is the one of the main traffic-related air pollutants(anthropogenic) and precursors forming photochemical smog (together with VOCs) and ground-level ozone, is currently under intensive investigations, so this trace gases in main concern of our study and is introduced in this chapter.

2.2. Nitrogen Oxides

Nitrogen oxides (NO_x : NO_2+NO) are one of the most important components in the atmosphere, which are produced in combustion processes, mainly through fossil fuel combustion or the direct combination of atmospheric oxygen and nitrogen at high temperatures. Lightning is a natural nitrogen oxide source (direct combination of oxygen and nitrogen). Microbial processes in soil are a small fraction of the natural source of nitrogen oxides.

Power plants and motor vehicles play an important role for NO_x emissions. Natural sources as agricultural and biomass burning emit ammonia, others like nitrate and ammonium salts are secondary products from NO, NO_2 and ammonia (ammonium NH^{+4} ion is an important component of the tropospheric aerosol). The primary pollutant (directly emitted) is mostly nitric oxide (NO) and a small fraction is nitrogen dioxide.

NO_x have a strong impact on the oxidative capacity of the atmosphere because they influence the abundance and partitioning of HO_x radicals (HO_x=OH+HO_2). Furthermore, they act as a catalysator in the formation of ozone (O_3) in the troposphere. However in the stratosphere, NOx enhance the degradation of the ozone layer. NO_x is mostly removed from the atmosphere in form of nitric acid (HNO_3) which is, besides sulfuric acid (H_2SO_4), an important component of acid rain. NO is oxidized by ozone in the atmosphere, on a time scale of several minutes. The nitrogen oxides are rapidly inter converted to each other during the daytime.

Nitrogen oxides are produced in the atmosphere whenever air is heated to temperatures higher than 2000K, e.g. in combustion processes. In this case, the thermal energy is high enough to dissociate O2 into atomic oxygen which reacts with molecular nitrogen to form NO:

$O + N_2 \rightarrow NO + N$ (2.1)

Another byproduct is N_2O can be generated. In the troposphere, N_2O is inert (lifetime of about 120 years) and thus, does not play a chemical role. However in the stratosphere, the strong UV radiation can dissociate N_2O (at λ <298 nm) yielding atomic oxygen for further reactions. NO, as it is produced in reaction 2.1, is rapidly oxidized by ozone to NO_2:

$O_3 + NO \rightarrow NO_2 + O_2$ (2.2)

NO_2 mostly yielded from reaction (2.2) can be photolyzed by UV radiation of the sun below 420 nm generating ozone (see reaction (2.3)). Under direct sun exposure at noon, this happens fast and the mean lifetime of NO2 only accounts to several minutes.

$NO_2 + h\nu\ (\lambda<420\ nm) \longrightarrow NO + O(3P)$ (2.3)

where O(3P) reacts rapidly with O_2 to ozone:

$O(3P) + O_2 + M \longrightarrow O_3 + M$ (2.4) with M as required collision partner (e.g. N_2 or O_2) due to conversation of energy and spin momentum. Since other reactions with O(3P) can be neglected, each NO_2 molecule leads to the generation of an ozone and NO molecule. However, according to reaction (2.2), NO and O_3 form NO_2 again. Finally, a photostationary state arises between NO_2 and NO which is referred to as the Leighton ratio (Leighton, 1961):

$$\frac{[NO]}{[NO2]} = \frac{jNO2}{kNO.[O3]} \qquad (2.5)$$

Typically, the Leighton ratio in the lower troposphere is between 0.5 and 1 depending on the ozone concentration and the photolysis frequency. With increasing height the ratio increases due to higher photolysis frequency of NO_2. In the photostationary state, on average ozone neither is formed nor destroyed. Net ozone production is observed if NO_x is sufficiently abundant to react with peroxy radicals, HO_2 and RO_2. In this case, the following reaction can occur:

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (2.6)$$

whereby the peroxy radicals are generated from oxidation of volatile organic compounds (VOCs), which are abundant in urban areas. To a very small amount (≈0.1%), it is assumed that also other products, such as HNO_3, can be produced in this reaction. Thus, ozone is produced by reaction (2.3) and (2.4), but not degraded by NO in the same extent. This can lead to the so-called photosmog with large amounts of ozone, oxidized VOCs and organic aerosols. However, peroxy radicals also can react with ozone to molecular oxygen and OH. But this only plays a role if the concentrations of NOx are very low:

$O_3 + HO_2 \rightarrow 2O_2 + OH$ (2.7)

Thus, it depends on the different abundances of NOx and VOCs if more ozone is produced by reactions (2.3) and (2.4) or destroyed by reaction (2.7). The decomposition product of NO_2 is mostly nitric acid (HNO_3) which is generated by the reaction with OH:

$NO_2 + OH + M \rightarrow HNO_3 + M$ (2.8)

Hence, this reaction is not only a sink for NO_2, but also for OH. Thus, NO_2 contributes to the degradation of the concentration of the hydroxyl radical. NO_2 can also be further oxidized to NO_3:

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (2.9)

However during daylight, NO_3 is degraded by photolysis within several seconds in two ways:

$NO_3 + h\nu \rightarrow NO + O_2$ (2.10)

$NO_3 + h\nu \rightarrow NO_2 + O$ (2.11)

and furthermore, by the rapid reaction with NO:

$NO_3 + NO \rightarrow 2NO_2$ (2.12)

At day, the photolysis and the NO concentrations prevent a significant level of NO_3 concentration. Yet by night, when no photolysis occurs so that also NO concentrations are low, NO_3 can accumulate in the atmosphere. Additionally, NO_3 can react with NO_2 yielding N_2O_5:

$$NO_3 + NO_2 + M \longleftrightarrow N_2O_5 + M \qquad (2.13)$$

NO_3, NO_2 and N_2O_5 are in a thermodynamic equilibrium which depends strongly on temperature (Finlayson-Pitts and Pitts jr., 2000). N_2O_5 is degraded mainly by reaction on water (droplet) surfaces (Mentel et al., 1996), and is an important process of NO_x on local and global scales.

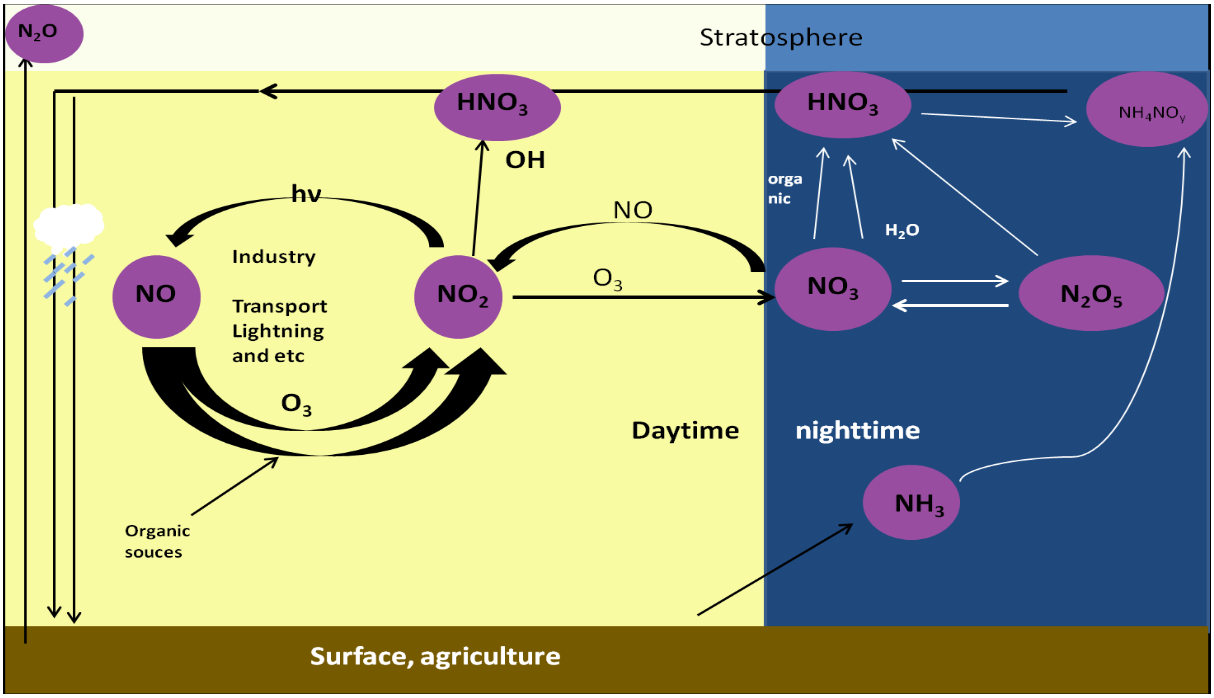


Figure 2.1: An overview about tropospheric nitrogen oxides chemistry during day and night.

A reaction, which produces nitrogen dioxide, is in the presence of HO_2 radicals. The oxidation of CO in the atmosphere by OH radicals produce HO_2 radicals:

$HO_2 + NO \rightarrow NO_2 + OH$ (2.14)

In the troposphere, under low NOx limit, the production rate of O_3 increases linearly with the NO concentration and independent from the CO level. In the high NO_x limit, the produced O_3 increases linearly with CO and HO_x, and it decreases with increasing NO_x (Seinfeld & Pandis, 2006).

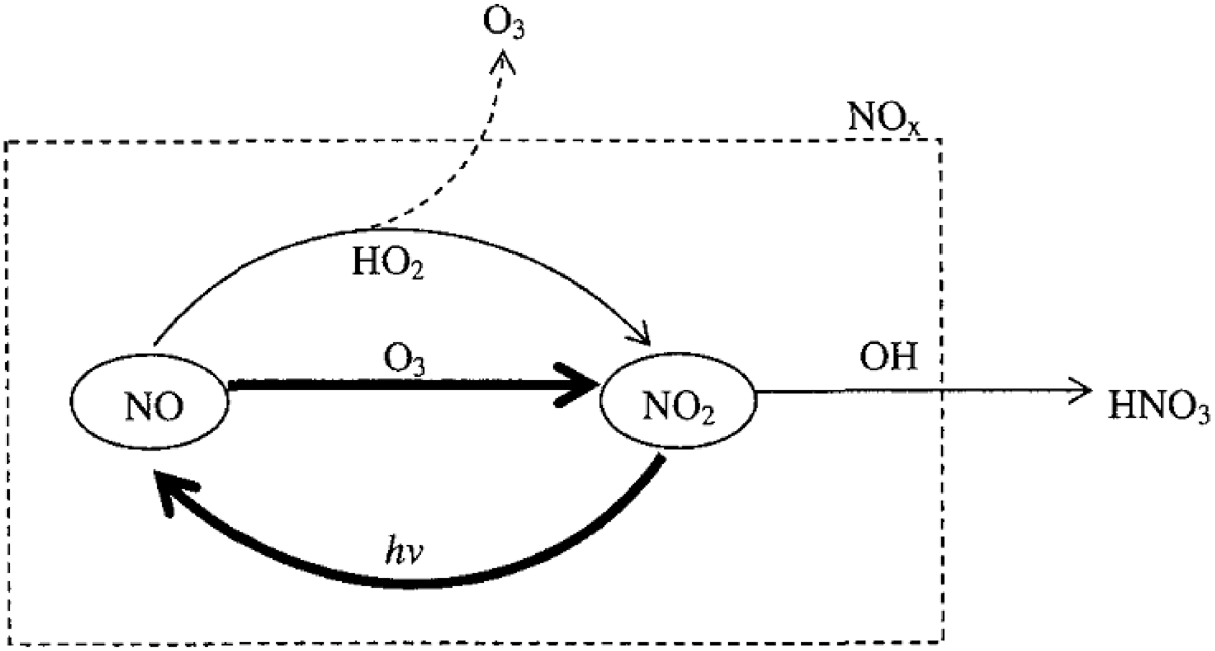


Figure 2.2: Important atmospheric reactions including nitrogen species (Seinfeld & Pandis, 2006).

2.3. Differential Optical Absorption Spectroscopy

2.3.1. DOAS Overview

The Differential Optical Absorption Spectroscopy (DOAS) is a very sensitive and widely used measurement technique to detect trace gases in the atmosphere (Perner and Platt, 1979; Platt, 1994). It was introduced by Platt et al. (1979) measuring atmospheric trace gases with an artificial light source. Since then, DOAS has been applied to measure concentrations of many trace gas for the first time, e.g. OH by Perner et al. (1976), HONO by Perner and Platt (1979) and Platt and Perner (1980), NO_3 by Platt et al. (1980), BrO in the stratosphere by Sanders et al. (1988) and in the troposphere by Hausmann and Platt (1994), IO by Alicke et al. (1999), and CHOCHO by Volkamer et al. (2005). A variety of other trace gases absorbing in the UV and the visible wavelength region can be detected as well (Platt, 1994), e.g. NO_2, ClO, O_3, SO_2, CS_2, HCHO, OClO, H_2O, and NH_3. Most recently, CH_4 could be measured in the near IR wavelength region from satellite (Frankenberg et al., 2005) and from a ground-based device (Woyde, 2007).

DOAS is based on the absorption of light traversing a gas volume and being attenuated characteristically for each trace gas in this volume. From the spectral position of these absorbing lines and their strengths, the trace gases can be identified and quantified. Because DOAS is capable of measuring the composition of ambient air in the open atmosphere without interaction caused by the measurement process, it can also detect highly reactive species, such as the free radicals OH, NO3, halogen oxides and NO2. Furthermore, DOAS is able to measure several trace gases simultaneously, which reduces measurement time and allows to analyse the different chemical components in the observed air mass.

Generally, DOAS can be performed actively, using artificial light sources, as well as passively with natural, extraterrestrial light sources, which is most commonly the sun owing to its high intensity in comparison, for instance, to the moon. Passive DOAS can be divided into scattered light measurements pointing somewhere to the sky and direct light measurements, which point directly onto the sun or the moon.

Active setups often use high pressure Xe-arc lamps, but most recently also light emitting diodes (LEDs) were introduced (Kern et al., 2006; Sihler, 2007), which need far less power, have a much longer life time, are easier to handle and have less spectral structures than the traditional Xe-arc lamps; however, their wavelength range is much more limited. The following list gives an overview on the most common DOAS applications:

Multi-Axis (MAX) and Zenith-Sky-DOAS measure scattered sunlight mostly from the ground and provide information on the concentration of trace gases in the atmosphere integrated along the light path. Zenith-Sky-DOAS instruments only point to the zenith and are suitable to investigate stratospheric absorbers. In contrast, MAX-DOAS measurements, on which this work is based, vary the viewing direction, are sensitive for trace gases in the troposphere and can deliver information on the altitude profile of trace gases. MAX-DOAS devices are easily to maintain and also suit to conduct long-term measurements. Since recently, these devices have been installed on different platforms, such as airplanes (AMAX-DOAS), vessels (SMAX-DOAS) and cars (Auto-MAXDOAS). This gives the possibility to observe atmospheric gases along the respective tracks.

Long path DOAS uses artificial light sources. Typically, light is sent out by a Newton telescope and is reflected by a retro reflector array usually in a distance of several kilometers, before it is received again. Thus, the measurement is constrained to the lowermost atmosphere. But in contrast to scattered light instruments, the derivation of concentrations and mixing ratios is easy and measurements by night are possible. It is adverse that the operation of long path DOAS devices requires a relatively large effort. By using several long path instruments together, tomography measurements can provide information on spatial distributions of trace gases. Multiple reflection cells (White cells) convolve the light path many times and, therefore, can measure trace gases of a small air mass parcel. The very young method Cavity Enhanced Absorption Spectroscopy uses this principle.

Satellite borne DOAS enables to receive a global picture of the spatial distribution of atmospheric trace gases. Instruments such as Global Ozone Monitoring Instrument (GOME) onboard the satellite ERS-2, the SCanning Imaging Absorbtion SpectroMeter for Atmospheric CHartographY (SCIAMACHY) onboard Envisat, the Ozone Monitoring Instrument (OMI) onboard NASA/EOS AURA and finally GOME2 onboard METOP measure reflected and in the Earth s atmosphere scattered sunlight (Nadir mode) and direct sunlight traversed the Earth s atmosphere (Limb mode), respectively.

Imaging DOAS enables to retrieve two-dimensional images of the distribution of trace gases. It has been applied to exhaust-gas plumes of power plants and volcanic plumes.

Balloon borne DOAS measurements use either scattered or direct sunlight. The latter requires a good alignment to the sun even in atmospheric turbulence. They are able to provide altitude profiles of atmospheric trace gases up to the stratosphere.

2.4. MAX-DOAS

DOAS is a technique of remote sensing allowing the determination of the abundance of atmospheric trace species by use of their structured absorption bands in the UV and visible spectral regions (Fraunhofer lines). It is one of the most widely applied spectroscopic methods in atmospheric research. This technique is based on the difference in absorption at different wavelengths. With the DOAS method, trace species are identified by absorption in their UV / visible absorption cross-sections. Relevant molecules include NO_2, O_3, HCHO, H_2O, O_4, or SO_2.

The fundamental principle underlying absorption measurements is the Lambert-Beer law: the attenuation of monochromatic radiation is related to the number of absorbing molecules in the optical path,

$$I(\lambda) = Io(\lambda)\, e^{-\alpha LC} \qquad (2.15)$$

Where "Io" is the incident flux, "I" is the measured flux, "α" is the absorption cross section of the targeted species, "L" is the distance over which the absorption takes place or optical path length and "C" is the concentration of the absorbing species (or density).

The presence of various gases, aerosols and scattering processes (Rayleigh, Mie and Raman) limit the application of Lambert Beer law. In atmospheric chemistry, differential optical absorption spectroscopy (DOAS) is used to measure concentrations of different trace gases. The illustration of DOAS Principle is given in Figure 2.3. (for details, see Platt, 1994)

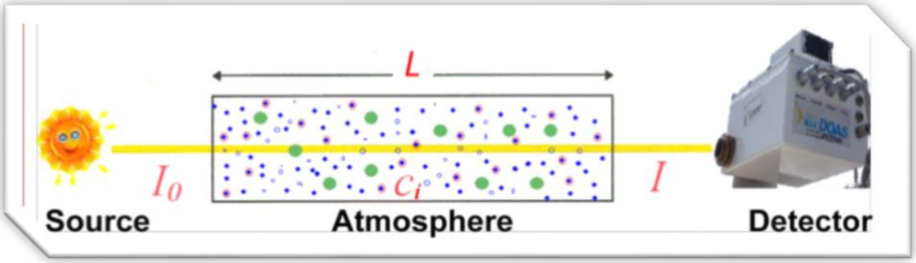


Figure 2.3: Illustration of DOAS Principle

In commercial analyzers, sophisticated signal processing is undertaken to account for interfering species and variability in atmospheric optical transmission conditions. Many species can be measured by the DOAS technique, but the most common configuration for ambient air monitoring is to measure NO_2, SO_2, O_3 and benzene.

2.4.1. The Lambert-Beer Law

The Lambert-Beer law (see equation (2.15)), on which absorption spectroscopy is based, describes how light is absorbed by matter. Three parameters determine the attenuation of light: the concentration c of the absorbing material, its cross section σ (i.e. the probability of absorption) and the length L of the light path through the absorbing material:

$$I(\lambda,L) = I_0(\lambda) \cdot e^{-c.\sigma.L} \qquad (2.16)$$

The light source mostly consists of the sun and the matter of the Earth s atmosphere. The sunlight traversing the atmosphere is both absorbed by the different trace gases i in the atmosphere and scattered. Scattering processes can be the Mie and Rayleigh scattering. A part of the incident light reaches finally the Earth s surface with the intensity I(λ,L):

$$I(\lambda,L) = I_0(\lambda) \cdot e^{-\int L0[\Sigma j\ \sigma j\ (\lambda,T,p).cj\ (l)+\varepsilon M(\lambda,l)+\varepsilon R(\lambda,l)]dl} \qquad (2.17)$$

where I(λ,L) and $I_0(\lambda)$ denote the wavelength dependent intensities after and before, respectively, passing the atmosphere; I(λ,L) is also dependent on the length of the light path assuming that more absorbing and scattering processes take place when the light path through the atmosphere is longer. $\sigma_j(\lambda, T, p)$ are the cross sections of the different trace gases, which are dependent on the wavelength λ, the temperature T and to a minor degree the pressure p. $c_j(l)$ are the concentrations of the different trace gases j along the light path. $\varepsilon_M(\lambda, l)$ and $\varepsilon_R(\lambda, l)$ stand for the extinction coefficients of the Mie and Rayleigh Scattering, respectively, which both are also wavelength dependent.

The Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) is a measurement technique that observes scattered sunlight under different elevation angles between zenith and horizon (Leser et al. 2003; Van Roozendael et al. 2003; Höonninger et al. 2004; Wagner et al. 2004). Using different elevation angles give us the possibility to derive the vertical distribution of trace gases.

2.4.2. Correction of the Spectra

The MAX-DOAS spectra have to be corrected before the analysis. These spectra have to be corrected by offset and dark current spectra, which are recorded by the same instrument.

a) Offset

The analogue-digital converter transforms the signals to digital form, and before this step, an offset is added to the measured spectra to avoid negative signals. Therefore this offset has to be subtracted from the spectra. An offset spectrum is a measured spectrum with a high number of scans and a short integration time.

b) Dark Current

This is the signal measured by the detector without illumination. This effect is caused by thermal excitation. The probability of this excitation is proportional to the Boltzmann function. To reduce the dark current signals, detectors are usually cooled to a constant temperature. IDC represents the dark current spectrum, which is a measured spectrum with one scan and a long integration time.

2.5. Recent studies on NO_2 pollution using Car-MAX-DOAS

Recently work on Nitrogen Dioxide monitoring has been done in Indian city of New Delhi by using car MAX-DOAS in April 2010 and January 2011. The Nitrogen dioxide concentrations were related to traffic congestion and other sources present in the study area. Further this nitrogen Dioxide monitoring was validated with satellite data. (Shaiganfar et al. 2011).

Another field campaign was conducted using MAX-DOAS observations via car journey from Brussels to Heidelberg in September, 2006. The distribution of the tropospheric NO_2 VCD was retrieved along the driving route with a spatial resolution of about 1 km. Three elevation angles (22°, 40°, and 90°) were used for spectral measurements. All three elevation angles showed consistency for NO_2 VCD retrieval, indicating that the geometrical approximation method is appropriate. Also the satellite validation for the ground base observations were done, which revealed that, “The comparison with OMI satellite observations yields rather fair agreement i.e. satellite observations are 25 to 100% larger than the AUTO-MAX-DOAS observations (Wagner et al. 2010).

During the month of July and August 2011, Nitrogen Dioxide measurements in the South-Eastern part of Romania have been observed. The experiment focused on areas with potential strong emissions of Nitrogen Dioxide since these are industrial zones or roads with heavy traffic. During the experiment it was found out that amount of Nitrogen Dioxide concentrations were mainly due to iron and steel industry away from cities, heavy traffic within the cities and ring roads near cities. (Constantin, et al. 2011)

2.6. Recent studies on NO_2 pollution in Pakistan

Since the environmental legislations in the country, some work has been done for air quality monitoring. Nitrogen Dioxide being on of criteria pollutant has been monitored within major cities of Pakistan. In Pakistan more than 70% of NO_2 pollution is being contributed by transportation, power plants and industries (GOP/IUCN, 1992). During 1995 to 2005 the growth rate for all motor vehicles in Pakistan has been 33.61% annually (Ilyas et al. 2007), which has worsened the ambient air quality in the country.

In order assess the ambient air quality situation in Pakistan, JICA and Pakistan Environmental Protection Agency (Pak-EPA) conducted air sampling in three cities (Lahore, Rawalpindi, Islamabad) of Pakistan in 2000. All the criteria pollutants were monitored during the study (i.e. Carbon Monoxide, Sulphur Dioxide, Nitrogen Oxides, Ozone, Particulate Matter and Hydrocarbons). The NO_x levels were found very high in the cities mainly due to traffic congestion. The most polluted city in terms of air quality was found to be Lahore (JICA, 2000).

Ambient air quality was also studied along various sections of N5 highway by Ali et al. in 2006. During the study various criteria pollutants (i.e. Carbon Monoxide, Sulphur Dioxide, Nitrogen Oxides, Particulate Matter and Noise Level) were monitored using different sampling techniques. NO_2 was sampled using glass impingers having tri-ethanolamine absorption solution using APM 410 & 415 Sampler. The NO_2 levels were found highest in the Lahore – Gujranwala Section of the highway with pollution increasing as we move from Gujranwala to Lahore along N5 highway. The same spatial trend was observed from the results of our study and also the satellite observation of the campaign day. The reason is that the Lahore – Gujranwala section is the busiest section of N5 highway in terms of traffic flow because Gujranwala is the junction to many roads that further lead to Lahore via this section of N5 highway.

Zafar et al. 2012 studied NO_2 pollution at various locations of the Islamabad and Rawalpindi city. The study was carried out in two phases as one monitoring was done in winter season and spring season. The study correlated the NO_2 pollution with traffic congestion and industrial activities of the twin cities.

Jahangir et al. 2013 study was focused at monitoring NO_2 pollution near public and private sector hospitals in the twin cities of Rawalpindi and Islamabad. The findings of the study were the NO_2 concentration was more near hospitals situated on the main roads due to traffic congestion.

According to ongoing research on ambient air quality at National university of Sciences and Technology (NUST) many initiatives have been taken to monitor air quality using Mini Max-DOAS instrument. NO_2 VCDs have been monitored along the N-5 highway and surrounding the cities of Lahore and Gujranwala with mobile monitoring (Shabbir et al. 2013). Also point source monitoring for NO_2, Formaldehyde (HCHO) and Ozone (O_3) have been done with Max-DOAS been mounted on building of Institute of Environmental Sciences and Engineering (IESE), NUST (Nisar et al. 2013). A database for NO_2 VCDs from satellites observation using OMI (2002 – Present) and GOME-2 (2007 - Present) data has also been established to study spatial and temporal trends on NO_2 pollution. 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 (Fatima et al. 2013).

Chapter 3

MATERIAL AND METHODS

3.1. MAX-DOAS

The Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) is a measurement technique that observes scattered sunlight under different elevation angles between zenith and horizon (Leser et al. 2003; Van Roozendael et al. 2003; Hönninger et al., 2004; Wagner et al. 2004). Using different elevation angles give us the possibility to derive the vertical distribution of trace gases.

3.2. Car MAX-DOAS instrument

The Mini-MAX-DOAS instrument is an automated and light weighted spectrometer intended for the spectral analysis of scattered sunlight. A stepper motor fixed outside the machine casing rotates the whole instrument to make it able to take measurements at different viewing angles. The entrance optics consists of a quartz lens of focal length f = 40 mm coupled to a quartz fiber bundle which leads the collected light into the spectrograph. The light is dispersed by a crossed Czerny-Turner spectrometer (USB2000+, Ocean Optics Inc.) with a spectral range from 320 - 460nm.

3.3. Field Campaigns:

Three field campaigns were conducted in order to complete the objectives of this study. Two field campaigns taken place within NUST on 12th November 2012 and 25th February 2013. Both days were clear days. Two field campaign of twin cities were conducted on 13th and 16th November 2012 and the days were clear day with little wind.

3.3.1. Field Campaigns in NUST:

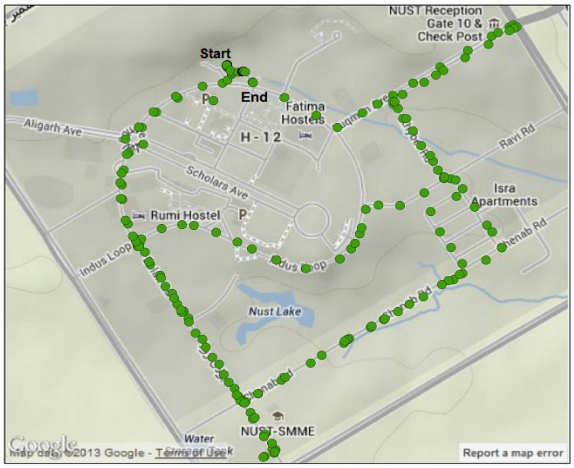
For the mobile observations measurements inside NUST Headquarters, the Mini-MAX-DOAS instrument was placed on the roof top of a car with the lens viewing backward.

The route for both days is shown in Fig. 3.1.

a)

Figure 3.1: Track Followed for the NUST Field Campaign a) 12th November, 2012 b) 25th February, 2013

b)



The sequence of elevation angles was set to: 8x22, 1x45, 1x90 for 12th November 2012 and for 25th February 2013 the elevation sequence was set to: 1×90^0, 4×30^0 and the time to make a single measurement was approximately 60 s. The temperature set point of the mini MAX-DOAS was 15 ^{0}C. A GPS logger was used to track the coordinates of the route along which the observations were made.

3.3.2. Overview on measurements around Islamabad and Rawalpindi

For the mobile observations measurements in Islamabad and Rawalpindi, the Mini-MAX-DOAS instrument was placed on the roof top of a car with the lens viewing backward. The field campaigns were conducted on 13th November, 2012 and 16th November, 2012. On 13th November, 2012 the route was done on G.T. Road till Gujranwala. Rawalpindi measurements were taken from that.

The measurements started from NUST H-12 Campus to Islamabad and around twin cities; the route is shown in Fig. 3.2 for 16th November 2012.

The sequence of elevation angles was set to: 1×90^0, 4×30^0 and the time to make a single measurement was approximately 60 s. The temperature set point of the mini MAX-DOAS was 15 ^{0}C. A GPS logger was used to track the coordinates of the route along which the observations were made.

The time to complete the track for 16th November, 2012 (Fig. 3.2.) took about 2 to 3 hours.

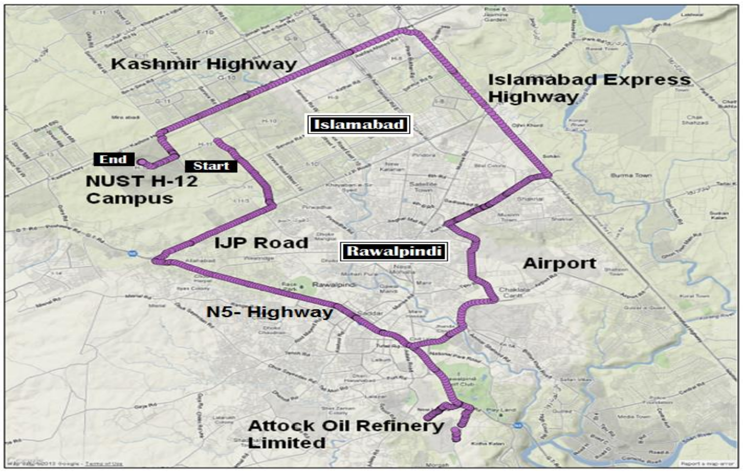


Figure 3.2: Track Followed for the 16th November 2012 Field Campaign

3.4. Processing of Research Work:

For the retrieval of the NO_2 tropospheric VCDs, their mapping and comparison with satellite data many software were used in order to meet the objectives of the study. Processing of research (Figure 3.3) and software used are mentioned below with details of its working.

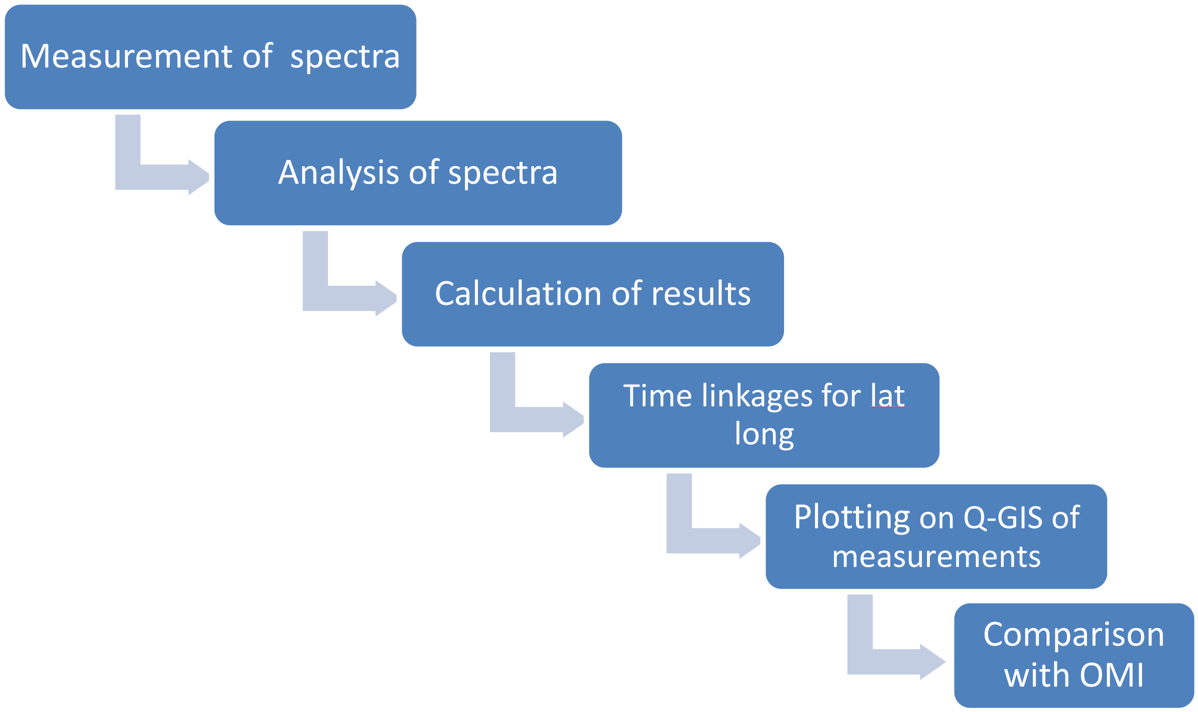


Figure 3.3: Processing of Research Work

3.4.1. Measurement of Spectra

Differential Optical Absorption Spectroscopy Intelligent System (DOASIS) is used to operate the Mini Max-DOAS during its measurements of spectra. It has various functions as to control stepper motor, integration time of spectrum and internal temperature of the spectrometer. In addition the spectrometer is operated be Ocean Optics Instrument (OOI) software. DOASIS is also used for Ring spectrum calculation which is later used in DOAS fit analysis. DOASIS is also used to measure dark current and offset for the spectrometer. These are used as zero correction for the spectra.

3.4.2. Analysis of Spectra

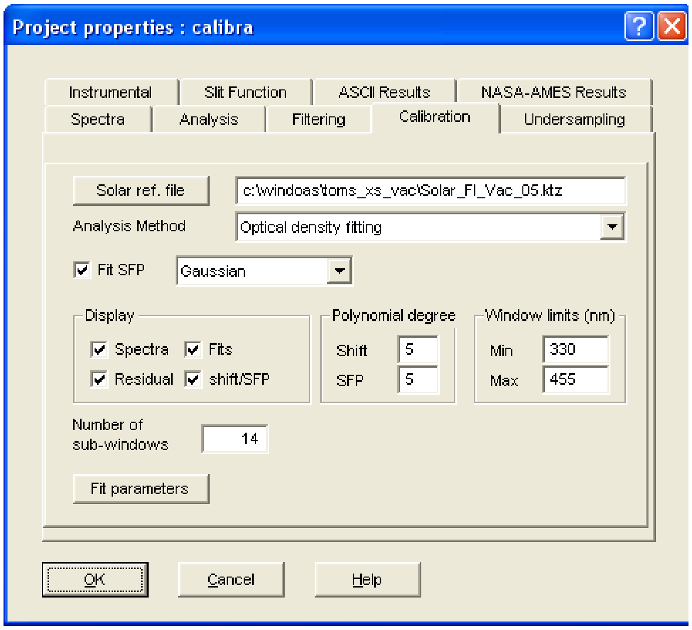
The measured spectra were analyzed using WinDOAS (Windows Differential Optical Absorption Spectroscopy) software for retrieval of Differential Slant Column Densities (DSCDs), (Platt and Stutz, 2008, Fayt and van Roozendael, 2001). A high resolution solar spectrum was used for wavelength calibration (Kurucz et al., 1984). A wavelength analysis window chosen for NO_2 was 405–455 nm. The trace gas absorption cross sections used for the DOAS fit were; NO_2 at 294K (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 Fraunhofer Reference Spectrum and a Ring

Spectrum (calculated from the Fraunhofer spectrum) were also included in the analysis for DSCDs.

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 performed by fitting a measured spectrum to a convoluted solar 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 (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.



Solar ref. file: c:\windoas\toms_xs_vac\Solar_FI_Vac_05.ktz
Analysis Method: Optical density fitting
☑ Fit SFP: Gaussian
Display: ☑ Spectra ☑ Fits ☑ Residual ☑ shift/SFP
Polynomial degree: Shift 5, SFP 5
Window limits (nm): Min 330, Max 455
Number of sub-windows: 14

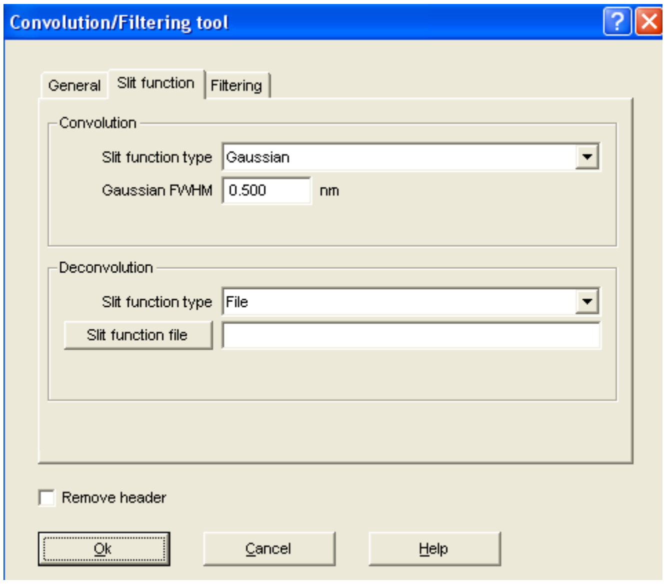
Figure 3.4: WinDOAS Calibration Window

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/SFP” indicates the polynomial degree used for interpolating the results of the individual sub-windows.

The calibration process is repeated twice to minimize the residual error of the calibration process. The entire measured spectrums are calibrated using the calibrated spectrum.

Wavelength Convolution: Convolution is a simple mathematical operation which is fundamental to wavelength processing operations. A number of trace gas cross sections are used e.g. NO_2 at 294K (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) are used for convolution of analysis wavelength.



Slit function type: Gaussian

Gaussian FWHM: 0.500 nm

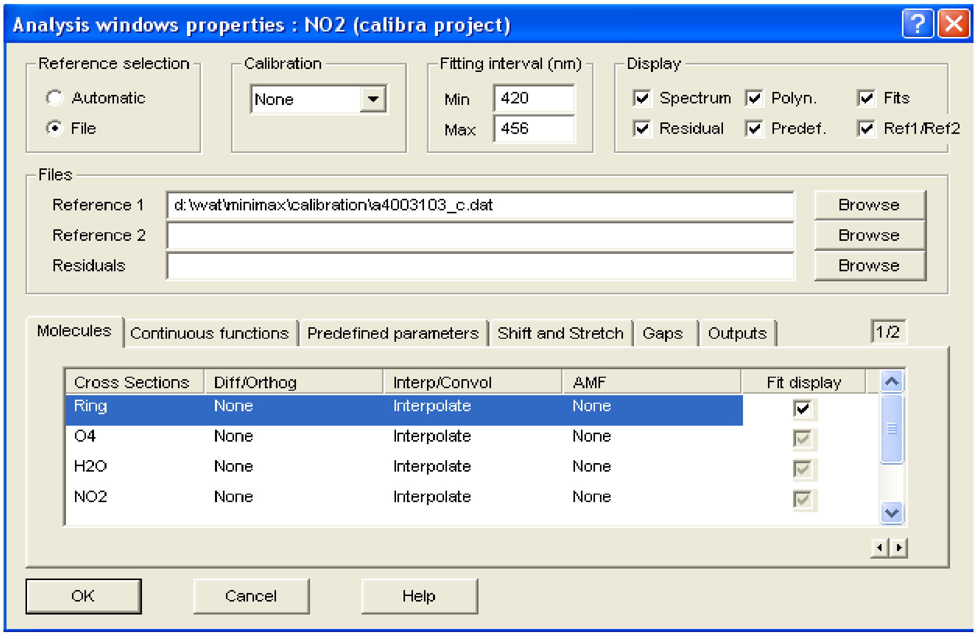
Slit function type: File

Figure 3.5: WinDAOS Convolution Window

We used the slit function type as Gaussian shape. In the case of NO_2, which is analyzed around 440nm, a FWHM of 0.5 nm is chosen.

NO_2 Analysis Window: The NO_2 analysis window was selected as 405 nm to 455 nm (Wagner et al. 2010). The calibrated spectrum is used as the reference spectrum for the analysis window. The path of all the cross sections are given in the Cross Sections Tab. The polynomial order of 5^{th} degree was used for our Nitrogen Dioxide 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 DSCD file is obtained as a result.



Analysis windows properties : NO2 (calibra project)

Reference selection

○ Automatic

● File

Calibration: None

Fitting interval (nm)

Min: 420

Max: 456

Display

☑ Spectrum ☑ Polyn. ☑ Fits

☑ Residual ☑ Predef. ☑ Ref1/Ref2

Files

Reference 1: d:\wat\minimax\calibration\a4003103_c.dat

Reference 2:

Residuals:

Cross Sections	Diff/Orthog	Interp/Convol	AMF	Fit display
Ring	None	Interpolate	None	☑
O4	None	Interpolate	None	☑
H2O	None	Interpolate	None	☑
NO2	None	Interpolate	None	☑

Figure 3.6: WinDAOS NO_2 Analysis Window

The trace gas cross sections used as DOAS fit for NO_2 analysis are as follows:

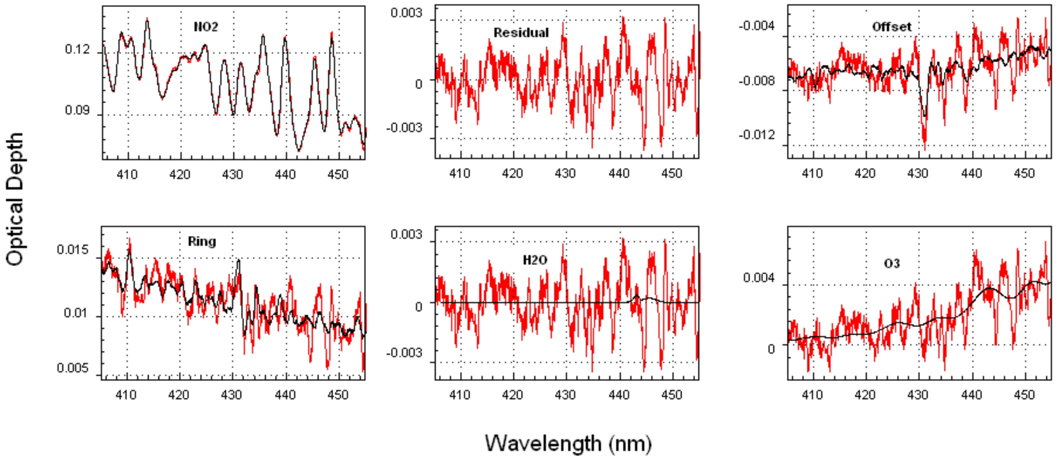
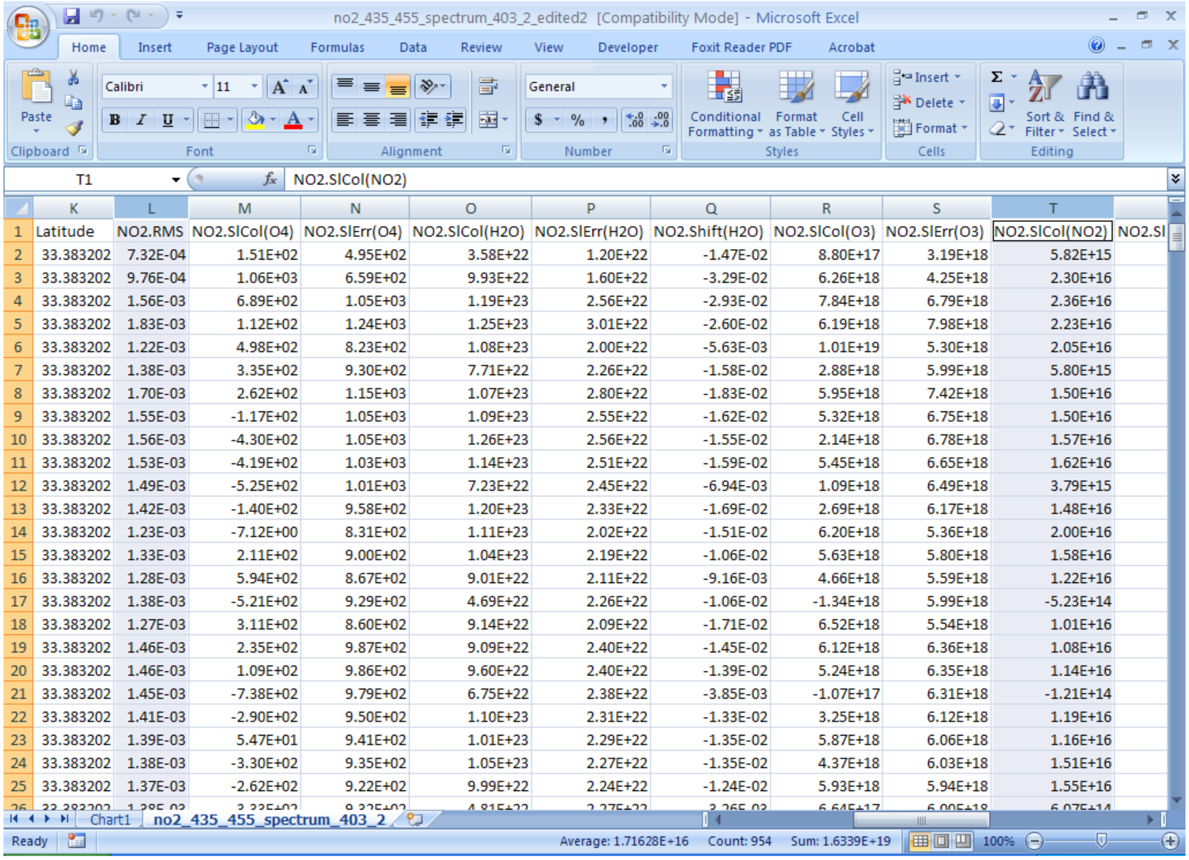


Figure 3.7: Typical Win-DOAS analysis window showing DOAS fit for our Field Campaign Data

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



T1 NO2.SlCol(NO2)

	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	

Average: 1.71628E+16 Count: 954 Sum: 1.6339E+19

Figure 3.8: Microsoft Excel Window showing NO_2 Root Mean Squares (RMS) and NO_2 (DSCD) values

3.4.3. Calculation of the tropospheric VCD using MS Excel

The tropospheric VCD can be obtained from the SCD using a geometric airmass factor (AMF). For the analysis of MAXDOAS observations we are concerned about the tropospheric vertical column density $\mathrm{VCD_{trop}}$.

$$\mathrm{VCD_{trop}} = \frac{\mathrm{SCD_{trop}}(\alpha)}{\mathrm{AMF_{trop}}(\alpha)} \qquad (3.1)$$

The SCD_{meas} (α) measured the SCD_{trop} (α) and SCD_{strat} (SZA). So SCD_{trop} (α) could be deduced from this equation below;

$SCD_{trop}(\alpha) = SCD_{meas}(\alpha) - SCD_{strat}(SZA)$ (3.2)

Since the Fraunhofer reference spectrum contains atmospheric trace gas absorptions, the result of the DOAS analysis represents the difference between the SCDs of the measured spectrum (SCD_{meas}) and that of the Fraunhofer reference spectrum ($DSCD_{ref}$), this difference is usually referred to as differential SCD (DSCD):

$DSCD_{meas} = SCD_{meas} - DSCD_{ref}$

$SCD_{meas}(\alpha) = DSCD_{meas}(\alpha) + DSCD_{ref}$ (3.3)

So after substituting the value of SCD_{meas} (α) in equation 2 becomes;

$SCD_{trop}(\alpha) = DSCD_{meas}(\alpha) + \mathbf{DSCD_{ref} - SCD_{strat}(SZA)}$ (3.4)

While $DSCD_{ref}$ is a constant (because a single Fraunhofer reference spectrum was used), SCD_{strat} (SZA) usually depends on the solar zenith angle. We will refer to the difference of the two unknowns $DSCD_{ref}$ and SCD_{strat} (SZA) as $DSCD_{offset}$ (SZA) in the following:

$DSCD_{offset}(SZA) = DSCD_{ref} - SCD_{strat}(SZA)$

The stratospheric SCD is added to the offset.

$DSCD_{ref} = DSCD_{offset}(SZA) + SCD_{strat}(SZA)$ (3.5)

3.4.3.1. Determination of the $\mathrm{DSCD_{ref}}$ and the stratospheric background

The Determination of the $\mathrm{DSCD_{ref}}$ and the stratospheric background is performed as described in Wagner et al., 2010. For each elevation sequence, pairs of 90° elevation and low elevation angles (here 30°) have to be selected. In our case, the 90° and the directly following 30° spectra are selected; the other 30° spectra are ignored.

For each of these pairs the following value is calculated:

$$\mathrm{DSCD_{offset}(SZA)} = \frac{\mathrm{AMF(90°) * DSCD(30°) - AMF(30°) * DSCD(90°)}}{\mathrm{AMF(30°) - AMF(90°)}} \qquad (3.6)$$

For many applications, radiative transfer simulations is used to retrieved the AMF, but in this research work the geometric approximation is used:

$$AMF\ \alpha = \frac{1}{Sin\ \alpha}$$

For the selected elevation angles, and using the geometric approximation, the AMF for the 30^0 and 90^0 becomes 2 and 1 respectively. Thus the equation 6 reduces to:

$\mathrm{DSCD_{offset}}$ (SZA) = DSCD (30°) – 2 * DSCD (90°)

Unrealistic values have to be removed. Especially near to strong emission sources, usually not the same air masses are observed at both elevation angles. This leads to strong negative or positive deviations. These ‘outliers’ have to be removed. Now the average of all values is calculated. This is the best estimate for the $DSCD_{ref}$. In our case it is 4.26e15 molecules/cm² for 16th November 2012.

The stratospheric AMF is calculated from the SZA according to the geometric approximation:

$$AMF_{strat} = \frac{1}{\cos(SZA)}$$

The stratospheric SCD is estimated assuming a typical stratospheric VCD.

3.4.3.2. Determination of the tropospheric NO_2 VCDs

The tropospheric VCD is calculated according to:

$$VCD_{trop} = \frac{SCD_{trop}(30°)}{AMF_{trop}(30°)}$$

With

$SCD\ (30°) = DSCD\ (30°) + DSCD_{ref} - SCD_{strat}$

$$VCD_{trop} = \frac{DSCD(30°) + DSCD_{ref} - SCD_{strat}}{AMF_{trop}(30°)}$$

The VCD_{trop} is calculated to yield the time series of NO_2 VCDs along the route (figure 3).

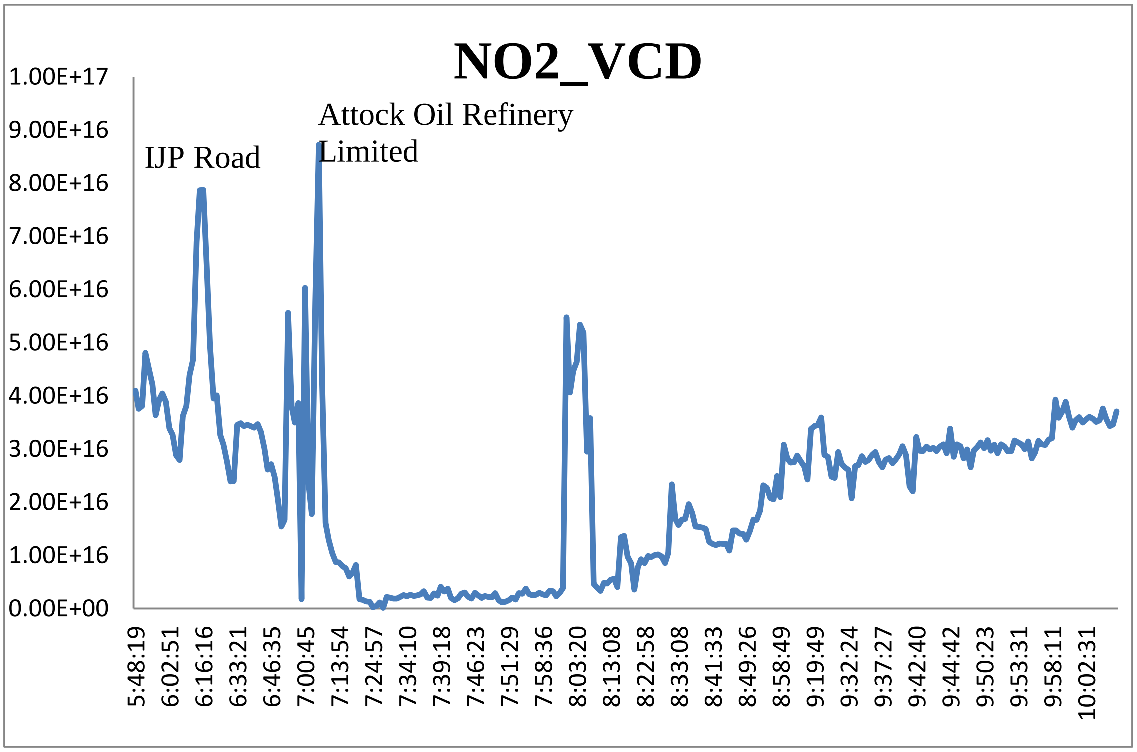


Figure 3.9: Time-series of NO_2 VCD on 16th November 2012

NO_2 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 NO_2 pollution over the project area.

3.4.4. Determination of the tropospheric NO_2 VCDs and Mixing Ratios

The tropospheric VCD is calculated according to the formula given by Eq. (3.7):

$$\mathrm{VCDtrop} = \frac{\mathrm{SCDtrop}(30°)}{\mathrm{AMFtrop}(30°)} \qquad (3.7)$$

In this study NO_2 mixing ratios from the retrieved NO_2 VCDs were also estimated. Since from car MAX-DOAS observations no information on the tropospheric NO_2 profile can be derived, the NO_2 layer height had to be estimated. Here we use a value of 500 m, which might be a good estimate close to strong emission sources (e.g. Wagner et al., 2011). In the first step the average NO_2 concentration is calculated:

$$[NO_2] = NO_2\ VCD / 5 \cdot 10^4\ cm \qquad (3.8)$$

Here $[NO_2]$ indicates the NO_2 concentration in units of cm^{-3}. $[NO_2]$ can be further converted into NO_2 mixing ratios (in units of parts per billion, ppb):

$$NO_2\ mixing\ ratio = [NO_2] / 2.5 \cdot 10^{10}\ cm^3 \qquad (3.9)$$

It should be noted that depending on the actual NO_2 layer height, the NO_2 mixing ratios derived from equations 3 and 4 can be subject to large uncertainties.

The resulting tropospheric NO_2 columns (molecules/cm^2), derived mixing ratios (ppbv) and its comparison with the Pakistan National Environmental Quality Standards (Pak-NEQS, Pak-EPA 2012) are presented in Figure 4.1 and Figure 4.2 in the next section for 13 and 16 November, 2012 respectively.

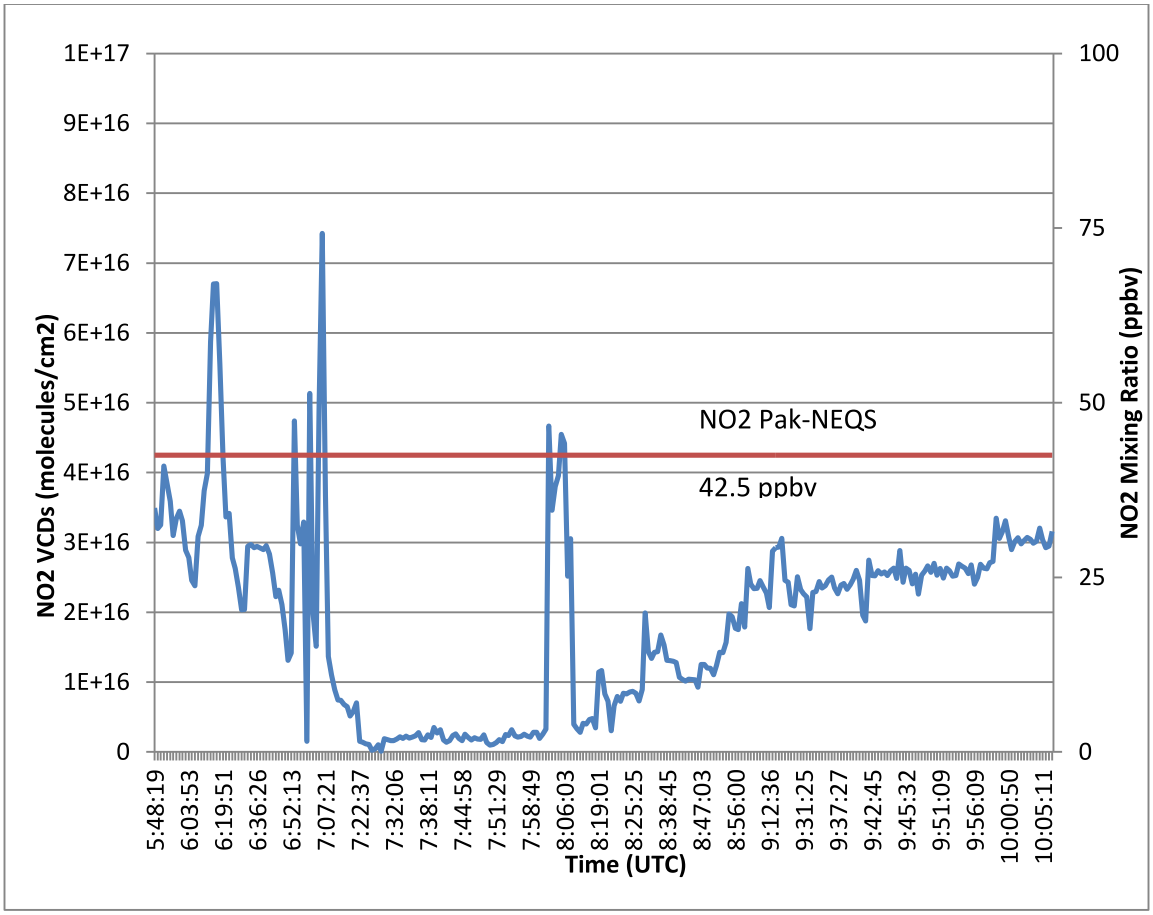
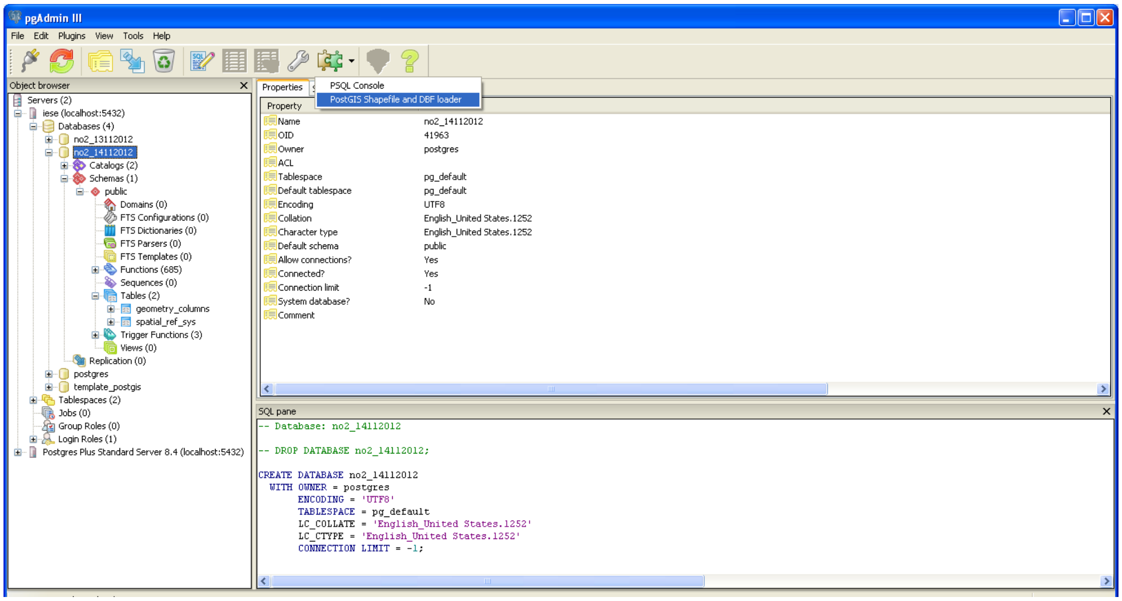


Figure 3.10: Nitrogen Dioxide VCDs (molec/cm^2) and Mixing Ratios (ppbv) on Islamabad-Rawalpindi route on 16th November,2012 and comparison of NO_2 levels with existing Pakistan National Environmental Quality Standards (Pak-NEQS)

3.4.5. Plotting of NO_2 VCD over Project Area

SQL Database: To plot the NO_2 VCD along NUST and Islamabad/Rawalpindi, the measured VCD needed to be plotted according to their coordinate of measurements. As the geographic coordinates were taken using a Global positioning System (GPS) logger and DOASIS don't have any geographic coordinates logging setup for capturing the coordinates along the field campaign route. This presented us with a problem to how to link the coordinates with the MaxDOAS measurements.

The problem was solved using the SQL Database. The time linkage was used to create link between instrument measurements and coordinates recorded. SQL queries were applied to our dataset in this regard. By applying these queries the NO_2 VCD were mapped using QGIS according to their coordinates along the routes.



Property	
Name	no2_14112012
OID	41963
Owner	postgres
ACL	
Tablespace	pg_default
Default tablespace	pg_default
Encoding	UTF8
Collation	English_United States.1252
Character type	English_United States.1252
Default schema	public
Allow connections?	Yes
Connected?	Yes
Connection limit	-1
System database?	No
Comment	

```
-- Database: no2_14112012

-- DROP DATABASE no2_14112012;

CREATE DATABASE no2_14112012
  WITH OWNER = postgres
       ENCODING = 'UTF8'
       TABLESPACE = pg_default
       LC_COLLATE = 'English_United States.1252'
       LC_CTYPE = 'English_United States.1252'
       CONNECTION LIMIT = -1;
```

Figure 3.1: SQL Database Window

Quantum Geographic Information System (QGIS): The NO_2 measurements were converted to shape-files to be mapped using QGIS. The plotted values were then used for source identification along the routes. Wind direction data was extracted from NASA global meteorological model (http://ready.arl.noaa.gov/READYamet.php) and incorporated in via ArcGIS.

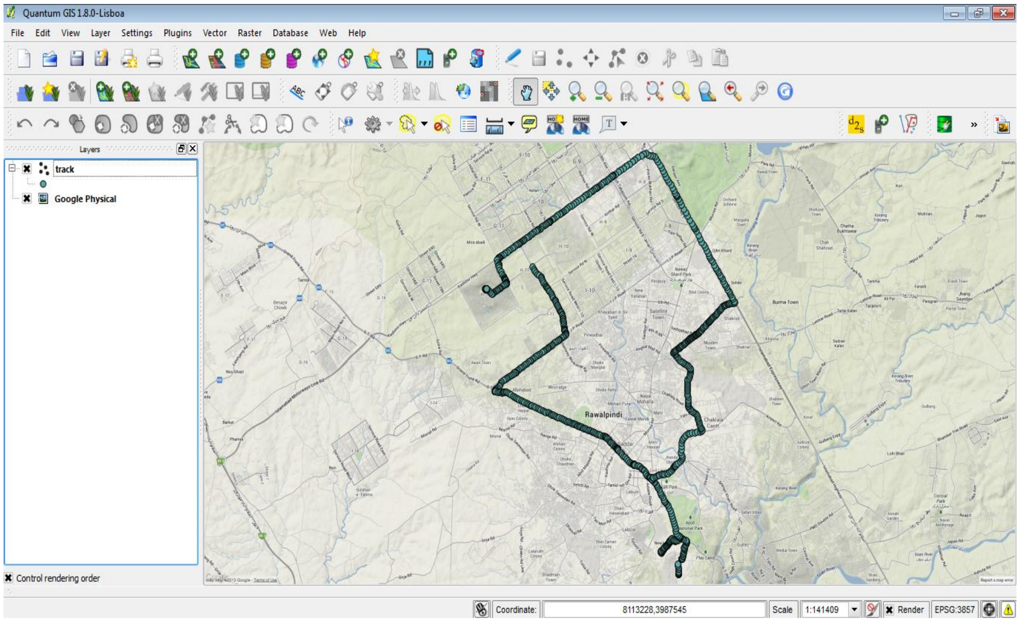


Figure 3.2: Quantum Geographic Information System (QGIS) Window

3.4.6. Satellite Validation of Max-DOAS Observations

Ozone Monitoring Instrument (OMI) observations were used for validation of Car Max-DOAS observations using ArcGIS. NO_2 car Max-DOAS have been successfully for satellite data comparison over various parts of the world (e.g. Shaiganfar et al. 2011; Halla et al. 2011; Boersma et al. 2007). In this study, OMI NO_2 tropospheric VCD level-2 product (OMNO2d.003) from NASA Goddard Earth Sciences Data and Information Services Center website (http://disc.sci.gsfc.nasa.gov/Aura) were used.

The data was downloaded as Comma Separated Value (.CSV) Format. This csv format was later converted to point data using ArcGIS. The satellite image was further used for comparison with car Max-DOAS measurements.

Chapter 4

RESULTS AND DISCUSSIONS

4.1. Nitrogen Dioxide VCD along Islamabad-Rawalpindi Route:

4.1.1. Field Campaign on 13 November, 2012

Tropospheric NO_2 columns (molecules/cm^2) measured along the car MAX-DOAS field campaign on 13 November, 2012 are presented in Figure 4.1. As mentioned earlier this field campaign was started from main campus NUST and was mainly conducted along the N5-Highway of Pakistan. Results exhibited peaks in NO2 columns along various segments of the N5-highway.

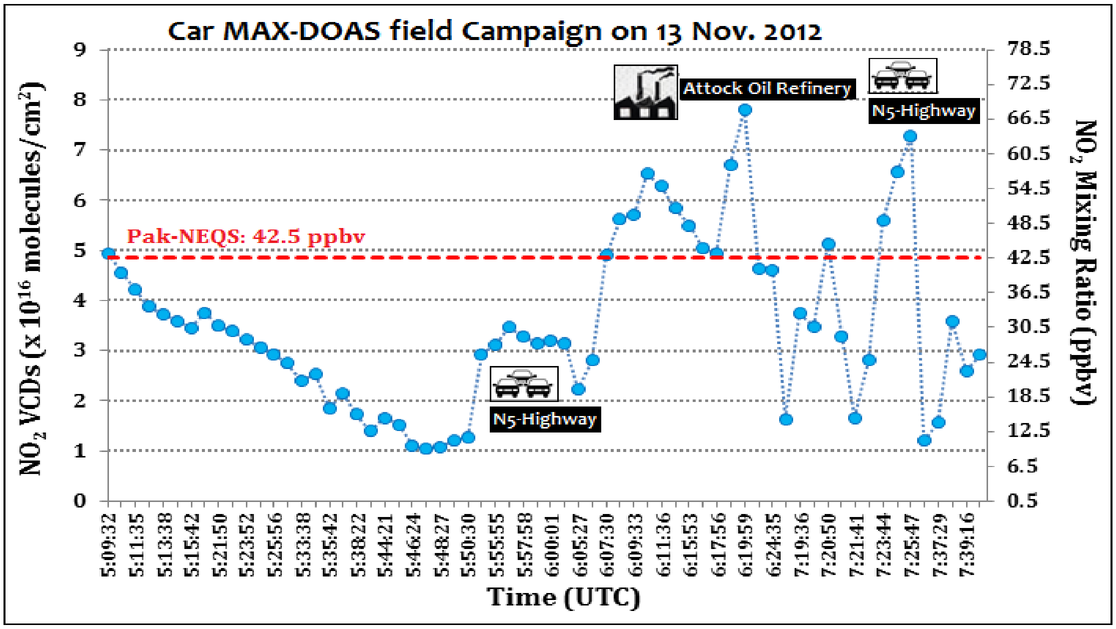


Figure 4.1: Nitrogen Dioxide VCDs (molecules/cm2) and Mixing Ratios (ppbv) within cities of Islamabad and Rawalpindi along the car MAX-DOAS route on 13 November, 2012.

Especially, the road segments in the city center and close to the Attock Oil Refinery Limited (AORL). The NO_2 VCDs were converted into surface mixing ratios by using method described in previous section and Eq. (3.8) and Eq. (3.9). The derived NO_2 mixing ratios were compared against the Pak-NEQS of 42.5 ppbv for NO_2 (Red dashed line). It clearly mentioned NO_2 pollution levels are exceeding the Pak-NEQS along the road segments in the vicinity of AORL and traffic congestion.

4.1.2. Field Campaign on 16 November, 2012

Second car MAX-DOAS field campaign conducted on 16 November, 2012 within twin cities of Islamabad and Rawalpindi. It started from main campus NUST preceded along the busy roads, city centers, airports and important industrial sectors of the both cities. The measured tropospheric NO_2 columns are presented in Figure 4.2. Results exhibited peaks in NO_2 columns along various segments of IJP and the N5-highway, close to landfill site, international airport and in the vicinity of AORL. Especially, the road segments in the city center and close to the Attock Oil Refinery Limited (AORL). The derived NO_2 mixing ratios were compared against the Pak-NEQS of 42.5 ppbv for NO_2 (Red dashed line). It clearly mentioned NO_2 pollution levels are exceeding the Pak-NEQS along the IJP road, landfill (open solid waste burning) site, N5-Highway and in the vicinity of AORL.

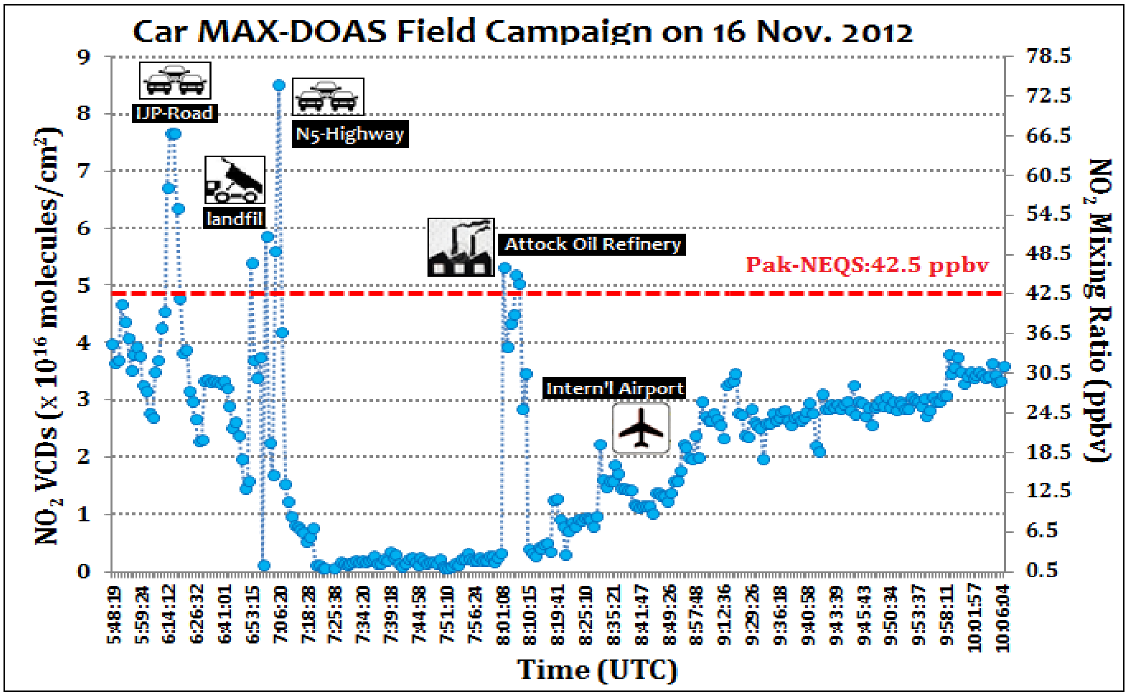


Figure 4.2: Nitrogen Dioxide VCDs (molecules/cm^2) and Mixing Ratios (ppbv) within cities of Islamabad and Rawalpindi along the car MAX-DOAS route on 16 November, 2012.

4.1.3. Spatial Analysis

Figure 5 represents the NO$_2$ VCD extracted from Car- MAX-DOAS measurements performed on 13 and 16 November, 2012. The high NO$_2$ VCDs are overplayed on Google map of Islamabad and Rawalpindi cities. The gaps within the car MAX-DOAS observations are due to interruptions caused by the bumpy roads and filtered out VCDs based on RMS values (data quality flag). On both occasions the highest NO$_2$ VCD was found within Rawalpindi. It was 80.1 × 10^{15} molecules/cm^2 (average value was 36.5 × 10^{15} molecules/cm^2) on 13 November, 2012 and 87.2 × 10^{15} molecules/cm^2 (average value was 22.4 ×10^{15} molecules/cm^2) on 16 November, 2012.

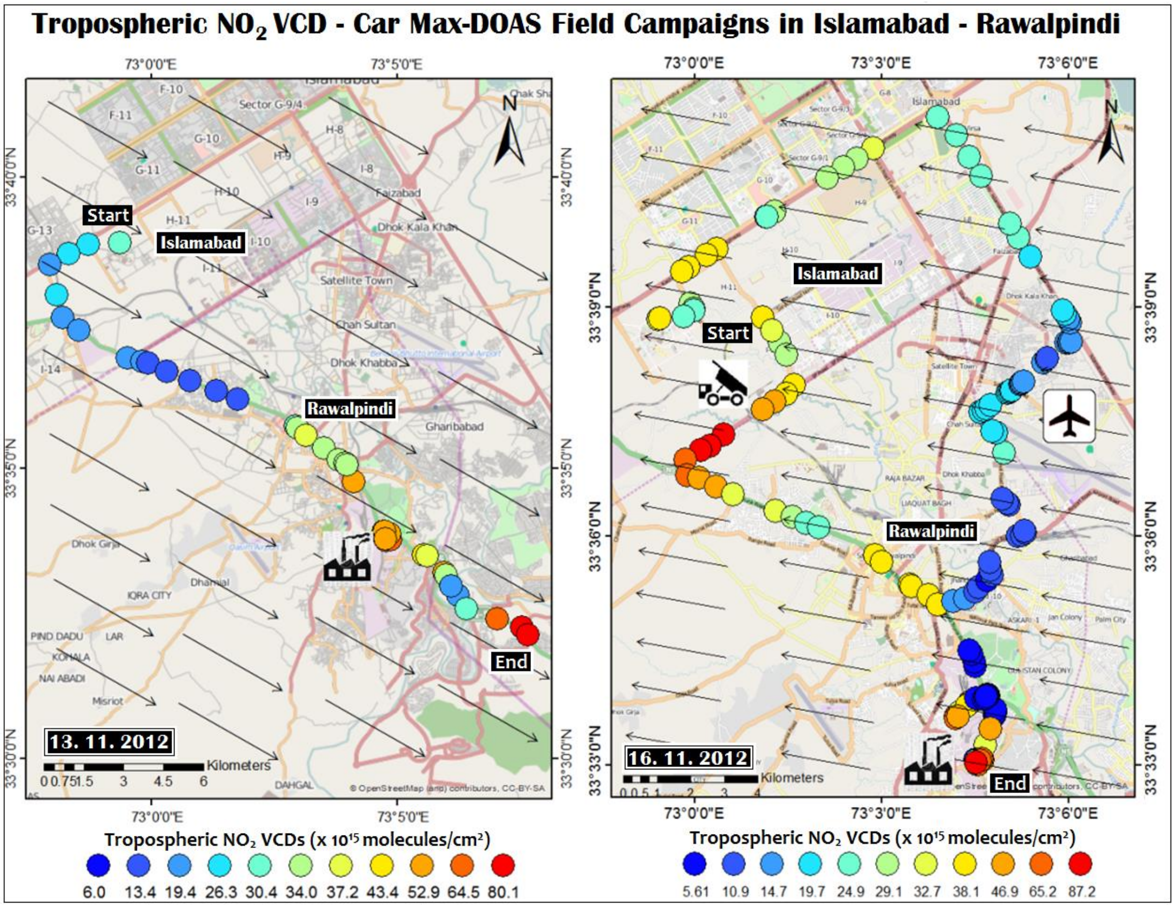


Figure 4.3: Tropospheric NO$_2$ VCDs measured on 13 and 16 November, 2012 within twin cities of Islamabad and Rawalpindi.

Especially, the larger peaks are observed along the road segments with heavy traffic, frequent traffic jam, Attock Oil Refinery and open solid waste dump sites. On average about 32309 vehicles enters the twin cities on daily basis (NHA, 2010) in addition to local vehicles making vehicular emissions as the major source of various air pollutants (Khawaja and Khan, 2005; Ilyas, 2007). Peaks in NO$_2$ concentrations observed along IJP road can be attributed to frequent traffic jam caused by ongoing construction of Pir Wadhai overpass and open solid waste dumping (landfill) site along the road. Oil refineries are also subjected to the pollution of many gases including NO_2 (CCME 2005). High NO_2 concentrations on both occasions in the vicinity of AORL are evident of the pollution cause by refinery itself. A Spatial gradient of NO_2 distribution over the field campaign domains can be clear identified from Figure 5. On 13 November 2016, south eastern while on 16 November, 2012 north western regions are exhibiting higher NO_2 levels. It was investigated by plotting wind data taken from NASA global meteorological model (http://ready.arl.noaa.gov/READYamet.php) for respective time and days as mentioned by black arrows in Figure 4.3. Spatial distribution of NO_2 VCD indicated very interesting behavior and role of meteorological parameters especially wind direction on both days. Besides stationary sources (landfill site, AORL), the wind direction and speed has caused the polluted air masses being transported to south eastern and north western regions of the study area on respective days. Surprisingly, on 16 November 2016, NO_2 measured close to international airport was not large as compared to other areas of the twin cities. Probably, it can be explained by the fact that most of international flights execute their flight operations during the night and as car-MAX-DOAS field campaign was conducted during noon time and was not able to measure high NO_2 levels caused by airport operations. As NO_2 owing shorter lifetime, night time NO_2 might have been converted to other species (NO, HNO_3) until the noon, and the measured quantities are only from the vehicular traffic and due to local flights coincident to car MAX-DOAS observation time. Therefore, in order to constrain NO_2 emissions from all sources and in all circumstances, continuous observations of air pollutants (NO_2 etc.) are mandatory and direly need in a region like Pakistan with no proper and regular air quality monitoring setup (ESoP, 2013).

4.1.4. Comparison with Satellite Observations

The observation of boundary layer pollution from satellite instrument is a great challenge. The main reason could be the increasing air density and aerosol concentration towards the surface, a significant amount of atmospheric scattering usually occurs within or above the trace gas layer.

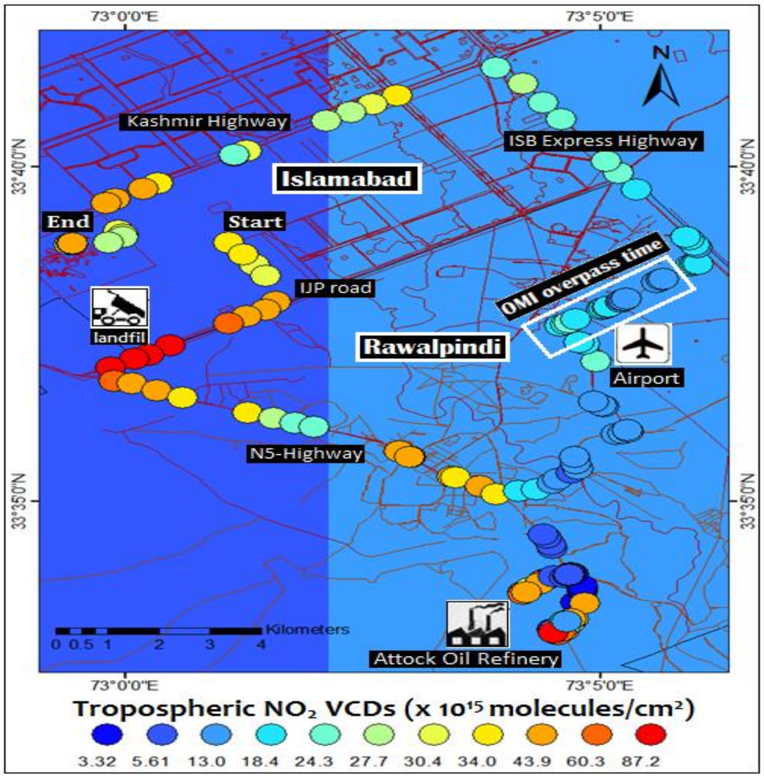


Figure 4.4: Tropospheric NO_2 VCD measured by OMI over Islamabad and Rawalpindi compared with Car MAX-DOAS measurements (coloured dots) on 16 November, 2012.

Thus the sensitivity of the satellite observation decreases towards the surface. Another reason could be that many satellite observations are influenced by the presence of clouds (shielding effect) which further decreases the satellite's sensitivity for trace gases close to the surface. Both effects can be corrected, but this correction requires precise information on the vertical distributions of the trace gases, aerosols and clouds, which is usually not available for same ground scene. Therefore, validation of satellite observations with in-situ and ground-based observations is highly needed. In this section, tropospheric NO_2 VCDs derived from car MAX-DOAS measurements are compared with ozone monitoring instrument (OMI) observations for respective days over the twin cities of Islamabad and Rawalpindi. Level-2 OMI data was downloaded from the NASA GES DISC website (http://disc.sci.gsfc.nasa.gov/Aura) for comparison with car MAX-DOAS observations. Satellite ground pixels usually extend over dimensions of 10 km to 100 km, the direct comparison between MAX-DOAS observations and satellite observations is further complicated by the horizontal gradients of the trace gas concentrations within the satellite ground pixel (Shaiganfar et al. 2011 and references there in). Thus, car MAX-DOAS is a valuable technique to measure the horizontal variability within a satellite ground pixel. Car MAX-DOAS have been successfully used for satellite comparison over various parts of the world (e.g. Shaiganfar et al. 2011; Halla et al. 2011; Boersma et al. 2007). In this study, only nadir pixel of size 10×24 km^2 and cloud fraction less 30 % was used. For detailed description of OMI products please refer to *Levelt et al.,* (2006) and *Boersma et al., (*2007). Figure 4.4 presents the comparison of OMI tropospheric NO_2 VCD with car MAX-DOAS measurements (coloured dots) on 16 November, 2012 over study area. The satellite validation becomes important for such major cities due to largest variability and strongest gradients (Chen et al. 2009) both on spatial and temporal scales. Two OMI pixels were used and referred them as western and eastern pixel. Satellite observations of tropospheric NO_2 was largely underestimated over twin cities. The maximum OMI VCDs for NO_2 over Islamabad and Rawalpindi was found to be 8.67×10^{15} molecules/cm^2 whereas car MAX-DOAS observed higher NO_2 VCDs in the range of 8.72×10^{16} molecules/cm^2. Especially, the comparison with western pixel is relatively poor than the eastern OMI Pixel. However, OMI observations compare well with car MAX-DOAS measurements of NO_2 columns (white rectangle in the F ig.6) close to the airport area which coincide with the OMI overpass time of 13:15 local time over Islamabad-Rawalpindi. So the observed difference could be due to that fact that satellite observed NO_2 columns are averaged over OMI pixel size (13×24 km^2) while car MAX-DOAS observations are just point measurement. Furthermore, differences are observed due to different observation time and due to reduced sensitivity of satellite observation towards the boundary layer pollution because of poor treatment of aerosols and clouds in the retrieval method. The most important thing to note is that tropospheric NO_2 VCDs is largely underestimated by satellite close to larger source like AORL and landfill site areas.

4.2. Nitrogen Dioxide VCD along NUST:

4.2.1. Field Campaign on 12th November, 2012

The first field campaign within NUST H-12 Campus was conducted on 12th November, 2012. The campaign was conducted around noon time. The measured tropospheric NO_2 columns are presented in Figure 4.5. The high NO_2 VCDs shown in figure 4.5 comes from the high traffic density on Kashmir Highway as the lens is viewing in backward direction (towards the road). The derived NO_2 mixing ratios were compared against the Pak-NEQS of 42.5 ppbv for NO_2 (Red dashed line). The values were within the Pak-NEQS.

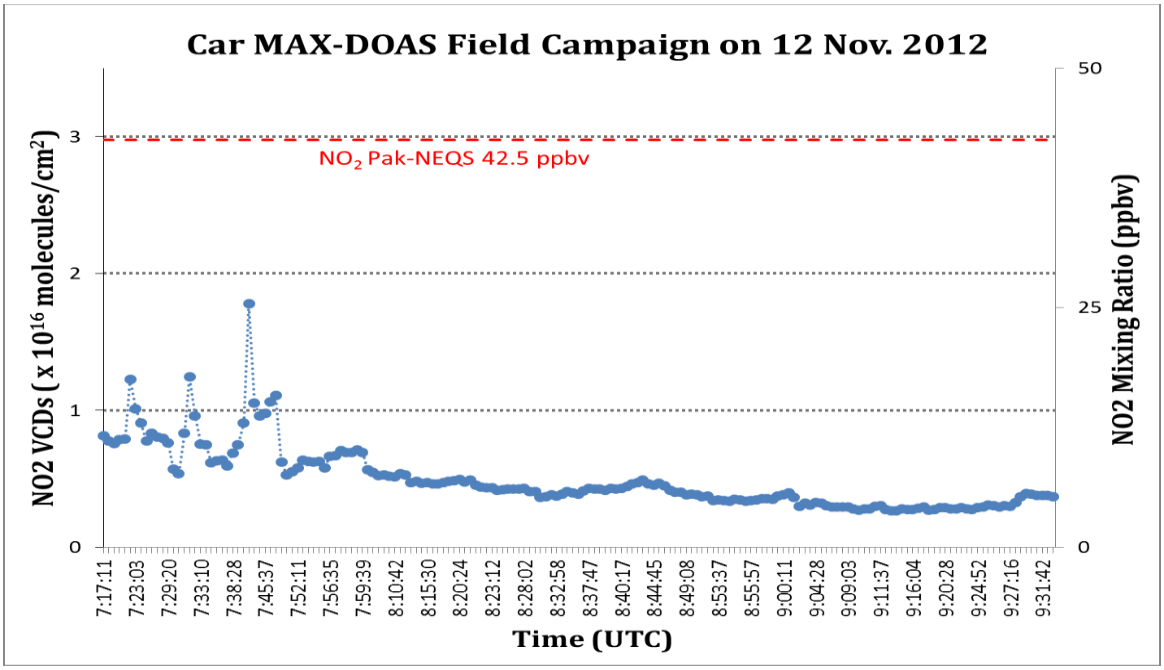


Figure 4.5: Nitrogen Dioxide VCDs (molecules/cm^2) and Mixing Ratios (ppbv) within NUST H-12 along the car MAX-DOAS route on 12 November, 2012.

4.2.2. Field Campaign on 25th February, 2013

Second field campaign within NUST H-12 Campus was conducted on 25th February, 2012. The campaign was conducted around 4 pm. The measured tropospheric NO_2 columns are presented in Figure 4.6. The maximum values of NO_2 VCDs are found in the area of frequent traffic passage way and when the lens was pointing backwards towards the IJP Road. IJP Road is a highly traffic prone road and wind direction towards the campus bring most of the NO_2 pollution towards the campus. The derived NO_2 mixing ratios were compared against the Pak-NEQS for NO_2 (Red dashed line).

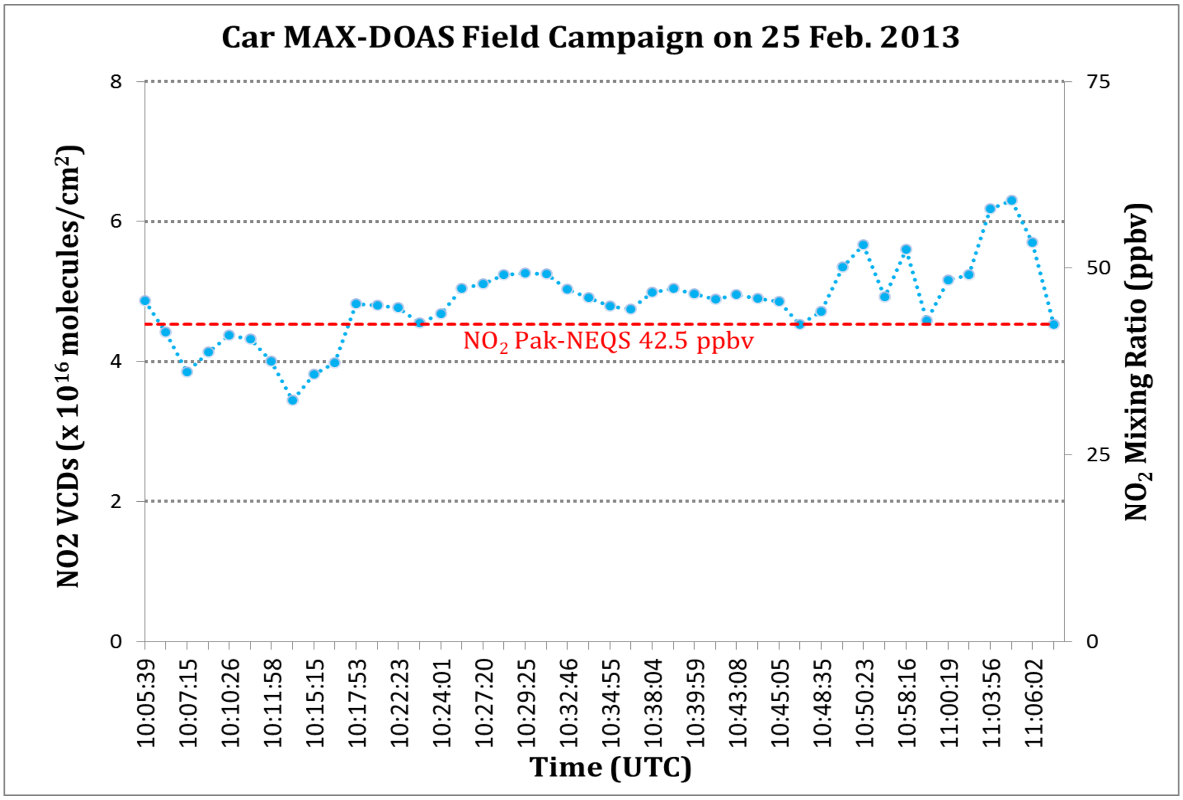


Figure 4.6: Nitrogen Dioxide VCDs (molecules/cm^2) and Mixing Ratios (ppbv) within NUST H-12 along the car MAX-DOAS route on 25 February, 2013.

4.2.3. Spatial Analysis

Figure 4.7 represents the NO_2 VCD extracted from Car- MAX-DOAS measurements performed on 12 November, 2012 and 25 February, 2013. The highest NO_2 VCD was found to be 29.9 x 10^{15} molecules/cm^2 and 69.4 x 10^{15} molecules/cm^2 and the average value was 8.29 x 10^{15} molecules/cm^2 and 53.4 x 10^{15} molecules/cm^2 for 12th November, 2012 and 25th February, 2013 respectively. The figure clearly shows that NUST is relatively clean area but high traffic densities on roads in surrounding i.e. IJP Road on west and Golra Moore and Kashmir Highway in the east causes the most of the high concentrations in the area.

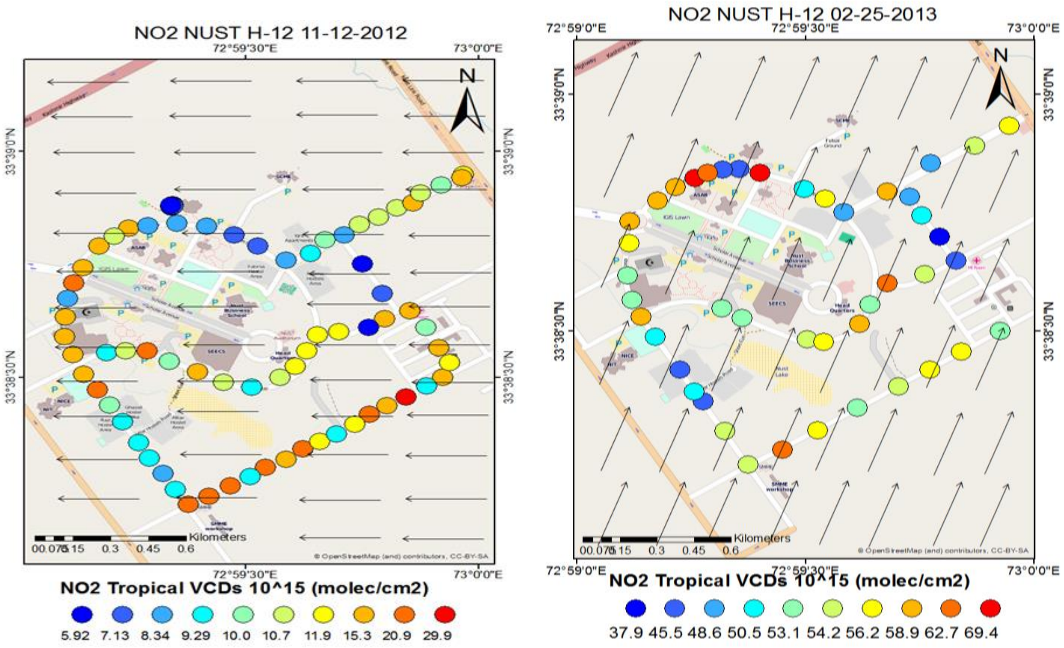


Figure 4.7: Tropospheric NO_2 VCDs measured on 12 November, 2012 and 25 February, 2013 within NUST H-12 Campus

Also the timing of the field campaigns mattered in the variation of results. On 12th November, 2012 the campaign was conducted in the late hours of morning so concentrations are very low. But on 25th February, 2013 the campaign was conducted around 4 pm which is rush hour time so the NO_2 concentrations are higher on that day.

4.2.4. Comparison with Ground-Based Observations

The results were furthermore compared with the work done at IESE. Ground based MAX-DOAS observations were made from the rooftop of IESE in which observations were made for the month of February and March 2013 from morning to evening. The work suggested that when the wind direction is from south south west and west south west then the pollution is high in NUST area (figure 4.8).

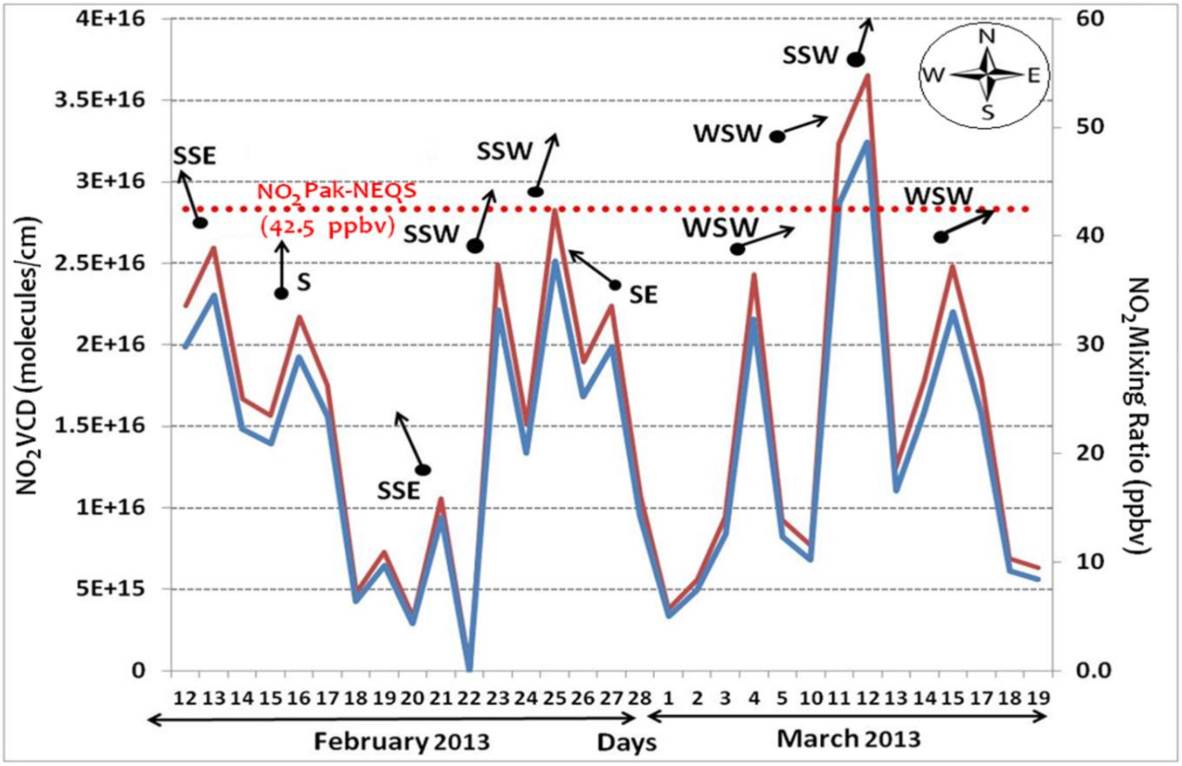


Figure 4.8: Ground based MAX-DOAS observations made at IESE, NUST

4.3. Ambient Air Quality in Twin Cities:

Nitrogen Dioxide being one of criteria pollutant has been monitored within major cities of Pakistan. In Pakistan more than 70 % of of NO_2 pollution is being contributed by transportation, power plants and industries (Khwaja and Khan, 2005; Ilyas, 2007; Ghuari et al., 2007). According to a recent study (Fatima, 2013) by using multi-sensor satellite observations during the time period of 2002-2012, indicated that NO_2 levels are highest near the urban centers of Pakistan. It identified temporal increase of 17 % per year in NO_2 columns over the cities of Islamabad and Rawalpindi. Other studies carried out in Pakistan on NO_2 pollution(e.g. Ali et al. 2008; Zafar et al. 2012; Ahmed and Aziz, 2013; Fatima, 2013; Jahangir et al. 2013; Shabbir, 2013; Nisar, 2013) are listed in Table1 and identified increasing number vehicle and consequent traffic as major source of NO_2 emissions in the twin cities.

Table 4.1: Recent studies carried out on Nitrogen Dioxide Pollution in Pakistan

Study	Location	Monitoring Month	Method	Concentration (ppb)		
				NO	NO_2	NOx
JICA, 2000	Lahore	April, 2000	Diffusion Samplers	88.4	68.2	156.6
	Islamabad	May, 2000		95.0	53.7	148.7
	Rawalpindi			69.0	5.7	74.7
Jahangir et al. 2013	Rawalpindi	March-June,2010	Diffusive Passive Sampling	-	23.9	-
	Islamabad			-	23.3	-
Zafar et al. 2012	Rawalpindi	January-February, 2011	Diffusive Passive Sampling	-	5.5	-
	Islamabad			-	8.1	-
	Rawalpindi	March-April, 2011		-	6.9	-
	Islamabad			-	10.3	-
Shabbir et al. 2013	N-5 Highway	November, 2012	Car Max-DOAS	17.90 (average)		
				62.88 (maximum)		
Nisar. 2013	Islamabad	February, 2013	Mini Max-DOAS	23.97		

In order assess the ambient air quality situation in Pakistan, JICA and Pakistan Environmental Protection Agency (Pak-EPA) conducted air sampling in three cities

(Lahore, Rawalpindi, Islamabad) of Pakistan in 2000. All the criteria pollutants were monitored during the study (i.e. Carbon Monoxide, Sulphur Dioxide, Nitrogen Oxides, Ozone, Particulate Matter and Hydrocarbons). The NO_x levels were found very high in the cities mainly due to traffic congestion. The most polluted city in terms of air quality was found to be Lahore (JICA, 2000).

Jahangir et al. 2013 study was focused at monitoring NO_2 pollution near public and private sector hospitals in the twin cities of Rawalpindi and Islamabad. The findings of the study were the NO2 concentration was more near hospitals situated on the main roads due to traffic congestion. The same trend is observed during car Max-DOAS field campaign the NO_2 levels are higher in urban centers having high traffic congestion.

Zafar et al. 2012 studied NO_2 pollution at various locations of the Islamabad and Rawalpindi city. The study was carried out in two phases as one monitoring was done in winter season and the other was done in spring season. The study correlated the NO_2 pollution with traffic congestion and industrial activities of the twin cities. As the concentration of NO_2 was found to be higher in spring season, it was inferred that the NO_2 levels are function to the rise in temperature. But with few exceptions, according to the study there were no correlations found between temperature and NO_2 levels.

According to ongoing research on ambient air quality at National University of Sciences and Technology (NUST) many initiatives have been taken to monitor air quality using

Mini Max-DOAS instrument. NO_2 VCDs have been monitored along the N-5 Highway with mobile monitoring (Shabbir et al. 2013). Also point source monitoring for NO_2, and Ozone (O_3) have been done with Max-DOAS been mounted on building of Institute of Environmental Sciences and Engineering (IESE), NUST (Nisar et al. 2013).

Compared with existing Pak-NEQS levels of 42.5 ppbv for NO_2, car MAX-DOAS measurements have identified the N5-Highway, IJP road, landfill site and areas in the vicinity of AORL were exceeding.

Table 4.2: Comparison of NO_2 concentrations along routes with Pak-NEQS

Sr. No.	Places	Average NO_2VCDs	Average NO_2 Mixing Ratio (ppbv)	Maximum NO_2VCDs	Maximum NO_2 Mixing Ratio (ppbv)
1.	NUST 12th November 2012	8.29 x10^{+15}	7.06	2.99 x10^{+16}	25.44
2.	NUST 25th February 2013	5.34 x10^{+16}	45.43	6.94 x10^{+16}	59.09
3.	Islamabad-Rawalpindi 13th November 2012	3.65 x10^{+16}	31.14	8.01 x10^{+16}	68.20
4.	Islamabad-Rawalpindi 16th November 2012	2.24 x10^{+16}	19.04	8.7209 x10^{+16}	74.25

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1.Conclusions

The Car MAX-DOAS observations along Islamabad and Rawalpindi were conducted in order to identify the nitrogen dioxide pollution levels within the study area. The observed elevated pollution levels in the urban areas of Pakistan are mainly due to traffic and population increase. In this work, NO_2 VCDs and their major sources have been discussed.

1. The cities of Rawalpindi and Islamabad had an international airport, a landfill site, and oil refinery along the route of field campaigns. Also the maximum NO_2 VCD of 87.2×10^{15} molecules/cm^2 (74.2 ppbv) and 80.1×10^{15} molecules/cm^2 (68.2 ppbv) were measured on 16th and 13th November, 2012 respectively. NO_2 concentrations calculated for car Max-DOAS indicated that the NEQS limits (42.5 ppbv) were violated at various locations due to traffic congestions and jams, around landfill sites, and industrial areas.
2. The NUST field Campaign shows that in November 2012 the pollution levels were lowered than the Pak-NEQs limits. But on 25th February 2013, maximum VCD of 70×10^{15} molecules/cm^2 (59.1 ppbv) were observed which is mainly due to the Kashmir Highway. NUST is relatively clean area but heavy traffic on surrounding roads causes pollution in this area.

3. Satellite validation was also done using tropospheric OMI NO_2 VCDs and car Max-DOAS observations. Generally, similar NO_2 spatial trends are found in both data sets, although satellite observations are found to be underestimated. The reason for this quantitative disagreement is mainly due to less sensitivity of satellite towards ground level pollutants. Also satellite observations are present over large area i.e. (13 x 24 km^2) in this case.

5.2.Recommendations

Following recommendations are suggested for further research in the field of ambient air quality monitoring in the country.

1. In order to improve and have better estimates of boundary level air pollution with the help of satellite remote sensing, such field campaign need to be done on regular basis worldwide and under different atmospheric conditions
2. This study is unique in a sense it was first time conducted in Pakistan and satellite observations of NO_2 column density within twin cities of Pakistan by suing car MAX-DOAS and are compared with satellite observations. This will help to provide basic information about NO2 pollution levels in Islamabad-Rawalpindi to various stakeholders concerned with environmental pollution issues in Pakistan.
3. The outcomes of this study will help to identify, a relationship between air pollutants and their sources. Pollution Control Techniques (PCTs) could be proposed especially areas with potential threats of air pollution.
4. The NO_2 pollution levels can be reduced by energy saving strategy, alternative fuels, improved combustion technology, use of catalytic converter technology in vehicles

are a few examples.

5. On State level, Mass transit system should be introduced in larger urban areas in order to control traffic pollution.
6. Besides, an effective media campaign to teach the public will improve the understanding and raise the concern for air quality. Educating school children, citizen groups etc. to study and monitor the situation shall be encouraged.
7. By conducting field campaign on monthly basis, the analysis of pollution trends over the whole year will help us to understand the seasonal cycles of trace gas concentrations. The data can be used as a baseline by other research organizations, environmental agencies and non-government organizations (NGOs) working on other aspects of air pollution impacts i.e. health impacts, climate change, mitigation and adaptation studies etc. It may provide guideline for regulatory authorities, policy makers and decision maker to review effective implementation of existing standards.

Chapter 6

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