CONTINUATION OF SATELLITE OBSERVATIONS OF NITROGEN DIOXIDE OVER PAKISTAN USING OZONE MONITORING INSTRUMENT DURING THE TIME PERIOD OF OCTOBER 2004 TO DECEMBER 2014

By

Rabbia Murtaza

NUST201362288MSCEE65213F

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

Master of Science

In

Environmental Sciences

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

(2015)

CONTINUATION OF SATELLITE OBSERVATIONS OF NITROGEN DIOXIDE OVER PAKISTAN USING OZONE MONITORING INSTRUMENT DURING THE TIME PERIOD OF OCTOBER 2004 TO DECEMBER 2014

By

Rabbia Murtaza

NUST201362288MSCEE65213F

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

Master of Science

In

Environmental Sciences

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

CONTINUATION OF SATELLITE OBSERVATIONS OF NITROGEN DIOXIDE OVER PAKISTAN USING OZONE MONITORING INSTRUMENT DURING THE TIME PERIOD OF OCTOBER 2004 TO DECEMBER 2014

Submitted by

Rabbia Murtaza

Has been found satisfactory for the requirements of the degree of

Master of Science in Environmental Sciences

Supervisor: ________________

Dr. Muhammad Fahim Khokhar

Assistant Professor

IESE, SCEE, NUST

Member:_____________

Dr. Muhammad Arshad

Associate Professor

IESE, SCEE, NUST

Member:____________

Dr. Salman Atif

Assistant Professor

IGIS, SCEE, NUST

I dedicate this thesis to my family

for their endless support and

encouragement

ACKNOWLEDGEMENTS

First of all, I am very thankful to Allah Almighty Whose benevolence has enabled me to complete my thesis in the best way and He gave me the understanding and patience to complete this work on time.

I would greatly acknowledge the enthusiastic supervision of my supervisor Dr.Muhammad Fahim Khokhar during my research work. Throughout my thesis, he provided encouragement, sound advice, good teaching and lots of good ideas. I would also like to thank my respective GEC members Dr. Muhammad Arshad and Dr. Salman Atif for their guidance and support.

I am very grateful to the superb staff of Institute of Geographic Information Systems (IGIS) for their outstanding efforts. This thesis would not have been possible without them because they provided me with all the knowledge of this work and the required software's. My sincere thanks goes to Population Bureau of Statistics for provision of data.

On a special note, I would like to thank Tropospheric Emission Monitoring Internet Service (TEMIS) for providing me with the updated satellite data.

In the end, I thank my entire family for providing a loving environment for me and I am indebted to my friends for providing a stimulating and fun environment to learn and making NUST the best university life for me.

Table of Contents

List of Abbreviations

NO_2	Nitrogen dioxide
OH	Hydroxyl
NTRC	National Transport Research Center
WHO	World Health Organization
GOME 2	Global Ozone Monitoring Experiment-2
RO_2	alkylperoxy radicals
EU	European Union
GOME	Global Ozone Monitoring Experiment
DOAS	Differential Optical Absorption Spectroscopy
IPCC	Intergovernmental Panel on Climate Change
VCDs	Vertical Column Densities
SCD	Slant Column Density
TEMIS	Tropospheric Emission Monitoring Internet Service
PBS	Pakistan Bureau of Statistics
AMF	Air Mass Factor
ACF	Auto Correlation Function
KPK	Khyber Pakhtun Khwa
SDPI	Sustainable development policy institute

List of Figures

List of Tables

Abstract

Spatial and temporal distributions of tropospheric NO_2 vertical column densities over Pakistan during the time period of 2002 – 2014 are discussed. Data products from three satellite instruments SCIAMACHY, OMI and GOME-2 are used. Further force was made on inter-satellite comparison for NO_2 observations over Pakistan. Minor differences are observed among the satellite instruments mainly attributed to difference in spatial resolution and overpass time. This study first time provides a database of tropospheric NO_2 column densities over Pakistan and useful for various stakeholders concerned with air quality and regulations. Temporal evolution of tropospheric NO_2 column densities over Pakistan is determined. Identification of different type of plausible NO_2 sources is also discussed. The results show a large NO_2 growth over the major cities of Pakistan, particularly the areas with rapid urbanization. The increase can be attributed to the anthropogenic emissions as these are the areas with high population, traffic density and industrial activities. Source identification revealed that use of fossil fuels for power generation, vehicular emissions and agriculture fires are significant source of tropospheric NO_2 in Pakistan.

CHAPTER 1

INTRODUCTION

1.1 Background

Air pollution is a combination of gases and solid particles in the atmosphere. Emissions from vehicles and factories, dust, pollen, soot suspend in the form of particles. Most of the pollutants are poisonous and cause severe health issues to the human lives. In today's era, air pollution is becoming rising issue around the globe. The ambient air quality is now at risk. Urban and indoor air pollution are registered as world's toxic pollution problems in Blacksmith Institute world's worst polluted places report which was published in 2008.

Rapid industrialization and urbanization are appreciably contributing to Pakistan's economy but also responsible for releasing large amounts of different gaseous pollutants. Heavy metals are causing reproduction problems in human beings. Nitrogen and Sulphur oxides are mainly coming from thermal power plants, industrial activities and biomass burning. The spatio temporal trend of nitrogen dioxide concentration is quite incomplete in Pakistan. So there is now a need to understand the atmospheric chemistry and spatio temporal variation in Pakistan when it comes to planning, policy and implementation on air quality.

1.2 Air Pollution

There is a remarkable economic development around globe since 1980s. The urbanization and industrialization has put thousands to millions of vehicles on roads. Tropospheric NOx has significant effect on air quality and acid deposition (Richter et al., 2005).

Global warming is affecting the atmosphere and people living around us. This effect is induced by the human activities. The world's temperature has risen clearly in the last 30 years (IPCC, 2007) because of enhanced greenhouse gas emanations coming from anthropogenic sources. These greenhouse gas emissions have increased upto 70% during the time period of 1970-2004.

Nitrogen and Sulphur dioxide are considered to be a component of smog. Acid rain is caused by the reaction of nitrogen oxides with water. The NOx and SOx reflect light, keep sunlight out and cool the earth. Developed countries have been working to reduce the levels of nitrogen dioxide, smog, and smoke in order to improve people's health status. But contrary to this, the lower level of NO_2 essentially make global warming worse. This effect is overstated when greenhouse gases trap the additional heat

Urbanized cities with large number of traffic vehicles emit nitrogen oxides into the atmosphere. In Los Angeles, the main source of acid rain is emissions from automobiles, while in Yosemite and Sequoia national parks, vehicular traffic is banned or forbidden to limit the amount of air pollution (Seinfeld et al., 2006).

1.3 Introduction to Nitrogen Oxides

Nitrogen oxides are considered as primary air pollution constituents. Nitrogen oxide directly comes from combustion processes. Nitric oxide (NO) and nitrogen dioxide (NO_2) referred as active nitrogen and combined together as NOx.

NOx plays crucial role in ozone+hydroxyl distribution in atmosphere. Nitrogen oxides take part in formation of ozone while in stratosphere they are precursor for ozone destruction. The hydroxyl radical converts primary discharges into secondary products that can be easily washed away from atmosphere by dry and wet deposition. So the OH radical is called atmospheric detergent (Richter et al., 2005).

1.4 NOx as Air Pollutant

NOx in grouping with hydrocarbons can lead to smog production in summer months. High smog concentrations is a threat to human life on earth. One of the hazardous components of smog is ozone. Health effects caused by smog are nose and throat irritation, coughing, painful breathing and reduced lung function while long term effects could be damage to lungs and immune system

1.5 Environmental Effects

The elimination mechanism of NOx from the atmosphere leads to formation of HNO_3 which causes acid rain. NOx deposition lead to increased nitrogen content in hydrosphere which is the main reason for algal bloom production in water bodies. This phenomenon is called eutrophication (WHO, 2007).

1.6 Objective of this Study

NO_2 tropospheric vertical column densities (VCDs) were extracted over Pakistan. Spatial maps were created in order to identify the major hotspots. NO_2 column values were correlated with its major sources i.e. thermal power plant, traffic count, and vegetation fire in Pakistan.

The objectives of this study were:

- Source identification of nitrogen dioxide from in Pakistan
- To observe the spatio temporal trend of nitrogen dioxide in Pakistan from 2004-2014

CHAPTER 2

LITERATURE REVIEW

2.1 Atmosphere

Atmosphere is made up of the thin layer of gases. Density decreases with altitude. Though the thickness of atmosphere is around 100 km but no set boundary or limit exists between atmosphere and outer space (Seinfeld et al., 2006).

The atmosphere is composed of nitrogen and oxygen and a small amount of argon while rest part contains water vapors, carbon dioxide (CO_2), methane (CH_4), noble gases and other trace constituents (Seinfeld et al., 2006). Tropospheric NO_2 is a key pollutant over all the megacities around globe. High traffic count, energy use and industrial production make them the major hotspot areas (Molina, 2004).

2.2 Tropospheric Nitrogen Dioxide

Troposphere is a Greek word tropo's means mixing. There is high dispersion of pollutants in this layer that is why it has to be considered whenever assessing the air quality. But, there is also dilution effect of pollutants so the harmful effects can be minimized to a local level. On the contrary, this can cause air pollution problems because pollutants travel from high production zones to those where pollution is fairly low (Khokhar, 2006).

NO_2 is a strong oxidant and has been listed as a criteria pollutant (US EPA, 1989). Since the pre-industrial era, there has been a five fold increase in NOx emissions and the most fast increase has been seen in Asia at the rate of 4-6% per year (Garg et al., 2001; Van aardenne et al., 1999).

Nitrogen dioxide (NO_2) has a significant role in radiative equilibrium of the Earth's atmosphere (WHO, 2007). The major sources of NO_2 emissions are soil, biomass burning, natural lightning, vehicle combustion and power plants. (Richter and Burrows, 2000).

The main source of NO_2 is NO coming from all the human being activities (Noxon, 1978). Denman and coworkers in 2007 stated that NOx emissions from burning of biomass and biofuel contribute 5.9 Tg N/year to the atmosphere which is estimated to be 15 % of the global NOx budget.

Solar ultraviolet radiations and hydroxyl radical are the dominant sink of NO_2 to form nitric acid, ozone, methane, and aldehydes called secondary pollutants (Kanaya et al., 2007). Industrialization and high population density are degrading the air quality of South Asia (Gurjar et al., 2008).

2.3 Satellite Retrieval of Nitrogen Dioxide Columns

Ul-Haq et al in 2014 measured spatio-temporal patterns of NO_2 over Pakistan using ozone monitoring instrument (OMI) during the time span of 2004–2008. Renuka et al. 2014 also analyzed temporal variations of tropospheric NO_2 over South India using GOME and OMI during 1996–2014. These authors found decreasing trend between eastern and western Ghats associated with changes in land use thus limiting the soil emissions of NO_2.

The ozone monitoring instrument (OMI) is used to evaluate the tropospheric NO_2 data (Wallace and Kanaroglou., 2009). NO_2 tropospheric columns were retrieved from OMI (Krotkov et al., 2006) satellite using the Differential Optical Absorption Spectroscopy (DOAS) (Richter et al., 2005; Khokhar et al., 2005; Wagner et al., 2004; Beirle et al., 2003; Perner and Platt, 1979). According to Vander A et al., (2008) an outflow of NO_2 by anthropogenic activities has been experienced over the oceans on the Eastern coasts of North America and China.

2.4 Urbanization in Pakistan

Urbanization in Pakistan is now at its peak in South Asia (SDPI, 2010). Road transport is carrying 91% of the passenger traffic and 96% of the cargo movements. From 2000 to 2010, the total number of vehicles on the roads grown from 4 to 9.8 million showing an increase of 145% (The world bank, 2006).

Pakistan's economy is profoundly dependent on the agricultural sector. The total farmed waste burnt is 1704.9 thousand tons per year in the rice-wheat cropping system in Pakistan contributing significant emissions of NO_2 (Tanvir and Bashir, 2013). NO_2 concentrations were higher than the World Health Organization (WHO) in Islamabad and Rawalpindi (Ahmed et al., 2011). The measurements done by satellites have worldwide coverage and their spatial and temporal resolution can meet such needs, especially, a country like Pakistan with no proper/regular air quality monitoring network (ESoP, 2013).

Around 50% is released from industry and traffic and 20% from biomass burning. Among natural sources, approx. 10% emissions are through lightning while 15% from soil due to the activity of microbes (Lee et al., 1997).

2.5 Lifetime of Nitrogen Dioxide

The lifetime of NO_2 ranges from a few hours to 1 day (Crutzen, 1979). It varies from hours to 10 days from continental boundary to upper troposphere. NO_2 lifetime is dependent on photolysis rate and amount of OH. Tropospheric NO_2 lifetime is upto 24 hours in winters and 6 hours in summers (Jaeglé et al., 2004). NOx has a significant role in atmospheric chemistry.

It forms secondary pollutants and acidity in environment. NO_2 has the ability to affect ozone and OH which is an important gas in the atmosphere. (Thompson, 1992; Logan et al., 1981).

2.6 Properties of Nitrogen Dioxide

NO_2 is gas with reddish brown color and has pungent smell, bitter odour (O'Neil, 2006; Genium, 1999; IPCS, 1997). It is brown liquid at temperatures below 21.15ºC and exists as a colorless solid below -11ºC (Lewis, 2002). It has high oxidizing capacity and is corrosive (IPCS, 1997); also noncombustible (Lewis, 2002).

The physical and chemical properties of NO_2 are given in Table 2.1.

Table 2.1: Physical and Chemical Properties of NO_2

S.No.	Property	Value	Reference
1.	Molecular weight	46.01 $g.mol^{-1}$	Lide, 2007; O'Neil, 2006
2.	Physical state	Clear colourless volatile liquid	Lide, 2007; O'Neil, 2006
3.	Melting Point	-9.3°C	Lide, 2007; O'Neil, 2006
4.	Boiling Point	21.15°C	Lide, 2007; O'Neil, 2006
5.	Density (liquid)	1.448 (at 20°C)	O'Neil, 2006
6.	Density (gas) (air=1)	1.58	O'Neil, 2006
7.	Vapour Pressure	58.66 kPa at 10°C 121 kPa at 25°C	RSC, 2007 HSDB, 2005
8.	Solubility in water	Reacts with water, decomposes forming nitric acid and nitric oxide	Lide, 2007; O'Neil, 2006
9.	Solubility	Soluble in concentrated sulphuric acid, nitric acid, carbon disulphide, chloroform	RSC, 2007; Lewis, 2000
10.	Conversion factors for vapour (at 25°C and 101.3 kPa	$1 mg.m^{-3}$ = 0.532 ppm 1ppm = 1.88 $mg.m^{-3}$	HSDB, 2005

2.7 Sources of Nitrogen Dioxide

Two main categories of nitrogen dioxide emissions are anthropogenic and natural sources. Global emissions for NOx in 1990 were presented by Olivier (1990).

Table 2.2 Global NOx Emissions

Table 1.1. Global sources of atmospheric NO_x in 1990 and their uncertainty ranges in TG [N] year^{-1}, adopted from Olivier et al. [1998]. *The lighting source is adopted from Boersma et al. [2005]. ** Uncertainty range is included in the surface fossil fuel combustions.

Source	Emission	Uncertainty range
Total anthropogenic sources	**31.1**	**16-46**
- Fossil fuel combustion (surface)	21.3	13-31
- Biomass burning	7.7	3-15
- Aircraft**	0.6	-
- Industrial processes**	1.5	-
Total natural sources	**11.1**	**6-35**
- Soil microbial production	5.5	4-12
- Lightning*	4.0	2-20
- Atmospheric NH_3 oxidation to NO_x	0.9	0-1.6
- Stratospheric destruction of N_2O	0.7	0.4-1
Total antr. + Natural	**42.2**	**22-81**

75% of the total global emissions are from anthropogenic sources. Most of the man made NOx emission occurs in combustion processes. On Northern Hemisphere, the fossil fuel combustion supplies the majority of the NOx emissions. 70% of the global anthropogenic NOx emissions are from fossil fuel combustion (Olivier et al., 1998).

2.7.1 Natural Sources

Soil emissions (oxidation of nitrogenous compounds present in the soil by different microorganisms), forest fires and lightning discharges (HSDB, 2005; Lee et al., 1997). Lightning and soil emissions account 10% and 15% of the total NO_2 emissions respectively (Lee et al., 1997).

2.7.2 Anthropogenic Sources

Combustion of fuels (coal, oil and natural gas) in vehicles or industrial processes (HSDB, 2007). Vehicles and industries are predicted to produce about 50% of NO_2, while biomass burning contributes about 20% (Lee et al., 1997). These sources mostly emit NOx in the form of NO with less than 10% NO_2 (IPCS, 1997).

2.8 Sinks of Nitrogen Dioxide

Wet and dry deposition and eliminate NOx from the atmosphere. The removal reaction of NOx is the production of HNO_3,

$NO_2 + OH \rightarrow HNO_3$ (1.1)

And then wet deposition of HNO_3. Nitric acid causes acidification. The removal process happens during day, mostly in summers, because hydroxyl; radical is produced by light and the lifetime is very short.

Anther removal phase is the production of N_2O_5.

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_2 + NO_3 \rightarrow N_2O_5$

$N_2O_5 + H_2O/\text{aerosol} \rightarrow 2HNO_3$

(Night + wintertime)

2.9 Health and Environmental Aspects

Different studies have found that a very small impact is present on the respiratory system of humans particularly on children but that result vanishes as the children grow (WHO, 1987).

NOx is precursor for the production of ozone and acid rain, plant injuries can occur. Nitric acid contributes Hydrogen (H+) ion levels in both dry and wet acid deposition, so NOx can contribute more significantly to acid deposition. NOx absorbs sunlight, starting the series of photochemical reactions that lead to the production of HNO_3. 90-95% (approx.) of NOx emitted through power plants is NO, which gradually forms NO_2 in the presence of O_3. (Schwartz and Zegler, 1990). The degree of harm caused by acid deposition is tough to guess, because the effects can vary depending upon the type of soil, the different plant species, conditions of atmosphere, insect population and different other factors. Stream ecosystems and freshwater lakes are being most evidently damaged through acid deposition. The pH of water can decrease due to acid deposition with possibly severe consequences for fishes, animals and different plants in water. The areas where there is fewer amounts of calcium and magnesium carbonate in soil, which can cause neutralization of acid rain, are the areas mostly at risk (Canada, 1987). The abrupt swifts in pH can help only a few fish species to survive; some affected lakes can even become completely devoid from fish life. NOx deposition in atmosphere is a considerable cause of those nutrients which can harm estuaries by causing anoxic conditions and algal blooms.

2.10 Ambient Standards and Guidelines

Standards for ambient NO_2 levels given by EU, WHO and USEPA are mentioned in

the following Table 2.3.

Table 2.3: Reference standards and guidelines for NO_2 ambient levels (micrograms per cubic meter)

S. No.	Standard or guideline	Annual average	24-hour average	1-hour average
1.	EU limit values (1985)	200_a	-	-
2.	US EPA standards (1990)	100_b	-	-
3.	WHO guidelines (1977)	-	-	$190\text{-}320_c$
4.	WHO guidelines for Europe (1987)	-	150	-
5.	NEQs (Pakistan) (Effective from 1st January, 2012)	40_d	80_d (42.5 ppbv)	-

a. 98th percentile calculated from the mean value per hour or per period of less than an hour taken throughout the year. **b**. Arithmetic mean **c**. Not to be expected more than once a month. Only a short term exposure limit has been suggested. **d**. 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) 1ppbv = 1.88 µg/m^3

Sources: European Community (1985); United States (1992), 40 CFR, part 60, WHO 1977, 1987

2.11 Ambient Air Quality of Pakistan

In Pakistan, air quality is a growing environmental issue. incompetent energy use, high population density and industrial activities without proper pollution control technologies are major reasons of deterioration of ambient air quality.

Pakistan is now trying to shift its base of economy from agriculture to industrial development. Air pollutants damage the environment. The industries of steel and cement are burning huge amounts of solid waste into the environment and the heavy overcrowded traffic is accountable for emission of gaseous pollutants, particulate matter and noise. Air pollution has resulted in increased cost of health, great losses to different properties and crops. Pakistan Economic Survey 2004 has declared the emissions from industries and vehicles as the main causes of air pollution.

Vehicle growth is about 12% annually and during the past two decades, the total number of automobiles increased from 0.8 to 5 million approximately (Lahore, 11 Oct 2004, IRIN). This can not only lead to regular traffic jams but can consequently increase the levels of air pollution in Pakistan.

Baseline air quality data was formulized in Lahore, Karachi, Rawalpindi, Islamabad, Quetta and Peshawar (Badar et al., 2004). The study was done with an aim to produce baseline levels of air pollutants in urban areas with different spatial and temporal parameters. Highest levels of NOx were reported in Lahore due to heavy traffic near the sampling sites. Many stationary sources like power plants were also the contributors.

In another study done by Ahmed et al., in 2011, NO_2 and O_3 levels were calculated in Islamabad and Rawalpindi from November 2009 to March 2011 using passive sampling in which NO_2 has shown seasonal variation. High NO_2 concentrations was reported in congested areas and those with heavy traffic. NO_2 was negatively related with temperature and rainfall and positively with relative humidity. NO_2 levels were above the permissible standards of WHO at all the sampling sites around the twin cities.

2.12 Studies o**n Nitrogen Dioxide by Satellite Data**

After the fast progress of remote sensing techniques such as differential optical absorption spectroscopy, the total NO_2 concentration in atmosphere can be obtained from ground as well as space. With the launch of Global Ozone Monitoring Experiment (GOME) in 1995 (Burrows et al., 1999b), the information of air pollution has been improved. After GOME, SCIAMACHY was launched in 2002 on Environmental Satellite (ENVISAT) (Bovensmann et al., 1999), OMI data was available from 2004 (Levelt and Noordhoek, 2002) while in 2006, GOME-2 was launched by Meteorological Operational Satellite (METOP) (EUMETSAT, 2009).

Satellite observation of tropospheric NO_2 has widespread value. The strong weekly cycles have been observed by different observational analysis (Beirle et al., 2003), biogenic emissions (Burrows et al., 1999; Ladstatter-Weissenmayer and Burrows 1998; Thomas et al., 1998) as well as discharge on continental scale (Richter and Burrows 2002; Leue et al., 2001).

NO_2 is a criteria pollutant (DEFRA, 2003) tropospheric NO_2 observations are being compared with ground data for maintaining local air quality (Blond et al., 2007). This was completed in Petersburg (Poberovskii et al., 2007), the Milan area (Ordonez et al., 2006), Moscow (Timofeev et al., 2000) Switzerland (Schaub et al., 2007; 2005), United Kingdom (Kramer et al., 2008). The assessment was prepared with the atmospheric data over Alps (Heue et al., 2005) Atlantic (Bucsela et al., 2008) Shanghai (Chen et al., 2009) South Eastern USA (Martin et al., 2004b), along N-5 Highway of Pakistan (Shabbir et al., 2013) and the twin cities of Pakistan (Mehdi et al., 2013; Nisar et al., 2013).

Soil NOx emissions were quantified using the NO_2 tropospheric data (Bertram et al., 2005; Jaegle et al., 2004); same study has been completed for shipping (Franke et al., 2009; Beirle et al., 2004a), power plants (Kim et al., 2009; 2006) and lightning (Martin et al., 2007; Sioris et al., 2007; Beirle et al., 2006; 2004c; Boersma et al., 2005; Thomas et al., 2003; Hild et al., 2002).

NO_2 VCDs were observed from space which can locate the efficacy of different legislative policies/plans and the accuracy of emission inventories. NO_2 trend was evaluated over the eastern Asian developing countries (Irie et al., 2005) particularly China (He et al., 2007; Zhang et al., 2007; van der A et al., 2006; Richter et al., 2005) in addition to the global trend (Hayn et al., 2009; van der A et al., 2008; Richter et al., 2005). A 50% increase in NO_2 emission over China has been reported by Richter et al., (2005) during the time period of 1996 – 2004.

The tropospheric NOx variability over Asia, mainly India has been observed by using a GOME NO_2 columns and 3-D chemistry meteorological model (Kunhikrishnan et al., 2004a).

2.13 Differential Optical Absorption Spectrometry (DOAS)

DOAS has been used for analyzing trace gases from the atmosphere by using spectras in Ultraviolet (UV), UV-Visible and near infrared spectral ranges which is considered to be the main idea behind DOAS. It was maintained for ground based measurements (Platt and Stutz, 2008; Platt et al., 1994) and has now been productively improved for space borne spectrometer measurements as well (Gottwald et al., 2006). The absorption from molecules was included to the logarithm ratio of the calculated radiance and straight solar irradiance without atmospheric absorptions. The resultant coefficient fits are those that are integrated number of molecule per unit of area along the light path of atmosphere for each gas constituent which is known as the slant column density (SCD). The SCD is dependent upon observation geometry, presence of clouds, sun’s position and reflectance from the surface. SCD has to be converted to Vertical Column Density (VCD) by dividing it with an air mass factor (AMF) which is calculated through a radiative transfer model. In principle, DOAS measurements can be applied to all gases that have appropriate narrow absorption bands in Ultra-Violet, UV-Visible and Infra-Red regions. But usually, the low concentration of these gases in the atmosphere along with the restricted signal to noise ratio limits the amount of trace gases which can be detected. The Figure 2.3 shows absorption cross sections of different trace gases which are regularly measured by DOAS.

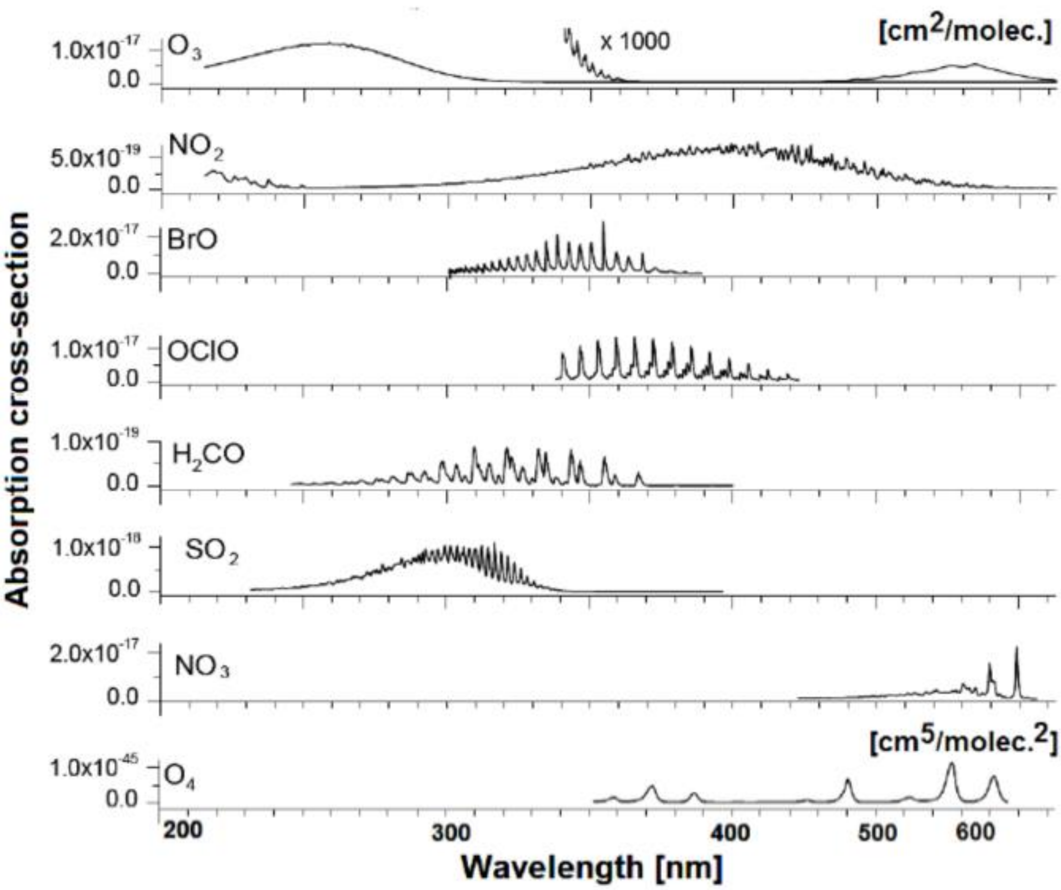

Fig 2.1: Absorption cross sections of various absorbers retrieved with the DOAS method (Platt and Stutz, 2008)

2.14 Satellite Instruments

Tropospheric NO_2 VCDs have been retrieved separately from different satellite instruments like GOME, GOME-2, SCIAMACHY and OMI by different groups (Richter and Burrows., 2002; Boersma et al., 2004; Martin et al., 2002; Bucsela et al., 2006). Tropospheric NO_2 VCDs shown in the following Figure 2.2. The definite enhancements can be seen over the major industrial and urban areas. Moreover, when observations of different satellites like

GOME-2, SCIAMACHY and OMI are combined, it can be helpful in the detection of different trends. The tropospheric NO_2 columns have increased over the industrial regions of China in the last decade. It has also been revealed by the same datasets that the emissions of NO2 have decreased in United States and Europe (Stavrakou et al., 2008; Richter et al., 2005; van der A et al., 2006 and 2008).

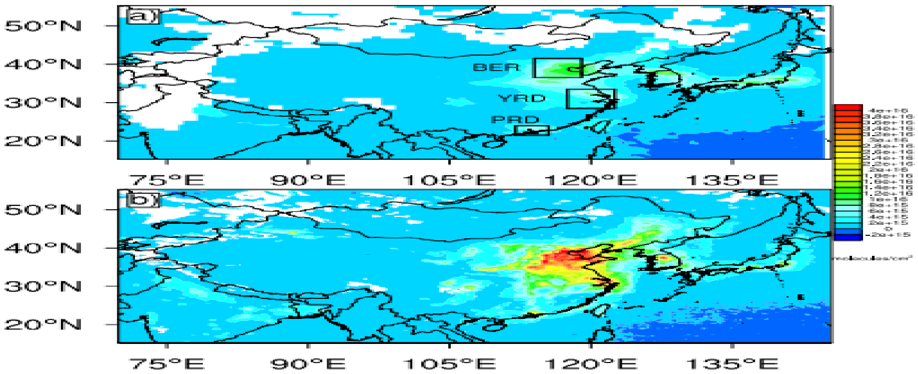

Fig 2.2 Yearly mean tropospheric excess column of nitrogen dioxide over China (a) 1996 (b) 2011. Boxes PRD, YRD and BER represent the three studied sub regions: the pearl river delta, the Yangtze river delta and the bohai economic rim

A nadir viewing spectrograph that estimates direct as well as backscattered sunlight in the UV-Vis region from 270 nm to 500 nm. The data set is available from October 2004 till now. It has a high spatial resolution of 13 × 24 km^2 (wide swath of measurement) with global coverage of one day. It has spectral range of 0.5 nm (Levelt et al., 2006).

SCIAMACHY is a passive remote sensing spectrometer which observes reflected, backscattered, emitted and transmitted radiation from Earth's surface and atmosphere, in wavelength ranges between 240 nm and 2380 nm. It has a spectral resolution of 0.25 nm in the UV and 0.4 nm in the visible. It makes nadir and limb measurements alternately. It provides global coverage within 6 days and more regularly at higher latitudes (Bovensmann et al., 1999). Its local crossing time is 10:00 am. The limb and nadir measurements is the special feature of SCIAMACHY which facilitates the measurement of vertical profiles from mesosphere down to troposphere at less spatial resolution while the total columns are measured at high spatial resolution. The nadir and limb scans are combined to give tropospheric columns (Beirle et al., 2010).

GOME 2 is an improved version of ESA's GOME-1 satellite; it is a nadir viewing UV-Visible spectrometer. The spectral range is between 240 and 790 nm while the spectral resolution is between 0.25 and 0.5 nm. Global coverage is provided within 1.5 days (Callies et al.,2000). While the orbit is illuminated, the satellite performs nadir measurement of atmosphere and scans the surface from east to west i-e, the forward scan and vice versa i-e, the backward scan. The local crossing time is 09:30 am.

CHAPTER 3

METHODOLOGY

3.1 Methodology and Data Sets

OMINO$_2$ (version, 2) monthly mean data was obtained from tropospheric emission monitoring satellite.

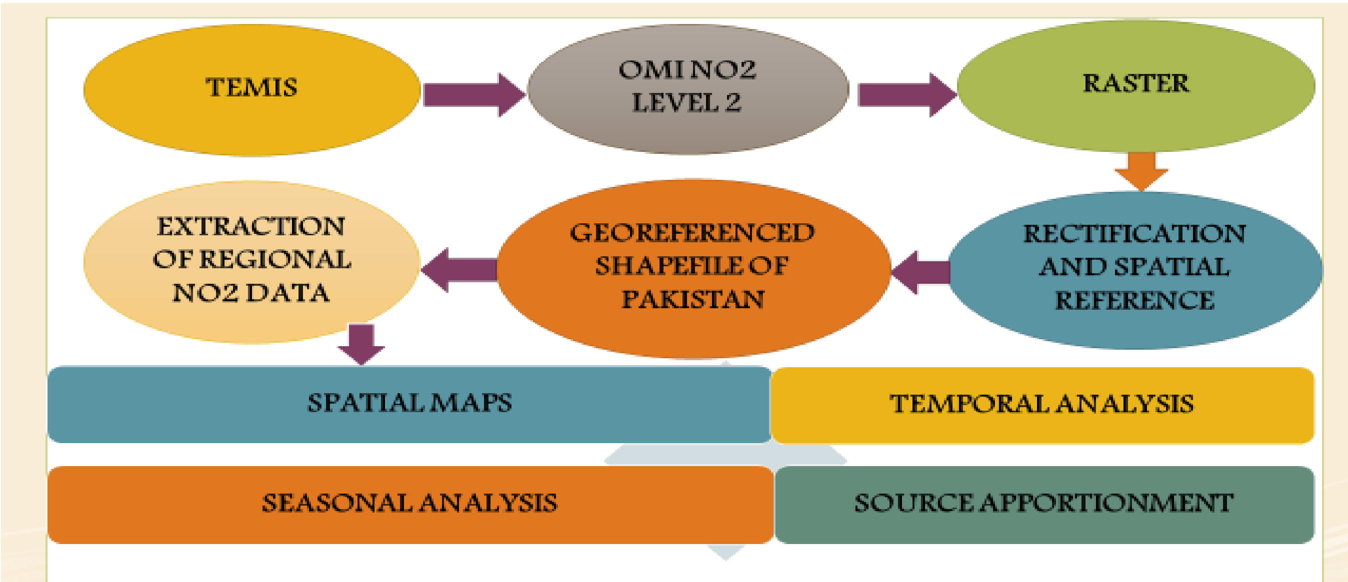

Fig 3.1 A flow chart presenting the method used to make maps of NO$_2$ VCDs

The ascii / text files were converted into raster images in ENVI 4.7. These raster images were georeferenced and WGS 1984 spatial reference was assigned in ArcGis 10.1. A georeferenced shapefile of Pakistan was added to extract regional NO$_2$ data from the global one. At the end spatial maps of NO$_2$ were created to have an idea about the major hotspot or polluted areas. The seasonal and temporal variations were also demonstrated in order to show that how the NO$_2$ column densities vary over time. Main features of OMI are summarized in Table 3.1

Table 3.1 Specifications of Ozone Monitoring Instrument (Richter and Burrows, 2002)

Instruments	**OMI**
Stand	Aura
Estimation Period	2004-till now
Crossing Equator at	1:45 pm
Spatial decree (km^2)	24×13
Spectral decree (nm)	0.5
Spectral Region	UV-Vis
Global reporting	1 day
Grid Size	0.25×0.25

3.2 NO_2 column densities retrieval by OMI/AURA

The NASA's Aura satellite team carries OMI, HIRDLS, TES and MLS. The satellite retrievals are usually in good arrangement with bottom-up emission inventories and in situ evaluations. Boersma et al., 2004 found a good association between OMI-NO_2 datasets and aircraft based NO_2. OMINO$_2$ Level-2 data product is used to observe the temporal evolution of tropospheric NO_2 over Pakistan. The data set was acquired from the Tropospheric Emission Monitoring Internet Service called TEMIS.

3.2.2 Ozone Monitoring Instrument

A nadir viewing spectrograph that estimates direct as well as backscattered sunlight in the UV-Vis region from 270 nm to 500 nm. The data set is available from October 2004 till now. It has a high spatial resolution of 13 × 24 km^2 (wide swath of measurement) with global coverage of one day. It has spectral range of 0.5 nm (Levelt et al., 2006). $OMINO_2$ level 2 data is based upon a better correction for across-track stripes and air mass factors (AMFs) obtained from calibration errors in the OMI backscattered reflectance. The previous studies indicated good data quality but also high biases upto 40%, because of faults and errors in the air mass factor calculations. DOAS method, was used to estimate tropospheric slant column densities (SCDs) by spectral fit to back scatter solar irradiance (Platt, 1994; Boersma et al., 2005; Bucsela et al., 2008) and by integrating slant columns into Chemistry transport Model (CTM) with wind fields and stratospheric chemistry. Tropospheric AMF was applied to convert slant column into vertical column. Surface albedo, cloud fraction, geometry and trace absorbers are the major constraints that affect the retrieval and contribute error.

3.3 Solar Irradiance and NO_2

Data of solar flux was taken from global UV-B radiation data set for macro-ecological studies (GLUV). The data product was mean spectral surface UV-B irradiance and erythermal dose level-2G data product for the time period of January 2004 to December 2013. HDF data was converted into CSVs and then the raster images were made. J/m^2 units were converted into $Watt/m^2$. The solar flux was then extracted over Pakistan.

3.4 Agricultural fires And NO_2

Active fire data (MCD14DL) was obtained from Nasa Earth Data and then the nitrogen dioxide column values were extracted over fire pixels. Spatial fire maps were created over

Pakistan from October 2004 to December 2014 to see the impact of agricultural fires and biomass burning on the column densities of nitrogen dioxide.

3.5 Population Data And NO_2

The mean population density data of land scan was used to correlate with NO_2 column densities. The data has resolution of 1km (30”×30”). It gives finest spatial distribution which exhibits the average 24 hours population (ambient population). The modelling mechanism includes the subsidiary datasets of villages, urban areas, slope, land cover and roads; sub-country level census is also included. These are the main indicators/factors of population distribution.

3.6 Thermal Power Plants And NO_2

Thermal power plants data was obtained from Population Bureau of Statistics. The geographical coordinates were assigned to each power generation facility in Google Earth which was saved as kmz. This kmz converted into layer in ArcGis 10.1. At every power plant, the nitrogen dioxide values were extracted.

3.7 Traffic Count And NO_2

The traffic count data (average over 24 hours) was taken from National Highway Authority (NHA). The geographical coordinates were assigned to each highway (starting toll plaza/entering point) in Google Earth which was saved as kmz. This kmz converted into layer in ArcGis 10.1. At every power plant, the nitrogen dioxide values were extracted and presented in the form of map. LandScan Population data (2010) was placed as a base map and over that the nitrogen dioxide values and traffic count bars were inserted which showed that the number of traffic vehicles are positively correlated with NOx emissions.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 An Overview of Pakistan's Economy

Pakistan lies in South Asia with population of more than 18 crore. It is considered to be sixth most populous state and has total area of 881913 sq.km. Its geographical coordinates are 33.66 N and 73.16 E. The energy is generated by WAPDA, KE and IPPs. It shares border with India, China, Iran and Afghanistan.

Urbanization in Pakistan is now at its peak in South Asia (SDPI, 2010). Road transport is carrying 91% of the passenger traffic and 96% of the cargo movements. From 2000 to 2010, the total number of vehicles on the roads grown from 4 to 9.8 million showing an increase of 145% (The world bank, 2006). Pakistan's economy is profoundly dependent on the agricultural sector. The total farmed waste burnt is 1704.9 thousand tons per year in the rice-wheat cropping system in Pakistan contributing significant emissions of NO_2 (Tanvir and Bashir, 2013).

4.2 Satellite Observations of NO_2 over Pakistan

A nadir viewing spectrograph that estimates direct as well as backscattered sunlight in the UV-Vis region from 270 nm to 500 nm. The data set is available from October 2004 till now. It has a high spatial resolution of 13×24 km^2 (wide swath of measurement) with global coverage of one day. It has spectral range of 0.5 nm (Levelt et al., 2006). NO_2 concentrations were higher than the World Health Organization (WHO) in Islamabad and Rawalpindi (Ahmed et al., 2011). The measurements done by satellites have worldwide coverage and their spatial and temporal resolution can meet such needs, especially, a country like Pakistan with no proper/regular air quality monitoring network (ESoP, 2013). Around 50% is released from industry and traffic and 20% from biomass burning. Among natural sources, approx. 10% emissions are through lightning while 15% from soil due to the activity of microbes (Lee et al., 1997).

A database of monthly and annual mean maps of tropospheric NO_2 VCDs over Pakistan was prepared from the observations of SCIAMACHY (03/2002-03/2012), OMI (10/2004 to 12/2014) and GOME-2 (10/2007 to 12/2014) instruments. Time series of monthly mean tropospheric NO_2 VCDs obtained from SCIAMACHY, OMI and GOME-2 observations is presented in Fig 4.1. A recent study by Hilboll et al., (2013) has related inter- instrumental differences to various factors such as aerosol load, surface altitude, and surface spectral reflectance. All of these factors along with different spatial resolution lead to instrument dependent NO_2 columns; underestimated in the case of poor spatial resolution (SCIAMACHY and GOME-2) as compared to OMI instrument with relatively finer spatial resolution. This is further reflected by the correlation calculated by applying bivariate fit (Williamson-York Method) (Cantrell, 2008) among each data sets. Especially, the correlation between OMI and SCIAMACHY. On other hand, correlation calculated for SCIAMACHY and GOME-2 (r= 0.84) is equally good as in case of OMI and SCIAMACHY observations. This might be due the reason that SCIAMACHY and GOME-2 overpass are with half an hour difference. While OMI overpass is in the early afternoon (13:45 LT) as compared to GOME-2 (09:30 LT) and SCIAMACHY (10:00 LT). Therefore, diurnal cycles of NO_2 and aerosols, as well as the different angular sampling (pixel orientation) of spectral surface reflectance (Hilboll et al., 2013) can cause the observed differences among the instruments in addition to treatment of the cloudy pixels. Because the cloud products used for SCIAMACHY and GOME-2 (with wider spectral range) and OMI (< 500 nm) are different, since OMI cannot measure in the red spectral range. This may further be the plausible reason for observed differences of the mean NO_2 from the different sensors.

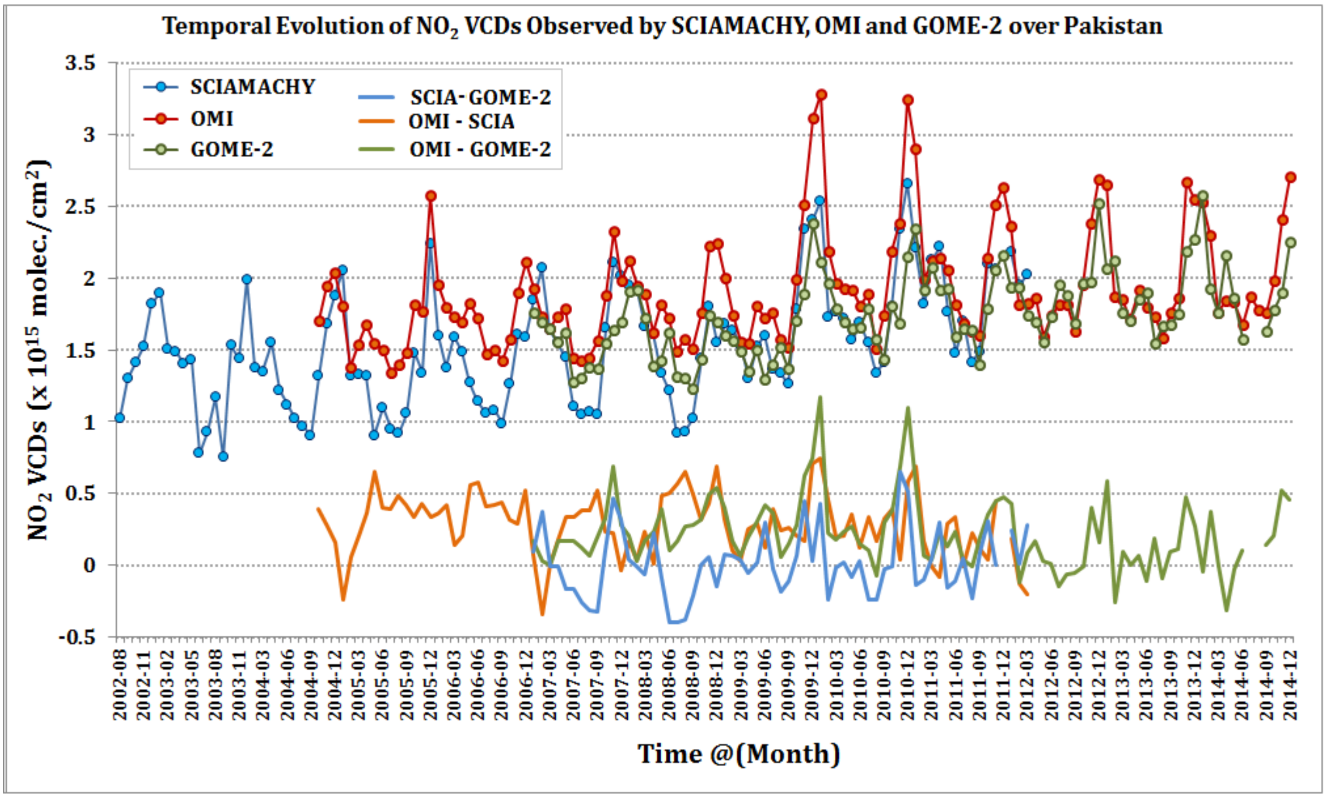

Fig 4.1. Temporal evolution of tropospheric NO_2 VCDs and comparison among SCIAMACHY (in blue), OMI (in brown) and GOME-2 (in green) over Pakistan during the time period of 2002-2014. The plain lines show the difference of GOME-2 (green) and SCIAMACHY (brown) from OMI observations and that of SCIAMACHY and GOME-2 (in blue) for respective time period.

The characteristics of these three satellites have been described in Table 4.1. It can be clearly seen that similar seasonal pattern but quantitatively different, is observed for all the three satellite instruments. NO_2 peaks in OMI data are larger as compared to those measured by SCIAMACHY and GOME-2 instrument. The difference of OMI data from GOME-2 (Green Solid line) and SCIAMACHY (Green Solid line) data and difference of SCIAMACHY from GOME-2 observations (Blue solid line) are also plotted in the Fig

4.1. The difference of GOME-2 with OMI is slightly larger than in the case of SCIAMACHY observations. It can be partially attributed to the difference in ground-pixel size of OMI, SCIAMACHY and GOME-2, as depicted by inset picture in Fig 4.2.

Table 4.1. Features of satellite instruments for the remote sensing of tropospheric NO_2 used in this study

Instrument	**SCIAMACHY**	**OMI**	**GOME-2**
Platform	**ENVISAT-1**	**AURA**	**MetOp**
Measurement Period	Aug. 2002- Mar. 2012	Oct.2004- Present	Jan 2007- Present
Equator Crossing local time	10:00 am	1:45 pm	09:30 am
Nadir resolution (km^2)	60 × 30	24 × 13[1]	80 × 40
Spectral region	UV-Vis-NIR-SWIR	UV-Vis[2]	UV-Vis
Global Coverage	6 days	1 day	1.5 days

[1]*at nadir and may exceed at far ends of the swath*

[2]*OMI covers only wavelengths <500 nm*

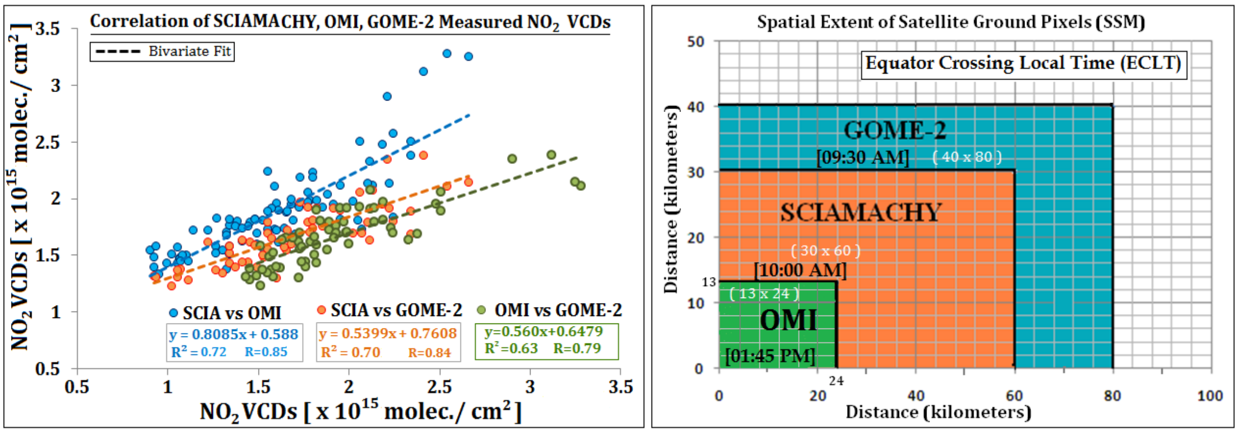

Fig 4.2. (left)- shows correlation of troposheric NO_2 VCDs observed by OMI & SCIAMACHY (Blue circle), SCIAMACHY & GOME-2 (Brown) and GOME-2 & OMI (Green circles). (Right)- shows the comparison of nadir ground-pixel size of OMI (13×24 km^2), SCIAMACHY (30×60 km^2) and GOME-2(40×80 km^2) instruments in standard scan mode (SSM) along with equator crossing local time of GOME-2(09:30 LT), SCIAMACHY (10:00 LT) and OMI (13:45 LT). Bivariate fit (see Cantrell, 2008) was applied in order to measure the correlation in each case.

Besides observed differences, all of these NO_2 data sets are significantly correlated with each other with correlations ($r > 0.79$) in each case. This indicates an overall good agreement in observed NO_2 VCDs over Pakistan among three satellite instruments which differ from each other in various aspects (see Table 4.1). Linear fits were applied to identify the relative temporal increase in the levels of tropospheric NO_2 columns during the selected time period. An overall statistically significant temporal increase in tropospheric NO_2 VCDs: 45% for SCIAMACHY (01/2003 - 01/2012), 30% for OMI (10/2004 - 10/2014) and 33% for GOME-2 (01/2007 - 12/2014) was observed. All of three data sets have shown an increasing trends but with different magnitudes because trends were calculated for different time periods subject to availability of observations (lifetime of the satellite instruments). The overall absolute increase in SCIAMACHY data was

$0.55\pm0.2 \times10^{15}$ molecules/cm^2 with annual increase at the rate of $0.61\pm0.02 \times10^{14}$ molecules/cm^2 per year, for OMI data was $0.5\pm0.19 \times10^{15}$ molecules/cm^2 with annual increase at the rate of $0.5\pm0.19 \times10^{14}$ molecules/cm^2 per year, and for GOME-2 data was $0.5\pm0.14 \times10^{15}$ molecules/cm^2 with annual increase at the rate of $0.71\pm0.2 \times10^{14}$ molecules/cm^2 per year. It has been observed that NO_2 VCDs during winters of 2010 and 2011 were higher than usual shown in Fig 4.1. Efforts were made to explore the most probable reason behind these anomalous peaks. A closer look in to the use of fossil fuels in Pakistan revealed that use of oil consumption by power sector was maximum during the year 2010 and 2011 shown in Fig 4.3. Pakistan with limited natural resources is facing severe energy/power crisis (10–12 hours of electricity load shedding in addition to natural gas outages). Pakistan is investing a lot of revenue to import fossil fuel such as furnace oil, coal, natural gas etc. to meet their industrial needs of electricity (Khattak et al., 2014).

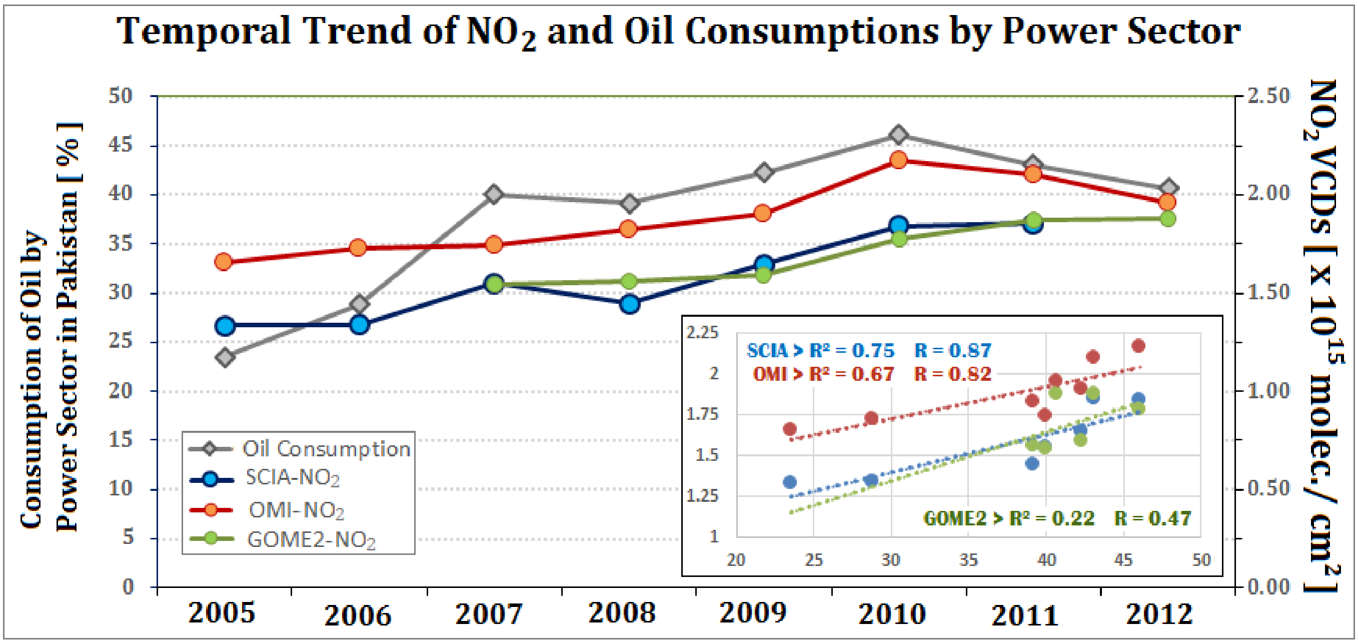

Fig 4.3. Share of oil consumptions by power sector in Pakistan (in grey) are compared with annul mean NO_2 VCDs from SCIAMACHY (in blue), OMI (in brown) and GOME-2 (in green) during the time period of 2005-2012. Oil Consumption in % is

shown along Primary Vertical axis while NO_2 VCD (molecules/cm^2) is shown along Secondary Vertical axis. Horizontal axis exhibiting time (Years). Nested pictures show the correlation among mean NO_2 VCD (molecules/cm^2) from all satellite instruments and oil consumption for power generation in Pakistan.

Consequently, it has caused adverse impacts on air quality environment of Pakistan by releasing other air pollutants such as CO, SO_2 and NO_2 etc. An increasing trend in oil- and gas-based power generation while a decreasing trend in the hydro-based power generation in Pakistan was reported.

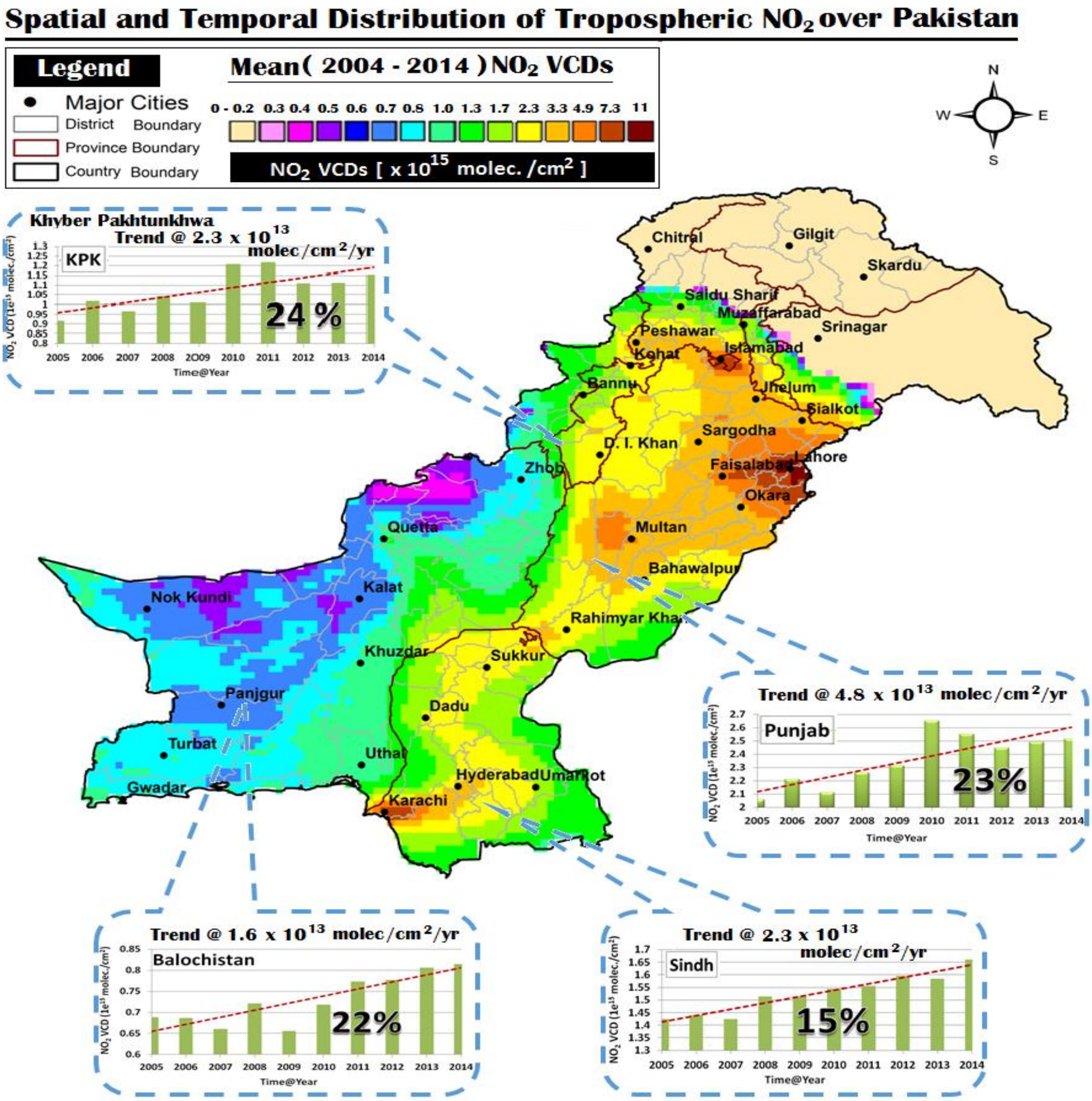

Fig 4.4. A multi-year mean map of tropospheric NO_2 VCDs from OMI observations from year 2004 to 2014. The temporal evolution of annually averaged tropospheric NO_2 columns over four provinces of Pakistan during 2005 to 2014 is presented by bar charts. Year 2004 was excluded because OMI observations were less than 12 months during the year 2004

Long-term mean map of OMI NO_2 column densities over Pakistan during the time period of 10/2004 – 12/2014 is shown in Fig 4.4 Major cities of Pakistan are shown with black circles. lifetime of NO_2 ranges up to 6 hours in summers and 18-24 hours in winters depending upon different meteorological factors like temperature, humidity, actinic flux and cloud cover. NO_2 is mainly removed from atmosphere by reaction with OH to form nitric acid. Seasonality in NO_2 concentration over Pakistan is driven by enhanced OH levels, wet scavenging during monsoon spells in summer and increased use of coal and biofuel for space heating, and decreased photolysis rate during winter months. Moreover it is also contributed by agricultural fires, biomass burning and biogenic emissions as explored by Khokhar et al., (2015) by using SCIAMACHY observations during the time period of 2002-2012. This study showed a different yearly growth in the levels of tropospheric NO_2 columns over different regions of Pakistan. Temporal increase in NO_2 VCDs was calculated in four major provinces (Punjab, Sindh, Balochistan, KPK- Khyber Pakhtunkhwa) of Pakistan separately (black, brown and grey line showing country, province and district boundary, respectively). Relative increase observed in tropospheric NO_2 column was in the following order: KPK (24% at rate of 2.4% per year with absolute increase of 2.3×10^{13} molecule cm^{-2} $year^{-1}$), Punjab (23% at rate of 2.3% per year with an absolute increase of 4.8×10^{13} molecules cm^{-2} $year^{-1}$), Balochistan (22% at rate of 2.2% per year with absolute increase of 1.6×10^{13} molecule cm^{-2} $year^{-1}$) and Sindh (15% at rate of 1.5% per year with absolute increase of 2.26×10^{13} molecule cm^{-2} $year^{-1}$). Temporal trend of tropospheric NO_2 over major cities of Pakistan is presented during the time period of 2004-2014 as listed in Table 4.2. NO_2 VCDs were extracted by using major cities shapefile of Pakistan. NO_2 VCDs for only one grid cell (0.25° × 0.25°) having co-ordinates exactly/close to the geographical co-ordinates of the respective city was selected. The largest increase has been observed over Islamabad followed by Lahore, Faisalabad and so on. These cities have high population density and traffic count hence showed higher NO_2 columns. Seasonal Mann-Kendel test was applied to test the statistical significance of calculated temporal change with 95% confidence interval. Statistically significant increasing trends are observed over all Pakistan, major provinces (Punjab, Sindh, KPK and Balochistan) and major cities (Lahore, Islamabad, Okara, Faisalabad, Hyderabad, Peshawar and Quetta) while mega city of Karachi is observed with statistically non-significant trend (Table 4.2). Twin cities of Islamabad and Rawalpindi exhibited the strongest relative increase of about 8% per year followed by Lahore with 6.4% per year observed by OMI instrument during the years 2004-2014. Similar trend of 44% per year over Islamabad and 23 % per year over Lahore observed by Tariq et al., (2014) by OMI instrument during the time period of 2004-2008. Khokhar et al., (2015) studied the strongest relative trend of about 8% per year over Islamabad/Rawalpindi for SCIAMACHY data (2002-2012) followed by the city of Lahore with 7% per year. In general, low NO_2 column values observed over Karachi followed by Hyderabad because low values may be related to more precipitation wash out, high moisture, and powerful sea breeze from Arabian coasts dispersing the NO_2 columns. More OH is produced due to increased precipitation rate thereby increasing photolysis rate and converts NO_2 into HNO_3. High NO_2 concentration in Islamabad, Lahore and Okara may be partially attributed to transboundary pollution from India, Afghanistan and Iran. Industries, fossil fuel burning, transport and power sectors are substantially contributing to pollutant emissions worldwide. Use of coal and furnace oil in power generation plants and industries contribute almost 45% and 32% in total NOx emissions. A recent study revealed that traffic/industrial activities, biomass burning, lightning and soil account 50%, 20%, 10%, and 15% of NO_2 emissions in Pakistan, respectively.

Table 4.2. Temporal Trend of NO_2 VCDs over major cities and Pakistan derived from OMI observation during the period of 2004–2014.

Region		Absolute Change in Tropospheric NO_2 VCDs ($\times 10^{15}$ molecules cm^{-2})		Relative Change in Tropospheric NO_2 VCDs (%)		p-value	Seasonal Mann Kendal Test Statistic (S)	Significance
		Total	Yearly	Total	Yearly			
Pakistan		0.4±0.3	0.04±0.03	28	2.7	< 0.0001	274	Yes
Provinces	**Punjab**	0.3±0.2	0.03±0.02	23	2.3	< 0.0001	224	Yes
	KPK	0.2±0.1	0.02±0.01	24	2.4	< 0.0001	203	Yes
	Sindh	0.2±0.1	0.02±0.01	15	1.5	< 0.0001	198	Yes
	Balochistan	0.1±0.1	0.01±0.01	22	2.2	< 0.0001	208	Yes
Major Cities	**Lahore**	3.7±2.6	0.37±0.26	65	6.4	< 0.0001	241	Yes
	Islamabad/ Rawalpindi	2.5±1.8	0.25±0.18	79	7.9	< 0.0001	236	Yes
	Faisalabad	0.6±0.4	0.06±0.04	18	1.8	< 0.0001	168	Yes
	Okara	0.7±0.5	0.07±0.05	32	3.2	< 0.0001	231	Yes
	Karachi	0.1±0.1	0.01±0.01	3.6	0.36	0.278	43	No
	Hyderabad	0.06±0.04	0.006± 0.004	2.6	0.26	0.013	97	Yes
	Peshawar	0.6±0.4	0.06±0.04	30	3	< 0.0001	190	Yes
	Quetta	0.2±0.1	0.02±0.01	27	2.7	0.001	128	Yes

4.3 Seasonal Analysis of NO_2

NO_2 lifetime is of about 6 hours in summers and 18-24 hours in winters depending upon different meteorological factors like temperature, humidity and cloud cover (Richter et al., 2005). NO_2 is removed from atmosphere in reaction with OH to form nitric acid. NO_2 concentration decreases in summers (Tariq et al., 2014) and increases in winters. Enhanced winter NO_2 values of might be attributed to increased anthropogenic practices. Moreover it is also contributed by agricultural fires, biomass burning and forest fires as discussed below. Fig. 4.5 exhibiting seasonal cycle of climatologically averaged NO_2 over Punjab, Sindh, Balochistan and Khyber Pakhtunkhwa. Blue rectangles indicating monsoon period. Winter maximum was observed in Punjab, Sindh and Khyber Pakhtunkhwa. This maxima might be attributed to cloud cover which decreases the removal of NO_2 through phenomenon of photolysis. There is enhanced usage of fossil fuels in winter season which might be another reason for high NO_2 concentration. Low NO_2 values were observed in Punjab, Sindh and Khyber Pakhtunkhwa because more OH is produced due to elevated temperature hence photolyzes NO_2 into HNO_3. As far as Balochistan is concerned it was examined with somewhat different chemistry. This province lies in west side of Pakistan which is known to receive less precipitation in monsoon. Thereby the elevated temperature level in monsoon causes more soil NO_2 emissions. So the NO_2 column values were getting gradually high in monsoon.

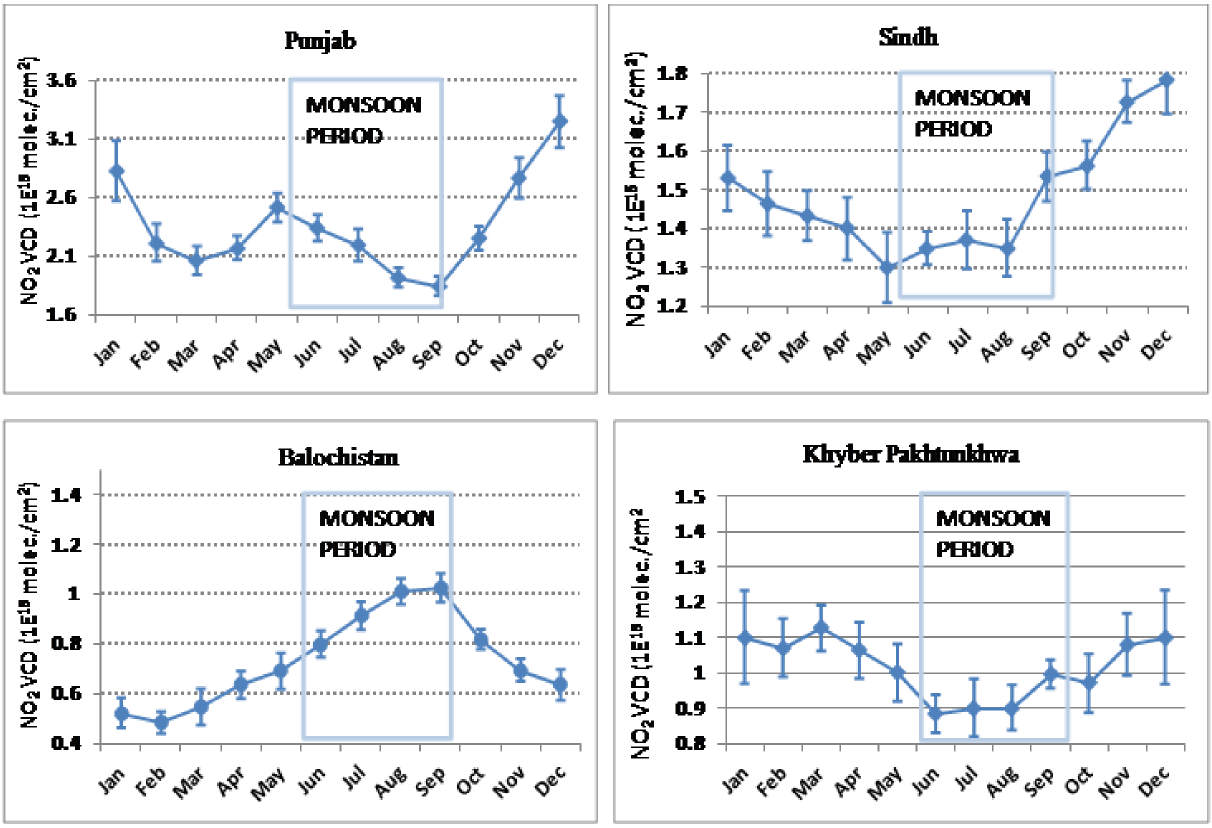

Fig 4.5. demonstrated seasonal cycle in tropospheric NO_2 VCDs over major provinces of Pakistan. Blue rectangles are signifying the monsoon period of the year. Error bars representing standard deviation.

4.4. Source Identification

This study also focuses on source apportionment when it comes to NO_2 emissions.

4.4.1. Agricultural Fires and NO_2

Agricultural fires emit aerosol particles, greenhouse gases and various trace gases into the atmosphere (Crutzen and Andreae, 1990). Post-harvest burning is a very common feature in South Asian region in order to make fields ready for next cultivation and a conservative method to get soil nutrients for next crop. Peak agricultural fire events occur to clear the agriculture residue during the months of April and May for wheat crop and November for rice paddies in Pakistan. In May, large scale crop residue burning is also stated by Ali et al. (2014) during wheat–rice rotation in the neighboring areas of Kasur, Shiekhupura, Narowal, and Mian Channu cities. Additionally, during monsoon season high temperature and humidity also contribute to soil emissions which are further enhanced by the application of fertilizers in the rice growing fields. For this purpose, MODIS active fire data (MCD14DL) data was downloaded from NASA (National Aeronautics and Space Administration - webpage https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms/active-fire-data). Fig 4.6 (a) shows the spatial distribution of total number of active fire events and mean map of OMI NO_2 observations during the time period of 2004–2014. It can be seen that regions with extensive vegetation fires are exhibiting enhanced NO_2 columns. Especially, regions of Punjab, Sindh and KPK provinces exhibited enhanced NO_2 columns consistent to the regions with fire hotspots caused by agricultural fires. Balochistan showed relatively low NO_2 columns because of limited agricultural activities in this region.

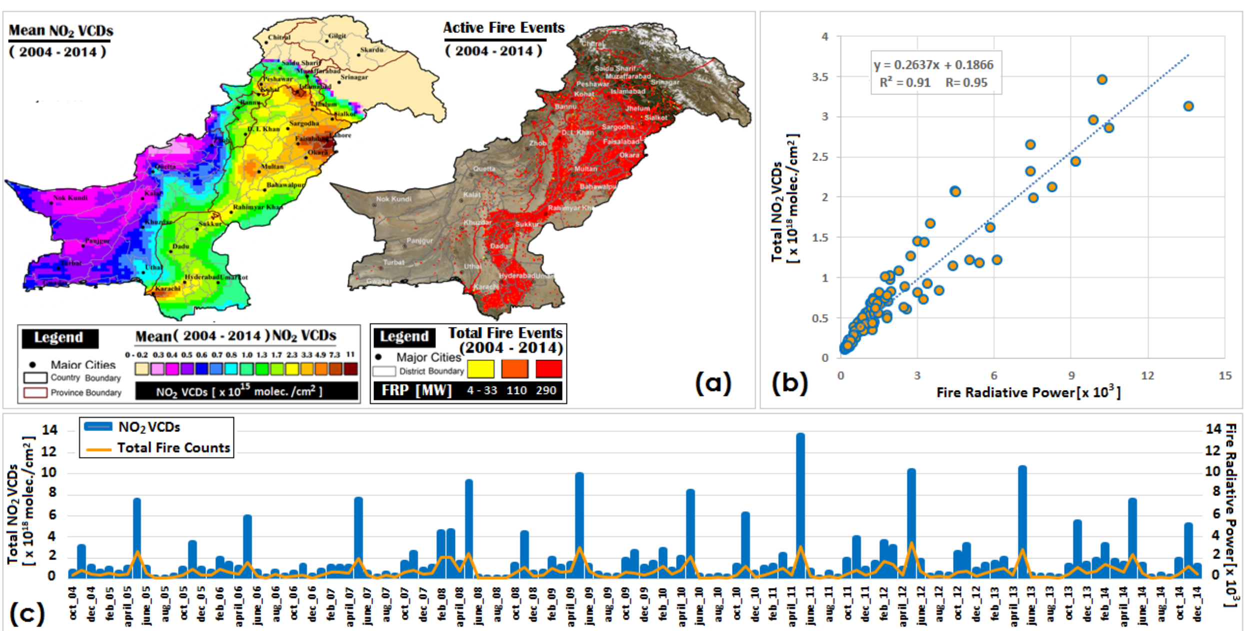

Fig. 4.6. (a) Long-term mean map of Active Fire from MODIS and NO_2 VCDs from OMI (2004-2014) instrument; (b) Correlation (r =0.95) between total/sum NO_2 VCDs and Fire counts in Pakistan is presented. NO_2 VCDs were sum over the pixels having fire events only; (c) Time series of Active Fire (in golden) and OMI NO_2 columns (in blue) are presented. Similar patterns and coincidence was observed in both fire counts and NO_2 columns.

Agricultural fires have shown remarkable impact on NO_2 column densities in Pakistan. Fig 4.6 (c) presents time series of Active Firm fire data (in golden) and OMI NO_2 columns (in blue). A significant correlation of 95% (R and R_2 = 0.95 and 0.91 respectively) is observed for total fire events across Pakistan and resulting NO_2 columns in Fig 4.6 (b). A brief summary of total number of fire counts, total and mean NO_2 columns and correlations between fire counts and resulting NO_2 columns from each province and all Pakistan is presented in Table 4.3. Both data sets exhibited significant correlation r with maximum from KPK and Balochistan. It is important to mention here that existing estimates for NOx emissions (EDGAR v4- although correlation between fires and NO_2 columns is significant in Punjab, Sindh and KPK Province but high NO_2 column density is relatively less contributed from agricultures fires (1% and underestimated too – Khokhar et al., 2015). High population density, industrial activities and traffic count as discussed in the following sections are the main sources of high NO_2 columns in Punjab followed by Sindh and KPK (Khokhar et al., 2015). While in Balochistan, region natural emissions from soil and lightning are predominant.

Table 4.3. Sum and mean vertical column densities of NO_2 for year 2004–2014 over pixels exhibiting fire activities across Pakistan.

Regions	Total No. of Fire Counts	Total/SumNO_2 VCDs ($\times 10^{18}$ molecules/cm^2)	Mean NO_2 VCDs ($\times 10^{15}$ molecules/cm^2)	r(r^2)
Pakistan	86701	241.74	2.39	0.95 (0.91)
Punjab	55251	184.44	2.77	0.97 (0.95)
Sindh	21194	400.08	1.85	0.97 (0.96)
KPK	4717	8.21	1.56	0.98 (0.97)
Balochistan	3727	6.04	1.22	0.980.97)

4.4.2. Solar UV-B Flux and NO_2 VCDs in Pakistan

Climate conditions have long been recognized as major drivers of meteorological processes such as temperature, humidity etc. The global solar flux data was obtained from glUV (Global UV- B Radiation Dataset for Macro ecological Studies from the webpage http://www.ufz.de/gluv/ details see Beckmann et al., 2014. The dataset (aaverage solar irradiance of the spectral surface UV-B irradiance and erythemal dose Level-2g product “omuvbg, v003”) was obtained during the time period of 2004 to 2013 with spatial resolution of 0. 25°×0.25°.

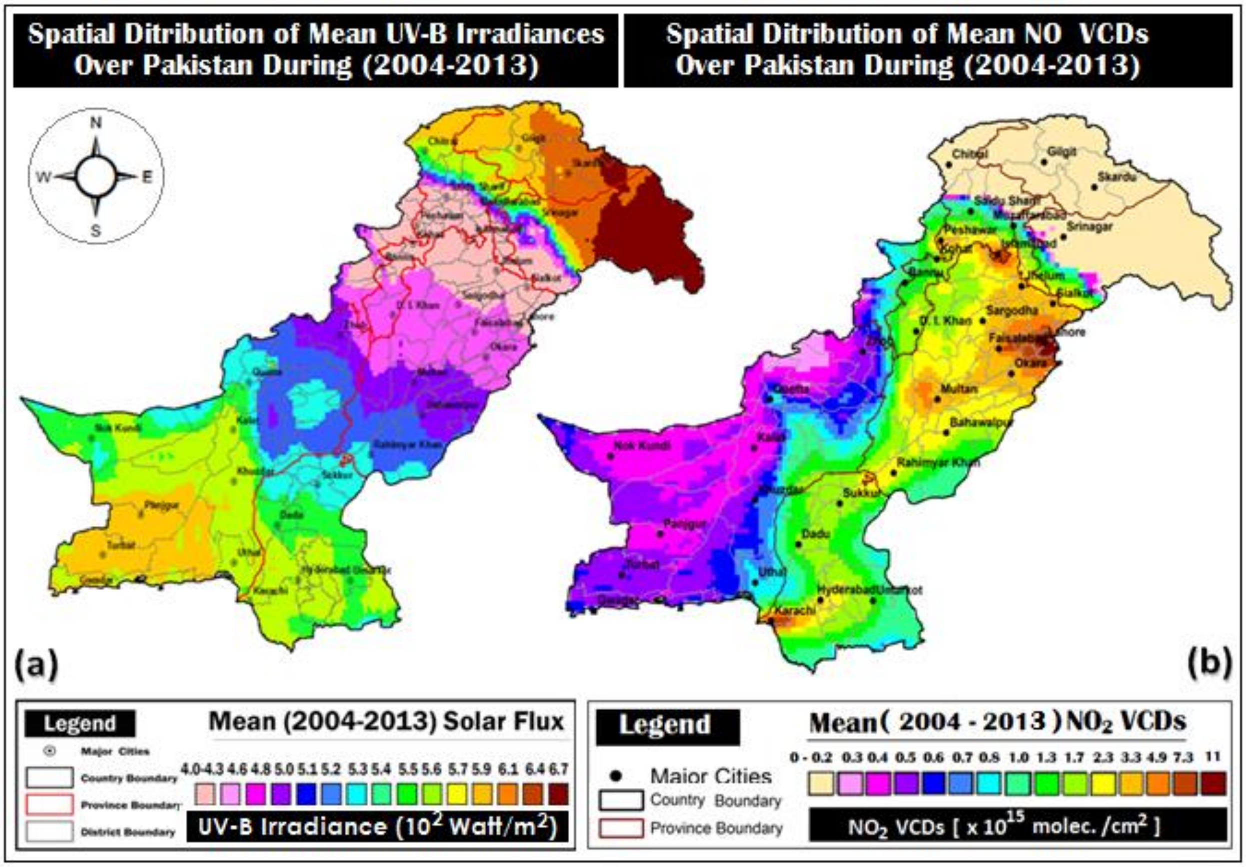

Fig 4.7. (a) Mean Solar Flux (UV-B) over Pakistan obtained from glUV (Global UV B Radiation Dataset for Macro ecological Studies); (b) long-term mean NO_2 VCDs over Pakistan during 2004 to 2013.

UV-B radiations has a range of 280-315 nm and stimulates the formation of reactive radicals such as OH and HO_2. Relative increase in OH is greatest at low NOx with decreasing sensitivity at high NOx (Seinfield and Pandis 2012). It plays an important role in the atmospheric chemistry and may convert primary pollutants into secondary pollutants such as oxidation of methane, isoprene and glyoxal into formaldehyde. In turn formaldehyde is photolysed to produce OH and other radicals (Seinfield and Pandis 2012) – a principal component that oxidizes most of the reactive gases, known as detergent of atmosphere and an important part of acid rain formation.

Fig 4.7 is showing mean solar flux in Pakistan during 2004 to 2013 obtained from glUV (Global UV B Radiation Dataset for Macro ecological Studies) and corresponding seasonal variation of NO_2 concentration over Pakistan during 2004 to 2013 observed from OMI instrument. Black dots are showing major cities. It is obvious that the northern areas are receiving high amount of UV-B radiations but anthropogenic activities here are very less. So lowest NO_2 column values were observed here. While in Punjab where the UV-B radiation is relatively lower and may cause relatively less OH production. It can be speculated that lower level of UV-B radiation might be partially responsible of enhanced levels of NO_2 over Punjab followed by KPK and Sindh in addition to large number of anthropogenic sources. In Balochistan, the UV-B radiations are significantly very high but due to low population density and vehicular emissions less NO_2 is observed.

4.4.3. Population and Vehicular Density

Population density (number of persons / km^2) data over Pakistan for the year 2010 was obtained from LandScan (Vijayaraj et al., 2008) and see webpage http://web.ornl.gov/sci/landscan/). It is quantified data based on night lights used as a proxy information. Pakistan shapefile was added to extract regional data of population density.

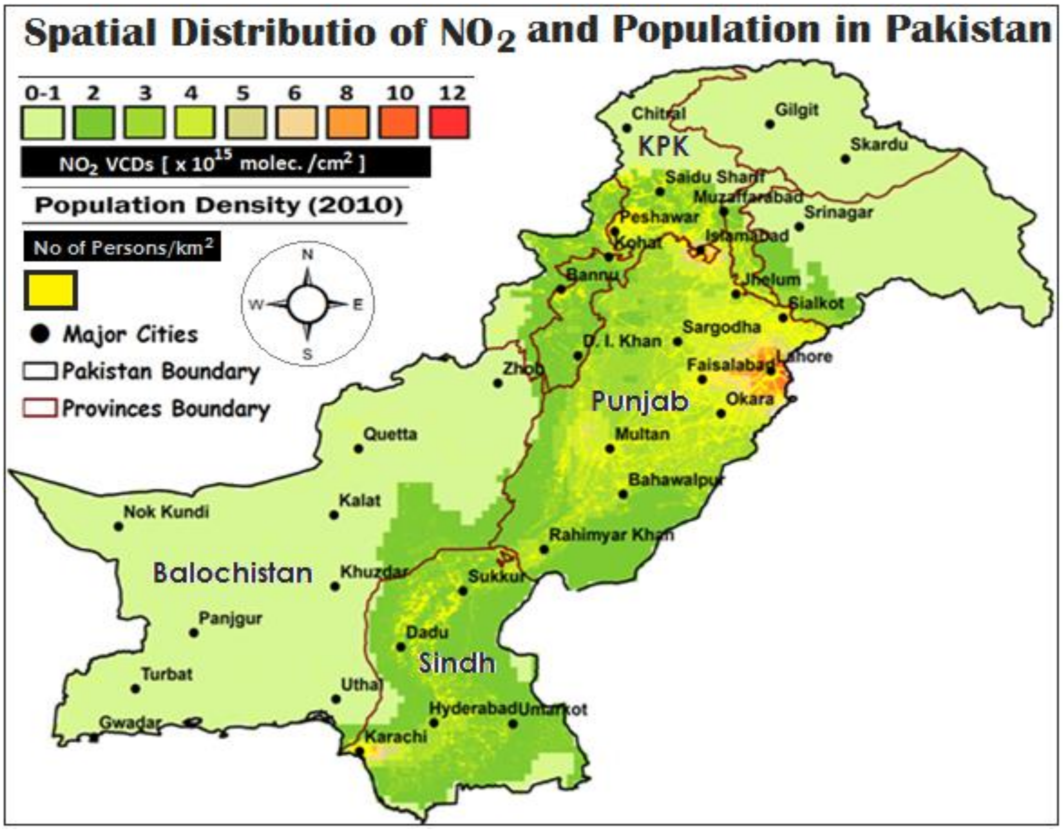

Fig 4.8 Showing Land Scan population density over Pakistan for year 2010. Green color exhibiting NO_2 VCDs while yellow color exhibiting population density. Black circles are indicating major cities across Pakistan. For details refer to (Vijayaraj et al., 2008 and see webpage http://web.ornl.gov/sci/landscan/).

It gives finest spatial distribution which exhibits average 24 hours population (ambient population). The modeling mechanism includes auxiliary datasets of villages, urban areas, slope, land cover, roads and sub-country level census is also included. Higher population densities are strongly associated with higher levels of automobile travel and consequent intense air pollution from cars and other highway vehicles. Fig 4.8 is showing the spatial distribution of population density and mean map of NO_2 VCDs for the year 2010. Yellow color is exhibiting population density. Black circles are indicating major cities across Pakistan. It can be seen that regions with extensive population density are also exhibiting enhanced levels of NO_2 columns. Especially, Punjab, exhibited enhanced NO_2 columns consistent to the regions with population density hotspots followed by Sindh and KPK. It is worth to mention that population density is also high over these regions and may serve as proxy information for air pollution. Similar behavior was reflected from the comparison between total number of vehicles and annual mean NO_2 VCDs during the time period of 2004-2014. Especially, measured correlation plot (R= 0.82) in the nested picture (Fig 4.9).

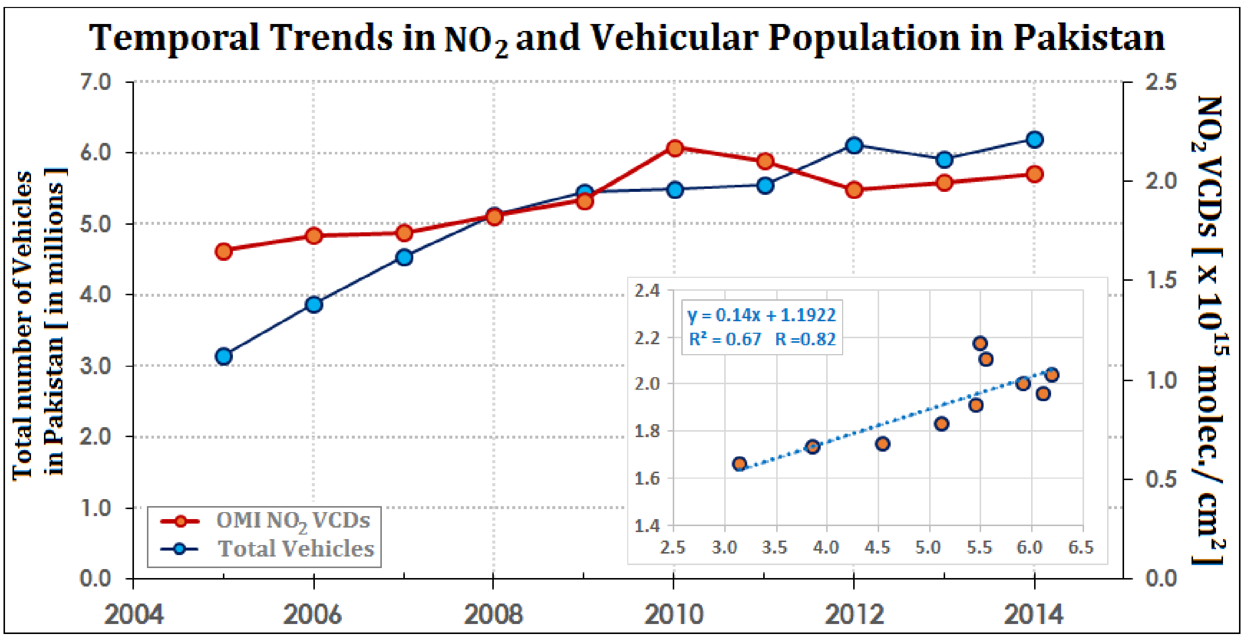

Fig 4.9. Comparison of annually averaged tropospheric NO_2 VCDs (in brown) retrieved from OMI observations with total number of vehicles (in blue) densities over Pakistan during the time period of 2005- 2014. Co-relation between NO_2 column densities and total number of vehicles (blue & brown dots) is presented in nested picture (vehicular data source; National Transport Research Centre of Pakistan)

It is worth to mention here that population density is also high over these regions which could the reason behind enhanced NO_2 VCDs. Table 4.4. exhibiting NO_2 column values and Average Traffic count (over 24 hours) passing at respective toll plaza for year 2013. The data of traffic count was obtained from National Highway Authority. It can be seen that regions with extensive traffic density are exhibiting enhanced NO_2 columns. Lahore (Punjab) was observed with highest NO_2 column value of 8.56×10^{15} molec./cm^2 followed by Karachi (Sindh) with 4.99×10^{15} molec./cm^2. Thereby, Lahore and Karachi exhibited enhanced NO_2 column values consistent to the regions with traffic density hotspots. Table 4.5. exhibited thermal power plants and corresponding NO_2 values across Pakistan. Location and owning companies of each power generation facility are also mentioned. It has been examined that highest NO_2 column value of 7.37×10^{15} molec./cm^2 and 5.85×10^{15} molec./cm^2 observed in GTPS Shahdara (Punjab) and Pakistan Steel Mills (Sindh) respectively during 2004-2014. It is worth to mention here that NO_2 column values are high where greater number of traffic flow and thermal power plants exist.

Table 4.4. exhibiting NO_2 column values (1e^{15} molec./cm^2) and Average Traffic count (over 24 hours) during 2013.

Name	NO_2 column values (1e^{15} molec./cm^2)	Average Traffic count (24 hours)
Multan	2.99	35938
Rahimyar Khan	2.08	19540
Lahore	8.56	46883
Rawalpindi	5.61	5267

Faisalabad	3.51	5717
DG Khan	2.35	8169
Kohala	2.80	3952
Kot Sarwar	3.85	4478
Khanewal	2.50	8554
Tarnol	4.17	11262
Hasanabdal	3.02	15961
Karachi	4.99	53287
Hyderabad	2.25	22982
Sukkur	1.96	26270
Larkana	1.79	23296
Ratodero	1.75	6093
N-5	4.31	6968
Kotri	1.99	4343
Kashmore	2.24	13025
Mansehra	1.58	6371
Nowshera	2.87	16781
Batkhela	1.19	9629
Besham	0.08	1361
Daraban	1.49	6258
Abbotabad	1.65	6897
Chakdara	1.19	7243
Khwazakhela	1.42	2062

Table 4.5. exhibited thermal power plants and corresponding NO_2 column values ($1e^{15}$ molec./cm^2) during 2004-2014. Location and owning companies are also mentioned.

Name of Power Plant	Location	Owned by	NO_2 column values ($1e^{15}$ molec./cm^2)
Gul Ahmed	Sindh	IPP	5.36
Roush Power	Punjab	IPP	2.58
Habibullah Power	Balochistan	IPP	0.85
Saba Power Plant	Punjab	IPP	5.13
Tapal Power	Sindh	IPP	2.58
Uch	Balochistan	IPP	1.44
Kohinoor Energy	Punjab	IPP	5.95
AES Pak Gen	Punjab	IPP	3.43
AES Lalpir	Punjab	IPP	3.29
TNB liberty power	Sindh	IPP	2.14
Shikarpur Power	Sindh	IPP	1.72
Atlas Power	Punjab	IPP	6.94
Attock Generation Limited	Punjab	IPP	4.82
Sitara Energy	Punjab	IPP	4.77
Fauji Kabirwala Power Station	Punjab	IPP	2.50

Pakistan Steel Mills	Sindh	IPP	5.85
Kot Addu Power	Punjab	IPP	3.76
Foundation Power	Sindh	IPP	2.14
Davis Energen	Punjab	IPP	2.42
Saif Power	Punjab	IPP	2.71
Gas turbine Power Station Kotri	Sindh	WAPDA	2.44
Thermal Power Station Guddu	Sindh	WAPDA	2.30
Thermal Power Muzaffargarh	Punjab	WAPDA	3.25
Thermal Power Station Jamshoro	Sindh	WAPDA	2.05
SPS Faisalabad	Punjab	WAPDA	3.96
GTPS Shahdara	Punjab	WAPDA	7.37
GTPS Faisalabad	Punjab	WAPDA	3.96
Lakhra Power Plant	Sindh	WAPDA	1.48
Korangi Thermal Power Station	Sindh	Karachi Electric	5.36
NGPS Multan	Punjab	WAPDA	3.26
Bin Qasim Power	Punjab	Karachi Electric	4.66
Gas Turbine Power	Sindh	Karachi	4.66

Station SITE	Electric

The level-2 data of of OMI instrument was used to prepare a database of NO_2 from 2004-2014 across Pakistan. Different trends were identified over provinces, major cities and whole Pakistan. The temporal trend, seasonality patterns and source apportionment or identification (with agricultural fires, solar flux, population density, traffic density and thermal power plants) were analyzed. Analysis were performed to identify temporal increase, seasonal cycles and source identification of tropospheric NO_2 columns across Pakistan. NO_2 column values were higher in Punjab, followed by Sindh and KPK depending upon entire population density, vehicles and industrial activities. Low NO_2 column values were observed in Balochistan because of low population density and anthropogenic activities. In general, the NO_2 column values were higher in eastern region and lower in western part because of difference in population and vehicles count. It is meaningful to discuss here that satellites have good attribute to spot atmospheric pollutants. Temporal trend and seasonal variation of NO_2 VCDs can be easily analyzed through this. Seasonal cycles demonstrated winter maximum in Punjab, Sindh and Khyber Pakhtunkhwa due to increased man-made activities while summer maximum observed over Balochistan because of enhanced NO_2 soil and lightning emissions. Winter maximum occurs because of less OH production (due to low solar intensity) to slowly remove NO_2 through photolysis while opposite trend has been observed in summers because of more OH production (due to increased solar flux) to quickly remove NO_2 from atmosphere. We have done source identification in current study such as agricultural fires, solar flux, population density, traffic density and thermal power plants. By using firm active fire data, it was concluded that agricultural fires, biomass burning and forest fires are the source of NO_2 emissions. Solar flux (obtained from glUV) indicated that UV-B radiations in Punjab and KPK are very low but NO_2 column values are high (due to high anthropogenic activities) while Balochistan was marked with high UV-B radiations but NO_2 column values are very low (less anthropogenic activities). As far as Sindh is concerned, direct relation has been observed between UV-B radiations and NO_2 column values-more automobiles, high population density. The overall statistically significant temporal increase of 28% was identified by OMI from 2004 to 2014. The overall absolute increase in OMI data was $0.45 \pm 0.31 \times 10^{15}$ molec./cm^2 with annual increase of $2.7 \pm 0.031 \times 10^{15}$ molec./cm^2 per year. Temporal analysis was also performed over major cities of Pakistan. A rising trend in NO_2 columns over major cities of Pakistan was calculated. Islamabad followed by Lahore, Okara, Peshawar, Quetta, Faisalabad, Karachi and Hyderabad exhibited the highest increase due to large amount of traffic and industrial activities during the study period. Karachi and Hyderabad were observed with low NO_2 column values as compared with other cities may be related to more precipitation wash out, high moisture, and powerful sea breeze from Arabian coasts dispersing the NO_2 columns. Temporal trend of about 6.8% was observed by Hilboll et al., (2013). NO_2 column values were compared with population density, traffic count and thermal power plants. High values (in Punjab followed by Sindh, KPK and Balochistan) are positively correlated where increased population density, traffic count and greater number of thermal power plants exist.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Level 2 data of OMI, SCIAMACHY and GOME-2 was obtained from TEMIS during the time period of October 2004 to December 2014. Spatial maps were made while seasonal and temporal variations were also identified over Pakistan.

Agricultural fires, population density and traffic count data were also correlated with NO_2 column densities. Punjab showed highest NO_2 concentration followed by Sindh, KPK and Baluchistan. Most of the agricultural fire events happen in Punjab followed by Sindh as discussed in the results section.

Thermal power plants are also considered as major source of NOx emissions and most of the power plants are located in Punjab and Sindh. Population density was also marked high in Punjab, Sindh and KPK. The present study will provide vital information to scientists, researchers and those organizations working on air pollution and air quality monitoring.

5.2 Recommendation

Some of the worth mentioning recommendations are:

1. Trees plantation activities should be promoted on larger scale.
2. Pollution control technologies such as scrubbers, bag houses and electrostatic chambers should be installed at every industry or facility.
3. Polluter pay principle should be encouraged

4. Local transport has to be promoted in order to reduce the pollutant emissions.

REFERENCES

Ahmad, S. S., Buker, P., Emberson, L., & Shabbir, R. (2011). Monitoring nitrogen dioxide levels in urban areas in Rawalpindi, Pakistan. *Water Air Soil Pollution*, 220(1–4), 141– 150.

Amlinger, F., Peyr, S., & Cuhls, C. (2008). Green house gas emissions from composting and mechanical biological treatment. *Waste Management & Research*, *26*(1), 47-60.

Aqeel, A., & Butt, M. S. (2001). The relationship between energy consumption and economic growth in Pakistan. *Asia-Pacific Development Journal*, *8*(2), 101-110

Badar , G., Lodhi, A. and Mansha , M. (2007). Development of baseline (air quality) data in Pakistan. *Environmental Monitoring Assessment*, 127, 237–252.

Beckmann, M.; Václavík, T.; Manceur, A.M.; Šprtová, L.; Wehrden, H.; Welk, E.; Cord, A.F. Gluv: A global uv-b radiation data set for macroecological studies. *Methods in Ecology and Evolution* **2014**, *5*, 372-383.

Beirle, S., Platt, U., Wenig, M. and Wagner, T. (2003). Weekly cycle of NO_2 by GOME measurements: a signature of anthropogenic sources. *Atmospheric chemistry and physics*, 3, 2225–2232.

Bertram, T.H., Heckel, A., Richter, A,. Burrows, J.P. and Cohen, R.C. (2005). Satellite measurements of daily variations in soil NOx emissions. *Geophysics research*, 32, L24812.

Boersma, K.F., Eskes, H.J. and Brinksma, E.J. (2004). Error analysis for tropospheric NO2 retrieval from space. *Geophysics research*, 109, (D04311).

Boersma, K.F. (2005), Satellite observations of tropospheric nitrogen dioxide; retrieval interpretation and modelling, Ph.D Thesis, Universiteitsdrukkerij Technische Universiteit Eindhoven, Eindhoven

Bovensmann, H., Burrows, J.P. Buchwitz, M. Frerick, J. Noël, S. Rozanov, V.V. Chance, K.V. and Goede A.H. (1999). SCIAMACHY - Mission objectives and measurement modes. *Atmospheric sciences*, 56(2), 127-150.

Bucsela, E. J., Perring, A. E., Cohen, R. C., Boersma, K. F., Celarier, E. A., Gleason, J. F. Veefkind, J. P. (2008). Comparison of tropospheric NO_2 from in situ aircraft measurements with near-real-time and standard product data from OMI. *Geophysics Research*, (1984–2012), 113(D16).

Burrows, J.P., Weber, M., Buchwitz, M., Rozanov, V., Ladstatter-Weissenmayer, A., Richter, A., DeBeek, A., Hoogen, R., Bramstedt, K., Eichmann, K.U., and Eisinger, M. (1999). The global ozone monitoring experiment (GOME): Mission concept and first scientific results, *Atmospheric Sciences*

Bylin, G., (1993), Controlled studies on humans, Scand. Work, *Environment and Health*, 19 , suppl 2, 37-43

Calkins, M. (2008). *Materials for sustainable sites: a complete guide to the evaluation, selection, and use of sustainable construction materials*. John Wiley & Sons.

Canada, Federal-Provincial Advisory Committee on Air Quality. (1987). Review of National Ambient Air Quality Objectives for Nitrogen Dioxide. Ottawa: Environment Canada.

Cantrell, C. Technical note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems. *Atmospheric Chemistry and Physics* **2008**, *8*, 5477-5487.

Chiusolo, M., Cadum, E., Stafoggia, M., Galassi, C., Berti, G., Faustini, A., and Mallone, S. (2011). Short-term effects of nitrogen dioxide on mortality and susceptibility factors in 10 Italian cities: the EpiAir study. *Environmental health perspectives*, *119*(9), 1233.

Crutzen, P. J. (1979). The role of NO and NO_2 in the chemistry of the troposphere and stratosphere. Annual review of earth and planetary sciences., 7, 443-472.

DEFRA. (2003). Nitrogen Dioxide in the United Kingdom. The Air Quality Expert Group, Department for Environment, Food and Rural Affairs, The Scottish Executive, The National Assembly for Wales and The Department of the Environment in Northern Ireland.

European Community. 1985. Directive 85/203, March 7. Brussels. Forster

Gadhavi, H. S., Renuka, K., Ravi Kiran, V., Jayaraman, A., Stohl, A., Klimont, Z., and Beig, G. (2015). Evaluation of black carbon emission inventories using a Lagrangian dispersion model–a case study over southern India. *Atmospheric Chemistry and Physics*, *15*(3), 1447-1461.

Garg, A., Shukla, P. R., Bhattacharya, S., & Dadhwal, V. K. (2001). Sub-region (district) and sector level SO_2 and NOx emissions for India: assessment of inventories and mitigation flexibility. *Atmospheric Environment*, 35(4): 703-713.

Genium Publishing Corporation (Genium). (1999). Genium's Handbook of Safety, Health and Environmental Data for Common Hazardous Substances, McGraw Hill, New York, NY.

Gazdar, M.N. (1989). State of environment and our common future in Pakistan. Science and Technology, Islamabad, 8, 1-6.

Gottwald, M. Bovensmann, M. et al. (2006). SCIAMACHY, Monitoring the Changing Earth's Atmosphere, DLR, Institut für Methodik der Fernerkundung (IMF).

Hilboll, A.; Richter, A.; Burrows, J. Supplementary material to "long-term changes of tropospheric no2 over megacities derived from multiple satellite instruments". *Atmos. Chem. Phys* **2013**, *13*, 1-3.

Huang, J., Zhou, C., Lee, X., Bao, Y., Zhao, X., Fung, J. and Zheng, Y. (2013). The effects of rapid urbanization on the levels in tropospheric nitrogen dioxide and ozone over East China. *Atmospheric environment*, *77*, 558-567.

He, Y., Uno, I., Wang, Z., Ohara, T., Sugimoto, N., Shimizu, A., and Burrows, J. P. (2007). Variations of the increasing trend of tropospheric NO_2 over central east China during the past decade. *Atmospheric Environment*, 41(23), 4865-4876.

Heue, K. P., Richter, A., Bruns, M., Burrows, J. P., Friedeburg, C. V., Platt, U., and Wagner, T. (2005). Validation of SCIAMACHY tropospheric NO_2 columns with AMAXDOAS measurements. *Atmospheric Chemistry and Physics*, 5(4), 1039-1051.

Human Population Growth and Greenhouse Gas Emissions. (2008). Wilson Center.

International Programme on Chemical Safety (IPCS). (1997). Environmental Health Criteria 188. Nitrogen Oxides 2nd Edition. Published under joint sponsorship of the United Nations Environment Program (UNEP), the International Labour Organisation (ILO), and the World Health Organisation (WHO). Geneva, Switzerland, ISBN 92 4 157188 0. Available at http://www.inchem.org/documents/ehc/ehc/ehc188.htm (accessed July 24, 2007).

IPCC (2007): Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996.

Jaeglé, L., Martin, R. V., Chance, K., Steinberger, L., Kurosu, T. P., Jacob, D. J., and Galy-Lacaux, C. (2004). Satellite mapping of rain-induced nitric oxide emissions from soils. *Geophysical Research: Atmospheres* (1984–2012)., 109(D21).

Khan, N.A. (1987). Emissions from mobile sources in Pakistan. Science and Technology, Islamabad, 6, 25-37.

Khokhar, M. F., Frankenberg, C., Van Roozendael, M., Beirle, S., Kühl, S., Richter, A., and Wagner, T. (2005). Satellite observations of atmospheric SO_2 from volcanic eruptions during the time-period of 1996–2002. Advances in Space Research, 36(5): 879-887.

Khokhar, M.F. (2006). Retrieval and Interpretation of Tropospheric SO_2 from UV/VIS Satellites Instruments, M.sc thesis, der Universität Leipzig.

Khokhar, M.F.; Yasmin, N.; Fatima, N.; Beirle, S.; Wagner, T. Detection of trends and seasonal variation in tropospheric nitrogen dioxide over pakistan. *Aerosol and Air Quality Research* **2015**, *15*, 2508-2524.

Krotkov, N. A., Carn, S.A., Krueger, A.J., Bhartia, P.K. and Yang, K. (2006). Band residual difference algorithm for retrieval of SO_2 from the Aura Ozone Monitoring Instrument (OMI). IEEE Trans. Geoscience and remote sensing, 44(5), 1259–1266.

Kunhikrishnan, T., Lawrence, M. G., von Kuhlmann, R., Richter, A., Ladstätter-Weißenmayer, A. and Burrows, J. P. (2004). Analysis of tropospheric NOx over Asia using the model of atmospheric transport and chemistry (MATCHMPIC) and GOME-satellite observations. *Atmospheric Environment*, 38(4), 581-596.

Lee, D. S., Kohler, I., Grobler, E., Rohrer, F., Sausen, R., Gallardo- Klenner, L., Olivier, J. G. J., Dentener, F. J. and Bouwman, A. F. (1997). Estimations of global NOx emissions and their uncertainties. *Atmospheric environment*, 31(12): 1735–1749.

Leue, C., Wenig, M., Wagner, T., Klimm, O., Platt, U. and Jähne, B. (2001). Quantitative analysis of NOx emissions from Global Ozone Monitoring Experiment satellite image sequences. *Geophysical Research: Atmospheres* (1984–2012)., 106(D6), 5493-5505.

Levelt, P. F., van den Oord, G. H. J., Dobber, M. R., M¨alkki, A., Visser, H., de Vries, J., Stammes, Lundell J., and Saari, H. (2006), The Ozone Monitoring Instrument, IEEE Trans. *Geoscience and remote sensing*., 44(5), 1093–1101.

Lewis, RJ. Sr. (2002). Hawley's Condensed Chemical Dictionary. 14th Edition, John Wiley & Sons, Inc., New York, NY.

Likens, G. E., Wright, R. F., Galloway, J. N., & Butler, T. J. (1979). Acid rain. *Sci. Am.;(United States)*, *241*(4).

Logan, J. A., Prather, M. J., Wofsy, S. C. and McElroy, M. B. (1981). Tropospheric chemistry: A global perspective. Journal of Geophysical Research: Oceans (1978–2012), 86(C8), 7210-7254.

Majid, H., Madl, P., & Alam, K. (2012). Ambient air quality with emphasis on roadside junctions in metropolitan cities of Pakistan and its potential health effects. *Health*, *3*(3), 79-85.

Martin, R. V., Chance, K., Jacob, D. J., Kurosu, T. P., Spurr, R. J., Bucsela, E. and Koelemeijer, R. (2002). An improved retrieval of tropospheric nitrogen dioxide from GOME. *Geophysical Research: Atmospheres*, (1984–2012), 107(D20), ACH-9.

Mittal, M. L., Sharma, C., & Singh, R. (2012). Estimates of emissions from coal fired thermal power plants in India. In *2012 International Emission Inventory Conference*, (13-16).

Moffet, R. C., Foy, B. D., Molina, L. A., Molina, M. J., & Prather, K. A. (2008). Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry. *Atmospheric Chemistry and Physics*, *8*(16), 4499-4516.

Nieder, R., & Benbi, D. K. (2008). Bidirectional Biosphere-Atmosphere Interactions. *Carbon and Nitrogen in the Terrestrial Environment*, 235-305.

Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., Hayasaka, T., (2007). An Asian emission inventory of anthropogenic emission sources for the period 1980e2020. Atmospheric chemistry and physics, 7, 4419-4444.

Olivier, J.G.J. , A.F. Bouwman, Van Der Hoek, K.W. and J.J.M. Berdowski (1998), Global Air Emission Inventories for Anthropogenic Sources of NOx, NH_3 and N_2O in 1990. *Environmental pollution*, *102*, 135-148 Parton, W.J., E.A. Holland, S.J. Del Grosso, M.D. Hartman, R.E. Martin, A.R. Mosier, D.S.

O'Neil, M. (2006). The Merck index : An encyclopedia of chemicals, drugs, and biologicals, 14th Edition, Merck Research Laboratories, Division of Merck & Co. Inc. Whitehouse Station, NJ.

Pakistan Strategic Country Environmental Assessment, The World Bank, 2006.

Perner, D. and Platt, U. (1979). Detection of nitrous acid in the atmosphere by differential optical absorption. *Geophysical Research Letters*. 6(12), 917-920.

Platt, U and Stutz, J. (2008). Differential Optical Absorption Spectroscopy: Principles and Applications (Physics of Earth and Space Environments). Springer-Verlag, Berlin, Heidelberg.

Poberovskii, A. V., Shashkin, A. V., Ionov, D. V. and Timofeev, Y. M. (2007). NO_2 content variations near St. Petersburg as inferred from ground-based and satellite measurements of scattered solar radiation. Izvestiya, *Atmospheric and Oceanic Physics*. 43(4), 505-513.

Ray, J. D. (2001). Spatial distribution of tropospheric ozone in National Parks of California: interpretation of passive-sampler data. *The Scientific World JOURNAL*, *1*, 483-497.

Richter, A. and Burrows, J.P. (2002). Tropospheric NO_2 from GOME measurements. *Advances in Space Research*. 29, 1673–1683.

Richter, A., Burrows, J. P., Nüß, H., Granier, C. and Niemeier, U. (2005). Increase in tropospheric nitrogen dioxide over China observed from space. *Nature*. 437(7055), 129-132.

Schwartz, J. and Zeger, S. (1990). Passive smoking, air pollution, and acute respiratory symptoms in a diary study of student nurses. *Am Rev Respir Dis*. 141(1), 62-67

Schneider, K., Turner, J. L., Jaffe, A., & Ivanova, N. (2010). Choke Point China: Confronting water scarcity and energy demand in the world's largest country. *Environmental*, *12*, 713.

Seinfeld, J. H. and Pandis, S.N. (2006). Atmospheric Chemistry and Physics: From air pollution to climate change, second edition, John Wiley and Sons, New-York.

Sheel, V., Lal, S., Richter, A. and John P. B. (2010). Comparison of satellite observed tropospheric NO2 over India with model simulations. *Atmospheric Environment*. 44, 3314-332.

Stavrakou, T., Müller, J. F., Boersma, K. F. and De Smedt, I. (2008). Assessing the distribution and growth rates of NOx emission sources by inverting a 10-yearrecord of NO_2 satellite columns. Geophysical Research Letters. 35(10), L10801.

Thomas, W., Hegels, E., Slijkhuis, S., Spurr, R. and Chance, K. (1998). Detection of biomass burning combustion products in Southeast Asia from backscatter data taken by the GOME spectrometer. Geophysical research letters. 25(9), 1317-1320.

Thompson, A.M. (1992). The oxidizing capacity of Earth’s atmosphere: probable past and future changes. *Science.* 256, 1157–1165.

USEPA (United States Environmental Protection Agency). (1989). National Air Quality and Emission Trends Report, 1990. EPA-450/4-91-023. Research Triangle Park, N.C.

USEPA (United States Environmental Protection Agency). (1990). National Air Quality and Emission Trends Report, 1990. EPA-450/4-91-023. Research Triangle Park, N.C.

Van Aardenne, J. A., Carmichael, G. R., Levy II, H., Streets, D. and Hordijk, L. (1999). Anthropogenic NOx emissions in Asia in the period 1990–2020. *Atmospheric Environment*, 33(4), 633-646.

Wagner, T., Von Friedeburg, C., Wenig, M., Otten, C.and Platt, U. (2002). UV-visible observations of atmospheric O_4 absorptions using direct moonlight and zenith-scattered sunlight for clear-sky and cloudy sky conditions. *Geophysical research*, 107(D20), 4424.

Wallace, J., & Kanaroglou, P. (2009). The sensitivity of OMI-derived nitrogen dioxide to boundary layer temperature inversions. *Atmospheric Environment*, *43*(22), 3596-3604.

WHO (World Health Organization). (1977). "Oxides of Nitrogen." Environmental Health Criteria 4. Geneva.

WHO (World Health Organization). (1987). Air Quality Guidelines for Europe. WHO Regional Publications, European Series 23. Copenhagen: WHO Regional Office for Europe.

Worlds worst pollution problem report. (2010). Retrieved from http://www.worstpolluted.org/files/FileUpload/files/2010/WWPP-2010-Report-Web.pdf on 11-12-15

Zia-Ul-Haq, S. Tariq, M. Ali, K. Mahmood, S. A. Batool, and A. D. Rana, "A study of tropospheric NO_2variability over Pakistan using OMI data," *Atmospheric Pollution Research*, 5, 4, 709–720, 2015.