Temporal Assessment of NO$_2$ Pollution Levels in Urban Centers of Pakistan by Employing Ground-Based and Satellite Observations

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ABSTRACT

This study presents the assessment of nitrogen dioxide (NO$_2$) pollution within the twin cities of Islamabad and Rawalpindi by using car MAX-DOAS (Multi Axis-Differential Optical Absorption Spectroscopy) instrument during two different scenarios of with and without the availability of CNG (compressed natural gas) fuel. Information perceived from this study can be used to get an idea about recent air quality conditions of twin cities and its repercussions on ecological and human health. International air quality monitoring field campaigns were conducted during November 2012 and December 2013. Results showed different concentrations of NO$_2$ (68.2, 74.25 and 93.65 ppb) at various locations of Islamabad and Rawalpindi cities, exceeded the Pak-NEQS levels of 42.5 ppb. High NO$_2$ concentrations can be attributed to emissions from an oil refinery, traffic congestion and solid waste dump site along IJP road, and due to non-availability of CNG during December 2013. Results compared with OMI satellite observations exhibited that NO$_2$ columns from OMI observations are largely underestimated.

Keywords: CNG fuel; Car MAX-DOAS; Satellite validation; Air pollution; Pak-NEQS.

INTRODUCTION

Air pollution is on a continuous rise in major cities of Pakistan (Khawaja and Khan, 2005; Ilyas, 2007; Khattak et al., 2014) mainly due to rapid growth in population, motor vehicles, and industrial sectors. The combustion processes in vehicles and industry are the major source of air pollutants such as sulfur dioxide (SO$_2$ – WHO, 2005; Johansson et al., 2008; Kalabokas et al., 2012; Khattak et al., 2014), carbon monoxide (CO – WHO, 2005; Seinfeld and Pandis, 2012), nitrogen oxides (NO$_x$ – WHO, 2005; Frins et al., 2012; Shabbir et al., 2015; Khokhar et al., 2015a) and particulate matter (PM – Khokhar et al., 2016a and references therein) in the air. Globally, nitrogen oxides (NO$_x$ = NO + NO$_2$) are released through combustion of fossil fuel, biomass burning, lightning and microbiological processes in soil (Lee et al., 1997; Boersma et al., 2005; HSDB, 2007). Natural emissions account for approximately 10% through lightning and 15% are from the soil due to microbial activities (Lee et al., 1997). About 50% of NO$_x$ is released from industry and traffic and 20–25% from biomass burning (Oliver et al., 1998).

Motor vehicle numbers are growing at a rate of 11% per annum in Pakistan (ESoP, 2013; Khokhar et al., 2015a). Over the last two decades, the number of motor vehicles has risen from 2.71 million to nearly 9.08 million. The high rise is observed in a two-stroke engine and diesel vehicles (Colbeck et al., 2010; ESoP, 2013). Motor vehicles account for about 90 percent of the total emissions of hydrocarbons, NO$_x$, particulate matter and CO in Pakistan (Ghauri et al., 2007).

Humans exposed to toxic air pollutants for longer time periods (Parekh et al., 2001; Shabbir and Ahmed, 2010) may experience cardiovascular disorders (Miller et al., 2007), asthma (Wiwatanadate and Liwsrisakun, 2011), chronic obstructive pulmonary diseases such as bronchitis/emphysema (Pope, 2000) and other respiratory diseases (Dominici et al., 2006). Nitrogen dioxide (NO$_2$) once released into the atmosphere; is involved in important photochemical processes (Jacob, 1999; Platt and Stutz, 2008; Seinfeld and Pandis, 2012), and is toxic to human health and the environment (El Sayed, 1994; WHO, 2003, 2005). It actively participates in tropospheric ozone formation and can affect the oxidizing capacity of the atmosphere by reacting with volatile organic compounds (Jacob, 1999; Seinfeld and Pandis, 2012). It is also considered as a precursor for the formation of photochemical smog and acid rain. Uncertainties exist in the assessment of the total release of air pollutants and their effects on local, regional, and global scales (Ravishankara et al., 2004; Shaiganfar et al., 2011; Seinfeld and Pandis

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2012 and references therein). In order to assess the air quality and its effect on human health and the environment, continuous measurements of air pollutants such as NO₂ is mandatory (El-Sayed, 1994; WHO, 2003; Ravishankara et al., 2004; WHO, 2005; Seinfeld and Pandis, 2012; Shabbir et al., 2015). This study presents the measurements of tropospheric NO₂ within the twin cities of Islamabad and Rawalpindi by using car MAX-DOAS (Ibrahim et al., 2010; Shaiganfar et al., 2011; Shabbir et al., 2015) instrument. Islamabad is the capital city and Rawalpindi is the third most populous city in Pakistan. The metropolitan area of Islamabad-Rawalpindi lies between longitude 72°45’–73°30’E and latitudes 33°30’–33°50’N. Rapid increase of population in both cities (combined population estimated in 1998 was 1.94 million (PBOS, 2000) as compared to 0.99 million in 1971) has produced extra stress on natural resources and caused adverse effects on the surroundings. Various studies (Khan from (WHO, 2014) stated that 3 out of top 20 polluted routes in both cities (combined population estimated in 1998 was 1.94 million (PBOS, 2000) as compared to 0.99 million in 1971) has produced extra stress on natural resources and caused adverse effects on the surroundings. Various studies (Khan et al., 2007; Ali and Athar, 2008; Hussain, 2010; Ahmed et al., 2011; Jahangir et al., 2013; Khattak et al., 2014; Shabbir et al., 2015) have stated industrialization and unprecedented increase in the transportation sector as the main probable reasons for worsening air quality of major cities in South Asia (e.g., Garg et al., 2001; Ricther et al., 2005; Badarinath et al., 2006; Kunhikrishnan et al., 2006; Ghude et al., 2009; Cheng et al., 2012) and across the world. Very few studies have been conducted within the twin cities of Islamabad and Rawalpindi and indicated that NO₂ is high along the roads with frequent traffic congestions and heavy traffic (Ahmed et al., 2011; Zafar et al., 2012; Jahangir et al., 2013; Shabbir et al., 2015). A recent study (Khokhar et al., 2015a) has identified a temporal increase of approximately 8% per year from SCIAMACHY observations over the twin cities of Islamabad and Rawalpindi during the time period of 2003–2011.

Two field campaigns involving international scientists from Max-Planck Institute for Chemistry (MPI-Ch) Mainz, Germany and Institutes of Environmental Sciences and Engineering (IESE), National University of Sciences and Technology (NUST) Islamabad, Pakistan were conducted on 13 and 16 November 2012. While the third field campaign was conducted on 13 December 2013. All of three campaigns were conducted by using Multi-Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS - Fayt and van Roozendael, 2001; Hönninger et al., 2004; Wagner et al., 2004; Wittrock et al., 2004; Brinksma et al., 2008 and references therein) instrument mounted on a car roof (Ibrahim et al., 2010; Shaiganfar et al., 2011; Shabbir et al., 2015). Main objectives of the field campaigns were: (1) to quantify the NO₂ concentrations within twin cities of Islamabad and Rawalpindi, (2) to identify the positive impact caused by use of CNG (compressed natural gas) fuel by motor vehicles on urban air quality of twin cities, (3) to identify the regions with enhanced NO₂ pollution levels exceeding Pakistan’s national environmental quality standards (Pak-NEQS) and (4) to validate car MAX-DOAS measurements of tropospheric NO₂ with satellite observations over the domain of field campaigns.

**MATERIALS AND METHODS**

Mini MAX-DOAS is a fully automated instrument designed to measure the spectra of scattered sunlight at various elevation of the viewing angle (i.e., the angle between the horizontal and the viewing direction). For further details about instrument refer to (Bobrowski et al., 2003; Plats and Stutz, 2008; Shabbir et al., 2015). The measurements were controlled through a laptop using the DOAS intelligent system (DOASIS) software (Kraus, 2006). The sequence of elevation angles was set to: 1 × 90°, 4 × 30° and the time taken for an individual measurement were about 60 seconds. GPS data logger was used to record the geo-coordinates and took about 3 hours to complete one full circle along the route. Fig. 1 is exhibiting the roots (black – on 13 November 2012; red – on 16 November 2012; Blue – on 13 December 2013) of all field campaigns conducted within twin cities of Rawalpindi and Islamabad.

The measured spectra were analyzed using the DOAS (Platt and Stutz, 2008) method in a wavelength window of 405–455 nm. The absorption cross sections of several trace gases (NO₂ at 294°K (Vandaele et al., 1996), H₂O at 290°K (Rothman et al., 2005), O₂ at 243°K (Bogunil et al., 2003), O₃ (Hermans et al., 1999), a Fraunhofer reference spectrum, a Ring spectrum (calculated from the Fraunhofer spectrum by using DOASIS) and a polynomial of fifth order were included in the spectral fitting process by using WinDOAS software (Fayt and van Roozendael, 2001). The wavelength calibration was performed by using only O₂ absorption cross-sections and highly resolved solar spectrum (Kurucz et al., 1984). A typical NO₂ DOAS fit results are shown in Fig. 2.

The temperature of the miniMAX-DOAS instrument was set at 15°C for all the measurements. DOAS retrieval is strongly sensitive to the temperature of the detector as temperature variations of 0.1°C can cause root mean square errors of 1 × 10⁻⁴ (Coburn et al., 2011). The retrieved differential slant column densities (DSCDs) were filtered qualitatively by selecting only the data with root mean square (RMS) values smaller than 3.0 × 10⁻³. Geometric approximation of air mass factor (AMF) was used in order to convert DSCDs into vertical column densities (VCDs - Wagner et al., 2010; Li et al., 2012). The true AMF can deviate from the geometric approximation (Wagner et al., 2010) because of varying aerosol load, clouds condition, and vertical trace gas profile. For our measurements, variations of AMF are expected to be small because NO₂ generally occurs near the surface.

**Estimation of Tropospheric VCDs**

Tropospheric NO₂ VCDs were determined from the retrieved DSCDs according to the procedure described by Wagner et al. (2010). From the tropospheric NO₂ SCDs the tropospheric VCDs (VCDₜₒ₉) were calculated in the following way:

\[
VCD_{trop} = \frac{SCD_{trop} (x)}{AMF_{trop} (x)}
\]
Fig. 1. Tracks of three car MAX-DOAS field campaigns: black line – on 13 November 2012, Redline – on 16 November 2012 and blue line on – 13 December 2013 conducted in twin cities of Rawalpindi and Islamabad. The geographic locations were recorded every 3 seconds with the help of GPS data logger. Symbols are indicating the locations of the landfill site, international airport, and Attock oil refinery limited.

with AMF_{trop} as the tropospheric air mass factor and can be estimated using the geometric approximation (Hönninger et al., 2004; Brinksma et al., 2008; Ibrahim et al., 2010; Wagner et al., 2010; Halla et al., 2011) given by Eq. (2):

\[
AMF_{trop} = \frac{1}{\sin(\alpha)}
\]  

(2)

where \( \alpha \) is the elevation/viewing angle. The uncertainties introduced by the geometric approximation depend on the viewing geometry and the aerosol load. They are typically in the order of up to 20\% (Shaiganfar et al., 2011; Wagner et al., 2011; Lie et al., 2012).

**Tropospheric NO\textsubscript{2} Mixing Ratios**

In this study, tropospheric NO\textsubscript{2} VCDs for corresponding DSCDs at the off-zenith elevation angle, i.e., \( \alpha = 30^\circ \) were derived only. The VCD_{trop} are calculated according to the formula given by Eq. (3):

\[
VCD_{trop} = \frac{SCD_{trop} (30^\circ)}{AMF_{trop} (30^\circ)}
\]  

(3)

Furthermore, NO\textsubscript{2} mixing ratios from the retrieved NO\textsubscript{2} VCDs were also estimated. From car MAX-DOAS observations, no information on the tropospheric NO\textsubscript{2} profile can be derived (the NO\textsubscript{2} layer height had to be
estimated). It was assumed that the NO₂ is confined into a box profile between the surface and 500 m, which might be a good estimate close to strong emission sources (e.g., Wagner et al., 2011, Lie et al., 2012). In the first step the average NO₂ concentration is calculated:

\[ [\text{NO}_2] = \text{NO}_2 \text{ VCD}/5 \times 10^4 \text{ cm} \]  

(4)

here \([\text{NO}_2]\) indicates the NO₂ concentration in units of cm\(^{-3}\). \([\text{NO}_2]\) can be further converted into NO₂ mixing ratios (in units of parts per billion, ppb) by using air number density:

\[ \text{NO}_2 \text{ mixing ratio (ppb)} = [\text{NO}_2]/2.427 \times 10^{10} \text{ cm}^3 \]  

(5)

here the number density of dry air (at 500 meters above ground level, \(T = 284.9^\circ\text{K}, P = 95460.8 \text{ Pa}\)) is equal to \(2.427 \times 10^{19} \text{ molecules cm}^{-3}\), and the NO₂ mixing ratio is given in parts per billion (ppb). It should be noted that depending on the actual NO₂ layer height, the NO₂ mixing ratios derived from equations 3 and 4 can be subject to large uncertainties (e.g., ± 20% Shaiganfr et al., 2011). The resulting tropospheric NO₂ columns (molecules cm\(^{-2}\)) derived mixing ratios in parts per billion by volume (ppb) and its comparison with the Pakistan National Environmental Quality Standards (Pak-NEQS, Pak-EPA, 2012) are presented in Figs. 3 to 5 and are discussed in the following sections.

RESULTS AND DISCUSSIONS

Field Campaign on 13 November 2016

On 13 November 2012, the field campaign was conducted along the route (black line in Fig. 1) started from the main campus of NUST, Islamabad and entered the city of Rawalpindi through National Highway 05 (N5-Highway) of Pakistan. It runs through the center of Rawalpindi city and cater major fraction of both light and heavy traffic. Rawalpindi is the third most populated city in the Punjab province of Pakistan with a large number of cottage industry, international airport, high traffic density and industrial complex of Attock Oil Refinery limited. Tropospheric NO₂ columns (molecules cm\(^{-2}\)) measured during the first car MAX-DOAS field campaign on 13 November 2012 are presented in Fig. 3. Results exhibited peaks/enhanced NO₂ columns along various segments of the N5-highway. Especially, the road segments in the vicinity of the city center and Attock Oil Refinery Limited (AORL). The NO₂ VCDs were converted into surface mixing ratios by adopting method described in previous section 2 and given by Eq. (4) and Eq. (5). The derived NO₂ mixing ratios were compared against the Pak-NEQS of 42.5 ppb for NO₂ (Red dashed line). It clearly mentioned NO₂ pollution levels were exceeding the Pak-NEQS along the road segments with traffic congestion and in the vicinity of AORL.

Field Campaign on 16 November 2012

A second field campaign was conducted on 16 November 2012 and measurements were started from NUST main campus Islamabad and proceeded along the route (red line in Fig. 1) within the twin cities. It covered almost all important sectors of both cities. For instance, Sectors I-10 and its neighboring I-9 are main industrial regions of Islamabad comprising of electric, oil, marble, steel rolling and textile industries. An expressway "Kashmir Highway" transects the Islamabad city from West to East passing through almost all sectors of Islamabad city and catering major fraction of the vehicular traffic. In the West, it connects to the grand trunk road (N5-Highway) coming from Peshawar and heading towards Lahore cities passing by the huge industrial complex of Attock Oil Refinery Limited. Also, it passes by the international airport and connects to the Islamabad Express Highway carrying most of the traffic heading towards the capital city. Another road which caters both HTV and LTV
Fig. 3. Nitrogen dioxide VCDs (molecules cm$^{-2}$) and mixing ratios (ppb) within twin cities of Islamabad and Rawalpindi along the car MAX-DOAS route on 13 November 2012. Red dashed line is indicating the existing Pakistan National Environmental Quality Standards (Pak-NEQS). Local time (LT) of the day for which observations were made is presented on x-axis.

Fig. 4. Nitrogen dioxide VCDs (molecules cm$^{-2}$) and mixing ratios (ppb) within twin cities of Islamabad and Rawalpindi along the car MAX-DOAS route on 16 November 2012. Red dashed line is indicating the existing Pakistan National Environmental Quality Standards (Pak-NEQS). Local time (LT) of the day for which observations were made is presented on x-axis.
vehicles of Islamabad and Rawalpindi is called Islamabad Junction Principal (IJP) road and was also monitored. The measured tropospheric NO₂ columns during second field campaigns are presented in Fig. 4. Results exhibited peaks in NO₂ columns along various segments of IJP and the N5-highway: close to the landfill site, international airport and in the vicinity of AORL. NO₂ mixing ratios were compared against the Pak-NEQS of 42.5 ppb for NO₂ (Red dashed line). It clearly indicated that NO₂ 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.

Field Campaign on 13 December 2013

A third field campaign was conducted on 13 December 2013 along the route (blue line in Fig. 1). The main objective was to monitor the NO₂ levels of similar areas of twin cities explored during the second car-MAX-DOAS field campaign. Due to ongoing construction activities for expansion of Kashmir Highway and Metro Bus mass transit system, we could not follow exactly the same route as in the case of the second field campaign. The measured tropospheric NO₂ columns are presented in Fig. 5. Results exhibited huge peaks in NO₂ columns along various segments of IJP, Kashmir Highway, Margalla road and the N5-highway. It is worth to mention that in various regions of twin cities the NO₂ columns were about an order of magnitude larger than previously monitored NO₂ levels during November 2012. The reasons behind these enormous NO₂ levels are discussed in the next section.

Spatial Analysis

Fig. 6 presents the comparison of NO₂ VCD retrieved from the car-MAX-DOAS measurements performed during November 2012 and December 2013. NO₂ VCDs are overlaid on Google map of Islamabad and Rawalpindi cities. Gaps within the car MAX-DOAS observations are due to interruptions caused by the bumpy roads and VCDs filtered out based on RMS values (data quality flag). Highest NO₂ VCDs were found within the city of Rawalpindi. It was 8.01 × 10¹⁶ molecules cm⁻² (average VCDs = 3.65 × 10¹⁶ molecules cm⁻²) on 13 November, 2012, 8.72 × 10¹⁶ molecules cm⁻² (average VCDs = 2.24 × 10¹⁶ molecules cm⁻²) on 16 November, 2012 and 11.3 × 10¹⁶ molecules cm⁻² (average VCDs = 6.05 × 10¹⁶ molecules cm⁻²) on 13 December, 2013. Especially, larger peaks are observed along the road segments with heavy traffic, frequent traffic jam and in the vicinity of Attock Oil Refinery and open solid waste dump site. As diurnal variation in the emissions of various air pollutants is also driven by anthropogenic activities such as peak traffic hours etc. In major cities of Pakistan, first episode of peak traffic hour is observed during 08:00 to 10:00 hours because a huge mass of people commutes from their homes to school, offices and business places. Second episode is observed during the afternoon hours around 14:00 to 15:00 hours when school activities are finished. Third episode is observed right after the second one around 16:00 to 17:00 hours when office/factory workers commute back to their houses. Besides locally registered vehicles, on average about 32309 vehicles enters

Fig. 5. Nitrogen dioxide VCDs (molecules cm⁻²) and mixing ratios (ppb) within twin cities of Islamabad and Rawalpindi along the car MAX-DOAS route on 13 December 2013. Red dashed line is indicating the existing Pakistan National Environmental Quality Standards (Pak-NEQS). Local time (LT) of the day for which observations were made is presented on x-axis.
Fig. 6. Presents the comparison of tropospheric NO₂ VCDs measured in November 2012 and December 2013 within twin cities of Islamabad and Rawalpindi. Car MAX-DOAS measurements are plotted over Google map of both cities. Arrows in each map show the wind direction for that particular day and time. Wind data is taken from NASA global meteorological model (http://ready.arl.noaa.gov/READYamet.php).

The twin cities on a daily basis (NHA, 2010) making vehicular emissions as a significant source of various air pollutants (Khawaja and Khan, 2005; Ilyas, 2007; Shabbir et al., 2015) in the study area. Peaks in NO₂ concentrations observed along IJP road can be attributed to a frequent traffic jam caused by ongoing construction of Pir Wadhy flyover and open solid waste dumping (landfill) site. Similarly, high levels of NO₂ were monitored during December 2013 along Margalla road, IJP roads, landfill site and segments of N5- and Kashmir Highways. Due to the expansion of Kashmir Highway and construction of new mass transit system (Metro Bus) within twin cities, traffic flow was quite slow and frequent traffic jams were common in the twin cities. Additionally, most of the traffic from Rawalpindi heading towards Islamabad was shifted from the conventional route (via 9th avenue) to Kashmir Highway via Margalla road. An interesting feature is observed during the month of December 2013. NO₂ levels were overall larger than previously observed during November 2012. Especially, the enhanced levels are observed along the busy roads of both cities. It was investigated and most probable reason was due to non-availability of compressed natural gas (CNG) as fuel for vehicles. As CNG fuel is relatively environment-friendly because it results in lowering the emissions of various air pollutants e.g., particulate matter, NOₓ, SO₂ (Suthawaree et al., 2012 and references therein). Pakistan is recently experiencing an extensive shortage of power and natural gas outages. Therefore, in order to facilitate the domestic usage (cooking and heating) of natural gas, commercial sales of natural gas for vehicles was banned for the period of December 2013 to February 2014. Various studies have reported the decrease in NO₂ emissions due to increased usage of CNG in vehicles (Ravindra et al., 2005; Goyal et al., 2006; Suthawaree et al., 2012; Agarwal, 2015). Similarly, an interesting feature was observed during the comparison of field campaigns conducted in twins’ cities during two different scenarios: i) on 16 November 2012 when CNG was available and ii) on 13 December 2013 when CNG was not available for vehicles. Enhanced NO₂ levels (maximum = 1.13 × 10¹⁷ molecules cm⁻² and average = 6.05 × 10¹⁶ molecules cm⁻²) observed for scenario when CNG was not available were about a factor of 1.3 larger than as compared to the scenario with available CNG (maximum = 8.75 × 10¹⁶ molecules cm⁻² and average = 2.24 × 10¹⁶ molecules cm⁻²). Therefore, the observed high levels of NO₂ during December 2013 are likely to be caused by the excessive use of conventional fuel (diesel and petrol) as compared to November 2012.

Oil refineries are also subjected to the pollution of many gasses including NO₂ (CCME, 2005). High NO₂ concentrations on all occasions observed in the vicinity of AORL are evident of the NO₂ pollution caused by refinery itself.

A spatial gradient of NO₂ distributions over the domain of field campaigns can be clearly identified from Fig. 6. On 13 November 2016, southeastern while on 16 November 2012 and 13 December 2013, north-western regions are exhibiting higher NO₂ levels. It was investigated by exploiting 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 Fig. 6. Spatial distribution of NO₂ VCD indicated very interesting
behavior and the role of meteorological parameters especially wind direction. Besides stationary sources (landfill site and AORL), the wind direction and speed has caused the polluted air masses being transported to southeastern and the north-western regions in the study area on respective days. Surprisingly, on both occasions, NO_2 columns observed in the vicinity of the international airport was not high as compared to other areas of the twin cities. Probably, it can be explained by the fact that most of the airlines execute their flight operations during the night. As car MAX-DOAS field campaign was conducted during noon time, therefore, it was not able to measure high NO_2 levels caused by airport operations during the night. Owing shorter lifetime, nighttime NO_2 might have been converted to other species (NO_3, N_2O_5, HNO_3 – Platt and Stutz, 2008; Seinfeld and Pandis, 2012) as well. 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 dire need of a country like Pakistan with no proper and regular air quality monitoring setup (ESoP, 2013; Khattak et al., 2014; Khokhar et al., 2015a, b; Khokhar et al., 2016b).

**Ambient Air Quality within Twin Cities**

Decent growth in industrial sector and rapid urbanization resulted in in rapid growth of infrastructure in cities together with growth in road transport. Due to the liberal leasing system adopted by the financial institutions, the density of transport has increased many folds on the roads of Pakistan. The present road infrastructure in many cities of Pakistan cannot cater the need of growing automobiles flow. The result is frequent traffic jams and consequent release of toxic air pollutant like NO_2, SO_2, CO and VOCs and deteriorated air quality in Pakistani cities (Khattak et al., 2014; Shabbir et al., 2015). According to the National Transport Research Center (NTRC), total number of registered vehicle increased by 220% from 1990 to 2011 (ESoP, 2013). Recent reports form (WHO, 2014) stated that 16 out of top 20 polluted cities are located in the Indian subcontinent (WHO, 2014) and among them 3 are from Pakistan.

Nitrogen Dioxide being one of the criteria pollutant has been monitored within major cities of Pakistan by few studies (e.g., Khan et al., 2007; Ali and Athar, 2008; Hussain, 2010; Ahmed et al., 2011; Jahangir et al., 2013). In Pakistan, NO_2 pollution is being contributed by transportation (54%), power plants (20%), industries (10%) and agriculture (6%) (Khwaja and Khan, 2005; Ghuari et al., 2007; Ilyas, 2007). According to a recent study (Khokhar et al., 2015a) by using multi-sensor satellite observations during the time period of 2002–2012, indicated that NO_2 levels are highest over the urban centers of Pakistan. It identified a temporal increase of 8% per year in NO_2 columns over the cities of Islamabad and Rawalpindi.

The studies carried out in Pakistan on NO_2 pollution (e.g., Ali et al., 2008; Zafar et al., 2012; Ahmed and Aziz, 2013; Jahangir et al., 2013; Khokhar et al., 2015a; Shabir et al., 2015) are listed in Table 1 and unanimously identified vehicles and frequent traffic jams as major source of NO_2 emissions (54% - Khawaja and Khan, 2005) in major cities of Pakistan. Main purpose was to summarize the temporal evolution of NO_2 pollution levels reported by the previous studies and to compare them against the Pak-NEQS of 42.5 ppb for NO_2.

Air quality issues regarding transport sector can be addressed partially if not completely by maintaining the better traffic flow and management/planning in the urban centers of Pakistan. Further improvements can be obtained by strict enforcement of vehicular emissions and traffic laws, implementation of catalytic converters to all vehicles, use of environment friendly fuels (e.g., low Sulphur and CNG), mass transit system and raising awareness among public about vehicle inspection and maintenance practices. As it can be clearly seen from the comparison presented in Fig. 6, low NO_2 columns were measured within the twin cities during November 2012 when CNG was available for vehicles as compared to NO_2 columns measured in December 2013 (when CNG was banned for vehicles in order to facilitate domestic user).

**Comparison with Satellite Observations**

Monitoring of boundary layer pollution (especially weak absorbing gasses such as NO_2, SO_2, BrO, HCHO, Glyoxal etc.) from satellite instrument is a great challenge (Platt and Stutz 2008). The main reason is reduced sensitivity of satellite instruments towards the boundary layer pollution because of increasing air density and aerosol, presence of clouds (Khokhar et al., 2005, 2008) and atmospheric scattering usually occurs within or above the trace gas layer. These effects can be corrected, but it requires precise information on vertical distributions of trace gasses, aerosols, and clouds, which is usually not available for the same ground scene of satellite observations. Therefore, validation of satellite observations with in-situ and ground-based observations is direly needed. In this section, tropospheric NO_2 VCDs derived from car MAX-DOAS measurements are compared with ozone monitoring instrument (OMI - Level-2 data downloaded from the NASA GES DISC website http://disc.sci.gsfc.nasa.gov/Aura). For a detailed description of OMI products please refer to Levelt et al. (2006) and Boersma et al. (2007). Satellite ground pixels usually extend over dimensions of 10 km to 100 km (OMI pixel size at nadir view = 13 × 24 km²), the direct comparison between MAX-DOAS observations and satellite observations is further complicated by the horizontal gradients of the trace gas distribution (Shaiganfar et al., 2011 and references therein). Thus, car MAX-DOAS is a valuable technique to measure the horizontal variability within a satellite ground pixel. It has been successfully used for satellite comparison over various parts of the world (e.g., Boersma et al., 2007; Kramer et al., 2008; Halla et al., 2011; Shaiganfar et al., 2011; Li et al., 2013; Ma et al., 2013). In this study, OMI observations for nadir pixels of size 13 × 24 km² and cloud fraction less 30% were used. Fig. 7 presents the comparison of OMI tropospheric NO_2 VCDs with car MAX-DOAS measurements (colored dots) on 16 November 2012 and 13
Table 1. Air quality monitoring studies carried out in major cities of Pakistan.

<table>
<thead>
<tr>
<th>Study</th>
<th>City/Region</th>
<th>Monitoring Month</th>
<th>Method</th>
<th>Maximum and Average NO₂ Mixing Ratios (ppb) and VCDs</th>
<th>Location of Maximum NO₂ Observed (lat., Lon.)</th>
</tr>
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<tbody>
<tr>
<td>JICA, 2000</td>
<td>Lahore</td>
<td>April 2000</td>
<td>Diffusion Samplers</td>
<td>68.2</td>
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<td></td>
<td>Islamabad</td>
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<td>Rawalpindi</td>
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<td>Rawalpindi</td>
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<td>Diffusive Passive</td>
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<td></td>
<td>Islamabad</td>
<td></td>
<td>Sampling</td>
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<td></td>
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<tr>
<td>Zafar et al., 2012</td>
<td>Islamabad</td>
<td>January–February, 2011</td>
<td>Diffusive Passive Sampling</td>
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<td>Islamabad Airport (33.5555°N, 72.8338°E)</td>
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<td>Rawalpindi</td>
<td>March–April, 2011</td>
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<td></td>
<td>Islamabad</td>
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<td>6.9</td>
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<td>Rawalpindi</td>
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<td>Nisar, 2013</td>
<td>IESE-NUST</td>
<td>February–March, 2013</td>
<td>mini MAX-DOAS</td>
<td>23.97 (avg.) 48.67 (max.)</td>
<td>IESE-NUST Site (33.6457°N, 72.9929°E)</td>
</tr>
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<td>Islamabad</td>
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<td></td>
<td>(VCD = 3.65 × 10¹⁶ molecules cm⁻²)</td>
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<tr>
<td>Shabbir et al., 2015</td>
<td>N-5 Highway (Islamabad to Lahore section)</td>
<td>November 2012</td>
<td>car MAX-DOAS</td>
<td>17.90 (avg.) 68.2 (max.),</td>
<td>Attock oil refinery (33.557°N, 73.0791°E)</td>
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<td>8.01 × 10¹⁶ molecules cm⁻²</td>
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<td>17.90 (avg.) 72.88 (max.)</td>
<td>Mahmood Boti Lahore (31.6078°N, 74.3933°E)</td>
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<td>9.92 × 10¹⁶ molecules cm⁻²</td>
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<tr>
<td>This Study</td>
<td>Islamabad and Rawalpindi</td>
<td>November 13, 2012</td>
<td>car MAX-DOAS</td>
<td>31.14 (avg.) 68.20 (max.)</td>
<td>Attok Oil Refinery (33.557°N, 73.0791°E)</td>
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<td>8.01 × 10¹⁶ molecules cm⁻²</td>
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<td>December 13, 2013</td>
<td>car MAX-DOAS</td>
<td>74.25 (max.) 93.65 (maximum)</td>
<td>IJP Road Islamabad (33.621°N, 73.005°E)</td>
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<td>8.72 × 10¹⁶ molecules cm⁻²</td>
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<td>51.56 (average)</td>
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<td></td>
<td></td>
<td>1.13 × 10¹⁷ molecules cm⁻²</td>
<td>N5-Highway (33.647°N, 73.012°E)</td>
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</table>
The satellite validation becomes important over larger cities due to large variability and strong gradients (Chen et al., 2009) of air pollutants on both spatial and temporal scales. Only two ground pixels of OMI were able to cover the spatial extent of field campaign domain and were used for comparison with car MAX-DOAS measurements on respective days. Both pixels were referred as a western and eastern pixel. Satellite observations of tropospheric NO$_2$ was largely underestimated over the twin cities. The maximum OMI VCDs for NO$_2$ over Islamabad and Rawalpindi was found to be $8.67 \times 10^{15}$ molecules cm$^{-2}$ whereas car MAX-DOAS observed higher NO$_2$ VCDs in the range of $8.72 \times 10^{15}$ molecules cm$^{-2}$ on 16 November 2012. Similarly, OMI observed maximum NO$_2$ VCDs of $7.96 \times 10^{15}$ on 13 December 2013 as compared to car MAX-DOAS observations of $11.3 \times 10^{16}$ molecules cm$^{-2}$. Especially, the comparison with the 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 rectangles in the Fig. 7) close to the airport area which coincides with the OMI overpass (around 13:00 local time) over Islamabad-Rawalpindi. So the observed difference can be attributed to spatial resolution because satellite observed NO$_2$ columns are averaged over a ground pixel of size ($13 \times 24$ km$^2$) while car MAX-DOAS observations are just point measurement. Furthermore, differences are observed due to different observation time (the difference is relatively smaller for satellite overpass 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. It is worth to note that tropospheric NO$_2$ VCDs are largely underestimated by satellite instrument close to a larger source like AORL, N5-highway and landfill site areas as compared to other areas and these findings are consistent with previous studies (e.g., Nisar, 2013; Shabbir et al., 2015).

**CONCLUSIONS**

Car MAX-DOAS observations were performed within the cities of Islamabad and Rawalpindi during November 2012 and December 2013. Enhanced NO$_2$ column densities were found on the road segments along landfill site, IJP road, Margalla road, N5-highway and in the vicinity of Attock Oil.
Refinery Limited. Higher levels of NO₂ concentrations are attributed to the traffic jam, open solid waste burning site, and industrial activities in the twin cities. Maximum NO₂ pollution levels of 67.03 ppb and 74.25 ppb were observed in the city of Rawalpindi during both field campaigns on 13 and 16 November 2012, respectively. Whereas, enormous high NO₂ concentrations of 93.65 ppb were found during field campaign on 13 December 2013. These high concentrations of NO₂ in twin cities are attributed to non-availability of CNG and frequent traffic jams caused by construction activities. Therefore, use of environmentally friendly fuels such as CNG should be encouraged in order to improve the air quality of urban centers of Pakistan in addition to other measures (e.g., proper management and maintenance of the vehicle fleet, traffic management etc.).

Comparison of tropospheric NO₂ VCDs between OMI and car MAX-DOAS observations revealed that satellite observations are found to be an order of magnitude lower. The difference is significantly larger over highly polluted regions and during December 2013. The reason for this quantitative disagreement is mainly due to less sensitivity of satellite towards ground level pollution. Also, satellite observations are representative of large area i.e., (13 × 24 km²) as compared to car MAX-DOAS observations, which represents only point observations. This study is unique in a sense that car MAX-DOAS field campaign was first time conducted in Pakistan and tropospheric NO₂ columns were compared with OMI satellite observations over twin cities of Pakistan. The outcome of this study will provide vital information about recent NO₂ pollution levels within the cities of Islamabad and Rawalpindi to various stakeholders concerned with air pollution issues and mitigation strategies in Pakistan.

ACKNOWLEDGMENTS

Authors gratefully acknowledge the Level-2 OMI data downloaded from the NASA GES DISC website (http://disc.sci.gsfc.nasa.gov/Aura). Very special gratitude goes to MPI-Ch Mainz, Germany for providing mini MAX-DOAS instrument and technical guidance, and to NUST and Pakistan Science Foundations (PSF) for providing partial financial support from MS research fund to conduct field campaign. Our acknowledgment will be incomplete without mentioning the Wind data, taken from NASA global meteorological model freely available at (http://ready.arl.noaa.gov/READYamet.php).

REFERENCES


