Simultaneous Observations of Nitrogen Dioxide, Formaldehyde and Ozone in the Indo-Gangetic Plain

Mriganka Sekhar Biswas¹,², Sachin Ghude¹, Dinesh Gurnale¹, Thara Prabhakaran¹, and Anoop S. Mahajan¹*

¹. Indian Institute of Tropical Meteorology, Ministry of Earth Sciences, Pune, 411008, India
². Savitribai Phule Pune University, Pune, India

Abstract

This study reports concentrations of nitrogen dioxide (NO₂) and formaldehyde (HCHO) retrieved using the Multi AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) technique and collocated observations of surface ozone (O₃) conducted over the Indo-Gangetic Plain (IGP). Observations were conducted during the 2014 monsoon period as a part of the Cloud Aerosol Interaction and Precipitation Enhancement Experiment (CAIPEEX). The average daytime NO₂ mixing ratio was 0.81 ± 0.20 ppbv (parts per billion by volume) (range: 0.08 ppbv to 6.06 ppbv). NO₂ was observed to decrease through the morning between 0600 to 0900 hours local time and then stabilise for the rest of the day. The average daytime HCHO mixing ratio was 1.93 ± 0.60 ppbv (range: 0.32 ppbv to 8.81 ppbv). Unlike NO₂, HCHO increased during the early morning driven by daytime photochemical formation from hydrocarbon precursors. The averaged O₃ mixing ratio during the daytime was 30.0 ± 13.0 ppbv (range: 2.7 ppbv to 81.9 ppbv) and 22.5 ± 10.2 ppbv (range: 1 ppbv to 63 ppbv) during the night time. Analyses using back trajectories found that the NO₂ mixing ratios during CAIPEEX-2014 were affected by long-range transport from thermal power plants situated about 110 km to the South. The HCHO mixing ratios and O₃ production did not show any indication of long-range transport but were instead dominated by local emissions. These observations suggest that in the rural IGP ozone concentrations are affected more by local sources than long range transport.

Keywords: Nitrogen dioxide; Formaldehyde; Ozone; Indo-Gangetic Plains;

Highlights
- Simultaneous observations of NO₂, HCHO and O₃ in the Indo-Gangetic plain (IGP)
- Power plants located ~110 km towards the south affect the local NO₂ concentrations
- HCHO concentrations are homogenous over the region
- Ozone concentrations are affected more by local sources than long range transport

* Corresponding author: Tel: +91 20 25904526
E-mail address: anoop@tropmet.res.in
INTRODUCTION

Nitrogen dioxide (NO$_2$) is one of the most important trace gases in the atmosphere (Crutzen, 1979). Apart from being an atmospheric oxidant and pollutant (Burnett et al., 2004), it acts as a precursor for ozone (O$_3$) (Crutzen, 1970) and affects the hydroxyl radical (OH) abundance through reactive photochemistry. As a pollutant, NO$_2$ is associated with various health hazards (World Health Organization, 2013) and contributes towards acid rain and nitrate aerosol formation. It plays an indirect role in secondary aerosol formation (Chan et al., 2010) and locally contributes towards changes in radiative forcing (Solomon et al., 1999), hence indirectly affecting the climate system. Elevated tropospheric NO$_2$ abundance usually coincides with other atmospheric pollutants and hence it can be used as proxy for atmospheric pollution in general (Mayer, 1999; Molina and Molina, 2004). Major anthropogenic sources of NO$_2$ include high temperature combustion of fossils fuels, biomass burning, industries, thermal power plants, automobiles etc. Forest fires, lightning and soil microbial processes are considered to be the main natural sources (Jaeglé et al., 2005). Formation of nitric acid (HNO$_3$) during the daytime, dinitrogen pentoxide (N$_2$O$_5$) hydrolysis during night along with dry deposition and transport are the dominant sinks of tropospheric nitrogen oxides (NO$_x$) (Finlayson-Pitts and Pitts, 2000; Jacob, 2000). Understanding of current emissions (Martin et al., 2006), evaluation of chemical transport models (Huijnen et al., 2010 and references therein; Zyrichidou et al., 2009), tracking changes in the anthropogenic emissions (Stavrakou et al., 2008; Wang et al., 2012) have been studied using satellite retrieved NO$_2$ columns. Observations of NO$_2$ (Constantin et al., 2013; Johansson et al., 2009; Wagner et al., 2010) using the Differential Optical Absorption Spectroscopy (DOAS) technique (Noxon, 1975; Solomon et al., 1987) have been reported at various locations around the world and in several cases have been used for retrieving vertical profiles of atmospheric NO$_2$.
Formaldehyde (HCHO) is the most abundant and smallest carbonyl compound observed in the troposphere (Hak et al., 2005 and references therein). It is an intermediate oxidation product of various volatile organic compounds (VOCs). HCHO has biogenic (e.g. vegetation), pyrogenic (mainly biomass burning) and anthropogenic (e.g. industrial emissions and automobiles) sources (Carlier et al., 1986; Fu et al., 2007; Hak et al., 2005; Herndon et al., 2005; Lee et al., 1997; Smedt et al., 2010). The background levels of HCHO are mainly sustained by oxidation of long-lived VOCs like methane, whereas the spatial variability of HCHO is primarily associated with the oxidation of shorter lived, reactive non-methane VOCs of biogenic (e.g., isoprene) or anthropogenic (e.g., butane) origin. Being an oxidation product, HCHO is an useful indicator of biogenic and anthropogenic emissions of hydrocarbons (Andreae and Merlet, 2001; Barkley et al., 2013; Geiger et al., 2002; Seco et al., 2007; Stavrakou et al., 2014, 2009). Photolysis and oxidation by OH radicals, yielding hydroperoxyl radicals (HO₂) and carbon monoxide (CO) (hence affecting the global CO budget and the oxidative capacity of the atmosphere), is the main removal process for atmospheric HCHO. Dry and wet depositions are the other important removal processes of HCHO (Atkinson, 2000). Being a crucial participant in tropospheric O₃ formation (thereby affecting air quality), the monitoring of the spatial and temporal variability of HCHO is essential (Abbot, 2003; De Smedt et al., 2008). Satellite observations of tropospheric HCHO columns have been successfully reported for over two decades (Chance et al., 2000; De Smedt et al., 2008; Palmer et al., 2001; Wittrock et al., 2006). These observations have helped study the spatial and temporal trends, and to estimate the emissions of VOCs (Barkley et al., 2013; Gonzi et al., 2011). Higher concentrations of HCHO associated with areas of dense
vegetation and biomass burning indicates that on a global scale the major sources are of biogenic origin (Vrekoussis et al., 2010).

O₃ plays an important role in atmospheric chemistry (Barrie et al., 1988; Crutzen, 1974, 1970; Logan et al., 1981). Surface O₃ is a major pollutant and a greenhouse gas affecting the global radiation budget (IPCC, 2007). In the troposphere, O₃ acts as a secondary pollutant formed in the presence of sunlight and its precursors e.g., NOₓ, VOCs etc. (Fishman and Crutzen, 1978). Stratospheric subsidence is another source of tropospheric ozone (Holton et al., 1995). Ozone participates in the formation of OH, thus affecting the oxidising capacity of the atmosphere. Increased levels of tropospheric ozone have an adverse effect on human health (Desqueyroux et al., 2002) and crop yield (Ghude et al., 2014; Morgan et al., 2006). Increase in anthropogenic emissions by fossil fuel combustion in power plants, large-scale industries and vehicular emissions have led to an increase in the surface O₃ concentrations over the past few decades (Peleg et al., 1997; Ryerson et al., 2001; Sillman and Samson, 1995). Solar radiation, higher water vapour content in the atmosphere, along with increased NOₓ and VOC concentrations leads to higher photochemical production of O₃ in the tropical regions (Andreae and Crutzen, 1997; Crutzen, 1970; Sánchez et al., 2005). NO₂ participates as a catalyst and in presence of solar radiation, photochemically dissociates to form NO (nitrogen oxide) and O(³P).

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}(³\text{P}) \quad \text{(R1)}
\]

The resultant oxygen atom then reacts with molecular oxygen to form O₃. On further reaction with the HO₂ radical, NO converts back into NO₂, which continues the catalytic O₃ production process.

\[
\text{O}(³\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{(R2)}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad \text{(R3)}
\]
O<sub>3</sub> also photolysis at wavelengths <310 nm to form O(1D), which then reacts with water vapour
to yield OH radicals.

\[ \text{O}_3 + h\nu \rightarrow \text{O} (1\text{D}) + \text{O}_2 \]  
(\text{R4})

\[ \text{O} (1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  
(\text{R5})

Oxidation of methane (and other NMVOCs) by OH radical forms HO<sub>2</sub> and HCHO (higher
aldehydes in case of NMVOC oxidation). Further photochemical oxidation of formaldehyde with
OH radicals also results in the formation HO<sub>2</sub> (R10-12).

\[ \text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]  
(\text{R6})

\[ \text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} \]  
(\text{R7})

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]  
(\text{R8})

\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \]  
(\text{R9})

\[ \text{HCHO} + h\nu \rightarrow \text{H} + \text{HCO} \]  
(\text{R10})

\[ \text{HCHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HCO} \]  
(\text{R11})

\[ \text{HCHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HCO} \]  
(\text{R12})

\[ \text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \]  
(\text{R13})

At night, in the absence of sunlight, O<sub>3</sub> reacts with NO<sub>2</sub> to form the nitrate radical (NO<sub>3</sub>), which
can eventually lead to the removal of NO<sub>x</sub> from the atmosphere as mentioned earlier

\[ \text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 \]  
(\text{R13})

The Indo-Gangetic Plain (IGP) region spans over ~21% of the Indian subcontinent land area,
accommodating ~40% of the Indian population (Nair et al., 2007). Coal-based thermal power
plants (Prasad et al., 2006), coal-based small and medium industries, biomass burning and bio-
fuel burning for domestic cooking (Reddy and Venkataraman, 2002) are the main sources for
atmospheric pollutants in the IGP. Precise knowledge of NO<sub>2</sub>, HCHO, O<sub>3</sub> sources and monitoring
of their abundance are very important to determine their exact role in atmospheric chemistry on a local, regional and global scale. Recent studies over India have studied the inter-annual variation of NO$_2$ and HCHO using several years of satellite based data (De Smedt et al., 2008; Ghude et al., 2013; Hilboll et al., 2013; Mahajan et al., 2015; Smedt et al., 2010). However, scant information from ground based instruments is available in India to validate the satellite observations (Mandal et al., 2012; Pandey et al., 1992; Reddy et al., 2012; Sharma et al., 2010). Ground based observations of HCHO in India are rare (Dutta et al., 2010; Khare et al., 1997a, 1997b) and further satellite validation is necessary, especially considering a model-satellite discrepancy (Mahajan et al., 2015). In a recent study, MAX-DOAS observations of NO$_2$ and HCHO have been reported from IGP region (Pantnagar, 29.03°N, 79.47°E) for the year 2017 (Hoque et al., 2018). The HCHO mixing ratios were found to be in the range of 2-4 ppbv for July and August 2017 and between 4-6 ppbv for September 2017. The NO$_2$ mixing ratios were found to be between 0.5-1 ppbv for July and August 2017 and less than 0.5 ppbv in September 2017. Various groups have conducted studies over India and reported elevated levels of O$_3$ during late autumn and winter, extending through May (Beig et al., 2007; Ghude et al., 2008; Jain et al., 2005; Lal et al., 2000; Mittal et al., 2007; Nair et al., 2002; Naja and Lal, 2002). Low altitude rural sites in India show maximum O$_3$ concentrations in the summer and winter, and minimum concentrations during the Asian Summer Monsoon (ASM) season (Debaje and Kakade, 2006; Reddy et al., 2011). In another recent study, decadal changes of surface ozone were reported over ~40 years (1973 - 2014) from Thiruvananthapuram (8.542° N, 76.858° E) in peninsular India (Nair et al., 2018). The ozone mixing ratios were found in the range of 10-20 ppbv for the month of July, August and September over the 40 years of observations.

In this study, we report the retrieval of NO$_2$ and HCHO using the Multi axis Differential Optical Absorption Spectroscopy (MAX-DOAS) technique along with surface O$_3$ observations carried
out during the Cloud Aerosol Interaction and Precipitation Enhancement Experiment (CAIPEEX-2014). We also investigate the effect of long range transport of O₃ precursors and ascertain the main drivers of O₃ over a rural site in the IGP.

MEASUREMENT SITE AND METHODS

MEASUREMENT SITE

The CAIPEEX-2014 campaign was carried out at the Rajiv Gandhi South Campus, Banaras Hindu University at Barkachha in Mirzapur district, Uttar Pradesh, 169 m above the mean sea level (25.06°N, 82.59°E; Figure 1). The site represents a rural location in the IGP with extensive grasslands and cropland surrounding the measurement location. The site is approximately 300 km south of the Himalayan range. It is located 47 km south-west of Varanasi City and 8 km south from Mirzapur. Further to the south, there are two large thermal power plants ~110 km from the site: Vindhyachal Thermal Power Station and Rihand Thermal Power Station (Figure 1). A state highway passes through the university campus about ~100 m from the observation site on the western side. Towards the south, at a distance of ~750 m is a marketplace, which attracts traffic during the day time. The Majhawati River flows on the eastern side of the measurement location. The climate in this region is predominantly dry (sub-tropical to dry). The winter season is short (December to February) and the summer is from March to June followed by monsoon (July to September) and a brief autumn spanning over October and November. The temperature peaks at ~48° C during the summer and drop to a low of ~4° C during December-January. The average annual rainfall at the site is 1059 mm, of which 90 % is received during the ASM period. The onset of ASM in this region is usually during the third to fourth week in June, and lasts up to end of September. Meteorological parameters (all in one weather sensor for temperature, RH and winds, radiation from Kipp and Zonen CNR4 net radiometer) were measured for the period of
23\textsuperscript{rd} July, 2014 to 20\textsuperscript{th} September, 2014 with a data gap during 15\textsuperscript{th} August, 2014 to 23\textsuperscript{rd} August, 2014 due to instrumental problems (Figure 3).

\textbf{OZONE MEASUREMENTS}

An O$_3$ analyser (Ecotech, model number EC9810) was used for surface O$_3$ measurements. It is a non-dispersive ultraviolet photometer, which alternately switches between a selective ozone scrubber in and out of the measuring stream and computes the ratio of transmitted light giving a measure of ozone concentration. The lower detection limit is 0.5 ppbv (parts per billion by volume; equivalent to nmol mol$^{-1}$) or 0.2\% of the concentration reading, whichever is greater; and the instrument has a precision of 1 ppbv or 1\% of reading, whichever is greater. The instrument was active from 23\textsuperscript{rd} July, 2014 to 7\textsuperscript{th} Jan, 2015. There was no significant data gap aside from power failures at the station, which lasted for short periods.

\textbf{MAX-DOAS INSTRUMENTAL SETUP}

MAX-DOAS is a passive DOAS technique where scattered sunlight along multiple viewing directions are analysed and combined to get the distribution of various trace gases. As the differential absorption patterns of individual absorbers are unique, simultaneous measurements of different absorbers can be made provided that the cross-interference from other absorbers and contribution from broad band scattering is eliminated. MAX-DOAS measurements at lower elevation angles are more sensitive towards lower tropospheric trace gas layers as the photons travel longer paths through the lower troposphere compared to higher elevation angles. The MAX-DOAS instrument (Envimes) used for this campaign has two ultra-low stray light 75 mm Avantes spectrometers. The first spectrometer covers a range between 306.08-468.77 nm and the
second spectrometer operates in the range of 441.91-583.36 nm. Both the spectrometers have a full width half maximum resolution of 0.6 nm and a 100 µm slit. The spectrometers are temperature stabilised with a deviation of <0.05°C (which were maintained at an average temperature of 20 °C).

The MAX-DOAS instrument was installed on the rooftop of a water tower at the campaign site, at a height of ~10 m above ground level. The scanner unit pointed towards the geometric north, with a clear line of sight to the horizon. Spectra were recorded between 23rd July, 2014 to 20th September, 2014, with a gap during 1st-2nd August, 2014 and 17th-25th August, 2014 due to instrumental issues. Each full scan measured scattered sunlight along 10 different elevation angles (90°,40°,20°,10°,7°,5°,3°,2°,1°,0.5°) when solar zenith angle (SZA) was less than 80°. For 80°<SZA<97°, sunlight spectra were measured only in the zenith direction. The exposure time per individual spectrum was calculated according to 70 % saturation of the charged coupled device (CCD) sensor. The total exposure per elevation angle was set to 60 seconds. The dark current, offset and calibration spectra were recorded at the end of every day and were used to correct the measured spectra. Nonlinearity of the spectrometers was also taken into account. All the results from the campaign are presented in local time (Indian Standard Time).

DOAS ANALYSIS SETTINGS

The measured spectra were pre-processed with Matlab® for dark current and offset correction and then analysed using the QDOAS spectral fitting software (Danckaert, 2014). Zenith spectra from each scan was taken as reference to remove the stratospheric contribution in off-axis measurements (Hönninger et al., 2004).
HCHO differential slant column densities (DSCDs) were retrieved in the 332-358 nm wavelength window. Although HCHO shows characteristic absorption in the ultraviolet spectral region of 240-320 nm, the above mentioned wavelength range was chosen to avoid interference from strong ozone absorption bands below 320 nm. For O₄ and NO₂ the 350-386 nm and 433-460 nm intervals were chosen. The details of the cross-sections used in QDOAS retrieval are mentioned in Table 1. For all the three fitting windows, a 3rd order polynomial and an offset with zero order were also fitted. A ring spectrum (Grainger and Ring, 1962) was fitted (Chance and Kurucz, 2010, (250° K)) in addition to the fourth power ring spectrum following (Wagner et al., 2009).

Examples of the fits for O₄, NO₂ and HCHO are shown in Figure 2.

Boundary layer volume mixing ratios (vmr) for NO₂ and HCHO were retrieved from the DSCDs using the O₄ DSCDs. DSCDs from elevation angle less than 3° were used as the DSCDs from higher elevation angles contain information from the free troposphere. Only scans with SZA less than 60° were taken into account. Standard atmospheric temperature, pressure and O₄ concentration profiles were used for calculation of the path length. The trace gas mixing ratios were then calculated over the path towards the north as per the methodology used by other groups in the past (Gómez Martín et al., 2013; Mahajan et al., 2012; Prados-Roman et al., 2015; Sinreich et al., 2010).

RESULTS AND DISCUSSIONS

METEOROLOGY

Figure 3 shows the time series for various meteorological parameters measured during the campaign. The left column shows the temperature, relative humidity and wind speed (top to
bottom) and the right column shows the atmospheric pressure, incoming solar radiation and wind
direction (top to bottom). There was a gap in the data from 14th August late afternoon to 24th
August morning due to instrumental issues. The average atmospheric temperature was 28.6 °C
with minimum and maximum temperatures of 24 °C and 36.7 °C, respectively. The average
atmospheric pressure was 982.6 hPa with minimum and maximum pressure of 973.6 hPa and
987.6 hPa. The average relative humidity was 78.2 % with minimum and maximum relative
humidity of 39.4 % and 94.5 %, respectively. The average incoming solar radiation was 192.2
Wm$^{-2}$. There were several cloud free days and even on days with clouds, several cloud free hours
were recognised using the spectrometer data along with a sky imager and these data were used to
retrieve mixing ratios from the DOAS analysis. The average wind speed was 2.1 m s$^{-1}$ with
minimum and maximum wind speeds of 0.17 m s$^{-1}$ and 6.86 m s$^{-1}$.

O$_4$

O$_4$ DSCDs were found to be higher at lower elevation angles, as expected. This is due to the fact
that the intensity of O$_4$ absorption is proportional to the square of the oxygen pressure. At lower
elevation angles photon travel longer paths in lower troposphere and interact more with
tropospheric absorbing species before reaching the instrument. There is a decrease in the O$_4$
DSCD in the lowest three angles (2°,1°,0.5°), indicating the presence of aerosols in the boundary
layer. This is in accordance with fact that the campaign happened during ASM season. The
average RMS and detection limit for O$_4$ DSCDs were 7 x 10$^{-4}$ and 3.1 x 10$^{42}$ molecule$^2$ cm$^{-5}$
respectively at the1° elevation angle. Average O$_4$ DSCD at 1° elevation angle was 1.4 x 10$^{43}$
molecule$^2$ cm$^{-5}$ with maximum DSCD of 2.5 x 10$^{43}$ molecule$^2$ cm$^{-5}$ (Figure 4). The O$_4$ DSCDs
were then used to estimate the path length and hence the trace gas mixing ratios, as described earlier.

**NO₂**

NO₂ DSCDs were also found to be higher at lower elevation angles (Figure 4). This, in conjunction with the O₄ DSCDs indicates that most of the NO₂ is present close to the surface with a decreasing gradient with altitude. For the lowest three elevation angles, the DSCDs do not increase with a decrease in elevation angle, which can be attributed to the presence of aerosols in the boundary layer, as indicated by the decreasing O₄ DSCDs. The average RMS and detection limit for NO₂ DSCDs were 6 x 10⁻⁴ and 3 x 10¹⁵ molecule cm⁻² at the 1° elevation angle. The average NO₂ DSCD at the 1° elevation angle was 1.5 x 10¹⁶ molecule cm⁻², with a maximum DSCD of 7.2 x 10¹⁶ molecule cm⁻² (Figure 4, bottom panel).

Using the method described earlier, NO₂ mixing ratios were estimated for elevation angles lower than 3° to get the contribution NO₂ within boundary layer near the surface (e.g. Wagner et al., 2004). The resulting time series for NO₂ is shown in Figure 5. The average NO₂ mixing ratio was 0.81 ± 0.20 ppbv (range of 0.08 ppbv to 6.06 ppbv). The average detection limit for NO₂ was 0.16 ppbv. NO₂ mixing ratios decreased from an early morning high until mid-day and increased again later in the day (Figure 6). This can be attributed to the daytime photochemical decomposition of NO₂ by solar radiation as discussed in the introduction (R1).

The average vertical column densities (VCDs) for NO₂, as observed by the satellite-based ozone monitoring instrument (OMI) were studied to understand the spatial distribution over the IGP region (Figure 7). The annually averaged satellite based NO₂ VCDs for 2014 was found to be 2.5
x 10^{15} \text{ molecule cm}^{-2} \) around the observation site, with highest NO_2 \text{ VCD} (3.4 \times 10^{15} \text{ molecule cm}^{-2}) found in the month of December. The lowest NO_2 \text{ VCD} (1.9 \times 10^{15} \text{ molecule cm}^{-2}) was observed in the month of February. During the months of July, August and September 2014, higher NO_2 \text{ VCDs} (\sim 8 \times 10^{15} \text{ molecules cm}^{-2}) were observed over the two thermal power plants situated towards the south of the measurement site, as compared to 2.2 \times 10^{15} \text{ molecules cm}^{-2} over the measurement site. To investigate the effect of long range transport from the thermal power plants on the observed NO_2 at the measurement site, we computed the 12 hour and 24 hour back trajectories reaching the site every hour using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (Draxler and Hess, 1998). The area around the measurement site was divided into five sectors, with geometric north being 0°, the sectors were: Sector-1: 305°-35°; Sector-2: 35°-75°; Sector-3: 75°-125°; Sector-4: 125°-185° and Sector-5: 185°-305° (Figure 1). The sector numbers 1 and 2 represent nearby the towns of Mirzapur (which is closest to the measurement site at a distance of 10 km) and the city of Varanasi (at a distance of 60 km) (Figure 1). Sector 3 represents a vegetated area towards the east of the measurement site. Sector 4 represents the region with the two thermal power plants and sector 5 represents the rural IGP region. For each of the 12/24 hour back trajectories, information about which sector the air parcel spends at least 70% of the total time before arriving at the measurement site was extracted. The box-whisker plot in Figure 8 (left column) shows the sector-wise contribution to the observed NO_2, where the air parcels spend at least 70% of its time (top and bottom panels correspond the 12 and 24 hour back trajectories respectively). The median for the corresponding sectors along with the 75th and 25th percentile values are indicated in the box. The whiskers correspond to the 2.7 sigma (99.3%) when the data are normally distributed. The median NO_2 value for air parcels passing over sector 4 was the highest (1 ppbv and 1.44 ppbv for 12 hr and 24 hr back trajectories), which indicates the transport of NO_2 from the power plants to
the CAIPEEX-2014 site. Sector 5 and sector 3 show the lowest median values (0.51 ppbv and 0.51 ppbv) for the 12 hr and 24 hr back trajectories, respectively. This is expected considering that there are no large sources of NOx in these two sectors.

All the sectors were found to have outliers beyond the upper 2.7 sigma limit. For the 24 hr back trajectories, sector 1 had 9.2%; sector 2 had 0.8%; sector 3 had 6.8%; sector 4 had 2.9%; sector 5 had 5.6% outliers. For 12 hr back trajectories sector 1 had 8.1%; sector 2 had 3.4%; sector 3 had 7.8%; sector 4 had 0.4%; sector 5 had 6%. The probable sources of the outliers were (1) contamination of the air parcels with air parcels coming from sector 4 (associated to high NO2 from the power plants), (2) local sources originating from automobiles as there was a road close to the measurement site. To test the first hypothesis, air parcels which travelled over the power plants, even though their residence time was larger in other sectors, were identified. The reasoning behind this was that if the power plants were the source of outliers then these air parcels would contain more outliers.

To identify the effect of powerplant emissions on NO2 outliers we check whether the airparcels from the powerplants have contaminated the air parcels which have travelled predominantly over other sectors. We identified the region over powerplant which show higher NO2 VCDs (> 6 x 10^15 molecule cm^-2) in the satellite observations. We found that a box within latitudes 23.5° - 24.5° and longitudes 82.5° - 83.5° contained the highest NO2 VCDs. We identified air parcels that have travelled through this box in past 12 hr or 24 hr. Figure 9 shows all the NO2 data (blue dots) along with the outlier NO2 data (red dots). Data points which correspond to air parcels passing through the box are represented with black dots. Outliers that correspond to air parcels passing through the box are represented with green dots. The top and bottom panels represent 12 hr and 24 hr back trajectory plots. Out of 48 days of observation, 35 days contained data points which were identified as outliers in the 12 hr back trajectories (total 480 outlier data points out of 7412
data points). For 24 hr back trajectories, 31 days contained outlier data points in the different sectors (total 465 outlier data points out of 7106 data points). For 12 hr back trajectories, on 8 days air parcels passed through the box containing high NO$_2$ VCDs (492 data points) and out of these 8 days only 3 days (43 data points) contained outlier data points. For 24 hr back trajectories, 6 days contained air parcels that passed through the box containing high NO$_2$ VCDs (255 data points) and out of which 2 days (15 data points) had outlier data points. This leads us to conclude that contamination of air parcels coming from power plants do not explain the outlier NO$_2$ data points. Hence, we conclude that the outliers are not caused by long range transport, but rather by local emissions.

The reason behind the fact that sector 4 contains the least outliers is that the median and sigma value (hence the 2.7 sigma value) are higher in sector 4 as compared to other sections due to higher emissions from the power plant. Most elevated NO$_2$ values caused by the local effect are within the 2.7 sigma range. It should be noted that for sector 2 the lack of outliers could also be a result of sampling bias as during ASM season the dominant wind pattern is south-westerly. However, for other sectors the median and sigma value (hence the 2.7 sigma value) are lower, and most elevated NO$_2$ values caused by local emissions are observed as outliers. It is thus highly probable that the main cause behind the presence of large outliers is local emissions from automobiles on the highway to the south or the nearby market place mentioned earlier.

**HCHO**

Similar to O$_4$ and NO$_2$, the HCHO DSCDs were found to have lower values for higher elevation angles except lowest 3 elevation angles of 2°, 1° and 0.5° due to the presence of aerosols in boundary layer. This indicates that most of the HCHO is present near to the surface with a decreasing gradient upwards, although the decrease was not as strong as that for NO$_2$ (Figure 4).
The average RMS and detection limit for HCHO DSCDs were $4.1 \times 10^{-4}$ and $1.06 \times 10^{15}$ molecules cm$^{-2}$, respectively, at the 1° elevation angle. The average HCHO DSCD at the 1° elevation angle was $3.56 \times 10^{16}$ molecules cm$^{-2}$ with a maximum DSCD of $8.06 \times 10^{16}$ molecules cm$^{-2}$ (Figure 4).

The average HCHO mixing ratio was found to be $1.93 \pm 0.60$ ppbv, with values ranging between 0.32 ppbv to 8.81 ppbv (Figure 5). The diurnal variation of HCHO is unlike NO$_2$; HCHO was found to increase through the morning till 11 am and then gradually decrease towards late evening (Figure 6). This can be attributed to daytime photochemical oxidation of VOCs to form HCHO (R6-R9). Photochemical oxidation is also the major sink process for HCHO (R10, R11), which is why after an increase in the morning hours, HCHO starts to reduce as destruction starts to dominate production.

The annually averaged satellite-based HCHO VCDs for 2014 was $11.2 \times 10^{15}$ molecule cm$^{-2}$ around the observation site, with the highest HCHO VCD ($15.6 \times 10^{15}$ molecule cm$^{-2}$) found in the month of November. The lowest HCHO VCD ($6.6 \times 10^{15}$ molecule cm$^{-2}$) was observed in the month of September. Satellite retrieved HCHO VCDs averaged for the months of July, August and September of 2014 of were found to be within $8-12 \times 10^{15}$ molecule cm$^{-2}$ around the observation site (Figure 7) without any larger spatial differences, making it more homogeneous as compared to NO$_2$. The box-whisker plot for HCHO (middle column, figure 8) with 12 hr back trajectories shows that sector 1 had the highest median value (2.34 ppbv) and sector 5 displayed the lowest median value (1.5 ppbv). For 24 hr back trajectories plot, sector 1 has the highest (2.29 ppbv) and sector 5 has the lowest (1.53 ppbv) median value. Compared to NO$_2$, the HCHO does not show significant differences between different sectors. This can also be seen in the satellite observations (figure 7). Unlike NO$_2$, which has a significant source in sector 4, there is no similar strong ‘point’ source for HCHO in any sector. The numbers of outliers are also lower for HCHO.
as compared to NO₂. For 24 hr back trajectories, sector 1 had 2.74%; sector 2 had 0.0%; sector 3 had 3.92%; sector 4 had 0.0% and sector 5 had 5.47% outliers. For 12 hr back trajectories sector 1 had 3.58%; sector 2 had 2.78%; sector 3 had 4.63%; sector 4 had 1.03% and sector 5 had 3.32% outliers. The source for HCHO outliers also seems to be local anthropogenic emissions which include biomass burning and emissions from automobiles.

**OZONE**

For this study, we analysed O₃ data for the period of 23rd July, 2014 to 20th Sept, 2014, which coincides with the MAX-DOAS observations. Being located near a highway, O₃ mixing were ratios observed to be affected by emission from vehicles. To discard effects from nearby emissions, ozone data was filtered for spikes from periods when vehicles passed close to the site. The filtered data was averaged every 10 minutes, to match the MAX-DOAS observations. Figure 6 shows the time-series for O₃ during CAIPEEX-2014 campaign.

The blue points in the plot represent the ozone for SZA < 90°, i.e. daytime ozone. The red points represent data for SZA > 90°, i.e. night time ozone. The average O₃ mixing ratio during daytime (solar zenith angle < 90°) was 30 ± 13 ppbv (range: 2.7 ppbv to 81.9 ppbv) and during the night time (solar zenith angle ≥ 90°) the mean was 22.5 ± 10.2 ppbv (range: 1 ppbv to 63 ppbv). The right hand panel in figure 6 shows the hourly diurnal variation of O₃ with the corresponding standard deviation. Observed O₃ levels were at the lowest during the early morning (0600-0700 hr) and increased during the daytime due to photochemical production. The O₃ mixing ratios reached a peak around 1200 hrs and remained elevated until 1600 hrs. In the presence of solar radiation, NO₂ photochemically dissociates to NO and O(3P) and results in the formation of O₃ as per reactions described in the introduction. During midday, ozone concentrations reach an equilibrium which continues until the late afternoon. During the evening there is a gradual
decrease due to the lack of photochemical production, which continues after sunset. At night O₃ oxidises olefins, NO, NO₂ etc., this adds to a decrease in the O₃ concentrations. The diurnal trend for ozone (Figure 6) matches with the previously observed pattern at sub-urban sites in India (Beig et al., 2007; Jain et al., 2005; Ojha et al., 2012; Reddy et al., 2011).

Figure 8 represents a box-whisker plot for daytime (SZA < 90°) O₃ from corresponding sectors as discussed above (top right plot is for 12 hr back trajectories and bottom right is for 24 hr back trajectories). For both 12 hr and 24 hr back trajectories, sector 1 and 2 have the highest and lowest median values (sector 1 with 40.7 ppbv and 38.5 ppbv for 12 hr and 24 hr back trajectories, respectively; sector 2 with 22.1 ppbv and 10.7 ppbv for 12 hr and 24 hr back trajectories, respectively).

It is well known that at low NOₓ concentrations O₃ formation is linearly proportional to NOₓ concentrations and is independent of VOC concentration (Chameides et al., 1992). Whereas, in regions with lower VOC concentrations, ozone production is inversely proportional to NOₓ but linearly proportional to VOCs. Chameides et al. (1992) reported that HCHO/NO₂ ratio can be indicative for surface ozone sensitivity towards NOₓ limited and VOC limited regimes. Using satellite based observation Martin et al. (2004), reported that HCHO/NO₂ ratio below one is an indication of VOC limited regime and above one is an indication of NOₓ limited regime for ozone formation. In a recent study, Schroeder et al. (2017) further studied the critical ratio for VOC and NOₓ limited regimes. They found that HCHO/NO₂ column ratio from 1.1 to 4.3 cannot be reliably classified as either NOₓ limited or VOC limited regimes depending upon regional variability. From satellite data, the HCHO/NO₂ column ratio was found to be more than 4 over the CAIPEEX-2014 site (bottom left and bottom right panels in figure 4). The average HCHO/NO₂ from the ground based instruments was found to be more than 2. Both the results indicate that the CAIPEEX-2014 site is most likely a NOₓ limited region, hence the ozone
formation should be dependent on the NO\textsubscript{x} concentrations (Martin et al., 2004), although the ratio is within the ‘uncertain range’. We studied the correlation between hourly averaged HCHO and ozone mixing ratios and a positive correlation ($R=0.65$, $p<0.001$) was observed over the observation period. The correlation between hourly averaged NO\textsubscript{2} and ozone mixing ratio displayed a slight negative correlation ($R = -0.2$, $P=0.005$). The correlation between daily averaged HCHO and ozone mixing ratios also yielded a positive correlation ($R=0.78$, $P<0.001$), while the correlation between daily averaged NO\textsubscript{2} and ozone mixing ratios was insignificant. Hourly averaged HCHO and NO\textsubscript{2} mixing ratio did not show any significant correlation suggesting different sources. The correlational analysis suggests that the ozone mixing ratios are more dependent on the HCHO mixing ratios, contrary to what is expected from the observed HCHO/NO\textsubscript{2} ratio. However, on close inspection of variations within short periods, it is found that ozone resembles neither that the variation of HCHO or NO\textsubscript{2}. As mentioned above, the O\textsubscript{3} back trajectories indicate higher daytime O\textsubscript{3} mixing ratios associated with air masses coming from sector 1, whereas NO\textsubscript{2} is higher in air masses from sector 4. This suggests that O\textsubscript{3} formation at the CAIPEEX-2014 site was more affected by local production than long range transport from the power plants, during which elevated NO\textsubscript{2} was observed. The city of Mirzapur (sector 1) being closer to the measurement site compared to the city of Varanasi shows an effect on the observed O\textsubscript{3} concentrations, as can be seen from the sectorial analysis.

CONCLUSIONS

In this study we report the retrieval of NO\textsubscript{2} and HCHO concentrations using the MAX-DOAS technique and surface O\textsubscript{3} measurements during the ASM season as a part of the Cloud Aerosol Interaction and Precipitation Enhancement Experiment (CAIPEEX-2014). We discuss the effect of long-range transport on NO\textsubscript{2} and HCHO mixing ratios and O\textsubscript{3} production during the campaign.
The average NO$_2$ mixing ratio was 0.81 ± 0.20 ppbv, ranging between 0.08 ppbv to 6.06 ppbv. Observations indicate that most of the NO$_2$ is present near the surface with a decreasing gradient upward. NO$_2$ mixing ratios decreased from the early morning till mid-day and increased during afternoon. From the satellite observations NO$_2$ emission hotspot were identified ~110 km towards the south of the CAIPEEX-2014 site, where two large the thermal power plant are present. We found that the air-parcels coming from the direction of the power plants showed higher NO$_2$ mixing ratios during the campaign. Local effects (emission from automobiles from a highway near the campaign site and emissions from the nearby market place) also resulted in high NO$_2$ mixing ratios. The average HCHO mixing ratio was found to be 1.93 ± 0.60 ppbv with values ranging between 0.32 ppbv and 8.81 ppbv. HCHO was found to increase in the morning until 11 am due to the daytime photochemical oxidation of VOCs to form HCHO. Satellite observations indicate that HCHO concentrations around the campaign site were almost homogeneous compared to NO$_2$. The average observed O$_3$ mixing ratios during daytime was 30 ± 13 ppbv (range: 2.7 ppbv to 81.9 ppbv) and was 22.5 ± 10.2 ppbv (range: 1 ppbv to 63 ppbv) during the night time. O$_3$ mixing ratios were found to be low in the early morning (0600-0700 hr) and increased during the daytime due to photochemical production, reaching the maximum around 12 pm. After reaching a maxima during noon, the O$_3$ mixing ratios were steady until 4 pm and decreased in the late afternoon and evening. The analysis indicates that the background surface O$_3$ mixing ratio is dependent on the HCHO mixing ratio. The sectorial analysis indicates that surface O$_3$ concentrations at the CAIPEEX-2014 site were not controlled by long range transport of precursor from any particular direction; rather local emissions contributed more towards the O$_3$ variability.

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Table 1: MAX-DOAS retrieval settings for the different species retrieved during the campaign.

<table>
<thead>
<tr>
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<th>HCHO</th>
<th>O₄</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fitting interval</strong></td>
<td>332-358 nm</td>
<td>350-386 nm</td>
<td>433-460 nm</td>
</tr>
</tbody>
</table>

*Chance and Kurucz (2010), 250°K and a secondary ‘Ring’ spectrum created using QDOAS ‘Ring’ tool from MAX-DOAS spectra then multiplying and normalised it with the 4th power of the intensity. Also for retrieval of all the species a third order polynomial and linear offset of zero order were used.*
Figure 1: CAIPEEX-2014 location with nearby cities and thermal power plants indicated. The area around the measurement site was divided into five sectors. The sector numbers 1 and 2 represent nearby the towns of Mirzapur (which is closest to the measurement site at a distance of 10 km) and the city of Varanasi (at a distance of 60 km). Sector 3 represents a vegetated area towards the east of the measurement site. Sector 4 represents the region with the two thermal power plants and sector 5 represents the rural IGP region.
Figure 2: DOAS fit for O₄, NO₂ and HCHO. (Top panel) O₄: 30/08/2014 08:03:43 hr; SZA-58.4°; Elevation angle- 10.0°; DSCD- 2.32 x 10⁴³ molecules² cm⁻⁵; RMS- 3.4 x 10⁻⁴. (Middle panel) HCHO: 30/08/2014 08:27:38 hr; SZA- 52.9°; Elevation angle- 3.0°; DSCD- 4.08 x 10¹⁶ molecules cm⁻²; RMS- 4.0 x 10⁻⁴. (Bottom panel) NO₂: 30/08/2014 08:09:56 hr; SZA-56.9°; Elevation angle- 0.5°; DSCD- 1.53 x 10¹⁶ molecules cm⁻²; RMS- 5.9 x 10⁻⁴.
Figure 3: Time series of various meteorological parameters measured during CAIPEEX-2014. The left column represents temperature, relative humidity and wind speed from top to bottom. The right column represents air pressure, incoming solar radiation and wind direction from top to bottom.
Figure 4: Slant column densities of O₄, HCHO and NO₂ from CAIPEEX-2014 campaign. Different colours represent measurements at different viewing elevation angles.
**Figure 5**: Time series for NO$_2$, HCHO and O$_3$vmr. The top panel shows NO$_2$ (blue dots) and HCHO (red dots) mixing ratio. Bottom panel shows daytime (blue dots) and night-time (red dots) O$_3$ mixing ratio.
Figure 6: Diurnal variation in NO$_2$, HCHO and O$_3$ mixing ratios during CAIPEEX-2014. The error bars represent the standard deviations.

Figure 7: Satellite-based (OMI) retrieved vertical columns of NO$_2$ and HCHO for the months of July, August and September 2014. (A) HCHO over the India. (B) HCHO over the CAIPEEX-2014 site. (C) NO$_2$ over the India. (D) NO$_2$ contour over the CAIPEEX-2014 site. (E) HCHO/NO$_2$ ratio over India. (F) HCHO/NO$_2$ ratio over the CAIPEEX-2014 site. ‘o’ represents the city of Varanasi and ‘+’ indicates the thermal power plants.
Figure 8: Box-Whisker plot of NO$_2$, HCHO and O$_3$ mixing ratios and the number of sectors where the air parcel has spent more than 70% of its time in last 12/24 hour. All the top panels correspond to the 12 hr back trajectory data whereas the lower panels represent last 24 hr back trajectory data.

Figure 9: Time series of NO$_2$ and NO$_2$ outliers from different sectors. The blue dots represent all NO$_2$ data; the red dots represent NO$_2$ outliers from different sectors; the black dots represent NO$_2$ from with parcels corresponding to power plant region; the green dots represent NO$_2$ outliers affected by emissions from the power plant region. The top and
bottom panels represent 12 hr and 24 hr back trajectory plots. Top and bottom panels represent 12 hr and 24 hr back trajectory plots.