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

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ABSTRACT

This study reports the 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) during the 2014 monsoon period as 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: 0.08–6.06 ppbv). NO₂ was observed to decrease during the morning between 06:00 and 09:00 local time and then stabilise for the rest of the day. The average daytime HCHO mixing ratio was 1.93 ± 0.60 ppbv (range: 0.32–8.81 ppbv). Unlike NO₂, HCHO, driven by daytime photochemical formation from hydrocarbon precursors, increased during the early morning. The average O₃ mixing ratio was 30.0 ± 13.0 ppbv (range: 2.7–81.9 ppbv) during the daytime and 22.5 ± 10.2 ppbv (range: 1–63 ppbv) during the nighttime. Analyses of the back trajectories indicated 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 but the HCHO mixing ratios and O₃ production were influenced by local emissions. These observations suggest that in rural IGP, ozone concentrations are affected by local emission rather than by long-range transport.

Keywords: Nitrogen dioxide; Formaldehyde; Ozone; Indo-Gangetic Plain.

INTRODUCTION

Nitrogen dioxide (NO₂) 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 (O₃) (Crutzen, 1970) and affects the hydroxyl radical (OH) abundance through reactive photochemistry. As a pollutant, NO₂ 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 NO₂ abundance usually coincides with other atmospheric pollutants, and hence, it can be used as a proxy for atmospheric pollution in general (Mayer, 1999; Molina and Molina, 2004). Major anthropogenic sources of NO₂ include

high temperature combustion of fossil fuels, biomass burning, industries, thermal power plants and automobiles. Forest fires, lightning and soil microbial processes are considered to be the main natural sources (Jaeglé *et al.*, 2005). Formation of nitric acid (HNO₃) during the daytime and dinitrogen pentoxide (N₂O₅) 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), the performance of chemical transport models (Zyrichidou *et al.*, 2009; Huijnen *et al.*, 2010, and references therein) and changes in anthropogenic emissions (Stavrakou *et al.*, 2008; Wang *et al.*, 2012) have been studied using satellite retrieved NO₂ columns. Observations of NO₂ (Johansson *et al.*, 2009; Wagner *et al.*, 2010; Constantin *et al.*, 2013) 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 NO₂ and also for validating satellite observations (Hönniger *et al.*, 2004; Frieß *et al.*, 2006; Wagner *et al.*, 2011; Hendrick *et al.*, 2014).

Formaldehyde (HCHO) is the most abundant and smallest

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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; Lee *et al.*, 1997; Fu *et al.*, 2007; Hak *et al.*, 2005; Herndon *et al.*, 2005; Smedt *et al.*, 2010). The background levels of HCHO are mainly sustained by oxidation of long-lived VOCs, such as 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 a useful indicator of biogenic and anthropogenic emissions of hydrocarbons (Andreae and Merlet, 2001; Geiger *et al.*, 2002; Seco *et al.*, 2007; Stavrou *et al.*, 2009; Barkley *et al.*, 2013; Stavrou *et al.*, 2014). 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; Palmer *et al.*, 2001; Wittrock *et al.*, 2006; De Smedt *et al.*, 2008). These observations have helped us study the spatial and temporal trends and to estimate the emissions of VOCs (Gonzi *et al.*, 2011; Barkley *et al.*, 2013). Higher concentrations of HCHO associated with areas of dense vegetation and biomass burning indicate that on a global scale, the major sources are of biogenic origin (Vrekoussis *et al.*, 2010).

O₃ plays an important role in atmospheric chemistry (Crutzen, 1974, 1970; Logan *et al.*, 1981; Barrie *et al.*, 1988). 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., NO_x or VOCs (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 (Morgan *et al.*, 2006; Ghude *et al.*, 2014). Increased anthropogenic emissions from fossil fuel combustion in power plants, large-scale industries and automobiles have led to an increase in the surface O₃ concentrations over the past few decades (Sillman and Samson, 1995; Peleg *et al.*, 1997; Ryerson *et al.*, 2001). Solar radiation and higher water vapour content in the atmosphere, along with increased NO_x and VOC concentrations, lead to higher photochemical production of O₃ in the tropical regions (Crutzen, 1970; Andreae and Crutzen, 1997; Sánchez *et al.*, 2005). NO₂ participates as a catalyst and, in the presence of solar

radiation, photochemically dissociates to form NO (nitrogen oxide) and O(³P).

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

O₃ also photolyses at wavelengths < 310 nm to form O(¹D), which then reacts with water vapour to yield OH radicals.

The oxidation of methane (and other NMVOCs) by OH radical forms HO₂ and HCHO (higher aldehydes in the case of NMVOC oxidation). Further photochemical oxidation of formaldehyde with OH radicals also results in the formation of HO₂ (R10)–(R12).

At night, in the absence of sunlight, O₃ reacts with NO₂ to form the nitrate radical (NO₃), which can eventually lead to the removal of NO_x from the atmosphere, as mentioned earlier.

The Indo-Gangetic Plain (IGP) region covers ~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 NO₂, HCHO and O₃ sources and the

monitoring of their abundance are very important for determining 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; Smedt *et al.*, 2010; Ghude *et al.*, 2013; Hilboll *et al.*, 2013; Mahajan *et al.*, 2015). However, scant information from ground based instruments is available in India to validate the satellite observations (Pandey *et al.*, 1992; Sharma *et al.*, 2010; Mandal *et al.*, 2012; Reddy *et al.*, 2012). Ground based observations of HCHO in India are rare (Khare *et al.*, 1997a, b; Dutta *et al.*, 2010), 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 the 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 of 4–6 ppbv for September 2017. The NO_2 mixing ratios were found to be between 0.5 and 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 (Lal *et al.*, 2000; Nair *et al.*, 2002; Naja and Lal, 2002; Jain *et al.*, 2005; Beig *et al.*, 2007; Mittal *et al.*, 2007; Ghude *et al.*, 2008). Low altitude rural sites in India show maximum O_3 concentrations during 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 months 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 O_3 precursors and ascertain the main drivers of O_3 over a rural site in the IGP.

MEASUREMENT SITE AND METHODS

Measurement Site

The CAIPEEX-2014 campaign was carried out on the Rajiv Gandhi South Campus of Banaras Hindu University in Barkachha, Mirzapur District, Uttar Pradesh, 169 m above mean sea level (25.06°N , 82.59°E ; Fig. 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 the city of Varanasi and 8 km south of Mirzapur. Farther to the south, there are two large thermal power plants ~110 km from the site: Vindhyachal Thermal Power Station and Rihand Thermal Power Station (Fig. 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 daytime. The Majhawati River

Fig. 1. CAIPEEX-2014 location with nearby cities and thermal power plants indicated. The area around the measurement site was divided into five sectors. Sectors 1 and 2 represent the nearby town of Mirzapur (which, at a distance of 10 km, is closest to the measurement site) and the city of Varanasi (at a distance of 60 km). Sector 3 represents a vegetated area to 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.

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–February), and the summer (March–June) is followed by the monsoon (July–September) and a brief autumn (October–November). The temperature peaks at $\sim 48^\circ\text{C}$ during the summer and drops to a low of $\sim 4^\circ\text{C}$ during December and 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 the end of September. Meteorological parameters were measured (using an all in one weather sensor for temperature, RH and winds) and a Kipp and Zonen CNR4 net radiometer for radiation for the period of 23 July 2014 to 20 September 2014, with a data gap during 15 August 2014 to 23 August 2014 due to instrumental problems (Fig. 3).

Ozone Measurements

An O_3 analyser (EC9810; Ecotech) 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 (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 the reading, whichever is greater. The instrument was active from 23 July 2014 to 7 Jan 2015. There was no significant data gap aside from power failures at the station, which lasted for short periods.

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 broadband 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 of 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 (maintained at an average temperature of 20°C) with a deviation of $< 0.05^\circ\text{C}$.

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 23 July 2014 to 20 September 2014, with a gap during 1–2 August 2014

and 17–25 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° and 0.5°) when the solar zenith angle (SZA) was $< 80^\circ$. For $80^\circ < \text{SZA} < 97^\circ$, 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 a 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 abovementioned wavelength range was chosen to avoid interference from strong ozone absorption bands below 320 nm. For O_4 and NO_2 , 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 three fitting windows, a third-order polynomial and an offset with a zero order polynomial was 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 O_4 , NO_2 and HCHO are shown in Fig. 2.

Boundary layer volume mixing ratios (vmr) for NO_2 and HCHO were retrieved from the DSCDs using the O_4 DSCDs. DSCDs from elevation angles $< 3^\circ$ were used, as the DSCDs from higher elevation angles contain information from the free troposphere. Only scans with $\text{SZA} < 60^\circ$ were taken into account. Standard atmospheric temperature, pressure and O_4 concentration profiles were used for the calculation of the path length. The trace gas mixing ratios were then calculated over the path towards the north per the methodology used by other groups in the past (Sinreich *et al.*, 2010; Mahajan *et al.*, 2012; Gómez Martín *et al.*, 2013; Prados-Roman *et al.*, 2015).

RESULTS AND DISCUSSIONS

Meteorology

Fig. 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 the late

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

HCHO	O ₄	NO ₂
<u>Fitting interval</u>		
332–358 nm	350–386 nm	433–460 nm
<u>Cross-sections used</u>		
HCHO: Meller and Moortgat (2000), 298°K	O ₄ : Greenblatt <i>et al.</i> (1990), 296°K	NO ₂ : Vandaele <i>et al.</i> (1998), 294°K and 220°K
O ₃ : Bogumil <i>et al.</i> (2003), 223°K and 293°K	NO ₂ : Vandaele <i>et al.</i> (1998), 294°K and 220°K	O ₃ : Bogumil <i>et al.</i> (2003), 223°K and 293°K
O ₄ : Greenblatt <i>et al.</i> (1990), 296°K	HCHO: Meller and Moortgat (2000), 298°K	CHOCHO: Volkamer (2005), 296°K
NO ₂ : Vandaele <i>et al.</i> (1998), 294°K	O ₃ : Bogumil <i>et al.</i> (2003), 223°K and 293°K	O ₄ : Greenblatt <i>et al.</i> (1990), 296°K
HONO: Stutz <i>et al.</i> (2000), 298°K	HONO: Stutz <i>et al.</i> (2000), 298°K	H ₂ O: Hitran (2009), 296°K
<u>Ring spectra</u>		
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 4 th power of the intensity. Also, for retrieval of all the species, a third order polynomial and linear offset of zero order were used.

Fig. 2. DOAS fit for O₄, NO₂ and HCHO. Top panel: O₄; 30 August 2014, 08:03:43; SZA = 58.4°; elevation angle = 10.0°; DSCD = 2.32×10^{43} molecules² cm⁻⁵; RMS = 3.4×10^{-4} . Middle panel: HCHO; 30 August 2014, 08:27:38; SZA = 52.9°; elevation angle = 3.0°; DSCD = 4.08×10^{16} molecules cm⁻²; RMS = 4.0×10^{-4} . Bottom panel: NO₂; 30 August 2014, 08:09:56; SZA = 56.9°; elevation angle = 0.5°; DSCD = 1.53×10^{16} molecules cm⁻²; RMS = 5.9×10^{-4} .

afternoon of 14 August to the morning of 24 August due to instrumental issues. The average atmospheric temperature was 28.6°C with a minimum and maximum temperature of 24°C and 36.7°C, respectively. The average atmospheric

pressure was 982.6 hPa with a minimum and maximum pressure of 973.6 hPa and 987.6 hPa, respectively. The average relative humidity was 78.2% with a minimum and maximum relative humidity of 39.4% and 94.5%,

Fig. 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.

respectively. The average incoming solar radiation was 192.2 W m^{-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 a minimum and maximum wind speed 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, photons travel longer paths in the lower troposphere and interact more with tropospheric absorbing species before reaching the instrument. There is a decrease in the O_4 DSCD at the lowest three angles (2° , 1° and 0.5°), indicating the presence of aerosols in the boundary layer. This is in accordance with

the fact that the campaign happened during the ASM season. The average RMS and detection limit for O_4 DSCDs were 7×10^{-4} and $3.1 \times 10^{42} \text{ molecules}^2 \text{ cm}^{-5}$, respectively, at the 1° elevation angle. The average O_4 DSCD at a 1° elevation angle was $1.4 \times 10^{43} \text{ molecules}^2 \text{ cm}^{-5}$ with a maximum DSCD of $2.5 \times 10^{43} \text{ molecules}^2 \text{ cm}^{-5}$ (Fig. 4). The O_4 DSCDs were then used to estimate the path length and hence the trace gas mixing ratios, as described earlier.

NO_2

NO_2 DSCDs were also found to be higher at lower elevation angles (Fig. 4). This, in conjunction with the O_4 DSCDs, indicates that most of the NO_2 is present close to the surface with a decreasing gradient with altitude. For the three lowest 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 O_4 DSCDs. The average RMS and detection limit for NO_2 DSCDs were 6×10^{-4}

Fig. 4. Slant column densities of O₄, HCHO and NO₂ from CAIPEEX-2014 campaign. Different colours represent measurements at different viewing elevation angles.

and 3×10^{15} molecules cm^{-2} at the 1° elevation angle. The average NO₂ DSCD at the 1° elevation angle was 1.5×10^{16} molecules cm^{-2} , with a maximum DSCD of 7.2×10^{16} molecules cm^{-2} (Fig. 4, bottom panel).

Using the method described earlier, NO₂ mixing ratios were estimated for elevation angles $< 3^\circ$ to get the contribution to NO₂ within the boundary layer near the surface (e.g., Wagner *et al.*, 2004). The resulting time series for NO₂ is shown in Fig. 5. The average NO₂ mixing ratio was 0.81 ± 0.20 ppbv (range: 0.08–6.06 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 (Fig. 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 (Fig. 7). The annually averaged satellite based NO₂ VCD for 2014 was found to be 2.5×10^{15} molecules cm^{-2} around the observation site, with the highest NO₂ VCD (3.4×10^{15} molecules cm^{-2}) found in the month of December. The lowest NO₂ VCD (1.9×10^{15} molecules cm^{-2}) was observed in the month of February. During the months of July, August and September 2014, higher NO₂ VCDs ($\sim 8 \times 10^{15}$ molecules cm^{-2}) were observed over the two thermal power plants situated to the south of the measurement site than over the measurement site ($\sim 2.2 \times 10^{15}$ molecules cm^{-2}). To investigate the effect

of long-range transport from the thermal power plants on the observed NO₂ at the measurement site, we computed the 12-hour and 24-hour back trajectories reaching the site every hour using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) 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: $305\text{--}35^\circ$; Sector 2: $35\text{--}75^\circ$; Sector 3: $75\text{--}125^\circ$; Sector 4: $125\text{--}185^\circ$ and Sector 5: $185\text{--}305^\circ$ (Fig. 1). Sectors 1 and 2 represent the nearby town 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) (Fig. 1). Sector 3 represents a vegetated area to 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-h back trajectories, information about where (sector-wise) the air parcel spends at least 70% of its total time before arriving at the measurement site was extracted. The box-and-whisker plot in Fig. 8 (left column) shows the sector-wise contribution to the observed NO₂, where the air parcel spends at least 70% of its time in a particular sector (the top and bottom panels correspond the 12-h and 24-h back trajectories, respectively). The median for the corresponding sector 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 NO₂ value for air parcels passing over Sector 4 was the highest (1 ppbv and 1.44 ppbv for

Fig. 5. Time series for NO₂, HCHO and O₃ vmr. The top panel shows NO₂ (blue dots) and HCHO (red dots) mixing ratios. The bottom panel shows daytime (blue dots) and nighttime (red dots) O₃ mixing ratios.

Fig. 6. Diurnal variation in NO₂, HCHO and O₃ mixing ratios during CAIPEEX-2014. The error bars represent the standard deviations.

Fig. 7. Satellite-based (OMI) vertical columns of NO₂ and HCHO for the months of July, August and September 2014. (A) HCHO over India. (B) HCHO over the CAIPEEX-2014 site. (C) NO₂ over India. (D) NO₂ contour over the CAIPEEX-2014 site. (E) HCHO/NO₂ ratio over India. (F) HCHO/NO₂ ratio over the CAIPEEX-2014 site. “o” represents the city of Varanasi, and “+” indicates the thermal power plants.

12-h and 24-h back trajectories), which indicates the transport of NO₂ 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-h and 24-h back trajectories, respectively. This is expected, considering that there are no large sources of NO_x in these two sectors.

All the sectors were found to have outliers beyond the upper 2.7 sigma limit. For the 24-h back trajectories, Sectors 1, 2, 3, 4 and 5 had 9.2%, 0.8%, 6.8%, 2.9% and 5.6% outliers, respectively. For the 12-h back trajectories, Sectors 1, 2, 3, 4 and 5 had 8.1%, 3.4%, 7.8%, 0.4% and 6% outliers, respectively. The probable sources of the outliers were (1) contamination of the air parcels with air parcels coming from Sector 4 (associated with high NO₂ from the power plants) and (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 power plant emissions on NO₂ outliers, we check whether the air parcels from the power plants have contaminated the air parcels which have travelled predominantly over other sectors. We identified the region over the power plants, which shows higher NO₂ VCDs ($> 6 \times 10^{15}$ molecules 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 the past 12 or 24 hours. Fig. 9 shows all the NO₂ data (blue dots) along with the outlier NO₂ data (red dots). Data points which correspond to air parcels passing

Fig. 8. Box-and-whisker plot of NO₂, HCHO and O₃ mixing ratios and the number of the sector where the air parcel has spent more than 70% of its time in the last 12/24 hours. All the top panels correspond to the 12-h back trajectory data, whereas the lower panels represent the 24-h back trajectory data.

Fig. 9. Time series of NO₂ and NO₂ outliers from different sectors. The blue dots represent all NO₂ data; the red dots represent NO₂ outliers from different sectors; the black dots represent NO₂ from parcels corresponding to the power plant region; the green dots represent NO₂ outliers affected by emissions from the power plant region. The top and bottom panels represent 12-h and 24-h back trajectory plots.

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-h and 24-h back trajectory plots. Out of 48 days of observation, 35 days contained data points which

were identified as outliers in the 12-h back trajectories (480 total outlier data points out of 7412 data points). For 24-h back trajectories, 31 days contained outlier data points in the different sectors (465 total outlier data points out of 7106 data points). For 12-h back trajectories, on

8 days, air parcels passed through the box containing high NO₂ VCDs (492 data points), and out of these 8 days, only 3 days (43 data points) contained outlier data points. For 24-h back trajectories, 6 days contained air parcels that passed through the box containing high NO₂ VCDs (255 data points), 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 NO₂ 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 fewest outliers is that the median and sigma values (2.7 sigma values limiting the whiskers) are higher in Sector 4 compared to other sections due to higher emissions from the power plants. Most elevated NO₂ 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 the ASM season, the dominant wind pattern is south-westerly. However, for other sectors, the median and sigma values (2.7 sigma values limiting the whiskers) are lower, and most elevated NO₂ 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 marketplace mentioned earlier.

HCHO

Similar to O₄ and NO₂, the HCHO DSCDs were found to have lower values for higher elevation angles, except the three lowest elevation angles of 2°, 1° and 0.5°, due to the presence of aerosols in the boundary layer. This indicates that most of the HCHO is present near the surface with a decreasing gradient upwards, although the decrease was not as strong as that for NO₂ (Fig. 4). The average RMS and detection limit for HCHO DSCDs were 4.1×10^{-4} and 1.06×10^{15} molecules cm⁻², respectively, at the 1° elevation angle. The average HCHO DSCD at the 1° elevation angle was 3.56×10^{16} molecules cm⁻² with a maximum DSCD of 8.06×10^{16} molecules cm⁻² (Fig. 4).

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 (Fig. 5). The diurnal variation of HCHO is unlike NO₂; HCHO was found to increase through the morning till 11:00 and then gradually decrease towards late evening (Fig. 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 VCD for 2014 was 11.2×10^{15} molecules cm⁻² around the observation site, with the highest HCHO VCD (15.6×10^{15} molecules cm⁻²) found in the month of November. The lowest HCHO VCD (6.6×10^{15} molecules cm⁻²) was observed in the month of September. Satellite retrieved HCHO VCDs averaged for the months of July, August and

September of 2014 were found to be within $8\text{--}12 \times 10^{15}$ molecules cm⁻² around the observation site (Fig. 7) without any larger spatial differences, making it more homogeneous compared to NO₂. The box-and-whisker plot for HCHO (Fig. 8, middle column) with 12-h 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 the 24-h back trajectory plot, Sector 1 has the highest (2.29 ppbv) and Sector 5 has the lowest (1.53 ppbv) median value. Compared to NO₂, the HCHO does not show significant differences between different sectors. This can also be seen in the satellite observations (Fig. 7). Unlike NO₂, which has a significant source in Sector 4, there is no similarly strong “point” source for HCHO in any sector. The numbers of outliers are also lower for HCHO compared to NO₂. For 24-h back trajectories, Sectors 1, 2, 3, 4 and 5 had 2.74%, 0.0%, 3.92%, 0.0% and 5.47% outliers, respectively. For 12-h back trajectories, Sectors 1, 2, 3, 4 and 5 had 3.58%, 2.78%, 4.63%, 1.03% and 3.32% outliers, respectively. 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 23 July 2014 to 20 September 2014, which coincides with the MAX-DOAS observations. Being located near a highway, O₃ mixing ratios were observed to be affected by emissions 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. Fig. 6 shows the time-series for O₃ during the 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., nighttime ozone. The average O₃ mixing ratio during daytime (solar zenith angle < 90°) was 30 ± 13 ppbv (range: 2.7–81.9 ppbv), and during the nighttime (solar zenith angle > 90°), the mean was 22.5 ± 10.2 ppbv (range: 1–63 ppbv). The right hand panel in Fig. 6 shows the hourly diurnal variation of O₃ with the corresponding standard deviation. Observed O₃ levels were at the lowest during the early morning (06:00–07:00) and increased during the daytime due to photochemical production. The O₃ mixing ratios reached a peak around 12:00 and remained elevated until 16:00. In the presence of solar radiation, NO₂ photochemically dissociates to NO and O(³P) and results in the formation of O₃ 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 contributes to a decrease in the O₃ concentrations. The diurnal trend for ozone (Fig. 6) matches with the previously observed pattern at sub-urban sites in India (Jain *et al.*, 2005; Beig *et al.*, 2007; Reddy *et al.*, 2011; Ojha *et al.*, 2012).

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

It is well known that at low NO_x concentrations, O₃ formation is linearly proportional to NO_x concentrations and is independent of VOC concentration (Chameides *et al.*, 1992), whereas in regions with lower VOC concentrations, ozone production is inversely proportional to NO_x but linearly proportional to VOCs. Chameides *et al.* (1992) reported that HCHO/NO₂ ratio can be indicative of surface ozone sensitivity towards NO_x limited and VOC limited regimes. Using satellite based observation, Martin *et al.* (2004) reported that HCHO/NO₂ ratio < 1 is an indication of VOC limited regime and > 1 is an indication of NO_x limited regime for ozone formation. In a recent study, Schroeder *et al.* (2017) further studied the critical ratio for VOC and NO_x limited regimes. They found that HCHO/NO₂ column ratio from 1.1 to 4.3 cannot be reliably classified as either NO_x or VOC limited regime, depending upon regional variability. From satellite data, the HCHO/NO₂ column ratio was found to be > 4 over the CAIPEEX-2014 site (bottom left and bottom right panels in Fig. 4). The average HCHO/NO₂ from the ground based instruments was found to be > 2. Both the results indicate that the CAIPEEX-2014 site is most likely an NO_x limited region; hence, the ozone formation should be dependent on the NO_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 hourly averaged NO₂ and ozone mixing ratio displayed a slight negative correlation ($R = -0.2$, $p = 0.005$). The daily averaged HCHO and ozone mixing ratios also yielded a positive correlation ($R = 0.78$, $p < 0.001$), while the correlation between daily averaged NO₂ and ozone mixing ratios was insignificant. Hourly averaged HCHO and NO₂ 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/NO₂ ratio. However, on close inspection of variations within short periods, it is found that ozone resembles neither the variation of HCHO nor NO₂. As mentioned above, the O₃ back trajectories indicate higher daytime O₃ mixing ratios associated with air masses coming from Sector 1, whereas NO₂ is higher in air masses from Sector 4. This suggests that O₃ formation at the CAIPEEX-2014 site was more affected by local production than long-range transport from the power plants, during which elevated NO₂ 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 O₃ concentrations, as can

be seen from the sectorial analysis.

CONCLUSIONS

In this study, we reported the NO₂ and HCHO concentrations, obtained via MAX-DOAS technique, as well as the surface O₃ concentrations measured during the ASM season as part of the Cloud Aerosol Interaction and Precipitation Enhancement Experiment (CAIPEEX-2014). We discussed the effect of long-range transport on the NO₂ and HCHO mixing ratios and on O₃ production during the campaign. The NO₂ mixing ratios ranged from 0.08 ppbv to 6.06 ppbv with an average of 0.81 ± 0.20 ppbv. Observations indicated that most of the NO₂ lay near the surface with a decreasing gradient upward. The NO₂ mixing ratios decreased from early in the morning till mid-day and then increased during the afternoon. Through satellite observation, an NO₂ emission hotspot was identified ~110 km to the south of the CAIPEEX-2014 site, where two large thermal power plants are located, and air parcels travelling from the direction of these power plants exhibited higher NO₂ mixing ratios. Local emissions (from automobiles on a highway near the campaign site and from a nearby marketplace) also contributed to the high NO₂ mixing ratios. The HCHO mixing ratios ranged from 0.32 ppbv to 8.81 ppbv with an average of 1.93 ± 0.60 ppbv. Due to the daytime photochemical oxidation of VOCs, which resulted in the formation of HCHO, the HCHO increased during the morning until 11:00. Satellite observations indicated that the concentrations of HCHO around the campaign site were almost homogeneous compared to those of NO₂. The average O₃ mixing ratio observed during the daytime and the nighttime was 30 ± 13 ppbv (range: 2.7–81.9 ppbv) and 22.5 ± 10.2 ppbv (range: 1–63 ppbv), respectively. The O₃ mixing ratios were low in the early morning (06:00–07:00) but increased during the daytime due to photochemical production, reaching their maximum values around 12:00. Following this peak, they remained steady until 16:00, after which they decreased through the evening. Furthermore, our results suggested that the background surface O₃ mixing ratio depended on the HCHO mixing ratio. Based on the sectorial analysis, surface O₃ concentrations at the CAIPEEX-2014 site were contributed by local emissions rather than long-range-transported precursors.

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