Year-long Concurrent MAX-DOAS Observations of Nitrogen Dioxide and Formaldehyde at Pune: Understanding Diurnal and Seasonal Variation Drivers

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ABSTRACT

Year-long observations of nitrogen dioxide (NO₂) and formaldehyde (HCHO) using the Multi-Axis Differential Absorption Spectroscopy (MAX-DOAS) technique are reported from Pune City, India. We studied the diurnal and seasonal variations, effect of biomass burning and the weekend effect on both species. NO₂ diurnal profiles displayed a traffic induced peak at ~09:00 hrs. HCHO also showed a morning peak ~10:00 hrs due to production from oxidation of VOCs in the presence of solar radiation. Both NO₂ and HCHO show the highest average concentrations during the winter (October, November, December, January and February—ONDJF), with mean mixing ratios of 2.0 ± 1.4 ppb and 3.0 ± 1.4 ppb, respectively. These observations suggest that a lower boundary layer (BL) height during ONDJF leads to higher concentrations of trace gases. During June, July, August, and September (JJAS), both trace gases show a minimum in their concentrations, with average mixing ratios for NO₂ and HCHO being 0.9 ± 0.6 ppb and 1.1 ± 0.7 ppb, most likely due to removal by wet deposition. There was no significant difference in both the trace gases on weekdays and weekends. Using back-trajectory analysis, we conclude that air parcels coming from regions of biomass burning increased the concentrations in Pune. Emissions from nearby industrial areas of Bhosari and Pimpri-Chinchwad increased NO₂ concentrations in Pune city. Finally, we compared the observations with previous reports over India and found that both HCHO and NO₂ concentrations are lower in Pune compared to the other large cities in India.

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Keywords: Formaldehyde, Nitrogen dioxide, Pune city, Seasonal variation, Diurnal variation, Biomass burning

1 INTRODUCTION

Reactive trace gases make up less than 0.1% of the atmosphere but affect it in numerous ways. Some trace gases act as greenhouse gas and contribute to climate change by changing the radiation budget (e.g., nitrous oxide (N₂O), ozone (O₃)) (Stocker *et al.*, 2013), while others affect atmospheric chemistry by participating in oxidation reactions (e.g., nitrogen dioxide (NO₂), hydroxyl radical (OH)) (Levy, 1971; Crutzen, 1974). Trace gases can also act as pollutants and pose a threat to human health (WHO, 2013; U.S. EPA, 2015). NO₂ and formaldehyde (HCHO) are two such important trace gases in the atmosphere. Being atmospheric pollutants and key ingredients in tropospheric O₃ synthesis, monitoring both trace gases is important for understanding and predicting urban air quality.

NO₂ has been associated with various health hazards and is considered to be an atmospheric pollutant (Burnett *et al.*, 2004; WHO, 2013). It is associated with acid rain (Irwin and Williams, 1988) and nitrate aerosol formation, affecting the turbidity of the atmosphere (Lin and Cheng, 2007). Being photo-reactive, tropospheric NO₂ dissociates in the presence of solar UV radiation, producing nitric oxide (NO) and a free oxygen radical. The oxygen radical subsequently reacts with an oxygen molecule to form O₃. NO gets oxidized to NO₂ through other photochemical reactions,

resulting in a catalytic chain reaction producing O_3 (Crutzen, 1970, 1979). Anthropogenic activities (e.g., fossil fuel burning in automobiles, thermal power plants, industries etc.) and emissions from biomass burning are major sources of NO_2 (Beirle *et al.*, 2003; Stavrakou *et al.*, 2008; van der A *et al.*, 2008; Lamsal *et al.*, 2011). Lightning, forest fires and soil microbial processes are the main natural sources of tropospheric NO_2 (Zhang *et al.*, 2003; Jaeglé *et al.*, 2005; Schumann and Huntrieser, 2007). Photo-dissociation, conversion to nitric acid (HNO_3), hydrolysis of dinitrogen pentoxide (N_2O_5), transport and dry depositions are the main sink processes (Finlayson-Pitts and Pitts, 2000; Jacob, 2000). Beig *et al.* (2007) reported NO_x observations from Pune city during 2003–2004. They reported peak NO_x concentration at 08:00–09:00 hours and substantial reduction in NO_x concentration during monsoon (1–3 ppb). The highest NO_x mixing ratio was found during December (60–70 ppb). Recently Anand *et al.* (2020) have reported NO_x observation from Pune during 2017 and found that the main sources of NO_x in Pune city are the automobile emissions. Various observational studies of NO_2 have been reported in the past from India, which are detailed in Table 1.

The smallest and the most abundant atmospheric carbonyl compound, HCHO, is also a potential pollutant (U.S. EPA, 2015) and an important component for tropospheric O_3 formation (Carter and Atkinson, 1987). Considering that HCHO is formed in the atmosphere as an intermediate oxidation product of various volatile organic compounds (VOCs), it can be used as a proxy for atmospheric VOCs. Biogenic VOCs have been identified as major sources of atmospheric HCHO (Carlier *et al.*, 1986; Fu *et al.*, 2007; De Smedt *et al.*, 2010). Anthropogenic sources and biomass burning are other important sources (Herndon *et al.*, 2005; Zhu *et al.*, 2017). Photolysis, oxidation by OH radicals, dry and wet depositions are the main loss processes (Lowe and Schmidt, 1983; Atkinson, 2000). Satellite based HCHO observations have been used to study trends, spatial variation of HCHO and its precursor VOCs (Chance *et al.*, 2000; Wittrock, 2006; De Smedt *et al.*, 2008; Zhu *et al.*, 2017; Shen *et al.*, 2019). In a recent study by Surl *et al.* (2018), the seasonal variation of HCHO columns over India was found to be highly correlated with monthly averaged surface temperature. The local relationship between isoprene emissions and HCHO production along with the correlation of HCHO columns with surface temperature inferred that the HCHO variability over India is controlled by biogenic emissions rather than anthropogenic emissions. Chaliyakunnel *et al.* (2019) used the GEOS-Chem model to interpret HCHO observations from OMI and GOME-2a over India and found that biogenic VOC emissions were overestimated by ~30–60% for 2009. However, in-situ observations of HCHO required for model and satellite validation are scant compared to NO_2 over India. The comparative discussion between the present study and previous reports has been presented in Table 2.

In this work, we study tropospheric HCHO and NO_2 over a one-year period from January-2018 to February-2019 at the Indian city Pune using the Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) technique (Platt and Stutz, 2008 and references therein). DOAS is a remote sensing technique for the measurement of various gas molecules which shows absorption spectra in the UV-Visible range of electromagnetic radiation. Being an useful and reliable technique it have been used for measurement of HCHO, NO_2 , sulfur dioxide (SO_2) etc. from both ground-based and satellite-borne instruments (Leue *et al.*, 2001; Hönninger *et al.*, 2004; Beirle *et al.*, 2011; Gonzi *et al.*, 2011; Frins *et al.*, 2012). In this manuscript, simultaneous observations of NO_2 and HCHO are being reported in Pune city for the first time, which aims at a better understanding of tropospheric chemistry (including ozone formation) in Pune city. A recent study (Anand *et al.*, 2020) has shown that the average ozone concentration over Pune is higher than the National Ambient Air Quality Standards for ozone (CPCB, 2009). Hence, here we study in detail the ratio HCHO and NO_2 to identify controlling factor for tropospheric ozone formation in Pune city. Seasonal and diurnal characteristics, along with different factors controlling the NO_2 and HCHO variations are explored. Unlike satellite observations, which have maximum one daily observation over a region, these continuous ground-based observations help to study diurnal variations on daily scale and identify if the ozone production can be controlled in a similar way throughout the day.

2 MEASUREMENT SITE AND METHODS

2.1 Measurement Site

The study was conducted in Pune City, India from 2nd January 2018 to 8th February 2019. Pune

Table 1. Previous studies on NO₂ from India.

Authors	Location	Period	Annual (ppb)	Summer (ppb)	Monsoon (ppb)	Post-monsoon (ppb)	Winter (ppb)
Singh and Kulshrestha (2014)	Delhi	October 2012–September 2013	13 ± 7.2	13	5.5		21
Tiwari <i>et al.</i> (2015)	Delhi	September 2010 August 2012	12.5				
Sharma <i>et al.</i> (2010)	Delhi	2008 (winter: 8–28 th February, 2008; summer: 7–30 th April, 2008; post-monsoon: 12–29 th October, 2008)		3.04 ± 1.10		3.21 ± 1.60	10.70 ± 3.25
Chate <i>et al.</i> (2014)	Delhi	December 2012					< 2–47
Kumar <i>et al.</i> (2004)	St. John's college, Agra (Urban, IGP region)	July 1999 to June 2001	4.6 ± 1.0	4.6 ± 0.6	4.1 ± 0.8		5.0 ± 1.2
	Dayalbagh, Agra (sub-urban, IGP region)	July 1999–June 2001	2.9 ± 0.8	3.0 ± 0.8	2.2 ± 0.4		3.4 ± 0.7
Mallik and Lal (2014)	Delhi	2005–2009	27.42 ± 6.98				
	Jodhpur		11.80 ± 0.96				
	Kolkata		30.93 ± 9.31				
	Guwahati		8.66 ± 1.94				
	Durgapur		31.47 ± 8.74				
	Nagpur		16.06 ± 3.82				
Kumar <i>et al.</i> (2016)	Mohali	winter 2011–12					daytime average: 12.0 ± 5.9; nighttime average: 16.7 ± 10.1
		Monsoon 2012				daytime average: 4.6 ± 2.4; night-time average: 6.7 ± 3.6	
Sinha <i>et al.</i> (2014)	Mohali	May 2012		10.7 ± 7.7 ppb			
Peshin <i>et al.</i> (2017)	Delhi	October 2010–December 2014		22.4 ± 19.3	21.0 ± 19.2	22.4 ± 19.3	17.7 ± 13.1
Behera <i>et al.</i> (2015)	Kanpur (semi-urban)	February–March 2004					13.24 ± 4.0
	Kanpur (urban)	February–March 2004					18.56 ± 8.08
	Kanpur (traffic)	February–March 2004					27.0 ± 7.13
	Delhi (semi-urban)	February–March 2004					24.83 ± 7.92
	Delhi (urban)	February–March 2004					39.62 ± 12.02
	Delhi (traffic)	February–March 2004					45.0 ± 12.18

Table 1. (continued).

Authors	Location	Period	Annual (ppb)	Summer (ppb)	Monsoon (ppb)	Post-monsoon (ppb)	Winter (ppb)
Ravindra <i>et al.</i> (2019)	Amritsar	27 th October–6 th December 2016				6.24 ± 0.71	
	Rohtak	27 th October–6 th December 2016				4.70 ± 0.47	
Beig <i>et al.</i> (2013)	Delhi (CWG-2010 center)	3 rd –15 th October, 2010				28.8 ± 13.7	
	Delhi (residential)	3 rd –15 th October, 2010				11.3 ± 5.3	
Hoque <i>et al.</i> (2018)	Pantnagar, (semi-urban, IGP region)	2017	0.5–1.5				
Biswas <i>et al.</i> (2019)	Rural IGP region	2014			0.81 ± 0.20 ppb		8 ± 1.6 ppb in September,
Singh <i>et al.</i> (2010)	Patiala	August 2006–January 2007 and August 2007–January 2008					35.6 ± 20.7 ppb in October, 48.4 ± 20.7 ppb in November, 33 ± 8 ppb in December
Pancholi <i>et al.</i> (2018)	Jodhpur	December 2012–November 2013		13.8 ± 3.2	7.4 ± 4.3	37.8 ± 18.6	16 ± 8.5
Kumar <i>et al.</i> (2020)	Mohali	January 2013–June 2017	8.2 ± 6.7				
Biswas <i>et al.</i> (2020)	Mahabaleshwar	25 th April–30 th May 2018		0.19 ± 0.06			
Present study	Pune	Jan, 2018–Feb, 2019	1.62 ± 1.24	1.56 ± 1.0	0.87 ± 0.60		2.0 ± 1.42

Table 2. Previous studies on HCHO from India.

Authors	Location	Period	Annual (ppb)	Summer (ppb)	Monsoon (ppb)	Post-monsoon (ppb)	Winter (ppb)
Dutta <i>et al.</i> (2010)	Kolkata	summer season of 2007–2008		19.3 ± 9.9			
Ghosh <i>et al.</i> (2015)	Kolkata	July, 2012–April, 2014	217				
Sarkar <i>et al.</i> (2017)	Darjeeling		9.5 ± 13.3				
Hoque <i>et al.</i> (2018)	Pantnagar, (semi-urban, IGP region)	2017	2–6				
Biswas <i>et al.</i> (2019)	Rural IGP region	2014			1.93 ± 0.60		
Khare <i>et al.</i> (2000)	Agra (semi-urban IGP region)	1994–1996	1.9 ± 1.2	2.2 ± 2.1	1.9 ± 1.1		1.9 ± 1.8
Khare <i>et al.</i> (1997a)	Agra (semi-urban IGP region)	February 1995					0.8 ± 0.5
Khare <i>et al.</i> (1997b)	Agra (semi-urban IGP region)	monsoon 1995–1996			1.4 ± 0.8		
Kumar <i>et al.</i> (2020)	Mohali	January 2013–June 2017	8.7 ± 7.5				
Biswas <i>et al.</i> (2020)	Mahabaleshwar	25 th April–30 th May 2018		1.6 ± 0.61			
Present study	Pune	January 2018–February 2019	2.64 ± 1.43	2.75 ± 1.32	1.12 ± 0.70		3.0 ± 1.37

is the 8th most populous city in India and its population has grown ~35% to 5.05 million in 2011 from 3.75 million in 2001 (Office of the Registrar General & Census Commissioner, India, 2011). On the west side of the Pune City is the Western Ghats mountain range. The megacity Mumbai is situated at a distance ~180 km along the western coast in the north-west direction, separated by the Western Ghats. The elevation is 560 m above sea level. On the north-east direction at ~12 km away is the Bhosari industrial complex and towards the north-west is the Pimpri-Chinchwad industrial complex ~11 km away. A MAX-DOAS instrument was installed on the roof of a hostel complex named Prithvi (Fig. 1). There is a road ~150 m towards the east of this building, overlooking academic institutions, residential complexes, and a hill. On the west, at ~1 km are commercial and residential complexes. Towards the north and south are academic campuses and residential complexes. The city center is situated towards the east-southeast direction ~7–10 km away from the measurement site. Fig. 1(A) shows the location of Pune city in India. Whereas Fig. 1(B) shows the satellite image around the MAX-DOAS observation site. The numbers 1–8 in Fig. 1(B) show the different sectors around the MAX-DOAS observation site. Fig. 1(C) shows the zoomed in view of MAX-DOAS observation site where the red arrow shows the viewing direction of the instrument.

There are three seasons observed in Pune (Gadgil and Dhorde, 2005). The summer period is classified as March, April and May (MAM), followed by the Indian Summer Monsoon (ISM) in June, July August and September (JJAS). The winter period spans over December, January and February. Ali *et al.* (2012) have reported a brief post-monsoon season including October and November, but in this present study we have merged the post-monsoon and winter season into a single season from October to February (ONDJF) as they have similar wind direction and temperature. The ISM season (JJAS) is responsible for the major rainfall over Pune with an average rainfall of 138 mm month⁻¹ (Revadekar *et al.*, 2015). The predominant winds during ONDJF, MAM and JJAS are north-easterly, north-westerly, and south-westerly.

2.2 MAX-DOAS Observations

The MAX-DOAS instrument was installed on the rooftop of Prithvi hostel (18.54°N, 73.80°E; ~30 m above ground). The scanner pointed towards 355° with respect to the geometric north.

Fig. 1. The location of the measurement site at the Prithvi hostel (18.54°N, 73.80°E) in Pune City. Panel 'A' represents the location of Pune city. Panel 'B' shows the Prithvi hostel location. The numbers 1–8 show the different sectors separated by the black lines. Panel 'C' represents a zoomed in location, with the MAX-DOAS viewing direction indicated by the arrow.

The MAX-DOAS instrument consists of two spectrometers operating in the 306.08–468.77 nm and 441.91–583.36 nm windows, respectively. The field of view (FOV) of the instrument is 0.2°. Further details of the instrument specification and calibration can be found in our previous report by Biswas *et al.* (2019). The observations in Pune City were conducted from 2nd January 2018 to 8th February 2019. There were occasional data gaps during the campaign period due to instrument malfunction or logistical issues. After quality control, a total of 257 days of successful MAX-DOAS observations were used for further analysis. There were three significant gaps in MAX-DOAS observations during 15th July–14th August 2018; 22nd August–10th September 2018; and 30th September–21st October 2018. Each scan measured scattered sunlight along eight different elevation angles (90°, 40°, 20°, 10°, 5°, 3°, 2° and 1°) when the solar zenith angle (SZA) was < 75°. The dark current, offset and calibration spectra were recorded every evening after the MAX-DOAS observations and were used to correct the measured spectra. The measured solar spectra were analyzed using the QDOAS software (Danckaert, 2014) to obtain differential slant column densities (dSCDs). Detection limit for dSCD calculations were calculated by dividing the absorption cross-section of trace gases by corresponding root mean square (RMS) of the residual structure from the DOAS analysis. A zenith spectrum from every scan cycle was used to remove the stratospheric contribution in off-axis measurements (Hönninger *et al.*, 2004). The spectral window for O₄, HCHO and NO₂ dSCD analysis were 350–386 nm, 332–358 nm and 415–440 nm respectively. The QDOAS analysis settings and the cross-sections used are described in our previous work (Biswas *et al.*, 2019). Examples of the fits for oxygen dimer (O₄), NO₂ and HCHO are shown in Fig. 2. The boundary layer volume mixing ratios for HCHO and NO₂ were calculated using 'O₄ methodology' (Sinreich *et al.*, 2010; Mahajan *et al.*, 2012; Gómez Martín *et al.*, 2013; Prados-Roman *et al.*, 2015; Biswas *et al.*, 2019). In the atmosphere, oxygen molecules form collision induced transient O₄. The O₄ concentration in the atmosphere is proportional to the square of the atmospheric pressure. Hence, O₄ dSCDs from different elevation angles give information of the average effective path lengths. Using O₄ dSCDs from lower elevation angles (3° and lower), information of average effective path lengths in the boundary layer can be obtained by dividing O₄ dSCDs with the mean O₄ extinction coefficient in the boundary layer. The trace gas mixing ratios are then calculated by dividing the trace gas dSCDs by these path lengths. The errors in the dSCD calculations from DOAS analysis are propagated to calculate the error in mixing ratios. The main sources of errors in the

Fig. 2. DOAS fits for O₄, NO₂ and HCHO. (Top panel) O₄: 15th April, 2018 13:28 hr; SZA: 23.0°; Elevation angle (EA): 3.0°; dSCD: $1.7 \times 10^{43} \pm 1.7 \times 10^{41}$ molecules² cm⁻⁵; RMS: 3.1×10^{-4} . (Middle panel) NO₂: 15th April, 2018 09:31 hr; SZA: 37°; EA: 3.0°; dSCD: $6.7 \times 10^{16} \pm 4.9 \times 10^{14}$ molec. cm⁻²; RMS: 4.9×10^{-4} . (Bottom panel) HCHO: 15th April, 2018 11:04 hr; SZA: 16.1°; EA: 3.0°; dSCD: $9.8 \times 10^{16} \pm 2.0 \times 10^{15}$ molec. cm⁻²; RMS: 3.4×10^{-4} .

DOAS technique come from random noise in spectra (associated with photon statistics and instrumental design), unexplained spectral structure, uncertainties in environmental conditions. Errors also be introduced during the DOAS analysis process from spectral fitting of absorptions cross-sections and measured scattered solar radiation (e.g., least square fit), separating fine band absorption spectra from broad band structures due to scattering, uncertainty in wavelength alignment and uncertainty in path length calculations. For detailed discussion on errors from DOAS analysis please refer to Platt and Stutz (2008). The mixing ratios of HCHO and NO₂ were calculated using the respective trace gas and O₄ dSCDs from scans measured at SZA < 75° and elevation angle ≤ 3°. Standard atmospheric temperature, pressure and O₄ concentration profiles were used for the calculation of the path length.

2.3 Fire Data

Fire data from Moderate Resolution Imaging Spectroradiometer (MODIS) aboard Terra and Aqua satellite was collected from National Aeronautics and Space Administration (NASA) Earth observations repository (NASA, 2020). Daily gridded fire count data (MOD14A1) at a $0.1^\circ \times 0.1^\circ$ resolution were used to study effect of pollutants transported from nearby fire events to the observation site. The data was downscaled to a $0.5^\circ \times 0.5^\circ$ spatial resolution. The grid points which did not show any fire counts were associated with 'no fire' events. For all the grid points over the Indian sub-continent, the median value of all the fire events was calculated. Grid points which had higher fire counts than the median value were considered to be associated to 'high fire' events. Grid points with fire counts less than median value were associated with 'low fire' events.

2.4 Back-trajectory Analysis

Back-trajectory analysis for air parcels reaching the observation site was carried out using Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler and Hess, 1998).

Daily gridded meteorological data of $0.5^\circ \times 0.5^\circ$ resolution from Global Data Assimilation System (GDAS) were used as an input for the HYSPLIT model. The back-trajectories for air parcels reaching the observation site every hour were calculated for past 24 hours.

3 RESULTS

The MAX-DOAS instrument was operational for the period between 2nd January, 2018 and 8th February, 2019. As the observations were conducted over more than a year, temporal variability was expected and observed in the analyzed results. We divided the data according to three seasons observed over Pune City as discussed earlier. Summer, monsoon and post-monsoon/winter seasons were observed during March to May (MAM); June, July to September (JJAS) and October to February (ONDJF) respectively. Henceforth in this paper, the three seasons will be abbreviated as the initials of the months mentioned above.

Fig. 3 shows the time series of O₄, HCHO and NO₂ dSCDs at different elevation angles. The top panel in Fig. 3 shows the time series of O₄ dSCDs. Table 3 represents the average trace gas dSCDs, RMS of residual structure at 1° elevation angle. The average O₄ dSCD and the RMS of residual structure at the 1° elevation angle during MAM were $1.5 \times 10^{43} \pm 2.2 \times 10^{41}$ molec.² cm⁻⁵ (ranging from 5.8×10^{42} molec.² cm⁻⁵ to 3.0×10^{43} molec.² cm⁻⁵) and 3.9×10^{-4} . During JJAS and ONDJF, the average O₄ dSCDs at the 1° elevation angle were $1.7 \times 10^{43} \pm 3.1 \times 10^{41}$ molec.² cm⁻⁵ (ranging from 4.0×10^{43} molec.² cm⁻⁵ to 2.8×10^{42} molec.² cm⁻⁵) and $1.1 \times 10^{43} \pm 2.2 \times 10^{41}$ molec.² cm⁻⁵ (ranging from 3.5×10^{43} molec.² cm⁻⁵ to 3.8×10^{42} molec.² cm⁻⁵). Corresponding mean RMS were 5.5×10^{-4} and 3.9×10^{-4} for JJAS and ONDJF, respectively.

The middle panel in Fig. 3 represents the time series of NO₂ dSCDs. The average dSCD and RMS of residual structure for NO₂ at the 1° elevations angle were $4.8 \times 10^{16} \pm 5.3 \times 10^{14}$ molec. cm⁻² (ranging from 1.4×10^{16} molec. cm⁻² to 1.0×10^{17} molec. cm⁻²) and 5.1×10^{-4} during MAM. The average dSCD and RMS of residual structure are the 1° elevation angle during JJAS were $3.3 \times 10^{16} \pm 5.5 \times 10^{14}$ molec. cm⁻² (ranging from 5.4×10^{15} molec. cm⁻² to 9.7×10^{16} molec. cm⁻²) and 5.0×10^{-4} respectively. During ONDJF, the average NO₂ dSCDs and RMS of residual structure at the

Fig. 3. Differential Slant Column Densities (dSCDs) of O₄, NO₂ and HCHO. Colours represent measurements at different viewing elevation angles.

Table 3. MAX-DOAS results (average dSCDs, dSCD ranges and RMS) for 1° elevation angle.

seasons	O ₄			NO ₂			HCHO		
	Avg. dSCDs (molec. ² cm ⁻⁵)	dSCD range (molec. ² cm ⁻⁵)	Avg. RMS	Avg. dSCDs (molec. cm ⁻²)	dSCD range (molec. cm ⁻²)	Avg. RMS	Avg. dSCDs (molec. cm ⁻²)	dSCD range (molec. cm ⁻²)	Avg. RMS
MAM	$1.5 \times 10^{43} \pm 2.2 \times 10^{41}$	$5.8 \times 10^{42} - 3.0 \times 10^{43}$	3.9×10^{-4}	$4.8 \times 10^{16} \pm 5.3 \times 10^{14}$	$1.4 \times 10^{16} - 1.0 \times 10^{17}$	5.1×10^{-4}	$5.0 \times 10^{16} \pm 2.8 \times 10^{15}$	$1.8 \times 10^{16} - 9.9 \times 10^{16}$	4.8×10^{-4}
JJAS	$1.7 \times 10^{43} \pm 3.1 \times 10^{41}$	$4.0 \times 10^{43} - 2.8 \times 10^{42}$	5.5×10^{-4}	$3.3 \times 10^{16} \pm 5.5 \times 10^{14}$	$5.4 \times 10^{15} - 9.7 \times 10^{16}$	5.0×10^{-4}	$2.6 \times 10^{16} \pm 3.7 \times 10^{15}$	$5.8 \times 10^{15} - 7.1 \times 10^{16}$	6.2×10^{-4}
ONDJF	$1.1 \times 10^{43} \pm 2.2 \times 10^{41}$	$3.5 \times 10^{43} - 3.8 \times 10^{42}$	3.9×10^{-4}	$4.5 \times 10^{16} \pm 5.2 \times 10^{14}$	$1.4 \times 10^{16} - 1.0 \times 10^{17}$	5.1×10^{-4}	$4.1 \times 10^{16} \pm 2.9 \times 10^{15}$	$9.7 \times 10^{15} - 8.0 \times 10^{16}$	5.0×10^{-4}

Fig. 4. Time series of (a) NO₂ and (b) HCHO mixing ratios throughout the measurement period. Monthly average mixing ratio of (c) NO₂ and (d) HCHO.

1° elevation angle were $4.5 \times 10^{16} \pm 5.2 \times 10^{14}$ molec. cm⁻² (ranging from 1.4×10^{16} molec. cm⁻² to 1.0×10^{17} molec. cm⁻²) and 5.1×10^{-4} respectively. NO₂ mixing ratios were calculated using the O₄ method. Fig. 4(a) shows the mixing ratios of NO₂ measured during the current study. The average NO₂ mixing ratio and detection limit during MAM were 1.6 ± 1.0 ppb (ranging from 0.4 to 7.8 ppb) and 0.1 ppb respectively. During JJAS the average NO₂ mixing ratio and detection limit were 0.9 ± 0.6 ppb (ranging from 0.1 to 6.4 ppb) and 0.1 ppb. The average NO₂ mixing ratio and detection limit during ONDJF were 2.0 ± 1.4 ppb (ranging from 0.3 to 10.6 ppb) and 0.1 ppb, respectively. The annual average NO₂ mixing ratio was 1.6 ± 1.2 ppb. Fig. 4(c) shows the monthly average NO₂ mixing ratios. January 2018 and July, 2018 showed the highest and the lowest monthly average NO₂ mixing ratios.

Bottom panel of Fig. 3 shows the HCHO dSCD time series. The average HCHO dSCD at 1° elevation angle during MAM, JJAS and ONDJF were $5.0 \times 10^{16} \pm 2.8 \times 10^{15}$ molec. cm⁻² (ranging

from 1.8×10^{16} molec. cm^{-2} to 9.9×10^{16} molec. cm^{-2} ; $2.6 \times 10^{16} \pm 3.7 \times 10^{15}$ molec. cm^{-2} (ranging from 5.8×10^{15} molec. cm^{-2} to 7.1×10^{16} molec. cm^{-2}); and $4.1 \times 10^{16} \pm 2.9 \times 10^{15}$ molec. cm^{-2} (ranging from 9.7×10^{15} molec. cm^{-2} to 8.0×10^{16} molec. cm^{-2}) respectively. The average RMS of residual structure at the 1° elevation angle for MAM, JJAS and ONDJF were 4.8×10^{-4} , 6.2×10^{-4} and is 5.0×10^{-4} respectively. The average HCHO mixing ratio and detection limit during MAM were 2.8 ± 1.3 ppb (ranging from 0.4 to 9.6 ppb) and 0.4 ppb respectively (Fig. 4, bottom panel). During JJAS, the average mixing ratio is 1.1 ± 0.7 ppb (ranging from 5.8 to 0.2 ppb) with the average detection limit being 0.4 ppb. The average HCHO mixing ratio and detection limit were 3.0 ± 1.4 ppb (ranging from 0.2 to 12.8 ppb) and 0.6 ppb during ONDJF. The annual average HCHO mixing ratio was 2.6 ± 1.4 ppb. Fig. 4(d) represents the monthly average HCHO mixing ratios. July and August 2018 showed the lowest monthly average HCHO mixing ratios while January 2018 showed highest average HCHO mixing ratio.

4 DISCUSSION

4.1 Seasonal and Diurnal Variations

The diurnal profiles of O_4 dSCDs showed a 'U' shape with two dSCDs maxima, early the morning and late evening, during ONDJF. Fig. S1(a) shows a typical day from ONDJF (7th Jan, 2018). During MAM, the diurnal profile of O_4 dSCDs turned into skewed 'W' shape with three daily dSCD highs, early morning, midday, and evening: indicating an increase in the aerosol loading during the daytime. Fig. S1(b) shows a typical day from MAM (20th Apr, 2018). At any specific wavelength and temperature, the dSCDs depends on the concentration, path length and absorption cross-section. More aerosols in the atmosphere lead to multiple scattering of photons, increasing the path length and resulting in higher dSCDs. Hence the relatively higher dSCDs during midday indicate an increase in aerosols during MAM due to higher emissions of VOCs (Harley *et al.*, 2001; Tarvainen *et al.*, 2005) leading to increase in secondary organic aerosol (SOA). In comparison, during JJAS the sky is cloudy due to monsoon. Photons hence undergo multiple scattering and path lengths get mixed up for different SZA. Hence there was no identifiable diurnal pattern in the dSCDs ('U' or 'W') during JJAS.

Fig. 5 shows the seasonal variation in the diurnal trends of HCHO and NO_2 mixing ratios and the HCHO/ NO_2 ratio. The left column of Fig. 5 shows the diurnal variation in the NO_2 mixing ratios during ONDJF, MAM and JJAS. For all the three seasons, the NO_2 mixing ratios are low in the early morning at 07:00 hrs (2.6 ± 0.7 ppb in ONDJF; 2.0 ± 0.8 ppb in the MAM and 0.9 ± 0.5 ppb in JJAS). They increase through the morning between 07:00–09:00 hrs, reaching the diurnal maximum for all the seasons at approximately 09:00 hrs (4.5 ± 1.6 ppb in ONDJF; 2.9 ± 1.4 ppb in the MAM and 1.4 ± 1.0 ppb in JJAS). The duration between 08:00–10:00 hrs has the maximum traffic density on the streets of Pune as it represents the beginning of office hours. After 09:00 hrs, the NO_2 starts decreasing and reaches the diurnal minimum at 14:00 hrs during ONDJF (1.2 ± 0.4 ppb), at 14:00 hrs during MAM (1.0 ± 0.2 ppb) and at 13:00 hrs during JJAS (0.6 ± 0.2 ppb). After this post noon minimum, NO_2 increases by a small amount in the late afternoon. The 09:00 hrs maxima in the diurnal profile of mixing ratio indicates the contribution from automobile emissions during the morning peak traffic. As the day progresses, an increase in the solar radiation leads to a low in the diurnal profile during noon time, driven by photochemistry. Beig *et al.* (2007) reported the diurnal variation of NO_x and CO over Pune from June 2003 to May 2004. Both NO_x and CO showed two daily maxima, one during the morning (08:00–09:00 hrs) and another during the late evening (20:00–21:00 hrs). Automobile emissions being the main source of NO_x and CO over Pune, the observed two peaks are indicative of traffic peak. Our observations capture the morning NO_2 peak but due to the lack of solar radiation (hence MAX-DOAS observations are not available) we do not expect to see the late evening peak.

The diurnal profile of NO_2 shows the lowest values during JJAS. This is due to the removal of NO_2 via wet deposition during monsoon. Using ERA5 reanalysis product (Hersbach *et al.*, 2020) we have studied the time series of total precipitation over $0.3^\circ \times 0.3^\circ$ box around the Pune observation site (Fig. S2(b)) and found that JJAS has highest rainfall compared to the rest of the observational period. NO_2 shows the highest values during ONDJF. During the winter months, due to the cooler temperatures, the boundary layer heights remain lower compared to warmer summer months

Fig. 5. Seasonal variation in the diurnal profile of (A, D, and G) NO_2 and (B, E, and H) HCHO mixing ratios and (C, F, and I) HCHO/ NO_2 ratio. The top, middle and bottom panels represent profiles during ONDJF, MAM and JJAS, respectively.

of MAM (Ali *et al.*, 2012a; Safai *et al.*, 2007). Hence NO_2 emitted near the surface gets trapped and leads to an increase in the concentrations. This is often observed in other pollutants during the winter months across India (Kumar *et al.*, 2004; Singh and Kulshrestha, 2014).

The middle column in Fig. 5 shows the diurnal variation in the HCHO mixing ratios during ONDJF, MAM and JJAS. In all the three seasons, the HCHO mixing ratios show similar diurnal variation, with the average HCHO mixing ratios showing minima in the early morning and late afternoon. In the early morning (07:00 hrs) the mixing ratios start increasing from low values (2.4 ± 0.4 ppb in ONDJF; 2.2 ± 1.0 ppb in MAM; and 0.9 ± 0.3 ppb in JJAS) and reach a maximum at 10:00 hrs in the morning (4.2 ± 1.4 ppb in ONDJF; 3.7 ± 1.5 ppb in MAM and 1.4 ± 1.0 ppb in JJAS). After 10:00 hrs, the HCHO concentrations decrease gradually until the late afternoon during ONDJF and JJAS, reaching minimum values of 1.8 ± 0.7 ppb and 0.7 ± 0.3 ppb respectively. The main reason for this is that in the morning, due to the presence of solar radiation, VOCs get oxidized to HCHO leading to an increase. Later in the day, with increasing solar radiation the photo-dissociation of HCHO also starts increasing, leading to a loss of HCHO. These two competing processes result in a decrease after a peak at 10:00 hrs in the morning.

The average diurnal mixing ratios are lowest during JJAS. Due to wet deposition during monsoon, the HCHO is lower. The average HCHO mixing ratios during ONDJF were the highest among all the three seasons, which as explained earlier is due to the low boundary layer heights in winter compared to the summer months of MAM.

The right-hand column in Fig. 5 shows the diurnal variation in the HCHO/ NO_2 ratios during ONDJF, MAM and JJAS. Past studies (Chameides *et al.*, 1992; Schroeder *et al.*, 2017) have established that the HCHO/ NO_2 ratio is an important indicator for identifying the sensitivity of ozone formation towards VOC and NO_x concentrations. At low NO_x concentrations, tropospheric O_3 formation is independent of the VOC concentrations and linearly proportional to NO_x concentrations, i.e., NO_x limited (Chameides *et al.*, 1992). Whereas, at low VOC concentrations, tropospheric O_3 formation is found to be linearly proportional to the VOC concentrations, i.e., VOC limited. Schroeder *et al.* (2017) reported that HCHO/ NO_2 ratio between 1.1 and 4.3 denotes border line regime for O_3 formation. HCHO/ NO_2 ratios less than 1.1 indicate a VOC limited regime, whereas values more than 4.3 indicate a NO_x limited regime for O_3 formation. Identifying the regime for O_3 formation is important from a policy perspective for controlling the air quality in a city. In Pune, observations show that for all the seasons, the HCHO/ NO_2 ratios remains less than 1.1 during early morning (07:00–09:00 hrs) indicating a VOC limited regime. The ratio increases through the day, reaching a maximum at approximately 13:00 hrs (2.1 ± 0.5 ppb in ONDJF; 2.5 ± 0.5 ppb in MAM and 1.9 ± 0.7 ppb in JJAS) and then decreasing again. This indicates that during most of the day, the HCHO/ NO_2 ratio remains in the border regime although it is in the VOC limited regime in the mornings and evenings. During JJAS the HCHO/ NO_2 ratios are the lowest, whereas during MAM they are highest. Beig *et al.* (2007) reported that surface O_3 concentration in Pune increases between 08:00–12:00 hrs,

reaching the daily maximum around noon due to photochemical synthesis in presence of high solar radiation. The HCHO/NO₂ ratios remain in the border regime during noon, hence controlling the emission of either HCHO or NO₂ will not have a large effect on reducing surface ozone concentrations, but rather both need to be reduced. However, during the mornings and evenings, reduction in HCHO i.e., the VOC concentrations can result in lower surface O₃ as it is a VOC limited regime. According to the National Ambient Air Quality Standards set by Central Pollution Control Board of India, the standard for ozone concentrations averaged over 8 hour exposure period is 100 µg m⁻³ or ~51 ppb (CPCB, 2009). In a recent study, Anand *et al.* (2020) have reported that during 2017, the 8 hour average (10:00–18:00 hours) ozone mixing ratios in some parts of Pune reached over 70 ppb, with peaks of ~92 ppb. These values are much higher than the national air quality standards and show the need to reduce ozone in Pune. The results from this study conclude that a reduction in VOC emissions is the most efficient method for reducing surface ozone in Pune.

4.2 Weekend Effect on HCHO and NO₂

In an urban atmosphere, concentrations of primary pollutants are usually found to be significantly lower during the weekends compared to weekdays as emissions from peak traffic are lower (Marković *et al.*, 2008; Han *et al.*, 2011; Sadanaga *et al.*, 2012; Seguel *et al.*, 2012). We studied if this phenomenon also existed over Pune for all the three seasons. Fig. 6 shows the seasonal variation showing the weekend effect for NO₂ and HCHO mixing ratios and the HCHO/NO₂ ratio. Considering that in Pune many of the offices follow a six-day working week (Monday–Saturday), we used observations only from Sundays to discern the weekend effect. Observations from all other days of the week except Sundays were used for computing an average diurnal profile for weekdays.

The left, middle and right column of Fig. 6 shows the seasonal variation in NO₂, HCHO and the HCHO/NO₂ ratio during weekdays and weekend. For all the three seasons the diurnal profiles of the average trace gas mixing ratios on weekdays and weekends are almost similar with small differences less than the standard deviation in the observations. Similarly, the diurnal profile of the average HCHO/NO₂ ratio on weekdays and weekends are also comparable during all the three seasons. Thus, the observations suggest that both HCHO and NO₂ do not show any considerable difference between weekdays and weekends in any of the seasons.

4.3 Effect of Fire Events on HCHO and NO₂

Open biomass burning and crop residue burning in India contributes to air pollution all over the country, even on a regional scale (Sharma *et al.*, 2017; Liu *et al.*, 2018; Bray *et al.*, 2019; Shaik *et al.*, 2019). Venkataraman *et al.* (2006) reported that open burning contributes about ~25% of the black carbon, organic matter, and carbon monoxide emissions over India. They are also responsible for ~9–13% of the PM_{2.5} emissions. Considering that biomass burning is an important source for

Fig. 6. Weekend effect on (A, D, and G) NO₂ and (B, E, and H) HCHO mixing ratio and (C, F and I) HCHO/NO₂ ratio. The top, middle and bottom panels represent profiles during ONDJF, MAM and JJAS, respectively.

Fig. 7. (A) Back-trajectories for past 12 hours reaching the observation site every hour during MAM season of 2018. (B) Average fire counts during a representative day of 8th May, 2018. (C) Diurnal plot of NO₂ mixing ratios during MAM with no fire (back-trajectories did not encounter any fires), all fire (back-trajectories encountered at least one fire event), high fire events (back-trajectories encountered fire events more than the median values of fire counts). (D) Represents a similar diurnal plot for HCHO.

atmospheric NO₂ and HCHO, we study the effects of open fire events on HCHO and NO₂ in Pune city. Numbers of fire events (0–30) were represented on every grid point. To quantify whether an observation at the site in Pune was affected by fire or not, corresponding HYSPLIT back-trajectories passing over locations where fires occurred in the last 12 hours were identified. Of the three seasons discussed above, the summer season (MAM) experienced the most fire events. Hence, we will be discussing the effect of fires only for MAM. Fig. 7(A) represents all the back-trajectories during MAM. Fig. 7(B) shows the fire counts for a representative day from MAM, 2018 (8th May, 2018) around the observation site during MAM. Fig. 7(C) represents the diurnal plot of NO₂ mixing ratios during MAM from the three scenarios of no-fire, all-fire and high-fire events. No-fire days showed the lowest NO₂ mixing ratios succeeded by all-fire events. Mixing ratios from high-fire events had the highest values for the trace gases. NO₂ mixing ratios from all the three types of fire events displayed the peak daily values at 09:00 hrs. The average NO₂ mixing ratios at 09:00 hrs were 2.7 ± 1.2 ppb, 3.2 ± 1.7 ppb, 3.8 ± 1.6 ppb for no-fire, all-fire and high-fire events, respectively. There was ~40% increase in the peak NO₂ mixing ratio in the high-fire observations as compared to the no-fire events during MAM. Fig. 7(D) represents diurnal plot of HCHO mixing ratios during MAM. HCHO mixing ratios shows daily maxima at 10:00 hrs during all the three types of fire events. Average HCHO mixing ratios at 09:00 hrs were 3.4 ± 1.5 ppb, 4.4 ± 1.4 ppb, 5.1 ± 1.1 ppb for no-fire, all-fire and high-fire events, respectively. During early morning and late afternoon hours there were no significant differences in the mixing ratios between no-fire, all-fire and high-fire events. This is most likely because crop residue burning generally starts in the morning and finishes by late afternoon, hence we found the strong fire signature in trace gas mixing ratios during 09:00–10:00 hours. There was an increase of 48% in the peak HCHO mixing ratio during MAM for high-fire events compared to no-fire events. This suggests that the fire events around Pune city contributed to an increase in the HCHO and NO₂ mixing ratios observed at the site.

4.4 Sectorial Analysis

To know whether the measured trace gases originated from any specific geographical region, we divided the space around the observation site into 8 sectors (Fig. 1). Considering the north to be 0°, the sectors were defined as: sector-1: 0°–45°; sector-2: 45°–90°; sector-3: 90°–135°; sector-4: 135°–180°; sector-5: 180°–225°; sector-6: 225°–270°; sector-7: 270°–315°; sector-8:

Fig. 8. Box-whisker plot of sector-wise NO_2 mixing ratios. All the top panels show 24 hour back-trajectory analysis and the bottom panels show the 12 hour back-trajectory analysis. The red '+' signs represent the outliers for the corresponding sectors.

315°–360°). The HYSPLIT back-trajectories were then used to identify air masses which spent at least 60% of its time in last 12 hours and 24 hours in any sector. The hypothesis is that if an air parcel spends 60% or more of its time in a sector, the air parcel will carry representative information from that sector compared to the other.

Fig. 8 shows the box-whisker plots of observations corresponding to the different sectors in which air parcels spent at least 60% of their time in the last 12 or 24 hours. The median value, 75th percentile and 25th percentiles values for each sector are shown in the box for corresponding sectors. The whiskers represent 2.7 sigma (99.3%) level of the data for corresponding sectors. The red '+' signs represents the outliers for each sector. During ONDJF, easterly wind prevails in Pune city, which is evident from the sector analysis. For 12 hour back-trajectories, 36.9% of the total observations were associated with the air parcels coming from sector 3 followed by sector 2 (22.6%) and sector 1 (4.8%). Figs. 8(A) and 8(D) show the analysis for the 24 hour back-trajectories and 12 hour back-trajectories for NO_2 during ONDJF. For both 24 hour and 12 hour back-trajectories, the highest median NO_2 corresponds to air parcels coming from sector 1 followed by sector 4. As described earlier, this could be due to a sampling bias as the number of observations associated with air parcels from sector 1 are far less compared to sectors 2 and 3. However, this sector also coincides with the Bhosari industrial region, situated to the north-east of the observation site at a distance of ~12 km and could contribute towards higher NO_2 at the observation site. For both 24 hour and 12 hours back-trajectories, the median NO_2 values for sector 3 are higher than sector 2. This indicates that the air-masses coming from sector 3 have higher NO_2 sources—this sector points towards the main city area as shown in Fig. 1 and hence higher concentrations of pollutants are expected. Sectors 2 and 3 contain many outliers. We found that 88.7% (92.3%) of the outliers from sector 3 (sector 2) occurred during 08:00–12:00 hours, which corresponds to the peak traffic hours, suggesting that the outliers are most likely from automobile emissions.

During MAM the prevailing wind direction is north-westerly. For 12 hour back-trajectories, 40.3% of the total NO_2 observations travel over sector 7, followed by sector 8 (18.5%) and sector 6 (7.7%). For both the 24 hour (Fig. 8(B)) and 12 hour (Fig. 8(E)) back-trajectories, the median NO_2 from sector 8 showed the highest value. This agrees with the fact that the Pimpri-Chinchwad industrial area is located ~12 km north-west of the observation site and hence the air parcels coming from that direction are expected to have more NO_2 . Sector 6, 7 and 8 show large number outliers as compared to the other sectors during MAM. 87.5% (75.14) outliers for sector 8 (sector 7) occur during 08:00 hrs–11:00 hrs, indicating that the outliers are probably from automobile emissions during the peak traffic periods, similar to ONDJF. During JJAS, south-westerly winds prevail in Pune due to the large-scale monsoon circulation. This is seen in the back-trajectory

data, with about 42.8% of the air parcels passing over sector 6, followed by sector 7 (23.7%) and sector 5 (6.0%) for the 24 hour back-trajectories. For the 24 hour back-trajectories (Fig. 8(C)), sector 7 shows highest median value. For the 12 hour back-trajectories sector 8 shows highest median values (Fig. 8(F)). Although this could be due to sampling bias resulting from a low number of trajectories passing over this sector, it also indicates emission of pollutants from the Pimpri-Chinchwad industrial region. 71.2% (54.4%) outliers from sector 7 (sector 6) for the 12 hour back-trajectories occurred during 08:00–12:00 hours, similar to the other seasons.

Fig. 9 shows a box-whisker plot for the sector-wise analysis of HCHO. Figs. 9(A) and 9(D) represent the HCHO box-whisker plots for the 24 hour and 12 hour back-trajectories respectively during ONDJF. In the case of HCHO during ONDJF, sector 4 shows the highest HCHO median, which could be due to a sampling bias (only 3% and 4.4% of air masses for 24 hr and 12 hr back-trajectories were from sector 4). Air masses from sector 3 and sector 2 account for most of the observations (36.9% and 22.6% respectively). Most of the outliers from sector 3 (96.2%) and sector 2 (99%) occurred during 08:00 hrs–12:00 hrs, similar to NO₂ and coinciding with automobile emissions from excess morning traffic. The total number of outliers from every sector, are much lower for HCHO than for NO₂ indicating that the HCHO outliers probably have different sources or less stronger sources compared to NO₂. While the spread of the whiskers from different sectors is more in case of HCHO, the spread is narrow for NO₂. This indicates that the spread in the values of the background concentrations of HCHO is larger than for NO₂, which shows a lower standard deviation. This implies that for elevated NO₂ the sources are most likely local as NO₂ has a photochemical lifetime of few minutes during day (de Foy *et al.*, 2015 and references therein). HCHO is produced by a multistep oxidation process of VOCs. Hence, VOCs transported from other regions can contribute to the locally observed HCHO. Additionally, the atmospheric lifetime of HCHO is of few hours (Zhu *et al.*, 2014), which adds to the observed variability in HCHO from different sectors. The higher spread in the higher variation in the background leads to a lower number of outliers (as more data points come within the 2.7 sigma limits). Figs. 9(B) and 9(E) represent the sector segregated 24 hour and 12 hour back-trajectories during MAM. During MAM, sector 2 (sector 4) show the highest median HCHO for the 24 hour (12 hour) back-trajectories. However, this could be due to a sampling bias as there are very few observations corresponding to the air parcels from those sectors. The largest number of air parcels travel over sector 7 and sector 8 (40.3% and 18.5% respectively). During JJAS, for both the 24 hour and 12 hour back-trajectories (Figs. 9(C) and 9(F)), sector 2 shows the highest HCHO median value. As mentioned above, this is probably resulting due to a sampling bias due to a low number of observations corresponding to the air parcels from those sectors. Just as for NO₂, air parcels from sector 6 and sector 7 show the largest number of HCHO observations during JJAS. The HCHO median values

Fig. 9. Box-whisker plot of sector-wise HCHO mixing ratios. All the top panels show the 24 hour back-trajectory analysis, and the bottom panels show the 12 hour back-trajectory analysis. The red '+' signs represent the outliers for the corresponding sectors.

for sector 7 are higher than sector 6. 97.14% (53%) of the outliers during MAM from sector 7 (sector 6) occurred during 08:00 hrs–12:00 hrs. In the case of HCHO, during MAM and JJAS the outliers are more spread throughout the day as compared to NO₂ which showed most of the outliers in the morning hours. This indicates that the sources of outliers for HCHO are different as compared to NO₂.

4.5 Comparison of Observations from Other Parts of India

Previous observations of NO₂ in India are presented in Table 1. We have not discussed observations of NO_x (NO + NO₂) and restricted our discussion to NO₂ observations reported from urban and semi-urban locations in India. In comparison with previous observations given in Table 1, the annually average NO₂ mixing ratio in Pune is lower than the urban sites of Delhi, Jodhpur, Kolkata, Guwahati, Durgapur, Nagpur, Mohali and Agra. The semi-urban locations in Indo-Gangetic plain (IGP) region (e.g., Kanpur, Agra) reported more NO₂ mixing ratio compared to Pune. IGP region has the highest population density in India and often associated with high level of pollution (Gautam *et al.*, 2007; Raatikainen *et al.*, 2014; Sen *et al.*, 2017). This indicates that Pune has cleaner atmosphere compared to other Indian cities. As expected, the semi-urban site at Pantnagar and high altitude region of Mahabaleshwar reported lower NO₂ mixing ratios (0.5–1.5 ppb and 0.19 ± 0.06 ppb respectively) as compared to the present study (1.6 ± 1.2 ppb). Like the present study, all the previously mentioned studies in urban regions (except Jodhpur) showed the highest NO₂ values during winter indicating BL controlled mixing ratio of trace gases. Interestingly, the NO₂ values during monsoon in Pune and in rural IGP were comparable. This shows that although the urban region of Pune has higher sources, wet scavenging during monsoon is effective at removing this pollutant from the atmosphere to bring it down to levels comparable to rural environment. The diurnal profiles of NO₂ from Delhi showed a similar automobile emission induced morning peak (at ~10:00 hrs) compared to the present study. Also biomass (crop residue) burning increases NO₂ mixing ratios in north-west India, whereas the impact is less in Pune.

Compared to NO₂, relatively fewer observations of HCHO have been made over India (Table 2). The annual average HCHO mixing ratio in Pune was lower than the megacity of Kolkata and the hill station of Darjeeling and Mohali, a city in IGP region. The high HCHO mixing ratio in Kolkata is probably due to high anthropogenic VOC emission from automobiles and Industries. Whereas HCHO in Darjeeling are oxidation product of biogenic VOCs from the forest around. The HCHO mixing ratios were comparable to Agra, Pantnagar and the rural IGP region. The HCHO diurnal profile of Pune was similar to the rural IGP region, with a morning peak at 10:00 hrs. HCHO from Mahabaleshwar, a high altitude station in western India showed lower values compared to Pune during summer period.

5 CONCLUSIONS

We report simultaneous MAX-DOAS observations of NO₂ and HCHO from Pune, an urban location in western India. The average NO₂ mixing ratio was the highest during ONDJF (2.0 ± 1.4 ppb) and the lowest during JJAS (0.9 ± 0.6 ppb). Like NO₂, the average HCHO mixing ratio was the highest during ONDJF (3.0 ± 1.4 ppb) and the lowest during JJAS (1.1 ± 0.7 ppb). The higher trace gas mixing ratios during ONDJF is due to a shallower boundary layer height, which leads to the gases getting concentrated. Wet deposition processes during JJAS are the main reason for lower mixing ratios during the monsoon period. The daily maximum NO₂ was found at ~9:00 hrs resulting from automobile emissions during peak traffic hours. HCHO showed a morning peak at ~10:00 hrs, which is due to emissions and the photochemical oxidation of VOCs. We found that HCHO/NO₂ ratio remains in VOC limited region for O₃ formation during 07:00–09:00 hrs but the ratio is in the border regime for rest of the day. This indicates that during early morning, controlling VOC emissions would be more effective towards controlling surface O₃ pollution. No significant difference in the concentration of trace gases was observed between weekdays and weekends. Air parcels coming from regions affected by open fires resulted in elevated concentrations of both NO₂ and HCHO within the Pune city. The emission from nearby industrial areas of Bhosari and Pimpri-Chinchwad also lead to higher NO₂ concentrations in Pune city, but no specific region was a significant contributor towards the HCHO concentrations.

Compared to other large cities in India, NO₂ concentrations were lower in Pune. But the diurnal profiles were similar with a morning peak at ~9:00 hrs. Most of the previous studies reported the highest NO₂ concentrations during winter and lowest during monsoon, which is similar to our findings in Pune. The observed HCHO concentration in Pune was comparable to other parts in India but lower than the city of Kolkata and hill station of Darjeeling. The HCHO diurnal profile from Pune showed similar pattern to the rural IGP region, with morning peak at ~10:00 hrs.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.200524>

REFERENCES

- Ali, K., Budhavant, K.B., Safai, P.D., Rao, P.S.P. (2012a). Seasonal factors influencing in chemical composition of total suspended particles at pune, India. *Sci. Total Environ.* 414, 257–267. <https://doi.org/10.1016/j.scitotenv.2011.09.011>
- Ali, K., Inamdar, S.R., Beig, G., Ghude, S., Peshin, S. (2012b). Surface ozone scenario at Pune and Delhi during the decade of 1990s. *J. Earth Syst. Sci.* 12, 373–383. <https://doi.org/10.1007/s12040-012-0170-1>
- Anand, V., Panicker, A.S., Beig, G. (2020). Gaseous pollutants over different sites in a metropolitan region (Pune) over India. *SN Appl. Sci.* 2, 1–19. <https://doi.org/10.1007/s42452-020-2472-2>
- Atkinson, R. (2000). Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ.* 34, 2063–2101. [https://doi.org/10.1016/S1352-2310\(99\)00460-4](https://doi.org/10.1016/S1352-2310(99)00460-4)
- Behera, S.N., Sharma, M., Mishra, P.K., Nayak, P., Damez-Fontaine, B., Tahon, R. (2015). Passive measurement of NO₂ and application of GIS to generate spatially-distributed air monitoring network in urban environment. *Urban Clim.* 14, 396–413. <https://doi.org/10.1016/j.uclim.2014.12.003>
- Beig, G., Gunthe, S., Jadhav, D.B. (2007). Simultaneous measurements of ozone and its precursors on a diurnal scale at a semi urban site in India. *J. Atmos. Chem.* 57, 239–253. <https://doi.org/10.1007/s10874-007-9068-8>
- Beig, G., Chate, D.M., Ghude, S.D., Mahajan, A.S., Srinivas, R., Ali, K., Sahu, S.K., Parkhi, N., Surendran, D., Trimbake, H.R. (2013). Quantifying the effect of air quality control measures during the 2010 Commonwealth Games at Delhi, India. *Atmos. Environ.* 80, 455–463. <https://doi.org/10.1016/j.atmosenv.2013.08.012>
- Beirle, S., Platt, U., Wenig, M., Wagner, T. (2003). Weekly cycle of NO₂ by GOME measurements: A signature of anthropogenic sources. *Atmos. Chem. Phys.* 3, 2225–2232. <https://doi.org/10.5194/acp-3-2225-2003>
- Beirle, S., Boersma, K.F., Platt, U., Lawrence, M.G., Wagner, T. (2011). Megacity emissions and lifetimes of nitrogen oxides probed from space. *Science* 333, 1737–1739. <https://doi.org/10.1126/science.1207824>
- Biswas, M.S., Ghude, S., Gurnale, D., Prabhakaran, T., Mahajan, A.S. (2019). Simultaneous observations of nitrogen dioxide, formaldehyde and ozone in the Indo-Gangetic Plain. *Aerosol Air Qual. Res.* 19, 1749–1764. <https://doi.org/10.4209/aaqr.2018.12.0484>
- Biswas, M.S., Pandithurai, G., Aslam, M.Y., Patil, R.D., Anilkumar, V., Dudhambe, S.D., Lerot, C., De Smedt, I., Van Roozendaal, M., Mahajan, A.S. (2020). Effect of boundary layer evolution on nitrogen dioxide (NO₂) and formaldehyde (HCHO) concentrations at a high-altitude observatory in western India. *Aerosol Air Qual. Res.* 21, 200193. <https://doi.org/10.4209/aaqr.2020.05.0193>
- Bray, C.D., Battye, W.H., Aneja, V.P. (2019). The role of biomass burning agricultural emissions in

- the Indo-Gangetic Plains on the air quality in New Delhi, India. *Atmos. Environ.* 218, 116983. <https://doi.org/10.1016/j.atmosenv.2019.116983>
- Burnett, R.T., Stieb, D., Brook, J.R., Cakmak, S., Dales, R., Raizenne, M., Vincent, R., Dann, T. (2004). Associations between short-term changes in nitrogen dioxide and mortality in Canadian cities. *Arch. Environ. Health* 59, 228–36. <https://doi.org/10.3200/AEOH.59.5.228-236>
- Carlier, P., Hannachi, H., Mouvrier, G. (1986). The chemistry of carbonyl compounds in the atmosphere—A review. *Atmos. Environ.* 20, 2079–2099. [https://doi.org/10.1016/0004-6981\(86\)90304-5](https://doi.org/10.1016/0004-6981(86)90304-5)
- Carter, W.P.L., Atkinson, R. (1987). An experimental study of incremental hydrocarbon reactivity. *Environ. Sci. Technol.* 21, 670–679. <https://doi.org/10.1021/es00161a008>
- Chaliyakunnel, S., Millet, D.B., Chen, X. (2019). Constraining emissions of volatile organic compounds over the Indian subcontinent using space-based formaldehyde measurements. *J. Geophys. Res.* 124, 10525–10545. <https://doi.org/10.1029/2019JD031262>
- Chameides, W.L., Fehsenfeld, F., Rodgers, M.O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D.R., Rasmussen, R.A., Zimmerman, P., Greenberg, J., Middleton, P., Wang, T. (1992). Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res.* 97, 6037–6055. <https://doi.org/10.1029/91JD03014>
- Chance, K., Palmer, P.I., Spurr, R.J.D., Martin, R.V., Kurosu, T.P., Jacob, D.J. (2000). Satellite observations of formaldehyde over North America from GOME. *Geophys. Res. Lett.* 27, 3461–3464. <https://doi.org/10.1029/2000GL011857>
- Chate, D.M., Ghude, S.D., Beig, G., Mahajan, A.S., Jena, C., Srinivas, R., Dahiya, A., Kumar, N. (2014). Deviations from the O₃-NO-NO₂ photo-stationary state in Delhi, India. *Atmos. Environ.* 96, 353–358. <https://doi.org/10.1016/j.atmosenv.2014.07.054>
- CPCB (2009). National Ambient Air Quality Standards. *Gaz. India*. <https://cpcb.nic.in/displaypdf.php?id=aG9tZS9haXltcG9sbHV0aW9uL1JlY3ZlZC10YXRpb25hbC5wZGY=>
- Crutzen, P.J. (1970). The influence of nitrogen oxides on the atmospheric ozone content. *Q. J. R. Meteorolog. Soc.* 96, 320–325. <https://doi.org/10.1002/qj.49709640815>
- Crutzen, P.J. (1974). Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air. *Tellus* 26, 47–57. <https://doi.org/10.3402/tellusa.v26i1-2.9736>
- Crutzen, P.J. (1979). The role of NO and NO₂ in the chemistry of the troposphere and stratosphere. *Annu. Rev. Earth Planet. Sci.* 7, 443–472. <https://doi.org/10.1146/annurev.ea.07.050179.002303>
- Danckaert, T. (2014). QDOAS Software user manual.
- de Foy, B., Lu, Z., Streets, D.G., Lamsal, L.N., Duncan, B.N. (2015). Estimates of power plant NO_x emissions and lifetimes from OMI NO₂ satellite retrievals. *Atmos. Environ.* 116, 1–11. <https://doi.org/10.1016/j.atmosenv.2015.05.056>
- De Smedt, I., Müller, J.F., Stavrou, T., van der A, R., Eskes, H., Van Roozendael, M. (2008). Twelve years of global observations of formaldehyde in the troposphere using GOME and SCIAMACHY sensors. *Atmos. Chem. Phys.* 8, 4947–4963. <https://doi.org/10.5194/acp-8-4947-2008>
- De Smedt, I., Stavrou, T., Müller, J.F., van der A, R.J., Van Roozendael, M. (2010). Trend detection in satellite observations of formaldehyde tropospheric columns. *Geophys. Res. Lett.* 37, L18808. <https://doi.org/10.1029/2010GL044245>
- Draxler, R.R., Hess, G.D. (1998). An overview of the HYSPLIT_4 modelling system for trajectories, dispersion, and deposition. *Aust. Meteorol. Mag.* 47, 295–308.
- Dutta, C., Chatterjee, A., Jana, T.K., Mukherjee, A.K., Sen, S. (2010). Contribution from the primary and secondary sources to the atmospheric formaldehyde in Kolkata, India. *Sci. Total Environ.* 408, 4744–4748. <https://doi.org/10.1016/j.scitotenv.2010.01.031>
- U.S. Environmental Protection Agency (U.S. EPA) (2015). Technical Support Document EPA's 2011 National-scale Air Toxics Assessment, 2011 NATA TSD.
- Finlayson-Pitts, P.J. (2000). *Chemistry of the Upper and Lower Atmosphere*, 1st editio. ed.
- Frins, E., Osorio, M., Casaballe, N., Belsterli, G., Wagner, T., Platt, U. (2012). DOAS-measurement of the NO₂ formation rate from NO_x emissions into the atmosphere. *Atmos. Meas. Tech.* 5, 1165–1172. <https://doi.org/10.5194/amt-5-1165-2012>
- Fu, T.M., Jacob, D.J., Palmer, P.I., Chance, K., Wang, Y.X., Barletta, B., Blake, D.R., Stanton, J.C., Pilling, M.J. (2007). Space-based formaldehyde measurements as constraints on volatile

- organic compound emissions in east and south Asia and implications for ozone. *J. Geophys. Res.* 112, D06312. <https://doi.org/10.1029/2006JD007853>
- Gadgil, A., Dhorde, A. (2005). Temperature trends in twentieth century at Pune, India. *Atmos. Environ.* 39, 6550–6556. <https://doi.org/10.1016/j.atmosenv.2005.07.032>
- Gautam, R., Hsu, N.C., Kafatos, M., Tsay, S.C. (2007). Influences of winter haze on fog/low cloud over the Indo-Gangetic plains. *J. Geophys. Res.* 112, D05207. <https://doi.org/10.1029/2005JD007036>
- Ghosh, D., Sarkar, U., De, S. (2015). Analysis of ambient formaldehyde in the eastern region of India along Indo-Gangetic Plain. *Environ. Sci. Pollut. Res.* 22, 18718–18730. <https://doi.org/10.1007/s11356-015-5029-y>
- Gómez Martín, J.C., Mahajan, A.S., Hay, T.D., Prados-Román, C., Ordóñez, C., MacDonald, S.M., Plane, J.M.C., Sorribas, M., Gil, M., Mora, J.F.P., Reyes, M.V.A., Oram, D.E., Leedham, E., Saiz-Lopez, A. (2013). Iodine chemistry in the eastern Pacific marine boundary layer. *J. Geophys. Res.* 118, 887–904. <https://doi.org/10.1002/jgrd.50132>
- Gonzi, S., Palmer, P.I., Barkley, M.P., De Smedt, I., Van Roozendael, M. (2011). Biomass burning emission estimates inferred from satellite column measurements of HCHO: Sensitivity to co-emitted aerosol and injection height. *Geophys. Res. Lett.* 38, L14807. <https://doi.org/10.1029/2011GL047890>
- Han, S., Bian, H., Feng, Y., Liu, A., Li, X., Zeng, F., Zhang, X. (2011). Analysis of the relationship between O₃, NO and NO₂ in Tianjin, China. *Aerosol Air Qual. Res.* 11, 128–139. <https://doi.org/10.4209/aaqr.2010.07.0055>
- Harley, P., Greenberg, J., Guenther, A. (2001). Seasonal temperature variations influence isoprene emission. *Geophys. Res. Lett.* 28, 1707–1710. <https://doi.org/10.1029/2000GL011583>
- Herndon, S.C., Jayne, J.T., Zahniser, M.S., Worsnop, D.R., Knighton, B., Alwine, E., Lamb, B.K., Zavale, M., Nelson, D.D., McManus, J.B., Shorter, J.H., Canagaratna, M.R., Onasch, T.B., Kolb, C.E. (2005). Characterization of urban pollutant emission fluxes and ambient concentration distributions using a mobile laboratory with rapid response instrumentation. *Faraday Discuss.* 130, 327–339. <https://doi.org/10.1039/B500411J>
- Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., Nicolas, J., Peubey, C., Radu, R., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Abellan, X., Balsamo, G., Bechtold, P., Biavati, G., Bidlot, J., Bonavita, M., Chiara, G.D., *et al.* (2020). The ERA5 global reanalysis. *Q. J. R. Meteorolog. Soc.* 146, 1999–2049. <https://doi.org/10.1002/qj.3803>
- Hönninger, G., von Friedeburg, C., Platt, U. (2004). Multi axis differential optical absorption spectroscopy (MAX-DOAS). *Atmos. Chem. Phys.* 4, 231–254. <https://doi.org/10.5194/acp-4-231-2004>
- Hoque, H.M.S., Irie, H., Damiani, A., Rawat, P., Naja, M. (2018). First simultaneous observations of formaldehyde and glyoxal by MAX-DOAS in the Indo-Gangetic Plain region. *Sola* 14, 159–164. <https://doi.org/10.2151/sola.2018-028>
- Irwin, J.G., Williams, M.L. (1988). Acid rain: Chemistry and transport. *Environ. Pollut.* 50, 29–59. [https://doi.org/10.1016/0269-7491\(88\)90184-4](https://doi.org/10.1016/0269-7491(88)90184-4)
- Jacob, D.J. (2000). Heterogeneous chemistry and tropospheric ozone. *Atmos. Environ.* 34, 2131–2159. [https://doi.org/10.1016/S1352-2310\(99\)00462-8](https://doi.org/10.1016/S1352-2310(99)00462-8)
- Jaeglé, L., Steinberger, L., Martin, R. V., Chance, K. (2005). Global partitioning of NO_x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions. *Faraday Discuss.* 130, 407. <https://doi.org/10.1039/b502128f>
- Khare, P., Satsangi, G.S., Kumar, N., Kumari, K.M., Srivastava, S.S. (1997a). Surface measurements of formaldehyde and formic and acetic acids at a subtropical semiarid site in India. *J. Geophys. Res.* 102, 18997–19005. <https://doi.org/10.1029/97JD00735>
- Khare, P., Satsangi, G.S., Kumar, N., Kumari, K.M., Srivastava, S.S. (1997b). HCHO, HCOOH and CH₃COOH in air and rain water at a rural tropical site in North Central India. *Atmos. Environ.* 31. [https://doi.org/10.1016/S1352-2310\(97\)00263-X](https://doi.org/10.1016/S1352-2310(97)00263-X)
- Khare, P., Singh, S.P., Maharaj Kumari, K., Kumar, A., Srivastava, S.S. (2000). Formaldehyde measurement at a suburban site of north central part of India. *Indian J. Radio Space Phys.* 29, 314–318.
- Kumar, R., Gupta, A., Maharaj Kumari, K., Srivastava, S.S. (2004). Simultaneous measurements of SO₂, NO₂, HNO₃ and NH₃: Seasonal and spatial variations. *Curr. Sci.* 87, 1108–1115. <http://www.jstor.org/stable/24108982>

- Kumar, V., Sarkar, C., Sinha, V. (2016). Influence of post-harvest crop residue fires on surface ozone mixing ratios in the N.W. IGP analyzed using 2years of continuous in situ trace gas measurements. *J. Geophys. Res.* 121, 3619–3633. <https://doi.org/10.1038/175238c0>
- Lamsal, L.N., Martin, R.V., Padmanabhan, A., Donkelaar, A. van, Zhang, Q., Sioris, C.E., Chance, K., Kurosu, T.P., Newchurch, M.J. (2011). Application of satellite observations for timely updates to global anthropogenic NO_x emission inventories. *Geophys. Res. Lett.* 38, L05810. <https://doi.org/10.1029/2010GL046476>
- Leue, C., Wenig, M., Wagner, T., Klimm, O., Platt, U., Jähne, B. (2001). Quantitative analysis of NO_x emissions from Global Ozone Monitoring Experiment satellite image sequences. *J. Geophys. Res.* 106, 5493–5505. <https://doi.org/10.1029/2000JD900572>
- Levy, H. (1971). Normal atmosphere: Large radical and formaldehyde concentrations predicted. *Science* 173, 141–143. <https://doi.org/10.1126/science.173.3992.141>
- Lin, Y.C., Cheng, M.T. (2007). Evaluation of formation rates of NO₂ to gaseous and particulate nitrate in the urban atmosphere. *Atmos. Environ.* 41, 1903–1910. <https://doi.org/10.1016/j.atmosenv.2006.10.065>
- Liu, T., Marlier, M.E., DeFries, R.S., Westervelt, D.M., Xia, K.R., Fiore, A.M., Mickley, L.J., Cusworth, D.H., Milly, G. (2018). Seasonal impact of regional outdoor biomass burning on air pollution in three Indian cities: Delhi, Bengaluru, and Pune. *Atmos. Environ.* 172, 83–92. <https://doi.org/10.1016/j.atmosenv.2017.10.024>
- Lowe, D.C., Schmidt, U. (1983). Formaldehyde (HCHO) measurements in the nonurban atmosphere. *J. Geophys. Res.* 88, 10844. <https://doi.org/10.1029/JC088iC15p10844>
- Mahajan, A.S., Gómez Martín, J.C., Hay, T.D., Royer, S.J., Yvon-Lewis, S., Liu, Y., Hu, L., Prados-Roman, C., Ordóñez, C., Plane, J.M.C., Saiz-Lopez, A. (2012). Latitudinal distribution of reactive iodine in the Eastern Pacific and its link to open ocean sources. *Atmos. Chem. Phys.* 12, 11609–11617. <https://doi.org/10.5194/acp-12-11609-2012>
- Mallik, C., Lal, S. (2014). Seasonal characteristics of SO₂, NO₂, and CO emissions in and around the Indo-Gangetic Plain. *Environ. Monit. Assess.* 186, 1295–1310. <https://doi.org/10.1007/s10661-013-3458-y>
- Marković, D.M., Marković, D.A., Jovanović, A., Lazić, L., Mijić, Z. (2008). Determination of O₃, NO₂, SO₂, CO and PM₁₀ measured in Belgrade urban area. *Environ. Monit. Assess.* 145, 349–359. <https://doi.org/10.1007/s10661-007-0044-1>
- National Aeronautics and Space Administration (NASA) (2020). Active Fires (1 day - Terra/MODIS) https://neo.sci.gsfc.nasa.gov/view.php?datasetId=MOD14A1_M_FIRE (accessed 18 June 2020).
- Office of the Registrar General & Census Commissioner, India (2011). Minist. Home Aff. Gov. India. <https://censusindia.gov.in/2011-Common/CensusData2011.html>
- Pancholi, P., Kumar, A., Bikundia, D.S., Chourasiya, S. (2018). An observation of seasonal and diurnal behavior of O₃–NO_x relationships and local/regional oxidant (OX = O₃ + NO₂) levels at a semi-arid urban site of western India. *Sustain. Environ. Res.* 28, 79–89. <https://doi.org/10.1016/j.serj.2017.11.001>
- Peshin, S.K., Sharma, A., Sharma, S.K., Naja, M., Mandal, T.K. (2017). Spatio-temporal variation of air pollutants and the impact of anthropogenic effects on the photochemical buildup of ozone across Delhi-NCR. *Sustainable Cities Soc.* 35, 740–751. <https://doi.org/10.1016/j.scs.2017.09.024>
- Platt, U., Stutz, J. (2008). Differential optical absorption spectroscopy - Principle and applications. Springer. <https://doi.org/10.1007/978-3-540-75776-4>
- Prados-Roman, C., Cuevas, C.A., Hay, T., Fernandez, R.P., Mahajan, A.S., Royer, S.J., Galí, M., Simó, R., Dachs, J., Großmann, K., Kinnison, D.E., Lamarque, J.F., Saiz-Lopez, A. (2015). Iodine oxide in the global marine boundary layer. *Atmos. Chem. Phys.* 15, 583–593. <https://doi.org/10.5194/acp-15-583-2015>
- Raatikainen, T., Hyvärinen, A.P., Hatakka, J., Panwar, T.S., Hooda, R.K., Sharma, V.P., Lihavainen, H. (2014). The effect of boundary layer dynamics on aerosol properties at the Indo-Gangetic plains and at the foothills of the Himalayas. *Atmos. Environ.* 89, 548–555. <https://doi.org/10.1016/j.atmosenv.2014.02.058>
- Ravindra, K., Singh, T., Mor, Sahil, Singh, V., Mandal, T.K., Bhatti, M.S., Gahlawat, S.K., Dhankhar, R., Mor, Suman, Beig, G. (2019). Real-time monitoring of air pollutants in seven cities of North India during crop residue burning and their relationship with meteorology and transboundary

- movement of air. *Sci. Total Environ.* 690, 717–729. <https://doi.org/10.1016/j.scitotenv.2019.06.216>
- Revadekar, J.V., Varikoden, H., Sapre, V.V. (2015). Variability in Summer Monsoon Rainfall over Pune, a Leeward Side Station of Western Ghats in India. *Vayu Mandal*.
- Sadanaga, Y., Sengen, M., Takenaka, N., Bandow, H. (2012). Analyses of the ozone weekend effect in Tokyo, Japan: Regime of oxidant ($O_3 + NO_2$) production. *Aerosol Air Qual. Res.* 12, 161–168. <https://doi.org/10.4209/aaqr.2011.07.0102>
- Safai, P.D., Kewat, S., Praveen, P.S., Rao, P.S.P., Momin, G.A., Ali, K., Devara, P.C.S. (2007). Seasonal variation of black carbon aerosols over a tropical urban city of Pune, India. *Atmos. Environ.* 41, 2699–2709. <https://doi.org/10.1016/j.atmosenv.2006.11.044>
- Sarkar, C., Chatterjee, A., Majumdar, D., Roy, A., Srivastava, A., Ghosh, S.K., Raha, S. (2017). How the atmosphere over eastern Himalaya, India is polluted with carbonyl compounds? Temporal variability and identification of sources. *Aerosol Air Qual. Res.* 17, 2206–2223. <https://doi.org/10.4209/aaqr.2017.01.0048>
- Schroeder, J.R., Crawford, J.H., Fried, A., Walega, J., Weinheimer, A., Wisthaler, A., Müller, M., Mikoviny, T., Chen, G., Shook, M., Blake, D.R., Tonnesen, G.S. (2017). New insights into the column CH_2O/NO_2 ratio as an indicator of near-surface ozone sensitivity. *J. Geophys. Res.* 122, 8885–8907. <https://doi.org/10.1002/2017JD026781>
- Schumann, U., Huntrieser, H. (2007). The global lightning-induced nitrogen oxides source. *Atmos. Chem. Phys.* 7, 3823–3907. <https://doi.org/10.5194/acp-7-3823-2007>
- Seguel, R.J., Morales S., R.G.E., Leiva G., M.A. (2012). Ozone weekend effect in Santiago, Chile. *Environ. Pollut.* 162, 72–79. <https://doi.org/10.1016/j.envpol.2011.10.019>
- Sen, A., Abdelmaksoud, A.S., Nazeer Ahammed, Y., Alghamdi, M.A., Banerjee, T., Bhat, M.A., Chatterjee, A., Choudhuri, A.K., Das, T., Dhir, A., Dhyani, P.P., Gadi, R., Ghosh, S., Kumar, K., Khan, A.H., Khoder, M., Maharaj Kumari, K., Kuniyal, J.C., Kumar, M., Lakhani, A., *et al.* (2017). Variations in particulate matter over Indo-Gangetic Plains and Indo-Himalayan Range during four field campaigns in winter monsoon and summer monsoon: Role of pollution pathways. *Atmos. Environ.* 154, 200–224. <https://doi.org/10.1016/j.atmosenv.2016.12.054>
- Shaik, D.S., Kant, Y., Mitra, D., Singh, A., Chandola, H.C., Sateesh, M., Babu, S.S., Chauhan, P. (2019). Impact of biomass burning on regional aerosol optical properties: A case study over northern India. *J. Environ. Manage.* 244, 328–343. <https://doi.org/10.1016/j.jenvman.2019.04.025>
- Sharma, D., Srivastava, A.K., Ram, K., Singh, A., Singh, D. (2017). Temporal variability in aerosol characteristics and its radiative properties over Patiala, northwestern part of India: Impact of agricultural biomass burning emissions. *Environ. Pollut.* 231, 1030–1041. <https://doi.org/10.1016/j.envpol.2017.08.052>
- Sharma, S.K., Datta, A., Saud, T., Saxena, M., Mandal, T.K., Ahammed, Y.N., Arya, B.C. (2010). Seasonal variability of ambient NH_3 , NO , NO_2 and SO_2 over Delhi. *J. Environ. Sci.* 22, 1023–1028. [https://doi.org/10.1016/S1001-0742\(09\)60213-8](https://doi.org/10.1016/S1001-0742(09)60213-8)
- Shen, L., Jacob, D.J., Zhu, L., Zhang, Q., Zheng, B., Sulprizio, M.P., Li, K., De Smedt, I., González Abad, G., Cao, H., Fu, T.M., Liao, H. (2019). The 2005–2016 trends of formaldehyde columns over China observed by satellites: Increasing anthropogenic emissions of volatile organic compounds and decreasing agricultural fire emissions. *Geophys. Res. Lett.* 46, 4468–4475. <https://doi.org/10.1029/2019GL082172>
- Singh, N., Mittal, S.K., Agarwal, R., Awasthi, A., Gupta, P.K. (2010). Impact of rice crop residue burning on levels of SPM, SO_2 and NO_2 in the ambient air of Patiala (India). *Int. J. Environ. Anal. Chem.* 90, 829–843. <https://doi.org/10.1080/03067310903023874>
- Singh, S., Kulshrestha, U.C. (2014). Rural versus urban gaseous inorganic reactive nitrogen in the Indo-Gangetic Plains (IGP) of India. *Environ. Res. Lett.* 9, 125004. <https://doi.org/10.1088/1748-9326/9/12/125004>
- Sinha, V., Kumar, V., Sarkar, C. (2014). Chemical composition of pre-monsoon air in the Indo-Gangetic Plain measured using a new air quality facility and PTR-MS: High surface ozone and strong influence of biomass burning. *Atmos. Chem. Phys.* 14, 5921–5941. <https://doi.org/10.5194/acp-14-5921-2014>
- Sinreich, R., Coburn, S., Dix, B., Volkamer, R. (2010). Ship-based detection of glyoxal over the remote tropical Pacific Ocean. *Atmos. Chem. Phys.* 10, 11359–11371. <https://doi.org/10.5194/acp-10-11359-2010>

- Stavrakou, T., Müller, J.F., Boersma, K.F., De Smedt, I., van der A, R.J. (2008). Assessing the distribution and growth rates of NO_x emission sources by inverting a 10-year record of NO₂ satellite columns. *Geophys. Res. Lett.* 35, L10801. <https://doi.org/10.1029/2008GL033521>
- Stocker, T.F., Qin, D., Plattner, G.K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (2013). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge, United Kingdom.
- Surl, L., Palmer, P.I., González Abad, G. (2018). Which processes drive observed variations of HCHO columns over India? *Atmos. Chem. Phys.* 18, 4549–4566. <https://doi.org/10.5194/acp-18-4549-2018>
- Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., Kulmala, M., Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P. (2005). Temperature and light dependence of the VOC emissions of Scots pine. *Atmos. Chem. Phys.* 5, 989–998. <https://doi.org/10.5194/acp-5-989-2005>
- Tiwari, S., Dahiya, A., Kumar, N. (2015). Investigation into relationships among NO, NO₂, NO_x, O₃, and CO at an urban background site in Delhi, India. *Atmos. Res.* 157, 119–126. <https://doi.org/10.1016/j.atmosres.2015.01.008>
- van der A, R.J., Eskes, H.J., Boersma, K.F., van Noije, T.P.C., Van Roozendael, M., De Smedt, I., Peters, D.H.M.U., Meijer, E.W. (2008). Trends, seasonal variability and dominant NO_x source derived from a ten year record of NO₂ measured from space. *J. Geophys. Res.* 113, D04302. <https://doi.org/10.1029/2007JD009021>
- Venkataraman, C., Habib, G., Kadamba, D., Shrivastava, M., Leon, J.F., Crouzille, B., Boucher, O., Streets, D.G. (2006). Emissions from open biomass burning in India: Integrating the inventory approach with high-resolution Moderate Resolution Imaging Spectroradiometer (MODIS) active-fire and land cover data. *Global Biogeochem. Cycles* 20, GB2013. <https://doi.org/10.1029/2005GB002547>
- Wittrock, F. (2006). The retrieval of oxygenated volatile organic compounds by remote sensing techniques.
- World Health Organization (WHO) (2013). Review of evidence on health aspects of air pollution – REVIHAAP Project 309. WHO Regional Office for Europe, Denmark.
- Zhang, R., Tie, X., Bond, D.W. (2003). Impacts of anthropogenic and natural NO_x sources over the U.S. on tropospheric chemistry. *Proc. Natl. Acad. Sci.* 100, 1505–1509. <https://doi.org/10.1073/pnas.252763799>
- Zhu, L., Jacob, D.J., Mickley, L.J., Marais, E.A., Cohan, D.S., Yoshida, Y., Duncan, B.N., Abad, G.G., Chance, K.V. (2014). Anthropogenic emissions of highly reactive volatile organic compounds in eastern Texas inferred from oversampling of satellite (OMI) measurements of HCHO columns. *Environ. Res. Lett.* 9, 114004. <https://doi.org/10.1088/1748-9326/9/11/114004>
- Zhu, L., Mickley, L.J., Jacob, D.J., Marais, E.A., Sheng, J., Hu, L., Abad, G.G., Chance, K. (2017). Long-term (2005–2014) trends in formaldehyde (HCHO) columns across North America as seen by the OMI satellite instrument: Evidence of changing emissions of volatile organic compounds. *Geophys. Res. Lett.* 44, 7079–7086. <https://doi.org/10.1002/2017GL073859>