Ambient ozone over mid-Brahmaputra Valley, India: effects of local emissions and atmospheric transport on the photostationary state

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Abstract This study presents the characteristics of ground level atmospheric ozone (O_3) over the rural mid-Brahmaputra Valley region of the northeastern India. Ozone and oxides of nitrogen ($NO_x = NO + NO_2$) concentration data were obtained from continuous measurement of O_3 and NO_x housed at the MAPAN-AQM station at Tezpur University. The meteorological parameters were obtained from the same station. The diel, monthly, and seasonal variations of O_3 were studied. The O_3 - NO_x photostationary state (*PS*) was carefully examined and it was found that the *net* O_3 concentration deviated substantially from the *PS* during the winter season. The

deviation could be attributed to local biomass burning, biogenic VOC emission from forest and agriculture, and long-range transport of peroxyacyl nitrate (PAN). The long-range transport has been ascertained by examining the ventilation coefficients (VC), which correlated with the steep growth of *net* O_3 concentrations in the morning hours. The HYSPLIT air mass back trajectories were used in concentration-weighted trajectory (CWT) analyses of O_3 to assess the long-range regional transport of O_3 precursors, which positively influenced local O_3 concentrations.

Keywords Ambient O_3 · NO_x · Photostationary state · HYSPLIT · Concentration-weighted trajectories

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Introduction

Ground level atmospheric ozone (O_3) is a criteria air pollutant and a major component of photochemical smog. Its formation depends on the chemistry of the precursors, viz., oxides of nitrogen ($NO_x = NO_2 + NO$), volatile organic compounds (VOC), and related species like carbon monoxide (CO), and prevailing meteorological conditions like solar radiation, air temperature, and wind (e.g., Allu et al., 2020; Geddes et al., 2009; Haagen-Smit, 1952; Khalil et al., 2018; Leighton, 1961; Paoletti et al., 2014; Singh et al., 2018; Wałaszek et al., 2018; Zhang et al., 2020). The VOC- NO_x - O_3

chemistry at the ground level atmosphere is well understood (e.g., Atkinson, 2000; Crutzen, 1974; Seinfeld & Pandis, 2016). NO_x and VOC are primary species that originate from natural and anthropogenic sources such as vehicular traffic and industrial fossil fuel burning, and through episodic events like biomass burning and volcanoes (e.g., Barletta et al., 2002; Khillare et al., 2005, 2008a, 2008b; Hoque et al., 2008; Li et al., 2017; Ling et al., 2014; Sillman, 1999; Srivastava et al., 2006; Steinbrecher et al., 2009). Ozone is formed through the photolysis of NO_2 and has a comparatively short lifetime in the air. However, its precursors can remain in the atmosphere for many days continuously forming ozone and resulting in long-range (often trans-boundary) transport (Wild et al., 2004; Young et al., 2013). Photochemical ozone production also occurs in rural and remote locations and in remote unpolluted areas (Crutzen, 1974).

Surface O_3 shows explicit diel and seasonal variations, which are governed by the photochemistry of its production and removal (Debaje et al., 2003; Lal et al., 2000; Zhao et al., 2021). Highly reactive hydroxyl ($\bullet\text{OH}$) and nitrate ($\text{NO}_3\bullet$) radicals are the important oxidative species in the troposphere during day and night, respectively. They are formed through reactions of O_3 (e.g., Aschmann et al., 2002; Atkinson et al., 1995). The $\bullet\text{OH}$ radical is the key species which initiates reactions of hydrocarbons (HC) and CO during the day, and in the process highly oxidizing peroxy radicals like $\text{HOO}\bullet$, alkyl peroxy radical ($\text{ROO}\bullet$), and acyl peroxy radical ($\text{RC(O)OO}\bullet$) are formed. These peroxy radicals compete with O_3 to oxidize NO to NO_2 leading to a situation where more O_3 is formed than is consumed. This process leads to the built up of O_3 during the day.

Two discrete regimes govern the ground level atmospheric ozone: (i) NO_x -sensitive regime, when the production of O_3 is sensitive to the concentration of NO_x , and (ii) VOC-sensitive regime, when the increase in the concentration of O_3 is a function of the concentration of VOC (Sillman, 1995; Finlayson-Pitts, 1999; Seinfeld & Pandis, 2016). If controls are applied to the wrong precursor, the O_3 concentrations can rise as has been seen in many places around the world since the COVID-19 pandemic led to substantial reductions in NO emissions in VOC-limited regions (e.g., Sicard et al., 2020; Sulaymon et al., 2021; Torkmahalleh et al., 2021).

Ground level atmospheric O_3 also affects carbon dynamics, ecological interconnections, and agricultural efficiency across the ecosphere (Schneider et al., 2017). High O_3 levels can lead to the closure of stomata, thereby reducing the uptake of gases affecting photosynthesis (Karnosky et al., 2003). Later, Ghude et al. (2014) reported reductions of crop yield in India due to surface ozone and, therefore, an agricultural economy like India's cannot ignore O_3 pollution.

Surface ozone is also an important greenhouse gas contributing to global warming and climate change (IPCC, 2013; Kulkarni et al., 2011; Zhao et al., 2020). The concentration of O_3 is changing in the global scale leading to an increase in the background concentrations, which influence the levels of local concentrations of O_3 and NO_2 (Clapp & Jenkin, 2001). There are reports of reduction of particulate pollution but O_3 remained constant or increasing, indicating the complexities in the O_3 pollution and, therefore, its control (e.g., Squizzato et al., 2018).

Ozone in the lower atmosphere is termed as "bad" O_3 for its adverse effects on human health and the environment. It was termed as lung irritant soon after its discovery (Bates, 1989). Health effects of increased concentration of O_3 include reduction of lung functions, increased respiratory problems, and inflammation. Long-term exposure of O_3 ultimately leads to chronic damage of the lungs in vertebrates (Lippmann, 1991). Ozone exposure can decrease the variability in heart rate of human beings thereby deteriorating the cardiac autonomic nervous system (Jia et al., 2011). The cardiovascular effects of ambient O_3 are found in animals, when exposed for a long duration, thereby altering their vascular tone (Chuang et al., 2009; Paffett et al., 2015; Robertson et al., 2013).

There has been limited literature addressing O_3 from India. More so, the reported studies are generally from major metropolitan areas, at sites that are often heavily influenced by local sources like traffic (e.g., Badarinath et al., 2009a, 2009b; Beig et al., 2013; Ganguly & Tzanis, 2013; Lal et al., 2012; Singla et al., 2011). There are a few studies on the ground level atmospheric O_3 from the Brahmaputra Valley region (e.g., Bharali et al., 2015; Bhuyan et al., 2014; Dumka et al., 2020; Pathak et al., 2016). Tyagi et al. (2020) examined the O_3 concentrations of three stations in northeastern India (including Tezpur) as well as surface temperatures and other meteorological

parameters. They concluded that there is significant transport of O_3 to the region; however, they did not address the air mass trajectory pathways/regions that contributed to higher O_3 .

Therefore, this study was taken up to determine the variability of ground level O_3 on a daily and seasonal basis in a relatively rural area of the mid-Brahmaputra Valley. Ozone has been assessed in terms of the NO_x - O_3 photostationary state to understand the processes that are driving the O_3 concentration. Concentration-weighted trajectory (CWT) analysis was done to identify likely source regions from where air masses carrying precursors originated and were subsequently transported to the region contributing to the formation of O_3 .

Methodology

The site

Ozone, NO and NO_2 , and meteorological variables were measured on the Tezpur University campus ($26^\circ 37' N$ and $92^\circ 50' E$) under the MAPAN (monitoring of atmospheric pollution and networking) program. The location of the study area along with illustrative air mass back trajectories during winter is shown in Supplemental Fig. S1. The diel patterns' atmospheric temperature through the year over the study area is shown in Fig. S2. The site is characterized as a rural residential/institutional area. The station is surrounded by villages and agricultural fields. Tezpur city had a population of about 2.0 million (Census of India, 2011). The moderately busy highways are at about 20 km and the eastern Himalayan ranges begin at 30 km on the north from the monitoring station. The region is still developing. Traditional biomass burning in homes, agriculture, and forest are seen in the surrounding areas of the study site previously reported by Bhuyan et al. (2018).

Methodology

Continuous hourly measurements of O_3 , NO, and NO_2 and meteorological parameters for two consecutive years (2013–14 and 2014–15) were used for the study. The O_3 measurements were made with a Serinus 10 ozone analyzer (Ecotech). This analyzer uses

non-dispersive ultraviolet (UV) absorption technology to measure O_3 with a sensitivity of 0.5 ppb and in the range of 0–20 ppm (Ecotech user manual, 2010; Dumka et al., 2020). The measurements of NO and NO_2 were made with a Serinus 40 Oxides of Nitrogen analyzer (Ecotech) that uses gas phase chemiluminescence detection. The concentration of NO_x is the sum of the concentrations of NO and NO_2 . This Serinus 40 analyzer measures with a sensitivity of 0.4 ppb with auto ranging of 0–20 ppm (Ecotech, 2011; Gilge, 2010; Yadav et al., 2014). Another important parameter estimated in this study was total oxidant ($OX = O_3 + NO_2$) that assists in understanding the O_3 behavior. Hourly average measurements of meteorological variables were made at the same station. The four seasons considered in the study were as per the India Meteorological Department (Laskar et al., 2016.): pre-monsoon (March–May), monsoon (June–September), post-monsoon (October–December), and winter (January–February).

The R package, Openair (Carslaw, 2018; Carslaw & Ropkins, 2012) was used for analyses and illustrations and in computing the polar plots. The air mass back trajectories were computed using TrajStat software that applies NOAA/ARL HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model to calculate back trajectories. The NCEP/NCAR Reanalysis data (<ftp://arlftp.arl.hq.noaa.gov/pub/archives/reanalysis>) were used to compute 72 h (3 days) back trajectories arriving at the site every hour (Draxler & Hess, 1998; Rolph et al., 2017; Stein et al., 2015). The time difference between UTC and local time was carefully adjusted so that the time of the measurement of concentration and the time of reaching the trajectory matched.

Concentration-weighted trajectory (CWT) analysis was applied where trajectories were weighted with associated concentrations. Each grid was assigned a residence-time-weighted concentration from the measured data associated with the trajectories that crossed that grid cell, as follows:

$$C_{ij} = \frac{1}{\sum_{l=1}^M \tau_{ijl}} \sum_{l=1}^M c_l \tau_{ijl} \quad (1)$$

where,

C_{ij} — average weighted concentration in the ij th cell.

l — index of the trajectory.

M — total number of trajectories.

C_l — concentration observed on arrival of trajectory l .

τ_{ijl} — time spent in the ij th cell by trajectory l .

In the cases of higher C_{ij} , it could be inferred that air masses that passed over the ij th cell were transporting that species leading to high concentrations at the receptor site. To reduce the effect of a small number of polluted trajectories, a weighting function was multiplied with the CWT (Wang et al., 2009).

Results and discussion

Concentrations

The concentrations of hourly O_3 , maximum O_3 of the day (O_3 max), NO , NO_2 , NO_x , and OX for the years 2013–14 and 2014–15 are shown in Fig. 1, and the descriptive statistics are given in Table S1. The 95th percentile O_3 concentrations were 43 ppb during 2013–2014 and 41 ppb during 2014–2015. The minimum concentration was 1 ppb during both the years. The 95th percentile NO_x concentrations were 15 ppb during 2013–2014 and 14 ppb during 2014–2015. Low NO_x and comparatively high O_3 are typical of remote locations where the production of O_3 is mainly governed by the NO_x concentration (Chameides et al., 1992). However, in a high NO_x regime like

an urban area, the production of O_3 is controlled by NO_x and VOC levels (Chameides et al., 1992; Sillman et al., 1990).

A summary of O_3 concentrations from the present study and related studies is provided in Table 1. Bhuyan et al. (2014) reported a maximum O_3 concentration of 43 ppb from urban Dibrugarh in the upper Brahmaputra Valley that was comparable to the present study values. Tezpur experienced higher maximum concentrations of O_3 compared to several regions of the Indian mainland, e.g., uplands of Udaipur (28 ppb; Yadav et al., 2014), city area of Ahmedabad (30 ppb; Lal et al., 2000), Coastal Tranquebar (37 ppb; Debaje et al., 2003), and semi-urban areas of Jodhpur (22 ppb; Pancholi et al., 2018). There are several reports of higher maximum concentrations of O_3 compared to the present study from the mainland India (e.g., urban areas of Pune; 5 ppb; Beig et al., 2007), urban commercial areas of Agra (72 ppb; Satsangi et al., 2004), semi-arid rural continental location of Anantapur (72 ppb; Reddy et al., 2012), and urban high-altitude area of Ooty (62 ppb; Udayasoorian et al., 2013). There were reports where the O_3 values were comparable to those in Tezpur. These locations include a rural mountain valley of Kannur (44 ppb; Nishanth et al., 2012), a busy urban industrial area of Lahore (41 ppb; Tabinda et al., 2016). Sarangi et al. (2014) reported average monthly O_3 concentrations in a remote high-altitude location of central Himalayas (Nainital, India) where concentrations were in the upper

Fig. 1 Box plot of measured concentrations for the years (a) 2013–2014 and (b) 2014–2015. The central solid lines inside the box represent median values of the respective species; the

whiskers are maximum (95th percentile) and minimum values excluding the outliers

Table.1 Comparison of ground level atmospheric ozone concentrations over mid Brahmaputra Valley region with concentrations reported elsewhere

Location	Land use	Max O ₃	Min O ₃	Reference
Tezpur, India (2013–2014)	Rural	43 ppb*	1 ppl	Present study
Tezpur, India (2014–2015)	Rural	41 ppb. *	1 ppb	Present study
Anantapur, India	Semi-arid rural, continental region	70.2 ± 6.9 ppbv (summer)	20.0 ± 4.7 ppbv (monsoon)	Reddy et al., (2012)
Kannur, India	Rural, valley of mountains	44 ppbv (winter)	18.5 ppbv (monsoon)	Nishanth et al., (2012)
Udaipur, India	Urban, hill range	28 ppbv (pre-monsoon)	19 ppbv (monsoon)	Yadav et al., (2014)
Dibrugarh, India	Urban, upper Brahmaputra basin	42.9 ± 10.3 ppb (March)	17.3 ± 7.0 ppb (July)	Bhuyan et al., (2014)
Ahmedabad, India	Urban, Industrial area	30 ± 3 ppbv (November)	12 ± 2 ppbv (Aug)	Lal et al., (2000)
Ooty, India	Urban, high altitude western ghats	62 ppb (March)	17 ppb (Aug)	Udayasoorian et al., (2013)
Jodhpur, Rajasthan	Urban, semi-arid desert	21.9 ppb (pre-monsoon)	12.6 ppb (monsoon)	Pancholi et al., (2018)
Agra, India	Urban, semi-arid commercial zone	72.3 ppb (November)	2.2 ppb (February)	Satsangi et al., (2004)
Tranquebar, India	Urban, coastal region	37 ppbv (May)	9 ppbv (October)	Debaje et al., (2003)
Pune, India	Semi-urban, industrial site	54.6 ppbv (February)	12.2 ppbv (August)	Beig et al., (2007)
Oki, Japan	Rural, small remote island	55 ppb (spring)	29 ppb (summer)	Pochanart et al., (1999)
Istanbul, Turkey	Urban, industrial area	32 ppb (summer)	8 ppb (winter)	Im et al., (2013)
Meadowlands, New Jersey	Urban, heavily industrialized	63 ppb (June)	0.2 ppb (November)	Roberts-Semple et al., (2012)
Namibia, Africa	Urban, high altitude	30 ppb (October)	11 ppb (March)	Zunckel et al., (2004)
Dhaka, Bangladesh	Urban, highly traffic congested	97 ppb (Winter)	16 ppb (monsoon)	Sikder et al., (2013)
Nepal	Urban, high altitude	60.9 ppbv (pre-monsoon)	38.9 ppbv (monsoon)	Bonasoni et al., (2010)
Lahore, Pakistan	Urban, busiest town, industrial area	41.36 ppb (June)	5.27 ppb (January)	Tabinda et al., (2016)
Barcelona, Spain	Urban, highly populated	24.51 ppb (June)	4.15 ppb (December)	Filella & Penuelas, (2006)
Giza, Cairo	Urban, industrial site	143 ppb (July)	50 ppb (January)	Khoder, (2009)
Marikana, South Africa	Urban, township	50.02 ppb (October)	21.07 ppb (April)	Kgabi & Sehloho, (2012)
Mohal-Kullu, India	Semi-rural	74.6 ± 23.2 ppb (summer)	16.0 ± 5.6 ppb (monsoon)	Kuniyal et al., (2021)
Telangana, India	Sub-urban	35.54 ± 7.16 ppbv (winter)	12.70 ± 3.55 ppbv (monsoon)	Kanchana et al., (2020)

*95th percentile concentration

range of values observed in the mid-Brahmaputra Valley. The proximity of Nainital to one of the most polluted regions of India, the Indo-Gangetic Plain (IGP) could have resulted in higher O₃ values in the hills. In another study from the Nepalese Himalayas, a maximum

O₃ concentration of 60 ppb was reported that could have been an outcome of the valley effect. In neighboring Bangladesh, Sikder et al. (2013) reported a high maximum O₃ concentration of 97 ppb in Dhaka. Therefore, it appears that the maximum ozone concentrations

varied in different locations likely related to the land uses. Although the station at Tezpur is a rural location, the maximum O_3 values were on higher compared to other similar locations of Indian subcontinent.

Diel and seasonal variations of O_3

The hour of the week of O_3 concentrations in the year 2014 (January to December) are shown in Fig. 2A. The hour of the week plot generally showed O_3 trends with single peak (maximum ozone) during the afternoons. The diel pattern of O_3 in 2014 is shown in Fig. 2B that shows a clear afternoon peak. This pattern is different from the trends of urban areas where the maximum ozone is experienced at midday (e.g., Dumka et al., 2020; Han et al., 2011; Reddy et al.,

2012; Yadav et al., 2014). The diel O_3 concentration variation followed the progression of temperature during the day shown in Fig. S2. Increased O_3 concentrations have been reported to follow the increase in atmospheric temperature (AT) (e.g., Coates et al., 2016). Temperature affects the O_3 formation by speeding up the rates of chemical reactions, e.g., $O_3 + NO + h\nu \rightarrow NO_2 + O$ is a function of temperature, which is the reaction that leads to the formation of O_3 by reaction with O_2 . AT also increases the rate of emission of biogenic VOCs (Sillman & Samson, 1995) as well as the evaporative emission of VOCs (Rubin et al., 2006).

The O_3 distributions across the days of the week (Fig. 2C) showed a small rise in the concentrations during Monday, Thursday, and Friday with the

Fig. 2 Variations in the concentrations of O_3 (mean O_3 and 95% confidence interval in mean): (a) variations in the hourly mean concentrations of O_3 as the days progressed in a week of the year (Monday to Sunday); (b) variations of hourly mean

concentrations of O_3 as the day of the year progressed; (c) concentrations of mean O_3 in weekdays (Monday to Sunday); and (d) monthly variations of mean O_3 concentrations (January to December, 2014)

concentrations decreasing only marginally on Tuesday, Wednesday, and during the weekends. Higher O_3 is observed on weekends due to reduction of NO_x emissions on weekends in a VOC-limited regime (Cleveland et al., 1974; Sicard et al., 2020; Wolff et al., 2013). The occurrence of higher levels of O_3 is termed as the “weekend effect.” The $\bullet OH$ radical initiated reactions of VOC play a key role here and a significant lowering of NO_x makes more $\bullet OH$ available to initiate the oxidation of VOCs leading to an increase in the ozone formation (Fujita et al., 2003). Also, the lack of titration of O_3 and the ability of the peroxides and peroxy radicals to cycle the NO more rapidly to the NO_2 to be photolyzed allows the formation of additional O_3 . Alternatively, lower weekend O_3 concentrations could be the result of NO_x reduction in a NO_x -limited regime.

The month-to-month O_3 pattern in 2014 is shown in Fig. 2D. It clearly shows pre-monsoon (April) O_3 concentrations maxima at this site (e.g., Crutzen, 1988; Dumka et al., 2020; Gilge et al., 2010; Yadav et al., 2014). The monthly average AT in the study area has been presented in Fig. S2(b). The maximum average monthly AT across the study region was seen during July–August. However, the ozone maxima were found during April when the temperatures were warm (20 to 30 °C) and enhanced photochemical reactions. Although AT has a role in increasing the O_3 formation through increasing the rate constants for important reaction, temperature also enhances the rates of biogenic emission of VOCs (e.g., Coates et al., 2016; Gu et al., 2020; Rubin et al., 2006; Sillman & Samson, 1995). The time series plots of the concentrations of O_3 , NO_x , NO_2 , and NO of the study period are given in Fig. S3. The pre-monsoon maximum of O_3 is clearly seen in these plots. However, maximum NO_x concentration was observed in the winter months. The meteorological conditions during the pre-monsoon favored the rise of O_3 concentration. The maximum concentration of O_3 was seen in the month of April when plants start growing strongly and emit more reactive VOCs. In this region, March–April are the main foliating months in the forests and tea plantations, which would lead to elevated emission of biogenic VOCs (BVOC) and impacting the O_3 formation (e.g., Wu et al., 2020). Also, there are controlled burning fires in the forests for management (Badarinath et al., 2009a). These fires emit large quantities of reactive organic compounds that also interact with the NO_x chemistry and O_3 formation (Singh et al., 1995). Previously, Tyagi et al. (2020)

examined O_3 with respect to AT of three stations in the northeastern India and did not find a dependency of O_3 on temperature. They inferred this discrepancy to the transport of O_3 into the region. However, the role of VOCs of both biogenic and anthropogenic origins cannot be overlooked in the present study.

Diel patterns of O_3 and O_3 - NO_x photostationary state

The O_3 - NO_x relationship can be explained by the following reactions after Leighton (1961):

Daytime O_3 , NO_2 , and NO equilibrate on a time-scale of a few minutes (Clapp & Jenkin, 2001) to reach a “dynamic” equilibrium called the “photostationary state” (PS), wherein $d[O_3]/dt = 0$ (Seinfeld & Pandis, 2016). If J_1 is the rate of the photodissociation of NO_2 including the light intensity (Eq. 2) and k_3 is the rate coefficient of the formation of NO_2 (Eq. 4), then the PS can be explained by the ratio $J_1/k_3 = [O_3][NO]/[NO_2]$, which will govern the concentrations of O_3 , NO_2 , and NO during the day. J_1 is a function of solar intensity so it includes a diel variability whereas k_3 is a function of temperature. The k_3 varies with temperature as given by Seinfeld and Pandis (2016):

$$k_3 (ppm^{-1} min^{-1}) = 3.23 \times 10^3 \exp[-1430/T] \quad (5)$$

However, the accumulation of O_3 in the lower atmosphere is more complicated, and reactions that convert NO to NO_2 with no-or-less destruction of O_3 are required for O_3 to accumulate. Ozone reacts with olefins to form Criegee intermediates that can decompose to produce $\bullet OH$ and peroxy radicals. The $\bullet OH$ radicals oxidize other VOCs and CO to form additional oxidizing radicals like $HOO^\bullet$ and $ROO^\bullet$. These oxidants convert NO to NO_2 without the destruction of O_3 (Eq. 4) as outlined in (Eq. 6) to (Eq. 11) (Atkinson, 2000; Greiner, 1967; Stedman et al., 1970):

There are external factors that can affect the *PS* including transport of O_3 , the nature and concentrations of VOCs, alternate generation of peroxy radicals such as photolysis of short-chain carbonyls, and local sources and transport of NO_x (Khalil, 2018). Due to these complexities, a “true” *PS* is rarely attained in the ground level atmosphere.

Thus, the *net* O_3 (measured O_3 concentration) and J_1/k_3 were plotted against time of day for the different

seasons to ascertain how the temporal variation of O_3 behaved relative to J_1/k_3 (Fig. 3). The *net* O_3 and J_1/k_3 attained a maximum during midday to the early afternoon hours, and then both parameters declined as the day progressed.

During the pre-monsoon and monsoon seasons (Fig. 3a, b), the *net* O_3 and J_1/k_3 attained their maxima and were about equal during midday to afternoon (1130 h to 1530 h local time). In this period, much of the NO_2 has photolyzed to give O_3 , and the *net* O_3 was a function of NO_x . These two seasons are much warmer seasons compared to the post-monsoon and winter periods, and the days are longer. Maximum sunshine and temperature occur during that time period (1130 h to 1530 h). It was also interesting to see that the maxima were attained long after the sunrise, which is the high traffic period of the morning hours.

During post-monsoon and winter seasons (Fig. 3c, d), the *net* O_3 and J_1/k_3 peaked for a shorter duration

Fig. 3 *net* O_3 (measured concentrations) and J_1/k_3 plotted against time of the day in different seasons: (a) pre-monsoon, (b) monsoon, and (c) post-monsoon, (d) winter.

at around 14:00 local time. During the post-monsoon *net* O₃ and J_1/k_3 were nearly equal at ~1400 h local time. However, during the winter, *net* O₃ and J_1/k_3 never became equal. During the peak hour, the levels of *net* O₃ were much higher than the J_1/k_3 during the winter month.

During all the seasons, the ratio (J_1/k_3) and *net* O₃ fell after the peak. The slopes of *net* O₃ and J_1/k_3 were not similar. The fall in the case of J_1/k_3 was much sharper than *net* O₃ and the levels of *net* O₃ remained higher than the ratio during the rest of the day. Also, *net* O₃ was found to be higher than J_1/k_3 during the period preceding the peak period. During the winter season, the *net* O₃ was always much higher than J_1/k_3 . This discrepancy points at the factors that cause deviations of *net* O₃ from the *PS*. Those factors include transport of O₃ and the role of VOCs. The activity of VOC and involvement of OH are local (Khalil, 2018), and OH generation and reactions of VOC degradation and production of O₃ in the process happens in situ. However, the VOCs and NO_x could be from both local emission and long-range transport.

The local sources of elevated levels of VOCs were biomass burning and biogenic emissions. The long-range transport of peroxyacyl nitrate (PAN) and other PAN homologues from the IGP can add NO_x and radicals in the region during the winter, which are important drivers of O₃ production.

Though biomass burning is prevalent in the region (Deka & Hoque, 2015), during the winter months, there is escalation in the biomass burning which is a major source of VOCs in the atmosphere. A unique festive biomass burning, locally known as *meji* burning during mid-January each year is a major emitter of particulate matter and gases (Deka & Hoque, 2014; Hoque & Deka, 2010) that also have implications on the oxidative behavior of the regional atmosphere and O₃ buildup in the winter period.

Biomass burning emits loads of oxygenated hydrocarbons like aldehydes, ketones, and alcohol which are important sources of free radicals linked with the reactivity of NO_x and ozone formation. Acetone alone can provide a high production of HO_x (•OH and HOO•) radicals thereby enhancing the production of O₃ (Singh et al., 1995). The alcohols also further undergo oxidation giving rise more reactive aldehydes and radicals that would favor O₃ formation explained by the following reaction (Singh et al., 1995):

Another important source of VOC in the winter months is agriculture. The whole of the Brahmaputra Valley region is widely cultivated with crops from the Brassicaceae family that are known to emit volatile organics (Gan et al., 1998; Mead et al., 2008). Rapeseed, cabbage, and radish are principal winter crops of the Brahmaputra Valley. There is a large area (0.276 million ha) under rapeseed cultivation (Das, 2015). Even the fallow lands are used for rapeseed since it is a hardy crop and does not need irrigation and excessive manuring. Similarly, large areas are under cabbage (33.24 kha) and radish (21.17 kha) (Horticulture Statistics Division, 2018). The Brassicaceae family is known to emit large volumes of CH₃Br and other organics (Gan et al., 1998; Mead et al., 2008). CH₃Br is a reactive gas and provides a source of radicals that convert NO to NO₂ and enhance the production of O₃ (Orlando et al., 1996), shown in Eqs. 14–16:

PAN is a source of NO_x and organic radicals in the remote atmosphere. The thermochemical stability of PAN depends on the temperature and is quite stable at low temperature. At 7 °C and NO₂/NO ratio of 2–20, the lifetime of PAN (τ_{PAN}) is ~19 to 120 h, and at 27 °C, τ_{PAN} is ~0.75 h to 4.4 h (Altshuller, 1993). Other PANs have similar lifetimes. Therefore, at low temperatures, PAN can be transported long-range and pump in NO_x and organic radicals to the remote regions. Analysis of the air mass back trajectories reaching the site during winter (Fig. S1) suggests that 28% of the trajectories traveled from the IGP region of India. The IGP is one of the most polluted regions of India from where aided by the low temperatures, there was likely transport to the study area of PAN. As the trajectories reached the site where the temperature is 10 °C to 24 °C in the winter, the PAN decomposed to NO_x and organic radicals (Eq. 17):

The ventilation coefficients (VC) calculated for winter month (January) as mixed layer height (MLH) $\times$ wind speed (WS), as illustrated in Fig. 4 show that the maximum VC is experienced at $\sim 9:00$ the morning and that is, then, there was a steep rise in the winter period concentration of *net* O₃.

Transport of O₃

Transport of O₃ also has a greater implication in the deviation of *PS* as seen in the period before and after the peak O₃ time of the day, wherein the O₃ concentrations were always higher than the ratio (J_1/k_3). The transport of O₃ to the station was examined by comparing (i) the polar plots of O₃ and NO₂ (for local transport) and (ii) the concentration-weighted trajectories (CWT) of O₃ (for regional transport representing the precursors like PAN). The polar plots of NO₂ were considered because O₃ is ultimately produced (through all photochemical processes) from the photolysis of NO₂. If O₃ was to be produced only from the photolysis of NO₂, the polar plots of O₃ and NO₂ would look similar. The polar plots of O₃ and NO₂ are given in Fig. 5, in which the concentrations are plotted against wind speed and wind direction.

Through the seasons, high O₃ concentrations were found to accompany high wind speed that suggests transport of O₃ to the site (Fig. 5a–d). However, stagnant conditions would also allow locally emitted NO to titrate the O₃. Alternatively, higher concentrations of NO₂ were observed under lower wind speeds (Fig. 5e–h). Only moderate and low levels of NO₂ were associated with high wind speeds indicating that the NO_x was locally emitted and dispersed under higher ventilation conditions. It is clear from the plots that higher O₃ and higher NO₂ were seen to be associated with winds from different directions. It was important to look at the polar plots of the winter season (Fig. 5d, h). As discussed in the previous section, in the winter season, O₃ did not show a diel pattern corresponding to J_1/k_3 (*PS*), and the O₃ concentration was much higher than J_1/k_3 . The polar plot of O₃ in winter shows that O₃ was higher when the wind speeds were high, a pattern that is different from the polar plot of NO₂. The wind directions with respect to high ozone and the direction with respect to high NO₂ were found to be different, which may be inferred as transport of O₃ to the site. There are previous reports that during the winter and pre-monsoon seasons, the region receives air mass trajectories that originated and/or passed over the IGP (Bhuyan et al., 2016; Deka et al., 2020) and bring high pollutant concentrations to the region (Omami et al., 2017; Rahman et al., 2020).

Fig. 4 Ventilation coefficient (VC) during winter period (January 2014). VC was calculated as $VC = MH \times WS$; MH was calculated by HYSPLIT

Fig. 5 Polar plots of O_3 (a–d: pre-monsoon, monsoon, post-monsoon, winter), and (b) NO_2 (e–h: pre-monsoon, monsoon, post-monsoon, winter): concentrations plotted against wind direction and wind speed during the study period

Fig. 6 Concentration-weighted trajectories (CWT) computed from 3-day HYSPLIT back trajectories reaching the site every hour for O_3 ; Tezpur station is shown as the black star

The HYSPLIT air mass trajectories reaching the site were weighted with the concentrations of O_3 , and the CWTs were computed (Fig. 6). It was clear from the CWT plot that when the trajectories originated or passed over the IGP, the Indian Himalayan region including Nepal, Bangladesh, and the Bay of Bengal, the site experienced higher O_3 concentrations (shown as colors above yellow). Moderate concentrations of O_3 (color codes green to yellow) were observed when the trajectories originated or passed over Myanmar, the Shillong Plateau, and the western regions of China. These results suggest that the O_3 concentrations are strongly affected when the trajectories originated or traveled over polluted regions transporting O_3 precursors such as PAN to the area.

Conclusions

Ambient O_3 concentrations of mid-Brahmaputra Valley showed vivid diel, monthly, and seasonal variations, which is not unusual. Ozone concentrations through days

and seasons do vary and should vary. However, the behavior of O_3 against the *PS* varied among seasons and O_3 of the days of the winter period deviated from the *PS* substantially. This deviation can be attributed to local emissions from biomass burning, VOCs from both biogenic and anthropogenic emissions, and long-range transport of O_3 precursors in the form of PAN and PAN homologues.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval There was no use of animals or animal products at any stage of this work.

Consent to participate There was no involvement of human subjects at any stage of this work.

Consent for publication This paper is an unpublished work and a product of original research. The paper has not been published in any language and not under consideration elsewhere. The authors have agreed to the submission and subsequent publication.

Competing interests The authors declare no competing interests.

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