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High ozone episodes at a semi-urban site in India: Photochemical generation and transport

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ABSTRACT

The present study focused on investigating the possible atmospheric conditions influencing the high ozone episodes over a semi-urban site (27.16° N, 78.08° E) in Agra, India during July 2014–June 2016. During the study period, average concentration of ozone was 32.3 ± 22.7 ppb, and concentrations of its precursors *viz* carbon monoxide (CO), nitrogen oxide (NO) and total nitrogen oxides (NO_x*) were 527.3 ± 482.7 ppb, 6.5 ± 8.2 ppb, and 12.1 ± 7.8 ppb, respectively. The maximum monthly average ozone concentration was observed in June (48.2 ± 31.0 ppb) and it was nearly three times higher than the minimum levels observed in December (16.7 ± 10.5 ppb). Considering high ozone episodes, 78 days exceed hourly ozone limit of 90 ppb specified by National Air Quality Standards (NAAQS, CPCB, 2009) for India while 75 days exceed the daily maximum 8 hourly ozone limit of 70 ppb or above (NAAQS, EPA, 2015). Trajstat model was used for air-mass cluster analysis during episodic days; five clusters of air-masses were identified and among them, the cluster from northwest direction had the maximum frequency (35.4%). During the study period, four different types of high ozone episodes were identified and explained using prevailing meteorology. The episodes were attributed to local photochemistry and/or transport.

1. Introduction

Rising level of trace gases due to rapid globalization and population outburst is a major concern for environmentalists. These rising levels frequently exceed air quality standards and are a threat to animals and vegetation. Among trace gases, tropospheric ozone is a harmful trace gas and its levels are increasing at the rate of 1–5 ppbv per decade in the Northern hemisphere (Cooper et al., 2014). Tropospheric ozone is a greenhouse gas as it absorbs solar radiation in 9–10 μm range (Wang et al., 1995; Beaney and Gough, 2002). Ozone has 1200–2000 times more radiative forcing as compared to CO_2 on per molecule basis (Schwarzkopf and Ramaswamy, 1993). It controls lifetime and chemical transformation of various trace gases through the production of OH· from water vapours (Levy, 1971). Tropospheric ozone is detrimental to human beings (Heal et al., 2013; Sousa et al., 2013), vegetations and crops (Tiwari and Agrawal, 2009; Avnery et al., 2011; Chaudhary and Agrawal, 2015). In Varanasi, India, Rajput and Agarwal (2005) reported reduction (32%) in yield of wheat crop and impaired seed quality due to high levels of ozone.

In the troposphere, ozone levels are predominantly due to two processes: Stratosphere to troposphere exchange (Lelieveld and Dentener, 2000) and photochemical generation from precursors: volatile organic compounds (VOCs), carbon monoxide (CO) and NO_x (Crutzen, 1974; Fishman, 1979). It is a challenging problem to control ozone levels because it is a secondary pollutant and its levels are affected by precursor concentrations as well as meteorological parameters (Yadav et al., 2016). In earlier studies high levels of ozone were considered to be associated with (i) rapid local photochemical production in hot and calm conditions (Dueñas et al., 2002; Shan et al., 2009; Li et al., 2017), (ii) transport from polluted areas (Wang et al., 2006; Saavedra et al., 2012) and (iii) special synoptic weather conditions like typhoon (Shan et al., 2009) and anticyclone (Flocas et al., 2009; Russo et al., 2014). Long range transport of ozone at regional scale is feasible due to its long lifetime (nearly 90 days) in the free troposphere (Fishman and Cros, 1991). It can be formed in transported air or aged air-masses from primary pollutants released from industrialized and urbanized areas (Cristofanelli and Bonasoni, 2009). The movement of air-masses is considered to play a role in governing the air quality (Kalabokas et al., 2008) by controlling the formation, transportation, and accumulation of air pollutants at local and regional scales (Flocas et al., 2009; Tang et al., 2017).

The tropical Asian region receives high amount of solar radiations and has high water vapour content in air (Crutzen, 1995), which is favourable for photochemical generation of ozone. This has led to the

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initiation of extensive studies on tropospheric ozone in India. Earlier studies in India, have reported diurnal variation, seasonal variation, relationship with precursors, effect of meteorological parameters on ozone levels and interaction of ozone with particulate matter (Lal et al., 2000; Naja and Lal, 2002; Srivastava et al., 2010; Ojha et al., 2012; Swamy et al., 2012; Sarangi et al., 2014) but the studies related to ozone episodes (Ganguly and Tzanis, 2012) are scanty. However, several studies reported and explained ozone episodes in other parts of the world (Gerasopoulos et al., 2005; Mateos et al., 2016). In Mediterranean region, high background ozone were observed in summer season and these levels were associated with long-range transport at the regional scale (Kouvarakis et al., 2002; Saliba et al., 2008; Kleanthous et al., 2014). In Galicia region of Iberian Peninsula few ozone episodes were associated with a high-altitude anticyclonic ridge which was associated with no cloud conditions and high temperature (Saavedra et al., 2012). Tsai and Liu (2013) observed severe ozone episodes over Taiwan and the episodes were linked with prevailing synoptic weather conditions. They observed three different ozone episodes; the first episode was due to north-eastward transport of ozone precursors under the influence of a frontal passage. The second episode occurred due to transport of O_3 during an anticyclonic passage. The third episode occurred as a result of departure of an anticyclone resulting in horizontal transport of O_3 and its precursors. In addition, the blockage of winds by central high mountains adds to local formation of ozone. In addition to above-mentioned studies, other studies have also reported episodic events to be associated with local photochemistry (Xu et al., 2008; Shan et al., 2009), synoptic meteorology (Carvalho et al., 2010; Monteiro et al., 2012) and long-range transport (Jaffe et al., 2004).

Several criteria have been used to identify ozone episodic event, the most common method is the identification of the days when ozone exceeds air quality standard of environmental agencies at a particular site. Shan et al. (2009) reported ozone episodes when hourly ozone concentration crosses 100 ppb (Chinese standard) limit at Jinan, China. Similar criteria were also followed by Carvalho et al. (2010) at Lamas d'Olo (rural mountain site), Portugal. Saavedra et al. (2012) considered two simultaneous criteria for identification of ozone episodes over Galicia region: hourly ozone concentration exceeding 150 μg m^{-3} and eight hourly ozone concentration reaching 120 μg m^{-3} or above. High ozone episodes have been explained by various methods including back trajectory analysis (Carvalho et al., 2010) and synoptic pattern classification (Saavedra et al., 2012).

Present work focused on ozone episodic events during July 2014–June 2016 with following objectives: (i) identification of high-ozone episodes, (ii) classification of air-masses through cluster analysis during episodic days, and (iii) analysis of four different types of ozone episodic events.

2. Measurements and techniques

Trace gases (O_3, NO_x*, and CO) measurements were carried out at the campus of Dayalbagh Educational Institute (semi-urban site) (27.16° N, 78.08° E), Agra located in North-central part of India. Agra has semi-arid climate as it is surrounded by Thar Desert on two third of its periphery. Map showing the location of sampling site in Agra, the site is about 6 km north of the urban and industrial area of Agra (Fig. S1). The sampling site is linked to the main city through one major road on which about 10^4 vehicles pass in a day. The National Highway NH-2 is about 2 km south to the site which has high vehicular density (10^6 vehicles per day). The site has four distinct seasons; summer (March to June), monsoon (July to September), post-monsoon (October and November) and winter (December to February). In the summer season, the temperature ranged between 20 and 47 °C (Avg 31.4 ± 6.9 °C) while relative humidity (RH) ranged between 18 and 75% (Avg 41.2 ± 20.8%). In the winter season, the temperature dropped to below 6 °C (Avg 17.4 ± 5.7 °C) and relative humidity ranged from 15 to 95% (Avg 72 ± 21%). In the post-monsoon season, temperature ranged from 11 to 39.5 °C (Avg 25.4 ± 6.7 °C) and RH ranged from 21 to 94% (Avg 54.9 ± 18.7%). In monsoon season, because of heavy rainfall, RH ranged from 22 to 98% (Avg 66 ± 18.9%) and temperature varied from 22 to 40 °C (Avg 30.2 ± 3.1 °C). The detailed description of the site has been discussed elsewhere (Verma et al., 2017a).

In-situ measurements of surface ozone, NO_x* and CO were made by continuously operating gas analyzers. The ozone analyzer (Thermo Scientific 49*i*) functions on the absorption of UV radiation at 254 nm and concentration of ozone is determined by following Lambert–Beer's law. In the O_3 analyzer, sample gas is split into two streams: the reference stream passes through scrubber which removes the ozone and the other stream (sample) goes to the detector directly. The solenoid valves alternate sample and reference gas streams every 10 s. The UV light intensity of each gas stream is determined by the detectors. The detection limit of ozone analyzer is 1.0 ppb, response time is 20 s and accuracy is ± 5%. The zero drift of ozone analyzer is < 1.0 ppb for 24 h. NO_x analyzer (Thermo Scientific 42*i*) works on the principle of chemiluminescence. In this analyzer, NO measurement is based on the reaction of NO with O_3 to form NO_2. The excited molecules of NO_2 show chemiluminescence which peak at nearly 630 nm and light intensity determine the concentration of NO. This method is specific for NO measurements, and NO_2 measurement was based on the conversion of NO_2 into NO using a molybdenum (Mo) convertor. But Mo convertor is not specific for NO_2, it also converts other oxides of nitrogen into NO (Xu et al., 2013; Mallik et al., 2015). Therefore it gives slightly high levels of NO_x (sum of NO and NO_2) and it can be considered as NO_x* (NO, NO_2 and other reactive nitrogen species) (Guo et al., 2013; Sarangi et al., 2014). The detection limit and response time of NO_x analyzer are 0.4 ppb and 80 s respectively for 60 s averaging time. The zero drift of NO_x analyzer is < 0.4 ppb for 24 h.

The CO analyzer is based on absorption of infra-red (IR) radiations at 4.67 μm by CO molecules. The analyzer generates a broad beam of IR radiation through a heated element. The detection limit and response time of CO analyzer are < 0.04 ppm and 60 s respectively for 60 s averaging time. The details on principles of these analyzers have been discussed elsewhere (Singla et al., 2011; Verma et al., 2017b). Zero and span calibrations of these analyzers are done on a weekly basis using zero air generator and dynamic gas calibrator (Teledyne T300).

Meteorological parameters viz. temperature, relative humidity, solar radiation and wind speed were recorded at the sampling site using Automatic Weather Station WM271 Data Logger at one hour interval.

Air-mass clusters were calculated using Geographical Information System (GIS) based Trajstat software (Wang et al., 2009). The meteorological files for running the model were extracted from GDAS archive derived from NCEP global data assimilation system (1 × 1°). The appropriateness of this model has already been discussed in earlier studies (Wang et al., 2015; Liang et al., 2016). As the study was performed at the ground level, therefore, back trajectory analysis was also performed at (height of Agra) 171 m AGL (above ground level) height for selected ozone episodic days. Three-day (72 h) back trajectories were used to perform the cluster analysis.

The pressure gradient was calculated using mean sea level pressure extracted from NCEP/NCAR reanalysis data (http://www.esrl.noaa.gov/psd/) available on a daily basis. Pressure gradient intensity is related to the efficiency of horizontal mixing. The surface pressure gradient intensity was calculated from grid point data of mean sea level pressure using NCEP/NCAR reanalysis data (Kallos et al., 1991; Flocas et al., 2009). Following the classification of surface pressure gradient given by Kallos et al. (1991), the episodes were placed in four classes: pressure gradient > 5 hPa/100 km as strong, pressure gradient = 1–5 hPa/100 km as moderate, pressure gradient = 0.5–1 hPa/100 km as weak while pressure gradient < 0.5 hPa/100 km as very weak. At the study site, no episode was characterized by strong and very weak pressure gradient. However, nearly 92% high ozone days were characterized by moderate pressure gradient, and 8.0% were characterized by the weak pressure gradient. These results substantiate