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Surface ozone scenario and air quality in the north-central part of India

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ABSTRACT

Tropospheric pollutants including surface ozone (O_3), nitrogen dioxide (NO_2), carbon monoxide (CO) and meteorological parameters were measured at a traffic junction (78°2′ E and 27°11′ N) in Agra, India from January 2012 to December 2012. Temporal analysis of pollutants suggests that annual average mixing ratios of tropospheric pollutants were: O_3 — 22.97 ± 23.36 ppbV, NO_2 — 19.84 ± 16.71 ppbV and CO — 0.91 ± 0.86 ppmV, with seasonal variations of O_3 having maximum mixing ratio during summer season (32.41 ± 19.31 ppbV), whereas lowest was found in post-monsoon season (8.74 ± 3.8 ppbV). O_3 precursors: NO_2 and CO, showed inverse relationship with O_3. Seasonal variation and high O_3 episodes during summer are associated with meteorological parameters such as high solar radiation, atmospheric temperature and transboundary transport. The interdependence of these variables showed a link between the daytime mixing ratios of O_3 with the nighttime level of NO_2. The mixing ratios of CO and NO_2 showed tight correlations, which confirms the influence of vehicular emissions combined with other anthropogenic activities due to office/working hours, shallowing, and widening of boundary layer. FLEXTRA backward trajectories for the O_3 episode days clearly indicate the transport from the NW and W to S/SE and SW direction at Agra in different seasons.

Introduction

In India, air pollution caused by gaseous pollutants has become a major concern in recent years, having human and environmental health effects (Lal, 2007; Saini et al., 2008, 2009, 2014; Sinha et al., 2015; Parkhi et al., 2016). Around 10% of the increased global warming potential of the atmosphere consequences from increases in surface ozone, however this value is very uncertain (Tropospheric Ozone Research (TOR) — 2 final report, 2003). Mixing ratio of O_3 is governed by natural and anthropogenic sources both, which includes: (a) downward transport of stratospheric ozone, (b) local chemistry: *in situ* surface ozone production from reactions of nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOC_s) from different sources and (c) long range transport (Reddy et al., 2008; Tang et al., 2009). Therefore, the O_3 mixing ratio in any given area results from a combination of formation, transport, destruction and deposition. The main sources of O_3 precursors: NO_x and VOC_s are vehicular, industrial and biomass emissions (Wang et al., 2004).

Nitrogen dioxide (NO_2) emitted from fossil fuel combustion reacts with oxygen present in the atmosphere photochemically to produce surface ozone in the troposphere, represented in set of Reactions (1)–(6) (Crutzen, 1970).

$$NO_2 + h\nu \xrightarrow{437\ nm} NO + O \quad (1)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (2)$$

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$$O_2 + h\upsilon \xrightarrow{245\ nm} 2O^{\bullet} \quad (3)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (4)$$

$$O_3 + h\upsilon \xrightarrow{310\ nm} O(^1D) + O_2 \quad (5)$$

$$O(^1D) + H_2O \rightarrow 2OH^{\bullet} \quad (6)$$

This photo-chemical reaction is initiated by the reaction of volatile organic compounds and carbon monoxide with hydroxyl ions present in the atmosphere, which produces RO_2 and HO_2 radicals in the atmosphere (Reactions (7)–(13)). RO_2 radical generated by the reaction of VOCs and hydroxide radical reacts faster with NO present in the atmosphere in comparison to O_3 molecule, which prevents the destruction of surface ozone in the atmosphere, during daytime.

$$RH + OH \rightarrow H_2O + R \quad (7)$$

$$R + O_2 + M \rightarrow RO_2 + M \quad (8)$$

$$RO_2 + NO \rightarrow NO_2 + RO \quad (9)$$

$$CO + OH \rightarrow CO_2 + H \quad (10)$$

$$H + O_2 \rightarrow HO_2 \quad (11)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (12)$$

$$\text{Net: } CO + 2O_2 \rightarrow CO_2 + O_3 \quad (13)$$

Apart from ozone precursors, changes in meteorological parameter: solar radiation (SR), wind speed (WS), atmospheric temperature (AT) also affect O_3 mixing ratio. O_3 exhibit pronounced seasonal cycles that varies with the latitude and altitudes. High mixing ratios of O_3 occur in summer (Oltmans et al., 2006), or in early spring/winter (Ahammed et al., 2006), whereas on a diurnal scale maximum O_3 mixing ratio was found during the noontime, when SR is maximum (Zvyagintsev, 2004; NRC, 1991).

Today, there are new threats to the environment which must be addressed with more sophisticated methods because of pronounced effects to human health. Therefore, the study of O_3 and its precursors is key for understanding the pollution levels in this tropical semi-arid region. In the present study, investigation of various aspects of O_3 pollution at a traffic junction site in Agra, India was conducted. The purpose of this work was to investigate the emission characteristics at different timescale (diurnal and seasonal), trends, assess relationships between the O_3 and meteorological parameters and identifying the most common sources of O_3 emission. The specific objectives of the study included: (1) Measurement of ambient O_3 and its precursors, (2) Identification of the main sources contributing to the elevated O_3 mixing ratio, (3) Quantitative evaluation of the effect of these sources on O_3 mixing ratio.

1. Methodolgy

1.1. Site description

The present work is an extension of a previous study to identify seasonal-variation of surface ozone and its precursors in Agra, India (Saini et al., 2014). Agra is in the central part of northern India, about 200 km south of the National Capital, New Delhi (Fig. 1). Geographical coordinated of Agra lies between 27°10′59.88″N 78°01′00.12″E with the height of 169 m above sea level (asl).

Agra has continental, subtropical and dry type climate. Meteorologically the year is divisible into four seasons: winter (January/February/March/December), summer (April/May/June), monsoon (July/August/September) and post-monsoon (October/November). Generally, the period between May to June is hottest period around the year. Though, July is the month of monsoon season but due to high humidity and clear sky (when it is not raining) is can be as hot as June. Detailed site description can be found in our previous publications (Saini et al., 2008, 2009, 2014).

1.2. Sampling protocol

For the measurement of pollutants' mixing ratios, a traffic junction site: Agra Nagar Nigam, Soorsadan crossing, Agra was selected in Agra. Sampling was done for a year from January to December 2012. Hourly mixing ratios of NO_2, CO, and O_3 were measured simultaneously with the instruments obtained from Ecotech, New Delhi, India. NO_2 was monitored with an analyzer (EC 9841), runs on the principle of measurement of the chemiluminescence formed by the oxidation reaction of NO with O_3. The mixing ratio of CO was monitored using non-dispersive infrared (NDIR) gas filter correlation technique based on the IR absorption (at 4.67 μm) by carbon monoxide molecules within its rotation–vibration absorption band by EC9830 monitor. The mixing ratio of ozone was measured using Ecotech analyzer (EC9810), based on the principle of measurement of absorption of UV radiation at 254 nm by ozone present in the sample air. Meteorological parameters were measured using met station: Met-One station, United States, located on the roof of Agra Nagar Nigam building, Agra (Taneja et al., 2008; Singh et al., 2014).

1.3. Air mass trajectories

Backward trajectory analysis is an important tool in determining the air mass parcel transport (Stohl et al., 1995; Stohl, 1998). To support the interpretation of O_3 behavior, backward trajectory analysis has been performed. Backward trajectories were drawn for the episodic days, having the extreme ozone mixing ratios. Trajectories were drawn using FLEXTRA model (Stohl et al., 1995) hosted by the Norwegian Institute for Air Research (NILU).

2. Results and discussion

2.1. Temporal variation of ozone

The basic dataset in the present study were recorded for 1-hr interval, which is represented in the form of descriptive statistics in Table 1. The seasonal variations can prove fruitful in the identification of different sources. In Fig. 2a, O_3 showed a well-defined seasonal variation pattern on a diurnal scale with high levels (32.41 ± 19.31 ppbV) during the summer and low (8.74 ± 3.8 ppbV) during the post-monsoon with an annual mean