

On low value of surface ozone during winter in Delhi

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In this paper, the main aim has been to explain the low value of surface ozone during winter in Delhi (28.38°N, 77.12°E). Surface ozone data of Delhi for the period 1990-2013 has been examined. Analysis of data shows that concentration of surface ozone is the lowest during winter (13.3 ppbv, parts per billion by volume, during December-January) and the highest in summer (25.35 ppbv during May-June). An attempt has been made to explain the low value of surface ozone during winter in terms of concentration of NO and NO₂. The low value of O₃ is explained when [NO₂]/[NO] ratio is ~1 and high value of surface ozone is explained when this ratio is ~2. The low value of [NO₂]/[NO] ratio and surface ozone during winter is due to the presence of fog. Also, during 1990-2013, surface ozone has been found to have an increasing trend ~ 0.3 ppbv/year.

Keywords: Surface ozone, Nitrogen oxide, Fog

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1 Introduction

The quality of air, we breathe in, is deteriorating day by day by human activities. This is due to the release of toxic gases, like oxides of nitrogen (NO_x), CO, CH₄ and non-methane hydrocarbons (NMHCs) into the atmosphere. Oxides of nitrogen and CO are emitted by fossil fuel combustion in the automobiles and NMHCs due to incomplete combustion. Methane is emitted from paddy field, wetland, marshy land, termites, biomass burning, drains, etc. Oxidation of these pollutants produces ozone when NO_x concentration exceeds 10 pptv (parts per trillion by volume). In this process, two radicals, viz. OH and O¹D, play a major role. Though, a secondary pollutant, surface ozone, is also a dangerous pollutant, which if not in right amount, can cause vegetation injury, visible injury, pulmonary damage, asthma attacks and hazardous episodes to environment. Vingrazan¹ reviewed the available surface ozone data all over the world. The review revealed that regional feature in different regions was different depending upon the nature of the source and meteorological conditions. A number of studies on features of O₃ have been made by various researchers for various locations in India²⁻²⁵. These locations are Thiruvananthapuram (8.29°N, 76.59°E), Tranquebar (11.1°N, 79.54°E), Gadanki (13.5°N, 79.2°E), Anantapur (15°N, 78°E), Pune (18.3°N, 73.55°E), Haldia (22.05°N, 88.03°E), Kolkata (22.34°N, 80.24°E), Ahmedabad (23.2°N, 72.38°E),

Mt Abu (24.40°N, 72.45°E), Agra (27.10°N, 78.5°E), Udaipur (27.42°N, 75.33°E), Delhi (28.38°N, 77.12°E) and two stations in the Himalaya region, viz. Mohali (31.9°N, 77.12°E) and Kothi (32°N, 77.18°E). Geographical and meteorological conditions of these locations are different from one another. As for example, Mt Abu is a hill station; Tranquebar, Thiruvananthapuram and Haldia are situated in the coast; Delhi and Kolkata are highly polluted mega cities and are situated in Indo-Gangetic plain. In the diurnal side, it is almost established that surface ozone is maximum during daytime and minimum during night. In the long-term side, both decreasing and increasing trend have been reported from various locations. In the seasonal side, during winter, which is the subject of the present study, ozone has been found to be high at many places; but at places situated in Indo-Gangetic plains, this has been found to be low compared to other seasons. This is evident from Fig. 1, which is reproduced from an earlier study⁶. In this figure, a comparison of monthly averaged values of surface O₃ of Delhi has been made with those of Kolkata, Haldia, Ahmedabad, Pune and Thiruvananthapuram. It is seen in this figure that ozone concentration of Delhi and Kolkata is low during winter as compared to that of Ahmedabad, Haldia, Pune and Trivandrum. Delhi and Kolkata are located in the Indo-Gangetic plain, whereas Ahmedabad, Pune and Thiruvananthapuram are situated outside this plain.

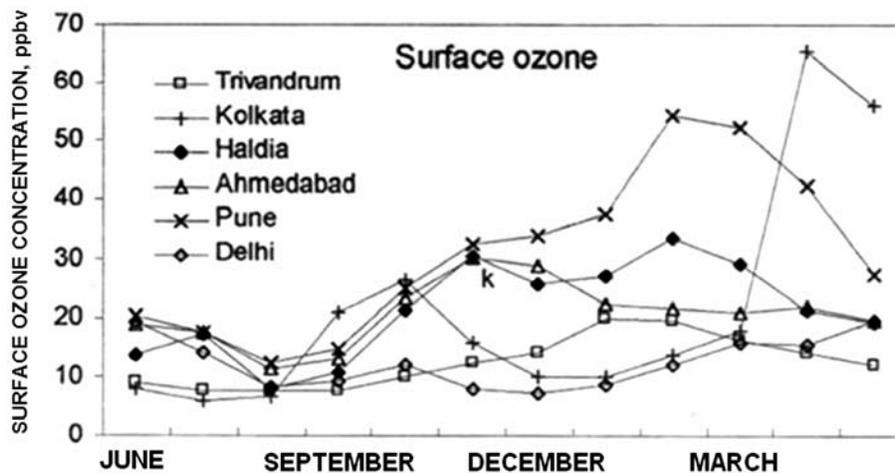


Fig. 1 — Monthly averaged values of surface ozone at different places of India

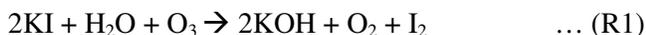
Low value of ozone is seen in all the stations during monsoon. That is understandable because pollution is washed away by the rain. After monsoon, ozone value starts increasing. But in Kolkata and Delhi, it decreases to a very low value during winter. Haldia is also located in the Indo-Gangetic plain and here also, it decreases during winter, but the decrease is not as much as in Kolkata and Delhi. That is because Haldia is a port city and it has the effect of sea breeze. The present study is based on the analysis of surface ozone data measured in Delhi from 1990 to 2013 (about 24 years).

2 Measuring site

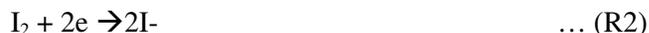
Measurements have been made at Delhi, which is the capital city of India. Its population is ~14 million covering an area of ~1483 km². It is surrounded by four satellite towns, viz. Faridabad, Gurgaon, Noida and Ghaziabad and is called the National Capital Region (NCR). The whole region is highly polluted by a large number of vehicular traffic, and small and big industries. A river, Yamuna, encompasses the eastern side of Delhi.

3 Measuring method

In this method, ambient air is drawn into a potassium iodide (KI) solution of an electrochemical cell (bubbler) with the help of a suction pump. Two electrodes (a cathode of platinum and an anode of silver) connected with an external circuit are dipped in the solution. A potential of 0.42 V is applied between the two electrodes. When air enters the solution, the ozone present in the air reacts with KI liberating free Iodine at the cathode:



This free iodine (I₂) takes two electrons, becomes I⁻ and flows to anode:



At the anode, I⁻ releases these two electrons and combines with silver (Ag) to form silver iodide (AgI).



These two electrons then flow in the external circuit and form ozone current. Thus, every molecule of ozone liberates two iodine atoms, which in turn results in a flow of two electrons in the external circuit. The ozone current is recorded in a chart recorder. The following equation is used to convert the ozone current into the partial pressure of ozone (P) in millipascals:

$$P = 4.308 \times 10^{-8} \cdot (i - i_b) \cdot t \cdot T \quad \dots (1)$$

where, t, is the time in seconds to pump 100 ml of air at a temperature T (in K); I, the current (in microampere); and i_b, the dark current (the output with ozone free air flowing through the sensor). The accuracy of the ozone measurement by this technique is about ±10%

4 Results

Figure 2 shows the monthly averaged values of surface ozone for Delhi from January 1990 to December 2012. Scatter in data is noticed. This is mainly due to the seasonal variation. To confirm this point, the data of all the years is averaged month wise. These are shown in Fig. 3(a) from January to December. It is seen in this figure that O₃ value

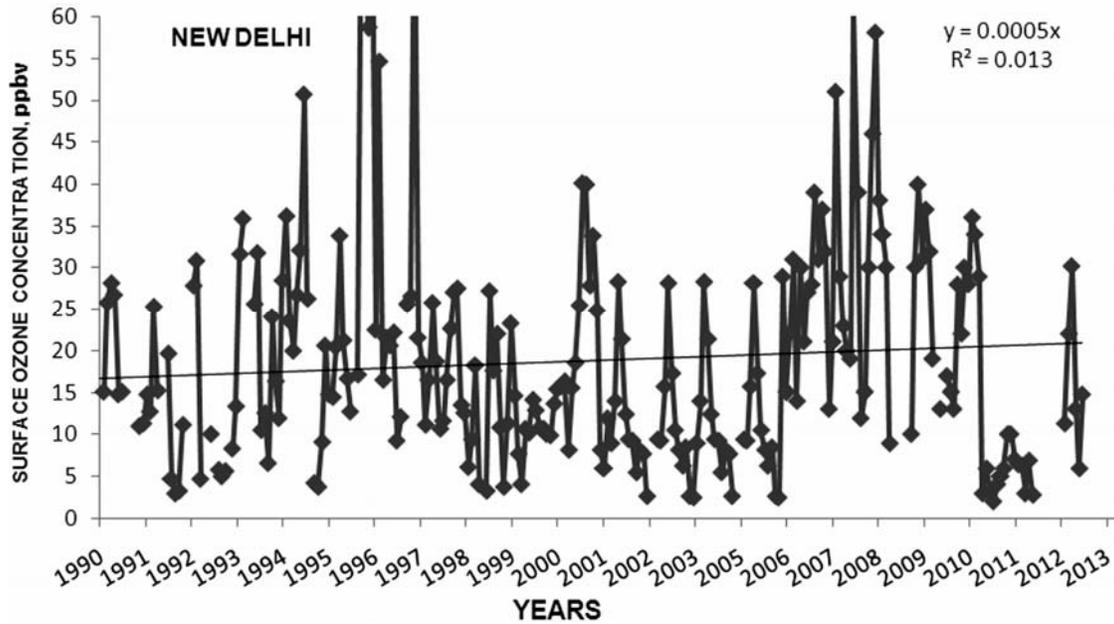


Fig. 2 — Monthly averaged values of surface ozone from January 1990 to December 2013 in Delhi

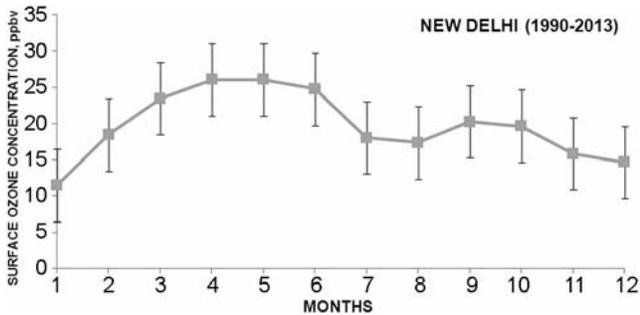


Fig. 3(a) — January to December monthly averaged values of surface ozone obtained from January 1990 to December 2013 data in Delhi

(11.5 ppbv, parts per billion by volume) starts increasing from January (winter), becomes maximum (26 ppbv) during April-May (summer), decreases to 18-17.3 ppbv during July-August (monsoon season), increases to 20.2-19.6 ppbv during September–October (post-monsoon period), and then decreases to 14.6 ppbv in December (winter). Season-wise, this picture is clearer in Fig. 3(b), where these data have been shown in bar graph. Here, winter corresponds to December and January; summer corresponds to May and June; monsoon corresponds to July and August; and post-monsoon corresponds to September and October. The ozone value is the lowest (13.3 ppbv) in winter (December-January) and the highest (25.35 ppbv) in summer (May and June). The straight line in Fig. 3(a) is the best linear fit to the data. An increasing long-term trend ~ 0.3 ppbv per year is also seen in this figure. It is significant at 90% confidence level.

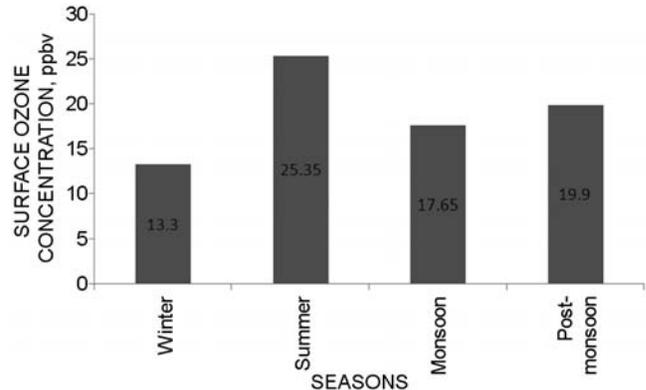
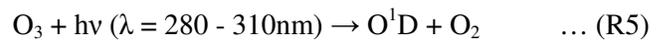


Fig. 3(b) — Bar graph of surface ozone values for four seasons

5 Theoretical model and Discussion

Surface ozone is a secondary pollutant, which is produced from primary pollutants, viz. NO_x , CO , CH_4 and NMHCs. The oxidation of these pollutants produces ozone when NO_x concentration is above a certain value. The oxidation channel, generally, starts with photo-dissociation of ozone molecule by UV radiation in the wavelength range (λ) 280 – 310 nm:



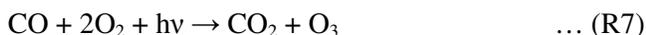
giving rise to atomic oxygen in the ^1D state. This atomic oxygen reacts with water vapour to give rise to OH:



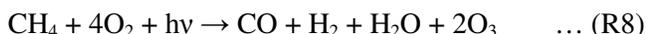
O^1D and OH are the two radicals, which play a significant role in the distribution of surface ozone in the troposphere even though their abundances are

small (O^1D is \sim a few molecules/cc to few tens of molecules and OH abundances are $\sim 10^5$ - 10^6 molecules/cc). This is illustrated as:

CO first reacts with OH to form H and CO_2 ($CO + OH \rightarrow H + CO_2$), which after a series of reactions produce ozone if there is sufficient NO_x :



CH_4 first reacts with OH to form CH_3 and H_2O ($CH_4 + OH \rightarrow CH_3 + H_2O$), which after a series of reactions produce ozone if there is sufficient NO_x :



Non-methane hydrocarbon (R) first reacts with O_2 to form its oxide in the presence of a third body ($R + O_2 + M \rightarrow RO_2 + M$), which after a series of reactions produce ozone if there is sufficient NO_x :



Details of these reaction series are presented by Subbaraya & Lal²⁶ and Brasseur & Solomon²⁷.

Emission of CO, NO_x and NMHC starts from the morning hours due to the start of the vehicular traffic. Then, their photo-oxidation starts and in that process NO_2 is produced. Simultaneously, the photo-dissociation of NO_2 also starts ($NO_2 + hv \rightarrow NO + O^3P$) yielding O^3P . Then, O^3P reacts with O_2 to form O_3 ($O^3P + O_2 + M \rightarrow O_3 + M$), which undergoes photo-dissociation leading to the formation of O^1D ($O_3 + hv \rightarrow O^1D + O_2$). This is a loss channel of O_3 . Another loss channel of O_3 is the reaction $O_3 + NO \rightarrow NO_2 + O_2$. O^1D , thus produced, reacts with H_2O to produce OH radical ($O^1D + H_2O \rightarrow OH + OH$). This radical then reacts with CO, CH_4 and NMHC. A product of these reactions then reacts with NO to form NO_2 leading to the production of O_3 . An example of how a product of CO forms ozone is:

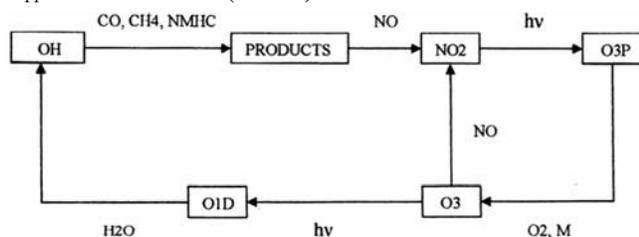
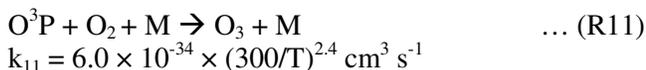
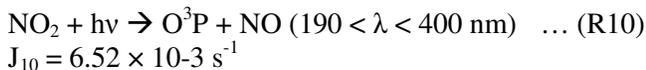
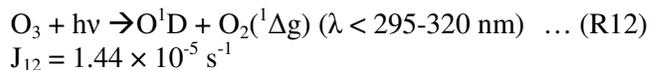


Fig. 4 — Simplified chemical scheme used for the model discussion



where, T, is the temperature; J_{10} , J_{12} , the photo-dissociation rates of NO_2 and O_3 ; and k_{11} and k_{13} , the coefficient of reactions R11 and R13. NO_2 , thus formed, is photo-dissociated and the reaction cycle from R10 repeats. The production and destruction of ozone by the oxidation process has been shown schematically in Fig. 4. During day, under steady state condition, O_3 concentration is given by Purkait *et al.*⁶:

$$[O_3] = J_{10} [NO_2] / (J_{12} + k_{13} \cdot [NO]) \quad \dots (2)$$

It is seen from this equation that $[O_3]$ depends on J_{10} , J_{12} , k_{13} , $[NO]$, $[NO_2]$ and T (because k_{13} is temperature dependent). If one takes the values of J_{10} , J_{12} and k_{13} from Sander *et al.*²⁸, it can be seen that the value of J_{12} is much less than that of $k_{13} \cdot [NO]$. Equation (2) then reduces to:

$$[O_3] = J_{10} \cdot [NO_2] / (k_{13} \cdot [NO]) \quad \dots (3)$$

Using Eq. (3), the values of O_3 have been calculated. In this calculation, the values of J_{10} and k_{13} have been taken from Sander *et al.*²⁸. Data of NO and NO_2 are not available from 1990-2013 corresponding to the period of ozone data. The values of T, NO and NO_2 used in this calculation are shown in Table 1. These are measured values for the year 2012 in the SAFAR project. The values of O_3 , thus, obtained are

Table 1 — NO, NO_2 , $[NO_2/NO]$ and temperature during 2012 measured in SAFAR project

Month	Temperature, °C	NO, ppbv	NO_2 , ppbv	$[NO_2/NO]$
January	7.7	17.1	8.1	0.47
February	9.7	15.6	7.6	0.49
March	15.2	23.5	8.6	0.37
April	21.7	32.5	5.8	0.18
May	26.4	30.2	6.7	0.22
June	30.6	7.3	3.0	0.41
July	28.6	6.1	2.0	0.33
August	26.4	8.2	2.0	0.24
September	25.1	8.3	2.0	0.24
October	18.5	27.6	10.5	0.38
November	12.2	40.8	9.0	0.22
December	9.1	26.6	6.1	0.23

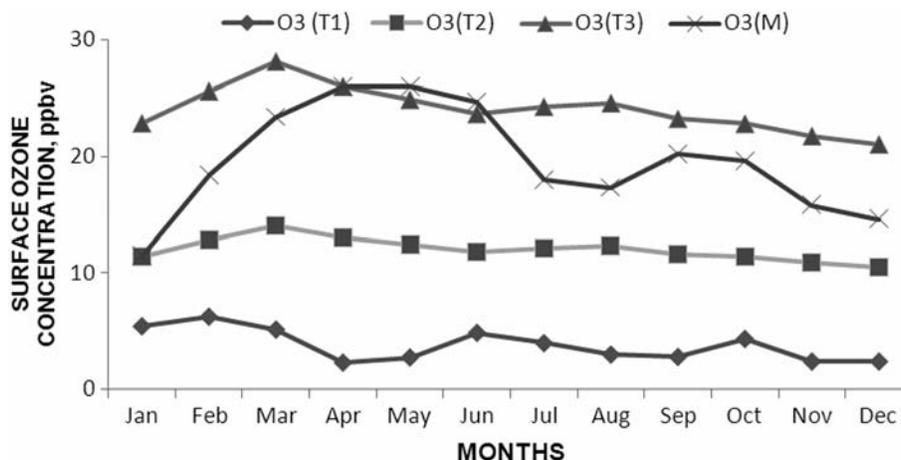
Fig. 5 — Measured and theoretical values of O₃

Table 2 — Measured and computed values of ozone for winter and summer

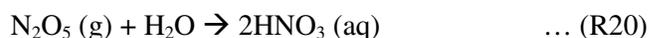
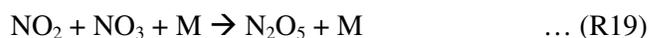
Season	O ₃ (M)	O ₃ (T1)	O ₃ (T2)	O ₃ (T3)
Winter	13.03	3.92	10.98	21.96
Summer	25.35	3.81	12.14	24.28

shown as curve O₃(T1) in Fig. 5 along with the measured value curve O₃(M). A comparison of O₃(T1) and O₃(M) shows that the present values are about 2-5 times lower than the measured values. Also, no appreciable seasonal variation is seen in these values. Nevertheless, a minor peak in February, June and October and minor dip in August, September and December is discernable. The winter (average of December and January) and summer (average of May and June) values are shown in Table 2.

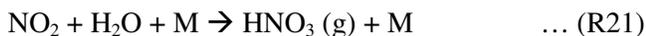
It is seen from Eq. (3) that [O₃] is directly proportional to [NO₂]/[NO] ratio. Mixing ratio of NO and NO₂ were measured in Delhi by Sharma *et al.*⁵ for different seasons. They reported [NO₂]/[NO] ratio is equal to 0.88 in winter and 0.14 in summer. Purkait *et al.*⁶ measured NO and NO₂ at Kolkata and Haldia. They reported that [NO₂]/[NO] ratio had both diurnal and seasonal variations. During December, around noon, they found this value to be ~5.8 at Kolkata and 0.6 at Haldia; and during summer, these values were about 1.5 times higher. The [NO₂]/[NO] ratio for curve O₃(T1) is 0.41 in June and 0.23 in December. The life time of NO and NO₂ near the ground is very low (~minutes) and they are in dynamical equilibrium. Therefore, measuring their values accurately is difficult. In view of no clear picture of the seasonal variation of [NO₂]/[NO] ratio, [O₃] has been calculated using Eq. (3) by taking different values of [NO₂]/[NO] ratio. In Fig. 5, two more

curves, O₃(T2) and O₃(T3) are shown, one corresponding to [NO₂]/[NO] = 1 and the other corresponding to [NO₂]/[NO] = 2. Agreement with measured values appears better when [NO₂]/[NO] ratio is increased from curve O₃(T1). Season-wise, the values of O₃ obtained from these calculations are also given in Table 2. It is seen from Table 2 that the present theoretical winter value comes close to the measured winter value when [NO₂]/[NO] = 1; and summer value when [NO₂]/[NO] = 2. This shows that [NO₂]/[NO] ratio (in other words concentration of NO₂ and NO) does not remain constant throughout the year; it has seasonal variation with highest value during summer and lowest value during winter. The emission of N₂O and NO, however, is unlikely to change during different seasons. Therefore, seasonal change in [NO₂]/[NO] ratio, which leads to the seasonal change in O₃, is due to the NO-NO₂ chemistry.

During winter, in Indo-Gangetic plain, the most of the days are covered by fog. The fog particle reduces the intensity of solar radiation to a great extent. The low value of solar flux decreases the photo-dissociation rate. Then, the loss of NO₂ through reaction R10 becomes slow and hence, [O³P] decreases. When [O³P] decreases, O₃ production decreases and hence, [O₃] decreases. During fog days, when solar radiation is low and reaction R10 is slow, NO₂ is lost, as in twilight time or during eclipse or during ozone hole period, through the following reactions²⁸ to form HNO₃:



In reaction R20, (g) means N_2O_5 is in gaseous state and (aq) means HNO_3 is in liquid state. It may be mentioned here that during foggy days, air is fully saturated with water vapour. Hence, during these days in winter, NO_2 is lost through reactions R18, R19 and R20 to form HNO_3 and hence, $[\text{O}_3]$ becomes low. During monsoon and post-monsoon period, when water content in the atmosphere is very high, NO_2 is likely to be lost through the following reactions to form HNO_3 :



This may explain the low value of surface ozone during monsoon and post-monsoon in comparison to summer.

6 Conclusion

Examination of surface ozone data in Delhi situated in Indo-Gangetic plain from 1990 to 2013 shows that its winter value is the lowest (13.3 ppbv during December-January) and the summer value is the highest (25.35 ppbv during May-June). There is also an increasing long-term trend ~ 0.3 ppbv/year. The low value of O_3 in winter is explained when $[\text{NO}_2]/[\text{NO}]$ ratio is ~ 1 and the high value of O_3 in summer is explained when this ratio is ~ 2 . In winter, solar flux reaching earth's surface decreases due to the presence of fog, which decreases the $[\text{NO}_2]/[\text{NO}]$ ratio and hence, $[\text{O}_3]$. The low value of surface ozone during fog days needs to be reproduced theoretically by a detailed chemical model. For that, accurate measured values of NO and NO_2 for a long period of time including fog days, which is sparse, are required. In that direction, data from SAFAR will be highly useful. It may be mentioned here that stratosphere-troposphere exchange (STE), long range-transport, deposition, and other precursors also affect ozone, which will be considered in detail chemical model study in near future.

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