Surface ozone measurements over Himalayan region and Delhi, North India

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Measurement of surface ozone concentration has been made at two Himalayan stations, Mohal (during 19-26 May 1999 and 20-25 May 2000) and Kothi (during 27 May - 1 June 1999 and during 27-31 May 2000) and at Delhi (during 2-5 June 2000). The study reveals that the average concentration of ozone at Mohal was 19.1 ppb during May 1999 and 26.1 ppb during May 2000. At Kothi, the average concentrations were 42.7 ppb and 23.0 ppb, respectively, and it was 38.3 ppb at Delhi. Diurnal variation of ozone at Mohal indicated the dominance of photochemical production mechanisms in both the years. Lack of diurnal signal was seen at Kothi over the period of observation in 1999 which suggests that there may be transport of ozone in the region from upper level of the atmosphere. During observational period in 2000, a weak diurnal variation of O₃ was observed. It suggests that apart from photochemical production of ozone, some other mechanisms also contribute considerably to the observed O₃ concentration. At Delhi also, the diurnal variation showed the influence of temperature on O₃ production. Variation of O₃ concentration with O₃ concentration at previous hour, temperature, relative humidity at previous hour and wind speed at individual locations and years showed a good degree of association of O₃ with these parameters.

Key words: Photochemical production, Industrial activity, Thunderstorm, Deposition mechanism

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1 Introduction

Ozone is characterized as one of the important trace species of both urban and rural atmospheres. It plays important role in atmospheric photo-chemistry and the aqueous phase chemistry of precipitation acidification. Elevated concentrations of ozone in the planetary boundary layer can adversely affect human health and the growth of plants. Considerable interest has culminated in the study of ozone on account of the above facts and also because it has been reported that ozone concentration has been increasing with the passage of time. Volz and Kley have pointed out that, in the northern hemisphere, the tropospheric O₃ concentration has been more than double over the past century, which has been attributed basically to the anthropogenic emissions of O₃ precursor gases like CH₄ and NOₓ.

It is well known that temperature has direct impact on the O₃ production rate. But, the temperature itself may not always be the direct cause for the increase in O₃ production. It may be a surrogate for other meteorological effects, such as, relative humidity, cloud coverage, lightning, atmospheric stability, stagnation, wind speed and solar intensity. Higher temperatures also increase the emission rate of ozone precursors. Also, the concentration of O₃ at previous hour may be expected to influence the concentration of O₃ at the current hour. Therefore, the present work aims at studying surface ozone concentration and its variation with different meteorological parameters at the two higher elevation locations of the Himalayan region, viz. Mohal (near Kullu, Himachal Pradesh) and Kothi (near Manali, Himachal Pradesh). Surface ozone observations made at Delhi have also been included in the present study.

2 Experimental sites and data collection

The geographical locations of the three sampling sites, viz., Mohal, Kothi and Delhi are shown in Fig.1. Mohal (31°54' N, 77°07' E, 1150 m asl) and Kothi (32°19' N, 77°11' E, 2530 m asl) are located in the hill state of Himachal Pradesh, India, among the high vegetative cover of the northwestern Himalayan region with an inter-distance of about 56 km. Kullu and Manali are the tourists spots in Kullu valley located near Mohal and Kothi, respectively. The sampling sites are surrounded on all sides by high hills. In summer, air is normally dry during daytime, but humidity starts increasing with decreasing solar intensity towards evening hours. Till morning, humidity level is found to reach even to 80%. Orographic lifting of air is the main weather activity,
causing mostly development of thunder clouds and rainfall in the region during summer. At Mohal, wind speed is normally of fluctuating nature, but at Kothi, it is normally high. Gusty wind is frequently observed there. The sampling site at Mohal was the terrace of G. B. Pant Institute of Himalayan Environment and Development, at a height of about 6 m above the ground, whereas the sampling site at Kothi was the front lawn of the solitary guest house there.

The sampling site at Delhi (28°37'N, 77°12'E; 217 m asl) was the terrace of the New Delhi Branch of Indian Institute of Tropical Meteorology (IITM), Pune, at a height of about 5 m above ground level. The adjoining region is almost plain. It is situated in a region which has been variously classified as Monsoon and Upland Savanna or Dry Sub-humid. The climate of this area clearly shows the influence of its inland position. The day temperatures, on average, are highest in May but the monthly mean temperature is highest in June when night temperatures are also the highest. Precipitation occurrence in this region in the month of June is solely due to the air-mass thunderstorms which occur randomly over the area. About 100 m away, on the front side, there is an exclusive residential complex. The traffic on the road, which is 50 m away, has considerably increased with the passage of time. At a distance of about 6 km in the south-west, an industrial complex is located where the industrial activity has increased.

Surface ozone was monitored at Mohal during 19–26 May 1999 and 20–25 May 2000, at Kothi during 27 May–1 June 1999 and 27–31 May 2000 and at Delhi during 2–5 June 2000 by UV-photometric ozone analyser (Thermo Environmental Model 49, USA) using the absorption of 0.254 μm radiation. Ambient air was sampled at a flow rate of 1.01 pm through a 0.45 μm cellulose filter paper attached to the instrument with a teflon tube. The instrument was calibrated periodically by the built-in ozonator (ozone generator) using pure zero grade air. Error range of the instrument is ±1ppb. With the help of this instrument hourly ozone concentration in the surface layer was recorded. Meteorological parameters like temperature, humidity and winds were recorded hourly, using manually-operated weather monitor during the experimental period of year 1999 and using an automatic weather monitor during the experimental period of 2000.

The data were compiled to study the distribution of ozone concentrations at all the three locations. Diurnal variation of ozone and the variation of ozone with different meteorological parameters were also investigated.

3 Results and discussion
3.1 Frequency distribution of ozone concentration at Mohal, Kothi and Delhi

Figure 2 shows the frequency distribution of ozone concentration in different concentration ranges observed at Mohal and Kothi during 1999 and 2000 and at Delhi during 2000. Frequency of occurrence of O₃ concentration at Mohal during May 1999 was maximum (23.2% each) in the concentration range 9-15 and 15-21 ppb and minimum (3.6%) in the range 39-45 ppb, whereas during May 2000 it was maximum (27.1%) in the range 27-33 ppb and minimum (1.4%) in 51-57 ppb. Average concentrations during above two years were 19.1 ppb and 26.1 ppb, respectively. The higher percentage of occurrence towards higher concentrations during 2000 is mainly because of the higher temperature during the period of observation in 2000 than that in the year 1999. Range of variation of ozone was also more in the year 2000.

Maximum percentage (35%) of occurrence of O₃ concentration at Kothi during May 1999 was in the concentration range 33-39 ppb and minimum (3.3%) in 39-45 ppb. Its average concentration was 42.7 ppb. On the other hand, during May 2000 the frequency
was 35.4%, the maximum, in each of the range 15-21 ppb and 21-27 ppb concentration range and 1.0%, the minimum, in 39-45 ppb concentration range. Average concentration during 2000 was 23.0 ppb.

Frequency of occurrence of O₃ concentration at Delhi during June 2000 was maximum (21.1%) in the concentration range of 33-39 ppb and minimum (2.8%) in 39-45 ppb. Average concentration was found to be 38.3 ppb. Its range of variation is between 9 and 69 ppb. The observed O₃ distributions at all three locations were attempted to fit standard distributions but, except Kothi 2000 data, no other data followed the standard distribution. Kothi 2000 data followed log-normal distribution at 5% level of significance.

3.2 Diurnal variation of ozone at Mohal, Kothi and Delhi

The variation of ozone, within a day, may be helpful in delineating the processes responsible for ozone formation or loss at a particular location. So, mean values of ozone evaluated at every hour of the day for the period under study of individual years at Mohal, Kothi and Delhi have been plotted against time of their occurrence (Fig. 3). It is evident from Fig. 3 that the minimum value of ozone at Mohal occurred at 0500 hrs IST in both the years 1999 and 2000. However, minimum value observed in the year 2000 was slightly less than that observed in the year 1999. The O₃ concentration started increasing and was found to be maximum at 1500 hrs IST in 1999 and at 1400 hrs IST in 2000. The concentration of O₃ in the year 1999 remained almost unaltered during 1400-1800 hrs IST. This is indicative of the fact that although there was decrease in the concentration of ozone caused by decrease in the photochemical activity during evening hours, ozone was replenished by its production due to increase in ozone precursors introduced in the surface layer by vehicular emissions. Similar feature was observed in the year 2000 also. In the year 1999, the concentration was found constant over a period during 2100-2300 hrs IST also. This was solely because of the lightning activity on some occasions during this period in the vicinity of the observational site. Sudden increase of about 3 ppb in the concentration of ozone as observed at 1900 hrs IST in the year 2000 was also associated with the lightning which occurred during 1800-1900 hrs IST. Afterwards, the concentration went on decreasing till its minimum at 0500 hrs IST. The overall picture of the diurnal variation reflects that the substantial portion of the ozone in the surface layer of Mohal was contributed through photochemical production, but the lightning also contributed occasionally to the total ozone concentration in the region. Even though the trend of diurnal variations in both the years was similar, the concentration level of ozone during 2000 was always (except during 0400-0600 hrs IST) more than those during 1999. The reason lies in the fact that the period of observation during 2000 was relatively dry and hot in comparison to the observation period during 1999 (Fig. 4). The average temperature and humidity over the period of observation during 2000 were 27°C and 55.6%, respectively, whereas during 1999 they were 22.9°C and 62.8%, respectively.

There was a lack of diurnal signal at Kothi in 1999 and the variations in temperature and humidity were not found to affect much the variation of ozone.
concentration. Daytime mean ozone was 39.7 ppb with standard deviation of 2.7 ppb, whereas nighttime mean ozone was 42.1 ppb with standard deviation of 2.1 ppb. The comparable concentrations of day and nighttimes, rather more during night with relatively small perturbations about their means, rule out the possibility of the dominance of photochemical production mechanism in the surface layer of Kothi during the observation period of 1999. The result suggests that there may be influence of some other mechanisms, may be either ozone rich air advection, subsidence of ozone from aloft, tropospheric-stratospheric intrusion or exchange as explained by Aneja et al.\textsuperscript{19}. They have also observed diurnal variation of ozone at two high elevation locations of Mt. Mitchell (e.g., Site 1—at an altitude of 2006 m asl, and Site 2—at an altitude of 1760 m asl) and have found a weak reverse signal for Site 1, whereas lack of diurnal signal for Site 2. Mean value of ozone at every hour at both the high altitude stations studied by Aneja et al.\textsuperscript{19} was high in comparison to the corresponding mean value recorded at a low lying station. The present result in this respect tallies with it. Natural surroundings of the observational site where the life time of ozone is approximately 10 days or may be as high as 50 or 60 days, may also be
attributed to the stability of ozone concentration observed at Delhi. The argument as given earlier of the sustenance of the previously generated ozone in the surface layer of Kothi on account of its being natural surroundings with very limited human activity is again emphasized on the basis of the observations of ozone concentration made during May 2000. Though diffuse diurnal pattern is observed in that year with minimum value of 17.3 ppb at 0400 hrs IST and maximum value of 28.8 ppb at 1200 hrs IST, the variation about the mean concentration over the period of observation was less with standard deviation of 3.8 ppb. The daytime average is 24.3 ppb with standard deviation of 3.8 ppb, whereas nighttime average is 19.9 ppb with standard deviation of 1.6 ppb.

The diurnal pattern of O₃ concentration at Kothi in the year 2000 reveals that one of the effective mechanisms of the presence of ozone in the region may be the photochemical mechanism. Slow rate of increase (decrease) of ozone concentration from minimum (maximum) to maximum (minimum) may be explained on the basis of diurnal variation of temperature and humidity at Kothi during this year (Fig. 4). Both the parameters have very less range of variation over the major period of observation. The difference between the variations observed during the above two years implies influence of different ozone production mechanisms caused by the different weather conditions over the region.

The salient features observed in the diurnal pattern of ozone concentration at Delhi were its minimum value of 12.3 ppb at 0500 hrs IST and maximum value of 63 ppb at 1500 hrs IST with almost steep slope of increase from minimum to maximum and decrease from maximum to minimum. The time of observed minimum value of O₃ coincided with the time of minimum temperature, but the time of maximum value of O₃ did not coincide with the time of maximum temperature, since the maximum temperature, which normally occurs around 1500 hrs IST during this period, occurred at 1700 hrs IST due to the presence of dust haze and the clouds. Although, the photochemical mechanism of ozone production is understood to be one of the effective mechanisms at Delhi, but the temperature at Delhi during the observational period is not found to show its strong relationship with the ozone, as the ozone at previous hour does with it (Table 1). But at the same time, it can also be argued that apart from many other influencing parameters, the temperature would have played a major role in the production of ozone at previous hour. Thus, the present observation of diurnal variation implies, at first glance, that there is substantial photochemical ozone production at Delhi. Temperature rise beyond certain limit is understood to have led to the saturation of photochemical production of ozone. At the same time, it can also be expected that there could have been the deficiency of ozone precursors at the time when temperature would have risen up.

3.3 Variation of current ozone with ozone at previous hour, temperature, humidity at previous hours and wind speed at Mohal, Kothi and Delhi

Variation of ozone concentration (O₃) at Mohal, Kothi and Delhi with ozone concentration at previous hour (O₃prev), dry bulb temperature, commonly referred to in the text as temperature (T), relative humidity at previous hour (RHprev) and wind speed (WS) is shown in Fig. 5. The correlation coefficients with significant levels between ozone and the above parameters related with the ozone for all the locations are given in Table 1. Ozone at previous hour is

<table>
<thead>
<tr>
<th>Location and period of observation</th>
<th>Correlated parameters</th>
<th>Correlation coefficient</th>
<th>Significant level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohal</td>
<td>O₃ &amp; O₃prev.</td>
<td>0.87</td>
<td>0.001</td>
</tr>
<tr>
<td>19-26 May</td>
<td>O₃ &amp; T</td>
<td>0.75</td>
<td>0.001</td>
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<tr>
<td>1999</td>
<td>O₃ &amp; RHprev.</td>
<td>-0.78</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>O₃ &amp; WS</td>
<td>-0.009</td>
<td>Not significant</td>
</tr>
<tr>
<td>Mohal</td>
<td>O₃ &amp; O₃prev.</td>
<td>0.88</td>
<td>0.001</td>
</tr>
<tr>
<td>20-26 May</td>
<td>O₃ &amp; T</td>
<td>0.78</td>
<td>0.001</td>
</tr>
<tr>
<td>2000</td>
<td>O₃ &amp; RHprev.</td>
<td>-0.65</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>O₃ &amp; WS</td>
<td>0.46</td>
<td>0.1</td>
</tr>
<tr>
<td>Kothi</td>
<td>O₃ &amp; O₃prev.</td>
<td>0.52</td>
<td>0.001</td>
</tr>
<tr>
<td>27 May to 1 June 1999</td>
<td>O₃ &amp; T</td>
<td>0.39</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>O₃ &amp; RHprev.</td>
<td>-0.42</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>O₃ &amp; WS</td>
<td>0.16</td>
<td>Not significant</td>
</tr>
<tr>
<td>Kothi</td>
<td>O₃ &amp; O₃prev.</td>
<td>0.87</td>
<td>0.001</td>
</tr>
<tr>
<td>27-31 May</td>
<td>O₃ &amp; T</td>
<td>0.68</td>
<td>0.001</td>
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<tr>
<td>2000</td>
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<td>-0.35</td>
<td>5.0</td>
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<tr>
<td></td>
<td>O₃ &amp; WS</td>
<td>0.28</td>
<td>Not significant</td>
</tr>
<tr>
<td>Delhi</td>
<td>O₃ &amp; O₃prev.</td>
<td>0.94</td>
<td>0.001</td>
</tr>
<tr>
<td>2-5 June</td>
<td>O₃ &amp; T</td>
<td>0.67</td>
<td>0.001</td>
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<tr>
<td>2000</td>
<td>O₃ &amp; RHprev.</td>
<td>-0.62</td>
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<tr>
<td></td>
<td>O₃ &amp; WS</td>
<td>0.31</td>
<td>Not significant</td>
</tr>
</tbody>
</table>
considered in this study as one of the parameters associated with the current concentration of ozone due to the fact that fraction of it may additively contribute to the ozone concentration at every consecutive hours, since the ozone produced at any moment is not possibly destroyed completely within an hour in the natural surroundings and at least a part of it may be expected to add to the freshly formed ozone. The temperature explains the photochemical activity or decomposition of ozone. Relative humidity at previous hour, though mostly has negative impact on ozone production, under certain condition it can also accelerate the formation of ozone. In this analysis, the correlation coefficient between ozone and relative humidity at previous hour has always been found to be more than that between ozone and relative humidity at current hour. As such, we have considered RH at previous hour as one of the parameters in place of RH at current hour. Wind also may cause either to increase ozone at particular location due to advection of ozone-rich air or to decrease ozone due to advection of ozone-rarefied air. Although we have taken into account only the wind speed recorded at the station and not the advection term, the present analysis can at least give an idea of the influence of wind on the concentration of ozone at the observational site. The limitation of the present data set is that it does not include any chemical indicator to show its impact on ozone production. This limitation is fully appreciated and only broad conclusions have been drawn.

It may be seen from Fig. 5 and Table 1 that ozone at Mohal has direct relationship with the ozone at previous hour and temperature but inverse relationship with relative humidity at previous hour during observations of 1999 and 2000. During 1999 wind speed does not show any relationship with ozone but during 2000 it shows positive relationship

![Fig. 5—Co-variation of ozone, ozone at previous hour, temperature, relative humidity at previous hour and wind speed at Mohal, Kothi and Delhi (■ O₃ (ppb); ● O₃ (ppb); △ T (°C); ▼ RHₚᵥ (%) and ○ WS (m/sec)](image)
with correlation coefficient 0.46, significant at 1% level. Similar results have been reported by Aneja et al.\textsuperscript{19}. The result indicates that the previously observed ozone helped in increasing the current level of ozone concentration. Also, as a strong source mechanism for the production of ozone was provided by the temperature, so a sink mechanism for it was provided by humidity. Wind during the year 2000 seemed to be advected from a region of comparatively higher ozone concentration.

In case of variation plot of Kothi 1999, it may be seen that the association of ozone with $O_{3\text{prev.}}$, $T$ and RH$_{\text{prev.}}$ is similar to that observed at Mohal, but the degree of relationship with any of the related parameters is not strong except for $O_{3\text{prev.}}$. Ozone relationship with wind speed is insignificant. Thus, an inference can be made that only a small portion of the observed ozone is photochemically produced at Kothi during 1999. Major portion of it is expected to come in the region through some other atmospheric processes. However, during the year 2000 the variation analysis shows a similar picture as observed for Mohal. Apart from major contribution made from ozone at previous hour, photochemical production mechanism is also understood to be effective. A small but significant contribution of ozone is also made through advection of air from surroundings. As seen in earlier cases, humidity is negatively related with ozone concentration and may be expected to cause reduction in ozone through deposition mechanism.

At Delhi, the observed variation in ozone with ozone at previous hour, temperature, humidity at previous hour and wind speed indicates that each parameter had significant relation with ozone. Even on being both the source and the sink mechanisms effective (Table 1), appreciable concentration of ozone was observed here and that may be caused by a number of thunderstorm activity during the course of observation. Strong wind is also expected to bring, in the region, an appreciable portion of the observed ozone.

4 Summary and conclusion
The study of surface ozone at Mohal, Kothi and Delhi reveals the following:

Frequency distribution of the concentration of ozone at Mohal indicates its maximum occurrence to lie in the range of 9-21 ppb during 1999 and in the range of 27-33 ppb during 2000 with their average values of 19.1 ppb and 26.1 ppb, respectively. At Kothi, maximum occurrence of ozone was in the concentration range of 33-39 ppb during 1999 and in the range of 15-27 ppb during 2000. The maximum frequency of occurrence of ozone at Delhi was found to lie in the range 33-39 ppb.

Diurnal variation of ozone at Mohal clearly indicates the dominance of photochemical ozone production mechanism in the region over any other mechanisms. Lack of diurnal variation at Kothi was observed during 1999 which suggests the influence of some other ozone production mechanisms in this region besides photochemical mechanisms. A weak diurnal signal was observed at Kothi during 2000.

Ozone concentration at Delhi was found to be minimum at 0500 hrs IST and maximum at 1500 hrs IST. Diurnal variation of ozone at Delhi indicates that photochemical production mechanism was effective in the region. However, beyond a certain limit, effectiveness of temperature in the ozone formation slacks off.

Ozone concentrations at previous hour, temperature and relative humidity at previous hour have been found to determine a major portion of the observed ozone at almost all the locations. In some cases wind was also found to influence ozone concentration.

It is concluded that at low altitude stations like Delhi and Mohal, photochemical ozone production mechanism is dominant. Thus, the measurement of precursor gases such as NO$_2$, CH$_4$, and CO and the accountability of thunderstorm activity and the local anthropogenic activity causing generation of precursor gases of ozone will be very helpful to have an idea about proportionate impact of precursor gases on the photochemical production of ozone and about future scenario of ozone in the region. At a high altitude location like Kothi, apart from the impact of precursor gases several other factors like prevailing surroundings, topography, advection and weather parameters also play important role for the occurrence of $O_3$ in the region. So, the consideration of these factors in the future study of ozone will help in understanding the true reason of weak or absence of diurnal cycle of ozone as observed in the present study.

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