3 Results

3.1 Surface ozone

3.1.1 Diurnal variation in surface ozone concentration

The diurnal variations in $O_3$ concentration were characterized by high value (15.3-68.6 ppbv) during daytime and low value (4.3-20.6 ppbv) during late evening and morning time. The maximum concentration of $O_3$ in diurnal monthly mean was observed as 68.6 ± 21.9 ppbv at 16:00 h IST in May followed by 58.1 ± 18.7 ppbv at 16:00 h IST in April and 57.5 ± 16.3 ppbv at 16:00 h IST in June. However, the daytime minimum concentration of $O_3$ was 15.3 ± 10.7 ppbv in August. The detailed results for the diurnal monthly mean are presented in Figure 3.1.

Fig. 3.1. Monthly averaged diurnal variation in surface ozone at Mohal during January 2010 to December 2012 (_n_ = indicates number of observation days in a month)
3.1.2 Meteorological effects on temporal variation in surface ozone

The hourly maximum concentration of surface ozone was observed to be 126 ppbv on 4 May, 119 ppbv on 3 May and 115 ppbv on 15 May, 2010. Additionally, these values were observed 101 ppbv on 8 June, 98 ppbv on 26 April, and 97.8 ppbv on 10 June, 2011. Recently, in 2012, the surface ozone concentration was observed 65.4 ppbv on 31 March, 61.8 ppbv on 1 April and 60 ppbv on 18 May. Daily maximum surface ozone was observed as 75 ± 30 ppbv on 4 May followed by 74 ± 35 ppbv on 26 May and 68 ± 22 ppbv on 3 May in the year 2010. In 2011, the surface ozone values were calculated to be 72.3 ± 20.3 ppbv on 26 April, 51.2 ± 23 ppbv on 27 April and 41.2 ± 20 ppbv on 5 June. However, in 2012, these values among the highest values of a year went down up to 36.7 ± 9 ppbv on 13 March, 35 ± 13 ppbv on 23 March and 34.8 ± 10 ppbv on 21 May. The detailed results for monthly variation in surface ozone concentration at Mohal is shown in Table 3.1.

Table 3.1. Monthly average surface ozone concentration with one sigma deviation, maximum, minimum and number of observations; January 2010 to December 2012.

<table>
<thead>
<tr>
<th>Month</th>
<th>Surface ozone (ppbv)</th>
<th>Surface ozone Minimum (ppbv)</th>
<th>Surface ozone Maximum (ppbv)</th>
<th>Surface ozone Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>27.3 ± 6.1</td>
<td>14.23</td>
<td>45.73</td>
<td>67</td>
</tr>
<tr>
<td>February</td>
<td>28.8 ± 7.4</td>
<td>10.44</td>
<td>47.67</td>
<td>77</td>
</tr>
<tr>
<td>March</td>
<td>32.7 ± 8.1</td>
<td>12.60</td>
<td>46.76</td>
<td>79</td>
</tr>
<tr>
<td>April</td>
<td>34.5 ± 10.8</td>
<td>14.09</td>
<td>72.34</td>
<td>89</td>
</tr>
<tr>
<td>May</td>
<td>38.4 ± 10.7</td>
<td>17.97</td>
<td>75.06</td>
<td>87</td>
</tr>
<tr>
<td>June</td>
<td>32.4 ± 10.4</td>
<td>14.40</td>
<td>59.81</td>
<td>87</td>
</tr>
<tr>
<td>July</td>
<td>23.8 ± 11.2</td>
<td>4.78</td>
<td>49.0</td>
<td>78</td>
</tr>
<tr>
<td>August</td>
<td>13.3 ± 4.4</td>
<td>2.0</td>
<td>25.25</td>
<td>41</td>
</tr>
<tr>
<td>September</td>
<td>12.2 ± 1.3</td>
<td>3.3</td>
<td>22.0</td>
<td>46</td>
</tr>
<tr>
<td>October</td>
<td>23.5 ± 8.9</td>
<td>6.3</td>
<td>37.4</td>
<td>50</td>
</tr>
<tr>
<td>November</td>
<td>23.2 ± 5.5</td>
<td>13.7</td>
<td>36.0</td>
<td>57</td>
</tr>
<tr>
<td>December</td>
<td>22.8 ± 9.2</td>
<td>10.13</td>
<td>39.9</td>
<td>54</td>
</tr>
</tbody>
</table>

The monthly pattern of surface ozone results showed an increase from January to May. The three years monthly average surface ozone was found to be maximum in May (38.4 ± 10.7
ppbv), which was followed by April (34.5 ± 10.8 ppbv) and June (32.4 ± 10.4 ppbv). Thereafter, average surface ozone starts decreasing up to September with a minimum value of 12.2 ± 1.3 ppbv. Furthermore, it again restarts to increase from October (23.5 ± 8.9 ppbv) to November (23.2 ± 5.5 ppbv) and shows a slight decrease in December (22.8 ± 9.2 ppbv) (Fig. 3.2). There was a good positive correlation of surface ozone with solar flux (r = 0.62) and temperature (r = 0.60). Relative humidity shows a negative correlation with surface ozone (r = -0.50) (Fig. 3.3). In the study area, the average wind speed ranges from a minimum of 0.10 ms\(^{-1}\) to a maximum of about 0.71 ms\(^{-1}\) during the study period. The monthly averages were in the range of 0.4 ms\(^{-1}\) to 1.0 ms\(^{-1}\). The wind speed was maximum during March to June in the valley. The correlation coefficient (r) was found with the value of 0.25 between average wind speed and surface ozone (Fig. 3.3d). It is made clear from the scatter plot that the wind speed at the study area played an insignificant role in reducing concentration of ozone by dispersion or transportation.

![Graph](image)

**Fig. 3.2.** Monthly averaged surface ozone concentration at Mohal
Fig. 3.3. Scattered plot showing the influence of: (a) solar flux, (b) temperature, (c) humidity and wind speed on surface ozone.
The high ozone concentration events during the study period is associated with the wind direction coming from the south-south west (211.2° to 240°C), as well as, the Punjab plain (Fig. 3.4a). Figure 3.4b represents the influence of monthly average rainfall on ozone during the study period. Furthermore, Figure 3.4b, shows that generally low ozone levels are associated with high rainfall.
3.1.3 Surface ozone on high and low insolation days

The seasonal variations in surface ozone are generally in good agreement with the variations in solar radiation. A systematic increase in both solar radiation and ozone is seen from January to May just before reaching the southwest monsoon in this region. Figure 3.5 shows variations for the period of January 2010 to December 2012 in terms of monthly average surface ozone associated with high and low insolation days and photochemical build-up.

![Ozone concentrations on high and low insolation days](image)

**Fig. 3.5.** Monthly variations in O$_3$ (all data monthly average January 2010-December 2012) showing on low and high insolation days and consequent photochemical build-up

During the period of observation, the average of O$_3$ on high insolation days was estimated to be 28.56 ppbv, whereas it was 23.87 ppbv on low insolation days. A large variance was noticed in a photochemical build-up of surface ozone in the present study region, which varied from 0.9 to 1.2 ppbv in rainy season and 6 to 13.0 ppbv in summer season. The largest ozone build-up was calculated 13.0 ppbv in May followed by 10.2 ppbv in June. However, its lowest value was 0.9 ppbv in August.

3.1.4 Surface ozone and water vapour content

Water vapour content (V, gm$^{-3}$) can be estimated from simultaneous measurements of temperature and RH by using the empirical relation given by Kneizys et al. (1980). Figure 3.6 shows the monthly variation of daytime V along with surface ozone. It can be seen that decrease
in ozone is associated with an increase of water vapour in the atmosphere. During the rainy season, it naturally increases up to high values of 17 gm⁻³.

Fig. 3.6. A plot for monthly variation in daytime water vapour (ρν) with O₃

3.1.5 Comparison in rate of change of surface ozone during morning and evening hours with other locations

The existing diurnal variations in average ozone mixing ratio at Mohal is evaluated in relation to other Indian urban (Delhi and Ahmedabad), rural (Gadanki and Joharapur) and rural coastal sites (Tranquebar and Thumba). In rural and rural coastal sites, the average rate of change in O₃ during evening hours (17:00-19:00 h IST) was observed lower than the morning hours (08:00-11:00 h IST) (Table 3.2). Similar results were observed at our experimental site, i.e., rate of change of O₃ concentration in the evening was lower (-4.1 ppb h⁻¹) than morning production rate (4.8 ppb h⁻¹). The average rate of production of O₃ during the morning as well as in evening hours was observed higher at Mohal than rural/rural coastal locations (Table 3.2).
Table 3.2. Monthly rate of change in surface ozone during morning (08:00-11:00 h IST) and evening hours (17:00-19:00 h IST) for the study period

<table>
<thead>
<tr>
<th>Experimental site</th>
<th>Rate of change at (08:00-11:00 h IST)</th>
<th>Rate of change at (17:00-19:00 h IST)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohal</td>
<td>+4.8 ppbv/h</td>
<td>-4.1 ppbv/h</td>
<td>Present study</td>
</tr>
<tr>
<td>Ahmadabad</td>
<td>+5.9 ppbv/h</td>
<td>-6.4 ppbv/h</td>
<td>Lal et al. (2000)</td>
</tr>
<tr>
<td>Delhi</td>
<td>+8.3 ppbv/h</td>
<td>-7.5 ppbv/h</td>
<td>Ghude et al. (2008)</td>
</tr>
<tr>
<td>Delhi</td>
<td>+4.5 ppbv/h</td>
<td>-5.3 ppbv/h</td>
<td>Ahammed et al. (2006)</td>
</tr>
<tr>
<td>Pantnagar</td>
<td>+5.6 ppbv/h</td>
<td>-8.5 ppbv/h</td>
<td>Ojha et al. (2012)</td>
</tr>
<tr>
<td>Dayalbag</td>
<td>+2.2 ppbv/h</td>
<td>-2.4 ppbv/h</td>
<td>Singla et al. (2011)</td>
</tr>
<tr>
<td>Gadanki</td>
<td>+4.6 ppbv/h</td>
<td>-2.6 ppbv/h</td>
<td>Naja and Lal (2002)</td>
</tr>
<tr>
<td>Joharapur</td>
<td>+4.5 ppbv/h</td>
<td>-3.3 ppbv/h</td>
<td>Debaje and Kakade (2006)</td>
</tr>
<tr>
<td>Thumba</td>
<td>+4.8 ppbv/h</td>
<td>-2.6 ppbv/h</td>
<td>Nair et al. (2002)</td>
</tr>
<tr>
<td>Tranquebar</td>
<td>+3.1 ppbv/h</td>
<td>-2.8 ppbv/h</td>
<td>Debaje et al. (2003)</td>
</tr>
</tbody>
</table>

3.1.6 Comparison with other observation sites in India

Seasonal variations in surface ozone observed at Mohal are compared with those at other sites namely Delhi (28.35° N, 77.12° E, 220 m amsl) (Ghude et al., 2008), Dayalbag (18.5°N, 73.81°E, 168 m amsl) (Singla et al., 2011), Gadanki (13.5°N, 79.2° E, 375 m amsl) (Naja and Lal, 2002), Mt. Abu (24.6°N, 72.7°E, 1680 m asl) (Naja et al., 2003b), Nainital (29.37° N, 79.45° E, 1958 m asl) (Kumar et al., 2010), Pune (18.54°N, 73.81°E, 550 m amsl) (Beig et al., 2007), Pantnagar (29.0°N, 79.5° E, 231 m amsl) (Ojha et al., 2012) and Trivandrum (8.55°N, 77° E, 2 m amsl) (David and Nair, 2011).

Fig. 3.7. Comparison of the observed monthly mean surface ozone variations at Mohal with the other country level sites- Gadanki, Delhi, Trivandrum, Nainital, Pantnagar, Dayalbag, Pune and Mount Abu
Furthermore, urban site (Delhi), semi-urban sites (Dayalbag, Pantnagar and Pune), rural coastal (Trivandrum) and rural (Gandki) are also compared with the present experimental semi-rural site (Fig. 3.7). Seasonally, the sites in the northern India (i.e., Pantnagar, New Delhi, Nainital and Dayalbag) also show high concentration of surface ozone in the summer as evaluated for Mohal (in the northwestern site) in contrast to southern India (Gadanki and Trivandrum), which shows higher concentrations of surface ozone during winter. Seasonally, the highest concentration was observed in the northern region as compared to the southern region in India. Thus, the process involved in controlling the surface ozone level over the northern region is different from the southern region.

3.1.7 Fire counts and surface ozone

The average fire counts results for the period 2010–2012 from MODIS Terra and Aqua satellites show their higher counts in the month of May, June, October and November (Fig. 3.8). The surface ozone concentration was observed 38 ppbv, 32 ppbv, 24 ppbv and 23 ppbv for the months of May, June, October and November, respectively, while the number of fire counts in the corresponding months was found to be 59, 27, 26 and 28.

![Fig. 3.8. Averaged MODIS Terra and Aqua fire counts for each month during 2010-2012 at Mohal](image-url)
3.1.8 Backward trajectory analysis for episode days

Besides local sources, contribution of external sources through the long range transport from different origin to the surface ozone episodes are also identified and analyzed. During the time of observation (2010-2012) six episodes are analyzed and plotted air mass trajectories are shown in Figure 3.9a. Two episodes of 2010, i.e., 3 May and 10 May are explained in detail (Fig. 3.9b and c).

Fig. 3.9. The backward trajectories: (a) ending at 0700 UTC on the daily highest surface ozone concentration days during 2010-12 and (b and c) ending at 0900 UTC on 3 May and 1600 UTC on 10 May of episode days of 2010.
3.2 Surface ozone and its precursor NO\textsubscript{x} (NO+NO\textsubscript{2})

3.2.1 Diurnal variation in O\textsubscript{3} and NO\textsubscript{x}

Figure 3.10a shows the variation of O\textsubscript{3} concentration in relation to NO, NO\textsubscript{2} and NO\textsubscript{x} concentrations. In general, the three years annually average O\textsubscript{3} concentration starts increasing gradually after sunrise (08:00-09:00 h IST), attains maximum concentration (42.3-46.0 ppbv) during daytime (12:00-16:00 h IST) and then gradually decreases. Figure 3.10b-d show the diurnal patterns of NO, NO\textsubscript{2} and NO\textsubscript{x}, respectively, corresponding to the same period. However, NO\textsubscript{2} concentrations show a bimodal peak and reaches a maximum (8-10 ppbv) at a time that coincides with the maximum automobile traffic in the morning and evening time, respectively and thus establishes an inverse relationship with O\textsubscript{3}.

Fig. 3.10. The variation of O\textsubscript{3} concentration in relation to NO, NO\textsubscript{2} and NO\textsubscript{x} concentrations
NO$_2$ concentration, as O$_3$ precursor lies in the range of 1.2 ppbv (May and July) to 4.7 ppbv (November) during daytime, which shows an increase from 2.2 ppbv (March) to 7.6 ppbv (November) during nighttime. In comparison, NO concentration is relatively very low, ranging from 0.3 ppbv (April) to 1.57 ppbv (November and September) during daytime and 0.2 ppbv (April) to 1.7 ppbv (September) during nighttime. However, the diurnal patterns of NO$_2$ and NO$_x$ are similar.

### 3.2.2 The correlation of O$_3$ with its precursor NO$_x$

Figure 3.11 shows the monthly average diurnal pattern of surface ozone and NO$_x$ for the study period (2011-2012). The daytime O$_3$ peak is observed broader and its values are higher from April to June with a seasonal mean value of 61.2 ± 8.5 ppbv in summer months. The rainy season was characterized by low O$_3$ concentration 23.9 ± 2.4 ppbv and relatively short duration of the peak.

![Fig. 3.11. The monthly average diurnal pattern of surface ozone and NO$_x$ for the study period 2011-2012](image)
The results during autumn months also show high diurnal value of 51.9 ± 9.5 ppbv for O₃ but the peak is less broader than summer months (Figure 3.12a), whereas higher NOₓ values appear in autumn (21.2±5.2 ppbv) followed by winter (14.3±9.5 ppbv) and lower values appear in rainy season (5.2±5.0 ppbv) (Figure 3.12b).

Fig. 3.12. Diurnal seasonal variation of (a) O₃ and (b) NOₓ

In any season, the decrease in NOₓ coincides with the increase in surface ozone. Figure 3.13 shows the seasonal variation of NOₓ against O₃ for morning (09:00-17:00h IST) and evening (18:00-08:00h IST). In all seasonal cases, O₃ and NOₓ were negatively correlated, with correlation coefficient >0.60. The correlation coefficient, y intercept and slope of O₃ and NOₓ during the morning and evening in different seasons are presented in Table 3.4.
Fig. 3.13. The seasonal variation of O₃ against NOₓ for daytime and nighttime hours

Table 3.3 The correlation coefficient, y intercept and slope of O₃ and NOₓ during the morning and evening in different seasons

<table>
<thead>
<tr>
<th>Seasonal Morning (09:00-17:00h IST)</th>
<th>Seasonal Evening (18:00-08:00h IST)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>Intercept</td>
</tr>
<tr>
<td>Autumn (n= 116)</td>
<td>-0.64</td>
</tr>
<tr>
<td>Winter (n=167)</td>
<td>-0.44</td>
</tr>
<tr>
<td>Summer (n= 109)</td>
<td>-0.67</td>
</tr>
<tr>
<td>Rainy (n=128)</td>
<td>-0.57</td>
</tr>
</tbody>
</table>
3.2.3 Chemical coupling of O$_3$, NO and NO$_2$

The chemical coupling of three species i.e., NO, NO$_2$ and O$_3$ concentrations are related by the following relation.

\[ \frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]} = \frac{J_1}{k_3} \]  

\[ J_1 = \frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]} / k_3 \]  

Where, $J_1$ is the rate of photolysis, which is a function of solar radiation intensity and $k_3$ is the rate coefficient for the reaction of NO with O$_3$, which is a function of temperature (T). Coefficient of $k_3$ varies as a function of temperature (T). Seinfeld and Pandis (1998) proposed the following equation for $k_3$. As expected, the variation of $k_3$ is similar to the variation of the mean air temperature.

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

In the study area, the mean value of $J_1/k_3$ varies between 0.003 and 0.010 ppm using equation 3.1. We estimated the value of $J_1$ using Eqs. 3.1, 3.2 and 3.3 and the dependence of $k_3$ on temperature and the value of $J_1$ varies between 0.2 and 0.6 (min$^{-1}$).

3.2.4 Variation of NO, NO$_2$ and O$_3$ with NO$_x$ concentration

The variations of daylight (08:00-19:00 h IST) and nighttime (20:00-07:00 h IST) concentrations of NO, NO$_2$ and O$_3$ (averaging time 30 minutes) with the level of NO$_x$ are presented by scattered plot with polynomial fit curve in Figure 3.14. The daytime highest concentrations of 5.9, 18.64, 69.05 and 25.46 ppbv and the nighttime concentrations of 6.8, 29.23, 44.78 and 35.28 ppbv were observed for NO, NO$_2$, O$_3$ and NO$_x$, respectively.
3.2.5 Dependence of local and regional OX (O₃+NO₂) contribution

In order to know the local and regional contribution of OX, the variation of mean OX versus NOₓ levels are plotted for the daytime and nighttime periods at Mohal (Fig. 3.15a and b). Regional OX concentrations (33.15 ppbv and 20.9 ppbv) have more impact at Mohal than local OX concentrations (0.465 ppbv and 0.012 ppbv) during daytime as well as in nighttime. Maximum local OX concentration was obtained in June during daytime and May in nighttime (Fig. 3.16a). Minimum daytime local OX was observed in February and September and nighttime in February and July at Mohal (Fig. 3.16b). Maximum regional OX concentration was observed in June during nighttime and May in daytime.
The highest value of OX and NOx were evaluated ~46.84 ppbv and ~2.6 ppbv during May, respectively. At night, maximum values were obtained in summer when NOx levels were higher i.e., OX~2.6 ppbv and NOx~4.6 ppbv.

**Fig. 3.15.** Variation of mean value OX concentration with NOx concentration: (a) daytime and (b) nighttime at Mohal
Fig. 3.16. Monthly variation of OX (O₃ + NO₂): (a) local and (b) regional during measuring period at Mohal

3.2.6 The relationship between NO, NO₂ and NOₓ

NOₓ and NO₂ show a linear correlation in comparison to NOₓ and NO. The correlation coefficient, i.e., r, is calculated 0.98 between NOₓ and NO₂ while it is observed 0.74 between NOₓ and NO. The detailed results for correlation coefficient are presented in Figure 3.17a and b. The daily variation of NO₂/NOₓ with NOₓ shows correlation coefficient of 0.68 (Fig. 3.18).
3.2.7 The difference between weekdays and weekend

Figure 3.19a and b also show the daily variation of the mean values of the NO$_x$ and OX concentration levels during weekdays and weekends. In comparison with weekends (WE), the
weekdays (WD) concentrations were higher for NO, NO$_2$ and NO$_x$, while an opposite trend was observed in the case of O$_3$ and OX concentration. In essence, the average maximum value of O$_3$ and OX concentration at weekends was higher than weekdays.

![Diurnal variation of mean value for weekdays and weekend: (a) of NO, NO$_2$ and (b) NO$_x$, OX at Mohal](image)

**Fig. 3.19.** Diurnal variation of mean value for weekdays and weekend: (a) of NO, NO$_2$ and (b) NO$_x$, OX at Mohal

### 3.3 Black carbon and particulate matter PM$_{10}$ and PM$_{2.5}$

#### 3.3.1 Daily and monthly mean variation of black carbon (BC) aerosol mass concentration

The daily average BC mass concentration for the entire study period (2010-2012) varies between 0.3 and 10.7 μg m$^{-3}$ with a mean value of 2.8 ± 1.67 μg m$^{-3}$. The results show a clear-cut monsoon minima and winter maxima in the valley. Figure 3.20 shows the daily variation in BC mass concentration at Mohal. The highest first three values of BC concentration were observed to be 10.7 μg m$^{-3}$, 9.7 μg m$^{-3}$ and 9.5 μg m$^{-3}$ in January at Mohal.
Fig. 3.20. Day-to-day variations in BC mass concentration at Mohal (red line indicates mean concentration, while blue lines indicate mean concentration ±std.)

The monthly mean variation of BC mass concentration from January 2010 to May 2012 is shown in Figure 3.21. The highest monthly mean variation in BC mass concentration was observed at 4.76 ± 1.99 µg m\(^{-3}\) in the month of January and the lowest was 2.27±1.04 µg m\(^{-3}\) in September.

Fig. 3.21. Variation in the monthly mean concentration of BC at Mohal during 2010-12
### 3.3.2 Diurnal annual and seasonal variations in BC aerosol mass concentration

The diurnal variation of BC during all the seasons showed two peaks, i.e., one during morning hours (07:00-09:00 h IST, 08:00 h IST) and other during evening hours (19:00-21:00 h IST, 20:00h IST). The primary peak is also known fumigation peak in the morning, while the secondary peak is less prominent during the evening. The highest mean value of diurnal BC (7.5 ± 3.8 µg m\(^{-3}\)) is observed to be in winter season during morning hour (Fig. 3.22). Seasonal mean value of BC mass concentration for the study period (during January 2010- December 2012) showed the maximum value of BC mass concentration as 7.5 ± 3.8 µg m\(^{-3}\) in winter, followed by 5.4 ± 3.4 µg m\(^{-3}\) in autumn, 4.5 ± 3.0 µg m\(^{-3}\) in summer and 3.3 ± 1.4 µg m\(^{-3}\) in rainy season (see Fig. 3.22). Detailed value of diurnal seasonal variation of BC mass concentration are shown in Table 3.4.

![Figure 3.22](image)

**Fig. 3.22.** Seasonal variation in BC mass concentration at Mohal during the study period from January 2010-December 2012 (_n^* indicates number of daily samples_)
Table 3.4. Diurnal seasonal variations in BC mass concentration during 2010 to 2012 at Mohal

<table>
<thead>
<tr>
<th>Season</th>
<th>Morning (08:00-09:00 h IST)</th>
<th>Evening (20:00-21:00 h IST)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>7.5 ± 3.8 ppbv (0900h IST)</td>
<td>6.1 ± 3.4 ppbv (2000h IST)</td>
</tr>
<tr>
<td>Summer</td>
<td>4.5 ± 3.0 ppbv (0800h IST)</td>
<td>3.7 ± 2.1 ppbv (2100h IST)</td>
</tr>
<tr>
<td>Rainy</td>
<td>3.3 ± 1.4 ppbv (0800h IST)</td>
<td>4.0 ± 1.7 ppbv (2100h IST)</td>
</tr>
<tr>
<td>Autumn</td>
<td>5.4 ± 3.4 ppbv (0800h IST)</td>
<td>5.5 ± 3.8 ppbv (1900h IST)</td>
</tr>
</tbody>
</table>

*Indicates the values when BC concentration was at peak

Fig. 3.23. The monthly mean diurnal variation of BC mass concentration January to December during the period 2010-2012

Diurnal monthly mean maximum concentration of BC was observed 9.8 ± 4.0 μg m⁻³ in January followed by 8.8 ± 5.8 μg m⁻³ in December and 6.2 ± 4.1 μg m⁻³ in November from 2010 to 2012, while its minimum concentration was observed in September with 2.7 ± 1.0 μg m⁻³ (Fig. 3.23).

3.3.3 Influence of meteorological parameters on black carbon

During the observation period, the correlation coefficient between BC and wind speed was found to be -0.44. Seasonally, it is varied from r = - 0.11 in summer to r = - 0.62 in winter. In winter, a significant correlation was observed as compared to other seasons. However, from
seasonal viewpoint, in winter there was found a good correlation ($r = -0.60$) between BC and wind speed (Fig.3.24a). The correlation coefficient of $r = -0.50$ were observed between temperature and BC in the winter season (Fig. 3.24b). The diurnal variation in BC with varying temperature and solar radiation showed an inverse relationship as is shown in Figure 3.25.

**Fig. 3.24.** Variation in BC mass concentrations with: (a) wind speed and (b) temperature during winter season

**Fig. 3.25.** Variation in BC and NO\textsubscript{x} with temperature and relative humidity

### 3.3.4 BC episodes and back trajectory analysis

The BC concentration on clean, average and episode days remained 15%, 30.4%, 53.7%; 14.5%, 30.7%, 54.68% and 13%, 31% and 55.6% for winter I (W I), winter II (W II) and winter III (W III), respectively (Fig. 3.26). The number of clean, average and episode days for W I, W II and W III were 16, 72, 27; 32, 103, 10 and 9, 75 and 16, respectively.
The numbers of episode days were more in W I than W II and W III. During winter season, the increase in BC concentration from clean to average days was ~1.8 times, while it was ~3.8 times from clean to episode days.

![Figure 3.26](image1.png)  
**Fig. 3.26.** Percentage of BC in clean, average and episode days

![Figure 3.27](image2.png)  
**Fig. 3.27.** The back trajectory ending at 03UTC over Mohal drawn on episode days of black carbon
During the W I, W II and W III, the highest concentrations were observed to be 10.68 µg m$^{-3}$, 9.70 µg m$^{-3}$, 9.4 µg m$^{-3}$ on 22$^{nd}$, 12$^{th}$ and 2$^{nd}$ January 2010 and 9.49µg m$^{-3}$, 7.98µg m$^{-3}$ and 7.07µg m$^{-3}$ on 12$^{th}$, 19$^{th}$ and 16$^{th}$ January and 3.9 µg m$^{-3}$, 3.8 µg m$^{-3}$, 3.7 µg m$^{-3}$ on 4$^{th}$, 22$^{nd}$ and 11$^{th}$ January 2012, respectively. Seven days back trajectory was plotted to analyze the origin of air masses for BC episodes (Fig. 3.27).

3.3.5 Influence of black carbon on surface ozone

The analysis of data showed statistically a negative correlation between O$_3$ and BC ($r = -0.44$). Furthermore, the results showed the ozone depletion by surface reactions on BC particles. The results are presented in Figure 3.28.

![Fig. 3.28. Scattered plot between O$_3$ and BC](image)

3.3.6 The impact of PM$_{10}$ and PM$_{2.5}$ on surface ozone

In this study, a negative correlation was obtained between daily mean values of aerosol and O$_3$ concentration. O$_3$ showed negative correlation with PM$_{10}$ and PM$_{2.5}$ mass concentration in winter i.e. $r = -0.65$, $r = -0.38$, respectively. In general, a positive correlation in summer was observed between O$_3$ and aerosol mass concentration (PM$_{10}$ and PM$_{2.5}$) due to transported aerosols with the correlation value of $r = 0.49$ and $r=0.44$, respectively (Fig. 3.29).
3.3.7 Mass fraction of BC in PM$_{10}$ and PM$_{2.5}$

The mass concentrations of PM$_{10}$ on monthly basis ranged from $19.4 \pm 8.3$ to $138.34 \pm 7.2 \mu g \text{ m}^{-3}$ (2010-2012), while PM$_{2.5}$ ranged from $13.94 \pm 5.43$ to $43.33 \pm 8.4 \mu g \text{ m}^{-3}$ during two years at Mohal. The monthly mean ratio of BC/PM$_{10}$ was evaluated 0.05 in September and 0.09 in January, while BC/PM$_{2.5}$ was observed 0.064 in August to 0.17 in June (Fig. 3.30 a and b). This indicates BC mass concentration contributed 9% as the maximum in PM$_{10}$ in January and 17% in PM$_{2.5}$ in June.
Results

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Fig. 3.30. Fraction of daily average BC in PM$_{10}$ and PM$_{2.5}$. The horizontal line represents the average PM$_{10}$/BC and PM$_{2.5}$/BC during the study period (January, 2011–December, 2012)

PM$_{10}$ concentrations on monthly basis ranged from 19.4 ± 8.3 to 138.34 ± 7.2 μg m$^{-3}$, while PM$_{2.5}$ ranged from 13.94 ± 5.43 to 43.33 ± 8.4 μg m$^{-3}$ during three years (2010-2012) at Mohal. Annually, BC contributed about 13% in PM$_{10}$ and 24% in PM$_{2.5}$ at Mohal. The correlation between BC and PM$_{10}$ as well as BC and PM$_{2.5}$ remained positive with correlation values of $r = 0.61$ and $r = 0.49$, respectively.

3.3.8 Daily and seasonal concentration of particulate matter- PM$_{10}$ and PM$_{2.5}$

The daily and seasonal concentration of PM$_{10}$ and PM$_{2.5}$ ranged between 19 to 188.5 μg m$^{-3}$ and 11 to 99.3 μg m$^{-3}$, respectively. The maximum daily PM$_{10}$
concentration at Mohal was 188 µg m⁻³ on December 29, 2012 followed by 169.4 µg m⁻³ on March 20, 2012 (Fig. 3.31).

The maximum daily PM⁰.₅ concentration at Mohal was 99.3 µg m⁻³ on May 29, 2011, followed by 99.2 µg m⁻³ on May 31, 2011. PM¹₀ concentration remained maximum in winter, while PM⁰.₅ remained maximum in summer.

**Fig. 3.31.** Daily concentrations of: (a) PM⁰.₅ and (b) PM¹₀ at Mohal
3.3.9 Seasonal concentration of BC, PM\(_{10}\) and PM\(_{2.5}\)

Seasonally, maximum concentrations of BC and PM\(_{10}\) were observed in winter (9.8 ± 1.04 µg m\(^{-3}\) and 53.7 ± 3.9 µgm\(^{-3}\)), while PM\(_{2.5}\) was observed with maximum concentrations in summer (42.9 ± 20.6 µgm\(^{-3}\)). Additionally, in rainy season all the particulate matters showed low values, i.e., BC, PM\(_{2.5}\) and PM\(_{10}\), respectively (Fig. 3.32).

![Graph showing mass concentration of BC, PM\(_{10}\) and PM\(_{2.5}\) during different seasons at Mohal.](image)

**Fig. 3.32** Mass concentration of BC, PM\(_{10}\) and PM\(_{2.5}\) during different seasons at Mohal

3.3.10 Investigation regarding transport of PM\(_{10}\) episodes at Mohal

The episodes days of PM\(_{10}\) aerosol on 31, December 2011 (92 µg m\(^{-3}\)) and 20, March 2012 (169 µg m\(^{-3}\)) were analyzed by plotting seven days back trajectory at 1400 UTC at three heights 500 m, 1000 m and 1500 m above ground level at Mohal. Images of terra MODIS satellite showing aerosol concentration over northwestern part of India at 550 nm are also drawn in Figure 3.33.
Fig. 3.33. Back trajectory ending at 04 UTC over Mohal: (a and c) plotted on 31 December 2011 and 20 March 2012 and (b and d) showing MODIS aerosol concentration over northwestern part of India at 550 nm on 31, December 2011 and 20, March 2012.

Figure 3.33a provides the information that air parcel reached on 31st December, 2011 at Mohal are coming through the IGP. Figure 3.33c shows that air parcels reached on 20th March 2012 at Mohal were passed through arid/or semi-arid region such as the Sahara and Thar deserts. Fig. 3.33b and d show MODIS aerosol concentration in the northwest region.
3.4 Ionic composition in particulate matter below 10 micron in size

3.4.1 Concentration and percentage distribution of ionic composition of aerosol of water-soluble ions in PM$_{10}$

In the present study, fifteen samples were analyzed from exposed filter papers for particulate matter of 10 micron size during January 2011-July 2012 at Mohal. Fig. 3.34 shows the detailed results of PM$_{10}$ concentration.

The highest concentration of PM$_{10}$ was observed on 7 January, 2011 with 138 $\mu$g m$^{-3}$ and 20 March, 2012 with 169.40 $\mu$g m$^{-3}$ in winter season. However, low concentration was noticed on 10 July, 2012 with 31.70 $\mu$g m$^{-3}$ in rainy season. Seasonally, maximum concentration was observed during the winter followed by autumn, summer and rainy seasons. The exposed filter papers were also analyzed for identifying the cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, NH$_4^+$), anions (F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) and transition metals (Zn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$). The ionic concentrations at Mohal during the year 2011 were found to be in decreasing order such as Na$^+$ > K$^+$ > Ca$^{2+}$ > NH$_4^+$ > Mg$^{2+}$ for cations, SO$_4^{2-}$ > Cl$^-$ > NO$_3^-$ > F$^-$ for anions and Zn$^{2+}$ > Cd$^{2+}$ > Cu$^{2+}$ > Co$^{2+}$ for transition metals. However, during 2012 the decreasing order of ionic concentration were calculated Na$^+$ > Ca$^{2+}$ > K$^+$ > NH$_4^+$ > Mg$^{2+}$ for cations, SO$_4^{2-}$ > NO$_3^-$ > Cl$^-$ > F$^-$ > NO$_2^-$ > PO$_4^{3-}$ for anions and Zn$^{2+}$ > Cd$^{2+}$ > Cu$^{2+}$ for transition metals.

![Figure 3.34](image-url)

**Fig. 3.34.** Concentration of PM$_{10}$ episodes analysed for ionic components during 2011-2012 at Mohal.
The results for ionic composition of the study area shows that $\text{SO}_4^{2-}$ is the most abundant chemical component in 2011 and 2012, which accounts for 29.33% and 36.45% of the total mass of the anion, respectively (Fig. 3.35). In general, the results show the highest percentage of cationic water soluble components in 2012 as compared to 2011. In anionic components, $\text{F}^-$ and $\text{Cl}^-$ show the 50% reduction in total water soluble mass in 2012 in comparison to 2011. The results show the percentage of $\text{F}^-$ as 1.621% and 0.831% in 2011 and 2012, respectively. The contribution of cations such as $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ and $\text{K}^+$ has shown increase in 2012 in contrast to 2011.

![Fig. 3.35. Percent of ionic composition among water soluble components in PM$_{10}$ during 2011-2012 at Mohal](image)

The percent contribution of inorganic constituents during the study period (2011-12) is shown in Figure 3.36. On average, among the ionic constituents, $\text{SO}_4^{2-}$ (32.89%) contributed maximum followed by $\text{Cl}^-$ (16.45%), $\text{NO}_3^-$ (13.91%), $\text{Ca}^{2+}$ (6.89%), $\text{Na}^+$ (15.37%), $\text{NH}_4^+$ (4.19%), $\text{F}^-$ (1.23%), $\text{Zn}^{2+}$ (0.77%) and $\text{Mg}^{2+}$ (0.44%).

The cations like $\text{K}^+$, $\text{NH}_4^+$ and $\text{Ca}^{2+}$ accounted for 18.3% of the total water soluble mass. The ionic balance of aerosol samples showed a decreasing trend of $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$ for anions and $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{NH}_4^+$ for cations. The contribution of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ found lower at Mohal in 2011 and as well as in 2012. Among the cations, $\text{Na}^+$ contributed the maximum 15.36% of the total mass concentrations. $\text{Ni}^{2+}$ and $\text{Pb}^{2+}$ are absent in the present study.
3.4.2 Marine influence on the composition of aerosol and non-sea salt fraction (NSS)

The ionic ratios of aerosols and corresponding values of seawater are shown in Table 3.5. The results show that the ratios of $K^+/Na^+$, $Ca^{2+}/Na^+$, $Mg^{2+}/Na^+$, and $SO_4^{2-}/Na^+$ are higher while $Cl^+/Na^+$ ratio is less than sea water. % NSS of $SO_4^{2-}$ (88.4%), $K^+$ (92.2%) and $Ca^{2+}$ (73.7%) are higher over Mohal, while 68% of $Cl^-$ and 35% of $Mg^{2+}$ are observed to be non-marine origin (see Eq. 2.7, Chapter 2).

**Table 3.5.** Ionic ratios of aerosols and corresponding values of seawater

<table>
<thead>
<tr>
<th></th>
<th>$Cl^-/Na^+$</th>
<th>$K^+/Na^+$</th>
<th>$Mg^{2+}/Na^+$</th>
<th>$Ca^{2+}/Na^+$</th>
<th>$SO_4^{2-}/Na^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>1.317</td>
<td>0.448</td>
<td>0.037</td>
<td>0.359</td>
<td>1.840</td>
</tr>
<tr>
<td>2012</td>
<td>0.804</td>
<td>0.506</td>
<td>0.041</td>
<td>0.544</td>
<td>2.464</td>
</tr>
<tr>
<td>Avg</td>
<td>1.071</td>
<td>0.475</td>
<td>0.040</td>
<td>0.448</td>
<td>2.140</td>
</tr>
</tbody>
</table>
3.4.3 Assessment of the source of aerosol composition and aerosol chemistry

The ideal molar ratio of $\text{NH}_4^+$/SO$_4^{2-}$, $\text{NH}_4^+$/NO$_3^-$ and $\text{NH}_4^+/\text{Cl}^-$ is 0.37, 0.29 and 0.50, respectively. The observed molar ratio value 0.14 for $\text{NH}_4^+$/NO$_3^-$ is higher than ideal; while for $\text{NH}_4^+$/SO$_4^{2-}$ and $\text{NH}_4^+/\text{Cl}^-$ observed molar ratios are 0.14 and 0.28, which are found lower than the ideal values, respectively.

<table>
<thead>
<tr>
<th>Ideal molar ratio</th>
<th>Observed</th>
<th>Possible source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{NH}_4^+$/SO$_4^{2-}$</td>
<td>0.37</td>
<td>0.14</td>
</tr>
<tr>
<td>2. $\text{NH}_4^+$/NO$_3^-$</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>3. $\text{NH}_4^+$/Cl$^-</td>
<td>0.50</td>
<td>0.28</td>
</tr>
</tbody>
</table>

3.4.4 Correlation between total cations and anions

The ratio of the sum of the concentrations of cation and anion in PM$_{10}$ was calculated. The calculated ratios were found to be ranging from 0.46 to 1.03 and 0.46 to 0.70 for the years 2011 and 2012, respectively. There is a positive correlation between the sum of the concentration of all cations and anions ($r = 0.95$ and $0.94$) during 2011 and 2012, respectively.

3.4.5 Neutralization factors

The neutralization factors (NF) of the acidic components of aerosol for $\text{NH}_4^+$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ by crustal components and ammonia is calculated by using the formula given by Saxena et al. (1996). This shows that during the year 2011 and 2012 in exposed PM$_{10}$ samples, the decreasing order of NF was $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+}$.
### Table 3.7. Neutralization factors for NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$

<table>
<thead>
<tr>
<th></th>
<th>NH$_4^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>0.089</td>
<td>0.121</td>
<td>0.007</td>
</tr>
<tr>
<td>2012</td>
<td>0.040</td>
<td>0.135</td>
<td>0.009</td>
</tr>
<tr>
<td>Mean</td>
<td>0.065</td>
<td>0.128</td>
<td>0.008</td>
</tr>
</tbody>
</table>

### 3.5 Satellite based observation

#### 3.5.1 Variation of surface ozone with tropospheric columnar and total columnar ozone

The monthly averaged value of surface ozone and tropospheric ozone are shown in Figure 3.39a and b, respectively.

![Graphs showing monthly averaged values of surface and tropospheric ozone](image.png)

**Fig. 3.37.** The surface, columnar ozone and its precursor- columnar NO$_2$: (a) monthly mean surface ozone (in ppbv), (b) tropospheric ozone (in DU), (c) tropospheric NO$_2$ and (d) total ozone (in DU) for the study period (January 2010-December 2012)
The results show almost similar variations which increased from March to May in case of surface ozone (peak in May) and March to June in case of tropospheric ozone (peak in June). The results show a decrease for surface ozone and tropospheric ozone in rainy season (July to September), which is followed by a further increase in autumn season (October and November).

Figure 3.37c shows the monthly mean tropospheric NO$_2$ (precursor of ozone) variation, which exhibits almost a seasonal pattern similar to that of tropospheric ozone. Seasonally, tropospheric NO$_2$ was observed to be maximum in spring and minimum in monsoon months, while its second maximum was in winter (Fig. 3.37c). Figure 3.37d shows a monthly mean variation of total ozone. The monthly mean total ozone showed an increased value from April to May, which was followed by a decreased value from October to November. The mean total ozone also showed a second peak in January and February.

![Scattered plot between tropospheric NO$_2$ and tropospheric ozone](image)

**Fig. 3.38.** Scattered plot between tropospheric NO$_2$ and tropospheric ozone
In computing correlation, there was found a positive correlation ($r = 0.60$) between tropospheric ozone and tropospheric NO$_2$. The detail results for correlation coefficient are presented in Figure 3.38.

3.5.2 The percentage contribution of tropospheric ozone to total ozone and surface ozone to tropospheric ozone

Figure 3.39 (a and b) show the monthly percentage contribution of tropospheric ozone to total ozone and surface ozone to tropospheric ozone, respectively. The contribution of tropospheric ozone to total column ozone ranged from 8% to 18% with its maximum value in June-July and minimum in January and February.

**Fig. 3.39.** The monthly percentage contribution of: (a) tropospheric ozone to total ozone and (b) surface ozone to tropospheric ozone
The present analysis shows a larger variation (16%–91%) in the contribution of boundary layer ozone to the total tropospheric column ozone, which indicates maximum contribution during January to March and minimum in the month of rainy months (August and September).

3.6 Investigation of transport for external sources

3.6.1 Air trajectory analysis

The 7-days back trajectories for different months are obtained at 0700 UTC form 1500 m above the ground level (Fig. 3.40).

Fig. 3.40. Monthly averaged 7-days air mass back trajectory at 1500m above ground level (AGL) for the year 2010-12
From this, it is obvious that the air mass movement during winter and autumn months are from west of the experimental site. The direction of air mass during summer is north-west and south-west and in rainy season it is from south-east or south-west.