5 Summary and Conclusions

Surface ozone, its precursor NO\textsubscript{x}, black carbon were measured at a semi-urban site Mohal in the northwestern Indian Himalaya during three years from January 2010 to December 2012. The ground based measurements were carried out using ozone analyzer, NO\textsubscript{x} analyzer and aethalometer. These data were analyzed using meteorological parameters, backward trajectories and satellite observations. Contribution of ground surface ozone to tropospheric ozone and tropospheric ozone to total columnar ozone have been estimated after analyzing satellite data. The relationship of surface ozone with chemical species such as NO\textsubscript{x}, BC and other particulate pollutants (PM\textsubscript{10} and PM\textsubscript{2.5}) were also investigated.

Diurnal variations of surface ozone show significance in-situ photochemical build-up at this site. The diurnal variations in O\textsubscript{3} were characterized by high concentrations (15.3-68.6 ppbv) during daytime and low concentration (4.3-20.6 ppbv) during late evening and morning time. Maximum diurnal monthly mean concentration of O\textsubscript{3} 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 and day time minimum concentration was 15.3 ± 10.7 ppbv in August. The seasonal variation in the monthly averaged surface ozone shows a systematic increase from January to May, decrease from July to September and then a slight increase during October- November. It is observed that surface ozone in May show maximum concentration and corresponding number of fire counts also stood to be maximum in May which could be due to the presence of additional ozone precursors from biomass burning and intense solar radiations. Hence, solar radiation, rainfall, backward trajectories and fire counts contribute to the seasonal variation at Mohal. The rate of change of O\textsubscript{3} concentration in the evening was lower (-4.1 ppbv h\textsuperscript{-1}) than morning production rate (4.8 ppbv h\textsuperscript{-1}). Urban sites generally show symmetric diurnal patterns, i.e., rate of change in ozone during morning and evening hours are similar, while rural sites are characterized by lower loss rates during evening than morning hours. The average rate of production of O\textsubscript{3} during morning as well as in evening hours at Mohal was observed to be higher than rural/ rural coastal sites (Gadanki, Joharapur, Tranquebar and Thumba) and less than urban sites (Ahmedabad and Delhi). The decrease in ozone during the evening time at Mohal is less than semi-urban site Pantnagar. The lower ozone loss rate in the evening suggests that ozone loss process could not be much stronger at Mohal due to low NO\textsubscript{x} emissions. At Mohal, magnitude of morning and evening
rate of change is almost similar and closely follows the behaviour as is shown by urban sites. The hourly maximum concentration of surface ozone was observed to be 126 ppbv, 119 ppbv and 115 ppbv. Daily maximum surface ozone was observed as 75 ± 30 ppbv followed by 74 ± 35 ppbv and 68 ± 22 ppbv. Observed surface ozone seasonality is in good agreement with the solar radiations. There was a good positive correlation of surface ozone with solar flux (r = 0.62) and temperature (r = 0.60). Low level of all the gases during August-September are mainly attributed to the arrival of southwest monsoon that brings cleaner marine air to the present study site. Relative humidity shows a negative correlation with surface ozone (r = -0.50) and also negatively correlated with water vapour content. 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°), as well as, the Punjab plain. During the observation period, the average surface ozone values for high insolation days was estimated using day time solar radiation data which were 28.56 ppbv, whereas on low insolation days surface ozone was 23.87 ppbv. The largest ozone build-up was calculated as 13.0 ppbv in May. However, its lowest value was 0.9 ppbv in August.

The black carbon concentration remains maximum in winter. This indicates a strong dominance of fine-mode size black carbon aerosols in winter which are attributed to anthropogenic aerosols, released into the atmosphere by biomass burning, forest fire at local levels and smoke aerosol transport from external source regions. Aerosols generated at one place are transported over long distances by wind and produce consequent effects at locations far away from the source. In this context, air trajectories play an important role in transporting dust aerosols and other pollutants. To investigate the influence of aerosol transport over Mohal, a multisensor approach in conjunction with back trajectory analysis is used. The past study reveals that in addition to local sources, the long range transport of aerosols also contributes to the existing columnar aerosols. The aerosol transport from different sources has played a major role in aerosol concentration over Mohal. The back trajectory analysis suggested that the highest AOD during pre-monsoon is due to high degree of human interference in the form of tourism and dust transport from the country lying in the northwestern part of India.
The high nighttime concentration of NO\textsubscript{x} is due to shallow nighttime boundary layer. The amplitude and duration of the peaks in ozone vary with seasons. Daytime ozone and nighttime NO\textsubscript{x} peaks are noticed during summer and autumn months respectively. Seasonal variations are associated with a clear-cut change in wind air flow pattern and air mass back trajectories. On seasonal basis, daytime surface ozone is positively correlated with that of nighttime NO\textsubscript{x}. During diurnal variation, ozone showed daytime high and nighttime low concentration; whereas NO\textsubscript{x} concentration showed bimodal peaks in a day, one in morning and second in evening. NO\textsubscript{x} concentration shows an inverse relationship with O\textsubscript{3}. In other words, surface ozone formation is faster than the process of destruction. The intercept shows low value during rainy season, which is probably attributed to less active photochemistry. Tropospheric ozone and NO\textsubscript{2} show similar seasonal patterns. Tropospheric ozone contributes to 8% to 18% of the total ozone with its maximum value in June-July and minimum in January and February at Mohal. Surface ozone near the Earth's surface contribute to 16% to 91% of the tropospheric ozone, with maximum contribution occurring during January to March and minimum in the rainy months (August and September) at Mohal.

A linear correlation is found between NO\textsubscript{2} and NO\textsubscript{x} as well as between NO and NO\textsubscript{x}. The NO\textsubscript{2}/NO\textsubscript{x} ratio decreased as NO\textsubscript{x} increased which could also support the VOC-sensitive nature of the region. The nature of the negative correlation between NO\textsubscript{x} and O\textsubscript{3} indicates that the study site is not NO\textsubscript{x} sensitive but possibly VOC sensitive. The level of OX concentration is influenced by NO\textsubscript{x}-independent and NO\textsubscript{x}-dependent contributions. The former is due to regional background of O\textsubscript{3} concentration and the later correlates with the local level of primary pollutants. During daytime, the regional background of O\textsubscript{3} concentration at Mohal is about 33.1 ppbv. Regional OX concentration has more impact in our region than the local oxidants. The daily average variations of NO, NO\textsubscript{2}, NO\textsubscript{x}, O\textsubscript{3} and OX (NO\textsubscript{2}+O\textsubscript{3}) in the semi-urban environment of the Kullu-valley is strongly affected by vehicular emissions, photochemistry activity and planetary boundary layer height. The highest mean concentration of primary pollutants was observed between 08:00-09:00h IST. In the evening, there is a second peak of NO, coinciding with the evening traffic flow (lower
concentration of NO than early morning) at around 20:00 and 21:00 h IST at Mohal. NO$_2$ concentration also showed a similar pattern as shown by NO. However, the second peak was higher than the observed peak in the early morning. It is probably due to more ozone available to produce NO$_2$ through reaction with NO. The levels of the pollutants observed in this study were much lower than those reported for previous winter periods, indicating that pollution control measures adopted by local government had effectively reduced emissions of gaseous pollutants. The low O$_3$ value in winter, especially at night, can be attributed to the lower temperature, weaker solar radiation and particularly the strong destruction of O$_3$ by chemical titration of NO from much higher emission of NO$_x$ which is related to heating in winter. The highest average NO and NO$_x$ concentrations observed during the whole measuring period occurred in night-time relatively with a large value in autumn and winter season. Also, from the measured values of NO, NO$_2$ and O$_3$, the rate of NO$_2$ photolysis is estimated. $J_l$, photolysis rate, was found to be between 0.2 and 0.6 (min$^{-1}$) in the study site.

The hourly mean concentration of OX is shown in terms of sum of a regional (NO$_x$-independent) contribution. During the period of observation, in this way, the slopes and intercepts of OX versus NO$_x$ plot represents the local and regional contribution, respectively which establish a settle point for understanding the oxidative dynamic of this semi-urban site. It was observed that regional contribution is more than local contribution during day and night in our study site, while local contribution is negligible during night. This shows that local contribution to OX levels depends directly on the level of NO$_x$ which mainly comes from vehicular exhausts. Maximum regional OX concentration was observed in May during nighttime and daytime respectively. While daytime, minimum regional OX concentration was observed in December and January and nighttime minimum was in August and September. Maximum local OX concentration was obtained in May during daytime as well as nighttime.

The daily average BC mass concentration for the entire study period (2010-2012) varied between 0.3 and 10.7 µg m$^{-3}$ with a mean value of 2.8 ± 1.67 µg m$^{-3}$. Seasonally, the highest mean diurnal value of BC (7.5 ± 3.8 µg m$^{-3}$) is observed in winter, followed by autumn (5.4 ± 3.4
µg m\(^{-3}\)) and summer (4.5 ± 3.0 µg m\(^{-3}\)) seasons. However, the lowest concentration was during rainy season (3.3 ± 1.4 µg m\(^{-3}\)). During whole of the observation period, BC shows moderate negative correlation with wind speed. However, in winter season there was a good correlation (r = -0.62) between BC and wind speed. Diurnal variation of BC concentration showed two peaks, one in morning between 08:00-09:00 h IST and other in evening at 20:00-21:00 h IST. The peaks in the morning and evening hours are attributed to the vehicular emissions arising from the rush traffic hours, increase in the local anthropogenic activities combined with nighttime residential cooking and heating.

On average, daily BC concentration accounted for 5.5% of the total PM\(_{2.5}\) mass and 9.14% of PM\(_{10}\) mass concentrations. The BC/ PM\(_{2.5}\) ratio varied from 1.2% to 33.3%, while BC/ PM\(_{10}\) ratio ranged from 1.0 to 17.34%. The mass concentrations of PM\(_{10}\) 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 the period of observation (2011-2012) at Mohal. On monthly basis, BC mass concentration at Mohal contributed 9.4% as maximum in PM\(_{10}\) in January and 14.3% in PM\(_{2.5}\) in January. Annually, BC contributed about 7% in PM\(_{10}\) and 9.7% 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 r = 0.61 and r = 0.49, respectively. In general, a negative correlation was obtained between daily mean values of aerosol and O\(_3\) concentration during the study period. O\(_3\) showed negative correlation with PM\(_{10}\) and PM\(_{2.5}\) mass concentration in winter (r = -0.65, r = -0.38), respectively. While a positive correlation in summer and autumn was observed between O\(_3\) and aerosol mass concentration (PM\(_{10}\) and PM\(_{2.5}\)) due to transported aerosols with the correlation value r = 0.49 and r = 0.44, respectively.

SO\(_4^{2-}\) contributed maximum (32.89%) from the total water soluble aerosol mass followed by Cl\(^-\) (16.5%), Na\(^+\) (15.4%) and NO\(_3^-\) (14%) among ionic constituents. The cations like K\(^+\), NH\(_4^+\) and Ca\(^{2+}\) accounted for 18.3% to the total water soluble mass. The ionic balance of aerosol samples showed a trend of SO\(_4^{2-}\) > Cl\(^-\) > NO\(_3^-\) > F\(^-\) for anions and Na\(^+\) > K\(^+\) > Ca\(^{2+}\) > NH\(_4^+\) for
cations. The contribution of cations such as Mg$^{2+}$, Ca$^{2+}$ and K$^+$ has shown a little increase in 2012. NSS Percentage 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. The ratio of Cl$^-$/Na$^+$ (1.07) in aerosols is less than sea-water indicating a deficiency of chloride relative to the sodium concentration. The loss of chloride ion from aerosol is mainly due to reaction of NaCl with H$_2$SO$_4$ and HNO$_3$ to produce HCl. 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. The study indicates that there is a possibility about climatic implications due to increasing local as well as transport of trace gases and aerosols in the northwestern Indian Himalaya.