Introduction

1 Introduction

Atmospheric ozone

Ozone is a reactive oxidant gas produced naturally in trace amounts in the Earth’s atmosphere. Atmospheric ozone is found in the lower two layers of the atmosphere (stratosphere and troposphere). Atmospheric ozone plays a critical role in maintaining ecosystems on the Earth’s surface. According to the Intergovernmental Panel on Climate Change (IPCC, 2001), it is regarded as the third most powerful greenhouse gas in the atmosphere after CO$_2$ and CH$_4$ with a radiative forcing of +0.35 Wm$^{-2}$. Further, it was realized that anthropogenically emitted substances have the potential to deplete the natural levels of ozone in the stratosphere. The anthropogenic emissions could lead to ozone increase in the troposphere which at elevated concentrations leads to respiratory effects in humans, whereas stratosphere ozone is essential for screening solar ultraviolet radiations. Surface ozone is a secondary air pollutant. It is not emitted directly into the air; rather it is formed by reaction of volatile organic compounds (VOC) and nitrogen oxides (NO$_x$) in presence of sunlight. The main sources of NO$_x$ are vehicular and industrial emissions (Wang et al., 2004). Surface ozone has an atmospheric lifetime of the order of days to weeks, which is generally longer than its precursors. Therefore, once formed surface ozone can be transported over a wider region. Moreover, the precursors emitted from elevated sources such as power plant stacks can also be transported to long distances, which accounts for the ozone presence outside the major urban centres and rural areas (Baumann et al., 2000). Consequently, the surface ozone problem is not only concerned in urban sites, but also in rural locations due to its persistent nature. This paradoxical dual role of ozone in the atmosphere can be regarded as ‘good’ ozone for stratospheric ozone and ‘bad’ for tropospheric ozone.

Most of the atmospheric ozone (about 90%) is found in the stratosphere where it plays a critical role in absorbing the ultraviolet radiations between 240-290 nm wavelengths. These radiations are biologically active and harmful to unicellular organism and also to the surface cell of higher plants and animals. A reduction in the stratospheric ozone leads to increased level of Ultraviolet B (UV-B) at the ground, which can lead to increased incidence of skin cancer in susceptible individuals. Surface ozone in the atmosphere has become one of the prevailing pollutants that harms the human health and ecosystem (Debaje et al., 2010; Avnery et al., 2011; Bates, 1994). It also affects
vegetation and ecosystems, leading to reduced growth and survivability of tree seedlings and increased plant susceptibility to disease, pests and other environmental stresses (Jacobson, 2002). Surface ozone is also regarded as one of the powerful oxidizing agents causing rapid deforestation and reducing life span of various materials (Hisham and Grosjean, 1991). It is considered to be a major precursor of reactive hydroxyl (OH) radicals, which determine the lifetime of many species in the atmosphere (IPCC, 2007).

1.2 Chemistry of surface ozone with its precursors

The surface ozone precursor gases (NO\textsubscript{X}, CO, CH\textsubscript{4} and VOC) are emitted from a wide range of anthropogenic (e.g. transport, fossil fuels, solvents) and natural (e.g. forests, wetlands, soils, lightning) sources. The primary sources for the emission of NO\textsubscript{X} include fossil fuel combustion from the stationary sources such as power generation, and in mobile sources such as road transportation. In 2000, road transport accounted for 33% of anthropogenic NO\textsubscript{X} emissions, while international marine shipping and energy combustion in power plants accounted for 19.0% and 17.0%, respectively (Cofala et al., 2007). Deforestation, and burning of the savannah and agricultural waste account for an half of the global anthropogenic emissions of CO. Biomass burning in the tropics also affects the regional and global distribution of tropospheric O\textsubscript{3} (Crutzen and Andreae, 1990). Two mechanisms have been proposed to account for the high rural emission of surface ozone (Subbaraya and Lal, 1998; Naja and Lal, 2002). One is the direct transport of surface ozone from urban areas, and the other is the transport of its precursors like NO\textsubscript{X}, VOC, CO, CH\textsubscript{4} and non methane hydrocarbon (NMHC) (Trainier et al., 1987), which accounts for insitu photochemical surface ozone production in rural area. The fuel combustion in the domestic sector and road transport in the commercial sector also account for the remaining emissions. The photochemical mechanism described above reveals that CO, NO\textsubscript{X} and hydrocarbons (HCs) gases play a key role in the production of surface ozone, hence, these gases are known as ozone precursors. Surface ozone is formed by the interaction of UV light from the sun and atmospheric nitrogen oxides.

Its production and concentration depend on the presence of primary pollutants (e.g. NO, NO\textsubscript{2}, NO\textsubscript{X}, etc.) as well as UV light.

In the troposphere, nitrogen dioxide (NO\textsubscript{2}) dissociates by sunlight absorption
(λ< 420 nm) to form reactive, ground state oxygen atoms, O (³P) and NO, while the O-atom reacts rapidly to form O₃, described by Equations (Eqs.) (1.1) and (1.2) (Calvert, 1984). Further, ozone can re-oxidize from NO to NO₂ by a catalytic process. The typical forms of the catalytic cycles are given by Eqs. (1.3) and (1.4) (Hewitt and Sturges, 1993) as explained below:

\[
\begin{align*}
\text{NO}_2 + h\nu (\lambda<420 \text{ nm}) & \rightarrow O(³\text{P}) + \text{NO} \quad (1.1) \\
O(³\text{P}) + O_2 (+\text{M}) & \rightarrow O_3 + (\text{M}) \quad (1.2) \\
O_3 + \text{NO} & \rightarrow O_2 + \text{NO}_2 \quad (1.3) \\
O + \text{NO}_2 & \rightarrow \text{NO} + \text{O}_2 \quad (1.4)
\end{align*}
\]

Where, M designates any other gaseous molecule {usually N₂, O₂, or H₂O in air} that collides with a newly formed molecule (e.g., O₃ from Eq. (1.2)), removes some of its excess energy, which was released as the new bond formed, and hence prevents redissociation of O₃. Eqs. (1.1) – (1.4) represent a closed system, which has the overall effect of partitioning NOₓ between its component, i.e., NO and NO₂. According to Eqs. (1.1) – (1.4), the equilibrium parameter exists and is constant under given initial emission rate (Cadle and Johnston, 1952; Leighton, 1961).

1.1 Atmospheric aerosols (Particulate pollutants- Black Carbon, PM₂.₅ and PM₁₀)

Climate change, one of the most burning issues over the globe, is considered to be primarily caused due to aerosols which help increase temperature rise and imbalance radiation budget of the atmosphere (IPCC, 2007; Jayaraman et al., 2010). Aerosol chemistry is one of the most interesting and rapidly expanding branches of modern sciences. Among the gaseous pollutants, surface ozone in the troposphere is a major component of urban smog. These suspended particles may be solid, liquid or gas is known as —aerosols. Some of them occur naturally originating from volcanoes, dust storms, forest fires and also from sea spray. Human activities such as the burning of fossil fuel and change in the natural cover of the surface also generate aerosols. Black carbon (BC), a heat absorbing aerosol, is a product of incomplete combustion of fossil fuel, biomass, agricultural waste and forest fire. It has a particulate uniform spherical shape of about 500 nm in diameter (Fu
et al., 2006). BC has been found responsible for the formation of ozone pollutants due to photochemical reactions in the troposphere (Li et al., 2005). The photolysis rate is generally reduced due to absorption by carbonaceous aerosols, particularly in the early morning and late afternoon with a high aerosol optical path. BC absorbs solar flux and is the second largest contributor to global warming after the green house gases (Jacobson, 2002). BC aerosols cause direct radiative forcing ranging from 0.27 to 0.54 Wm$^{-2}$ (IPCC, 2007). Biomass burning for agricultural and domestic purposes from the Indo-Gangetic Plain (IGP) region has been reported as a major source of BC emissions (Venkataraman et al., 2005). However, there are very few data available on BC aerosol from the Indian region (Latha and Badrinath, 2005; Tripathi et al., 2005; Ramachandran and Rajesh, 2007; Safai et al., 2007; Sreekanth et al., 2007). PM$_{10}$ and PM$_{2.5}$ have been reported with higher concentrations in winter which indicate relatively a longer residence time of particulate pollutants in the atmosphere due to low winds and low mixing height layer. Ganguly et al., (2006) from Ahmedabad (north west, India), Babu et al., (2007) from Trivandrum (south west, India), Sreekanth et al., (2007) from Visakhapatnam (south east India) and Pathak et al., (2010) from Dibrugarh (north east India) reported the fraction of BC aerosol mass concentration to the composite aerosol mass concentration around 7.0%, 10.7%, 10.0% and 7.5%, respectively. Annually, BC has been reported to contribute about 13.0% in PM$_{10}$ and 24.0% in PM$_{2.5}$ at Mohal (Sharma et al., 2013).

The scattering and absorption of solar radiations by aerosols play a major role in the Earth's radiation budget and climate forcing. The atmospheric aerosols are released into the atmosphere from anthropogenic (combustion of fossil fuel and biomass burning) as well as natural origin (volcanic eruption and wind dust transport). Furthermore, due to their varied sources of origin and formation mechanism they exhibit a large variability in their size distribution (Kedia and Ramachandran, 2009). At the global level, the natural sources of aerosols are dominant over the anthropogenic sources, while at the regional level anthropogenic sources of aerosol are significant (Ramanathan et al., 2001).

Sulphur dioxide within gaseous form of aerosol can be converted into sulphate in an aqueous phase. The pathways of aqueous phase are estimated to be responsible for more than half of the ambient sulphate concentration, while the remaining share of concentration is produced from
gas to particle conversion due to oxidation of \( \text{SO}_2 \) by \( \text{OH} \) (Walcek et al., 1990; Karamachandani and Venkatram 1992; Dennis et al., 1993).

Gas phase production of \( \text{HNO}_3 \) by the reaction of \( \text{OH} \) with \( \text{NO}_2 \) is well established and is 10 times faster than the \( \text{OH} \) reaction with \( \text{SO}_2 \). The peak daytime conversion rate of \( \text{NO}_2 \) to \( \text{HNO}_3 \) in a gas phase is 10-50\% per hour. Secondly, nitrate can be accounted by the following series of reactions:

\[
\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_3 + \text{NO}_2 & \leftrightarrow \text{N}_2\text{O}_5 \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O(aq)} & \rightarrow \text{HNO}_3 \text{(aq)}
\end{align*}
\]

These reactions occur in the nighttime, as during daytime \( \text{NO}_3 \) photolyzes rapidly. The \( \text{NO}_3 \) radical formed during the night time also reacts with a series of organic compounds and produces organic nitrates. \( \text{HNO}_3 \) is the main source of nitrate in precipitation. Furthermore, onethird \( \text{NO}_x \) and \( \text{SO}_2 \) portions are estimated to be removed by wet deposition.

About 10\% of the global atmospheric aerosol mass is generated by anthropogenic activity that is concentrated in the immediate vicinity and downwind of sources. The long-range transport of desert dust also contributes to the aerosol size distribution (ASD). However, the long-range transport of desert dust is season dependent and exhibits a large variability in the ASD (Kedia and Ramachandran, 2009; Kuniyal et al., 2009; Guleria et al., 2011a, 2011b, 2011c).

### 1.4 Interaction of aerosols (black carbon and PM$_{10}$) with surface ozone

In some of the studies, the negative correlations have been found between aerosol and surface ozone (Browell et al., 1988; Fendel et al., 1995; Latha and Badarinath, 2004). This reduction in aerosol concentration is due to an aggregate structure of soot particles, which offer a large specific surface area for heterogeneous interactions with surface ozone. The soot particles may significantly influence the tropospheric trace gas chemistry by its surface reaction and other reaction mechanism. The reaction mechanism involves the collision of ozone molecule with an
active site on the surface of carbon sample, which causes absorption of one of its oxygen atoms with the liberation of the resultant oxygen molecule. The adsorbed oxygen atom can then combine with another adsorbed oxygen atom to form molecular oxygen. This catalytic surface reaction of BC causes dramatic ozone depletion in the atmosphere (Fendel et al., 1995). High aerosol concentration significantly affects the chemical oxidation process, especially through the photodissociation (Li et al., 2005). Ozone sink into aerosol is a significant part of its destruction process which is characteristic of cold period (Girgzdiene, 1991).

In summer, a positive correlation was observed between \( \text{O}_3 \) and aerosol mass concentration due to high aerosol concentration from the transported aerosols. The high aerosol concentration at local level can be reported due to biomass burning and photochemical reactions, which accelerate \( \text{O}_3 \) production process. Moreover, the pollution loaded airmass in summer can cause a rise in \( \text{PM}_{10} \) concentration.

1.5 Meteorology and surface ozone

In general, seasonal variation in solar radiation remains in good agreement with the seasonal variation in surface ozone. It is also observed that the coupling of higher solar radiation with higher levels of precursor gases lead to enhanced daytime photochemical ozone production which results in relatively a higher surface ozone level in the spring and autumn seasons. A systematic increase in both solar radiation and surface ozone is observed from January to May. The arrival of monsoon is responsible for an abrupt fall in solar radiation and surface ozone concentration in June. The increase in nighttime concentration during spring months indicates an overall increase in the regional background of surface ozone (Kumar et al., 2011). Lower level of precursors (CO and \( \text{NO}_2 \)) from July to September are largely due to Asian monsoonal circulation, which lead to inflow of pristine marine air masses and also suppresses the photochemical activity through a widespread cloudy/rainy condition. Rainfall is more frequent during July to September which amounts to be about 50% of the total annual rainfall. Rainfall during late January to February has also led to decrease in surface ozone. Rainy season usually leads to decrease in solar radiation as well as surface ozone concentration. Similar seasonal variations in solar radiation and rainfall are also seen over the northern India. Further, the study carried out over the western and southern Indian region reported higher \( \text{O}_3 \) levels during late autumn and winter (Lal et al., 2000; Naja and Lal, 2002; Nair et al., 2002; Beig et al., 2007; Mittal et al., 2007; Kumar et al., 2010).
High level of O$_3$ concentration was also observed in Delhi, across the Indo-Gangetic Plain due to high level of pollutants and intense solar flux over India (Singh et al., 1997; Jain et al., 2005). Naja et al., (2003b), Sanchez et al., (2005) and Kumar et al., (2010) observed higher level of O$_3$ at high altitude sites due to in-situ or in-transport conversion of its precursors. This results in maximum concentration in May and minimum in August. Low altitude rural sites of India showed maximum concentration of O$_3$ in summer and winter as opposite to its minimum O$_3$ concentration in rainy season (Debaje and Kakade, 2006; Reddy et al., 2011).

1.6 Transport of surface ozone through air masses

In particular, ozone episodes typically occur during warm, sunny, and relatively stagnant weather conditions (Vukovich et al., 1977; Logan, 1989). The key pollutants as a result of this smog are gaseous pollutants such as ozone (O$_3$), nitrogen dioxide (NO$_2$), nitrous acid (HNO$_2$), nitric acid (HNO$_3$), peroxyacetyl nitrate (PAN) and polycyclic aromatic hydrocarbons (PAHs) (Wang et al., 2007). The transport of primary pollutants with downwind air masses provides more reaction time to produce secondary pollutants. The reaction mechanism includes gas to heterogeneous reactions to produce O$_3$ from NO$_x$ through photochemical reactions and SO$_2$ and NO$_x$ produce sub-micron aerosols through photochemical reactions (Seinfeld, 1986; Pilinis et al., 1987; Rastogi and Sarin, 2006; Lin et al., 2008). Airmass trajectory analysis has been increasingly used over the last two decades as a simple technique to indicate source regions of the airmasses arriving at a given experimental site. In case of ozone and its precursors, this technique is commonly used with precautions keeping in mind the shorter and more variable atmospheric boundary-layer and life cycle of the chemical species involved in this process. Surface ozone has a strong diurnal cycle in which it is formed during the day and depleted during the night. Trajectory plots are of a great value for identifying the pathways of air parcels and the potential source regions for ozone precursors. The urban plume can transport O$_3$ and its precursors and latter results in more photochemical O$_3$ production in the background atmosphere in the downwind rural area (Xu. et al., 2011). For example, backward trajectory analysis in urban site in the central–eastern China shows that surface ozone episodes are associated with the transport of air pollutants from the south-eastern coastal regions (Shan et al., 2009). In India, various groups have been involved to carry out long-term measurements of surface O$_3$, its various precursors and identified their sources through back trajectory analysis (Varshney and Aggarwal, 1992; Khemani et al.,1995; Lal et al.,
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2000; Naja and Lal 2002; Nair et al., 2002; Naja et al., 2003b; Jain et al., 2005; Beig et al., 2007; Ghude et al., 2008; Reddy et al., 2008; Kumar et al., 2010; David and Nair 2011; Singla et al., 2011).

The study region under the present context is frequently affected by transport of pollutants from the nearby continental emission sources, but the strongest pollution was due to long-range transport from the extra tropical Northern Hemisphere. The higher mixing ratios of trace gases are due to faster transport of air parcels from the source regions through free troposphere (Lal et al., 2007).

Transport of these continental emissions has been observed to alter the distributions of various trace gases over remote marine regions of the Pacific Ocean (Woo et al., 2003) and the Indian Ocean (Lelieveld et al., 2001). In the South Asia, meteorology in the winter season is dominated by high pressure and creates clear sky conditions and persistent northeasterly airflow (Krishnamurti et al., 1997). Further, the transport of pollutants and their chemical characteristics have been widely reported in the Asian continental outflow regime over the Arabian Sea and the Indian Ocean (Krishnamurti et al., 1998). Elevated levels of pollutants have been observed over the Indian Ocean due to air mass transport through the Bay of Bengal. Since the mid-1990s, ground and satellite based data have been suggesting that the amount of anthropogenic aerosols has decreased over the North America and Europe, but has increased over the parts of east and south Asia along with the atmospheric concentration of low latitude smoke particles (Mishchenko and Geogdzhayev, 2007). Badarinath et al., (2009a) observed radiative forcing in the range of 107.81 Wm^{-2} at surface over urban region of Hyderabad due to enhanced aerosols loading associated with the transport through airmasses due to burning of agricultural crop residues in the Indo-Gangetic Plain (IGP). Thick haze consisting of dust, BC, sulfate and fly ash aerosols are transported from the South Asia towards the Indian Ocean and accounts for significant perturbations in the regional radiation budget (Satheesh and Ramanathan 2000; Ramanathan et al., 2005). This mechanism suggests the weakening of monsoon circulation and reduction of monsoon rainfall with the future possibility of frequent droughts (Gautam et al., 2009).
1.7 Background of study

Gaseous pollutants and particulate pollution in the atmosphere play an important role in atmospheric dynamics. Aerosols and consequent temperature rise have increased the interests among the scientists today at worldwide level. In India, Indian Space Research Organization (ISRO) and other organizations have been playing an important role in initiating alike activities in different parts of the country. Speaking about ISRO- Geosphere Biosphere Programme (GBP) under ISRO, the work elements of atmospheric study by focusing on each component more closely and vigorously is divided in the form of separate projects under Specific Atmospheric Assessment Projects(SAAP).

![Fig. 1.1. Measurements of ozone and related trace gases in different regions. A network of environmental observatories in India under ISRO-GBP (AT-CTM) Programme (Source: www.esrl.noaa.gov/gmd/annualconference)](image)

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**Fig. 1.1.** Measurements of ozone and related trace gases in different regions. A network of environmental observatories in India under ISRO-GBP (AT-CTM) Programme (Source: www.esrl.noaa.gov/gmd/annualconference)
The entire atmospheric aerosol research programme has been organized into nine specific projects but the programmes relating to atmospheric sciences mainly exist such as Atmospheric Trace Gases Chemistry, Transport and Modeling (AT-CTM), Aerosol Radiative Forcing over India (ARFI) and Atmospheric Boundary Layer Network and Characterization (ABLNC). Among all of three, the programme in the Atmospheric Trace Gas Chemistry stands to be one of the most complex and least-studied area in climate change research. This research programme at nationwide level is being executed under the AT-CTM project by Physical Research Laboratory (PRL), Ahmedabad. This nationwide network programme is executed through research laboratories and universities through different scholars in atmospheric chemistry which is shown in Figure 1.1. Dibrugarh in Assam, Nainital in Uttarakhand and Mohal (Kullu) in Himachal Pradesh starting from the northeastern part to the northwestern part of the Indian Himalaya were established with a sole purpose of studying aerosol and trace gas chemistry in the Indian Himalayan Region. Similarly, the ARFI programme is being executed by SPL, Thiruvanthapuram mainly with the expertise of environmental physicists in various research institutions and universities (under Department of Physics) to study the interaction of aerosols with solar radiations in retrieving Aerosol Optical Depth (AOD) corresponding different spectral bands (ultraviolet to near infrared region) and black carbon aerosol in various geographical locations in India. There is an urgent need to characterize natural and anthropogenic aerosols in different geographical regions of India (Jayaraman et al., 2010).

It is a chemical composition and size of a particle which determine its efficiency to scatter and absorb radiation so these two aerosol properties are vital factors of investigation (Ramachandran et al., 2003) in atmospheric chemistry. A study conducted at Thumba showed on a long-term basis that the PM$_{10}$ levels were well within permissible limits set by several National Standards. But PM$_{2.5}$ levels were supposed to be critical. Further, the sub-micron aerosols contributed more than 80% of the total aerosol surface area irrespective to their mass type and implying their dominance in scattering properties (Moorthy and Pillai, 2004). The researchers from the Indian Institute of Chemical Engineering, Hyderabad in their study found that anthropogenic aerosols were dominating in PM$_{10}$ aerosols at Allahabad (Kulshrestha et al., 2005). The two important sites from the northwestern Himalayan region were selected for the measurements of ambient air quality parameters like Total Suspended Particulate Matter (TSP),
aitken nuclei (ultrafine) and their mass size distribution. At both the sites, it is found that TSP level has continuously been increasing (Kuniyal and Bhomick, 2005). Further investigations on AOD, surface ozone and TSP at Mohal and Kothi also revealed high values during tourist season (Gajananda et al., 2005).

It is obvious from aforesaid background that most of the work on aerosols pertain to its characterization in the Indian plains as well as in the marine environment. While the Himalayan ecosystem, especially in the hilly states like Himachal Pradesh, such studies are either sporadic in nature or very rare. Further, investigation on the near surface aerosol is scanty almost in the entire country. About 20 to 30% of the total global aerosol emissions to the atmosphere is due to mainly anthropogenic activities and substantial portion of these aerosols belong to fine submicron size (ultrafine or aitken) aerosols (IPCC, 2001). They live longer in the atmosphere and produce longterm global climatic change. However, the database so far generated and available till the date is not adequate to interpret and analyze longterm changes. Keeping in mind such scarcity in data, detailed studies on various aspects of ambient aerosols especially surface ozone, NOx (NO+NO2), black carbon and other particulate pollutants such as PM10 and PM2.5 and other meteorological parameters were taken into account under the present study.

1.8 Scope of the present work

The AT-CTM programmes at the National level is under operation by ISROGBP, ISRO, Bangalore. This country wide programme has made significant contributions in the trace gases measurement and climate change research programme which are going to execute by the Space Physics Laboratory (SPL), Vikram Sarabhai Space Centre (VSSC), Thiruvananthapuram as well as PRL, Ahmedabad. In India, surface ozone and its precursors are measured and studied recently by various scholars under AT-CTM project (Kumar et al., 2010; Nishanth and Satheesh, 2010; Kumar et al., 2011; David and Nair, 2011; Nishanth et al., 2011; Nishanth et al., 2012; Srivastava et al., 2012; Sharma et al., 2013; Swamy et al., 2013). In spite of the fact that mountainous areas are usually remote, marginal and measuring sites are located in the lower free troposphere (background conditions). These sites are often affected by polluted air masses from the urban areas. The aim of the observations of gaseous pollutants under the present activity is to obtain the first hand information, mainly about the surface ozone behaviour in the topographically fragile and ecologically delicate regions like the Himalaya. The identification of the potential role of
dynamic and chemical processes in the tropospheric ozone behaviour also continues to be a major problem and there is a need for a geographical extension of ozone measurement sites (Lindskog et al., 2003). At present, behaviour of tropospheric ozone around the globe is studied irregularly; however, there are still gaps in the geographical representativeness of ozone research (Kondratyev and Varotsos, 2001a and b). Longterm and numerous ozone data at worldwide level are available mainly for the North America, Europe, Japan and Russia. Outside these areas, ozone behaviour is investigated either to a considerably lesser degree or not at all. In the present research attempt, the author has conducted the study of the measurement of surface ozone, its precursor- NO\textsubscript{x}, particulate matter (such as black carbon PM\textsubscript{10} and PM\textsubscript{2.5} aerosol) and their relationship with the local meteorological parameters. This study helps to examine the concentration of these pollutants at Mohal (a semi-urban site) and correlation of surface ozone with its precursor- NO\textsubscript{x} and other particulate pollutants. This study also investigates transport of these pollutants over Mohal from outside the region. Due to a variety of ecosystems, surface conditions and aerosol properties, insitu observations of aerosols in this part of the Himalaya have been rare so far. The validation exercise of ground based observations with the satellite retrieved products from this part of the Indian Himalaya has therefore become more important among the trace gases, aerosol and climate change studies. Study of trace gases, aerosol and their impact assessment study especially in the Himalayan context is important because of its long mountain ranges which are topographically very fragile and act as a very delicate ecological entity. At the same time, it acts as an ecological guard of the Asian continent in many aspects. So it is termed as the third ice pole because of its huge water reserve in the form of snow. Unfortunately, the Himalayan glaciers in this ecosystem have been the first hit ecological biomes suffering due to ever increasing aerosols and its consequent warming effect in the region (Ramanathan et al., 2007; Ming et al., 2008). The present experimental site at Mohal in the northwestern part of the Indian Himalaya is a pioneering centre in the mountain region under ISRO-GBP, AT-CTM programme. In this direction, many other scholars have recently taken initiatives to add a new knowledge in the field of aerosol science.

Nowadays, this part of the Indian Himalaya has attracted a significant scientific interest among scientists due to lack of such data, transport of ever increasing anthropogenic aerosols from the Indo-Gangetic and the Punjab Plains, natural aerosols from the Thar Desert and the Great Sahara
to the Himalaya and their resultant adverse impact on the glaciers in this part of the globe (Gautam et al., 2009; Prasad et al., 2009).

1.9 Review of literature

Surface ozone (O$_3$) concentration and its changing behaviour have been reported in different parts of the world (Bojkov, 1988; Oltmans and Leavy, 1994; Xu et al., 2008; Wang et al., 2009). Appalachian mountain in the United States of America (Aneja et al., 1991), 17-different sites under the National Ozone Monitoring Programme in the United Kingdom (Bower et al., 1994), Athens in Greece (Cartalis and Varotsos, 1994), Zagreb in Yugoslavia (Lisac and Grubisic, 1991), southern part of the Alps (Vecchi and Valli, 1999) and Arosa in Switzerland (Staehelin et al., 1994) have been the important ones among them; Some alike measurements were also done in some of the high-altitude sites i.e., Mt. Fuji (3776m amsl), Waliguan (3810 m amsl) and Mauna Loa (3397 m amsl) (Tsutsumi et al., 1994; Oltmansa et al., 2006).

The damaging effect of surface ozone on crops was also studied in some rural parts of the world (Kelly et al., 1984; Debaje and Kakade, 2006). Biomass burning has been studied and considered to be a predominating factor in influencing ozone concentrations (Kirchhoff and Marinho, 1994). Satellite data can demonstrate the ozone concentrations in combination with the experimental work (Fishman et al., 1990). Surface ozone measurement in urban areas like in Jinan and China showed higher daytime ozone concentrations in summer (Shan et al., 2009). Furthermore, the average concentrations were found to be highest during summer months during late May up to early July till monsoon rain as compared to relatively lower concentrations during its downfall in August and September. Ozone concentrations can exceed the National Ambient Air Quality Standards (NAAQS) of 0.12 parts per million by volume (ppmv) during summer months.

The high ozone concentrations have high levels of SO$_2$ (~25 parts per billion by volume (ppbv)) and NO$_x$ (~11 ppbv) and the ozone concentrations increased from the lower elevations to the higher elevation (Aneja et al., 1991). In the Asian countries, India emits 778 GgN yr$^{-1}$ NO$_2$ (Akimoto and Narita, 1994). Atmospheric O$_3$, CO, SO$_2$ and Noy* (Noy* = NO + NO$_2$ + PAN + organic nitrate + HNO$_3$ + N$_2$O$_5$ + ...) were also measured during 1999–2000 at a rural/agricultural site in the Yangtze Delta of China (Wang et al., 2002). Measurements of surface ozone (O$_3$) and nitrogen oxides (NO$_x$) were conducted at Tae-ahn (TAP) and Chongwon (CHN) on the Korean
Peninsula, during the aerosol characterization experiment- Asian Pacific region (ACE-Asia) campaign, March–May 2001. The mean values of O₃ and NO₂ concentrations at TAP were 42 ppbv and 12 ppbv, respectively. The average O₃ diurnal variation of 17 ppbv at TAP indicates that the loss of O₃ was not pronounced during night. The highest NO₂ concentrations, with an average diurnal variation of 8 ppbv, occurred in the afternoon at 13:00-15:00 h IST (Kim and Chung, 2005). Ozone measured at two rural sites between January 2008 and November 2009 in the Iberian Peninsula plateau showed its seasonal variations with the lowest values during January and November. While high ozone concentrations were related to the high radiation intensity, temperature and wind directions (Notraio et al., 2011). Averaged hourly data of surface O₃ and its precursors like NOₓ monitored during 1987-2001 (07:00-15:00 h IST) in Athens, Greece at urban stations showed a negative trend of NO and NOₓ in winter but higher in summer. However, the negative surface ozone trend was reported in rural station with minimum NO and NOₓ in summer and maximum in autumn and winter. The mean seasonal wind-rose showed the dominating northward wind flow during June, which is the month of the lowest negative ozone trend in the rural station (Varotos et al., 2003).

Particulate matter in the form of TSP concentrations in the Federal Republic of Germany (FRG) was three times higher in February (64 µg m⁻³) compared to August (19 µg m⁻³) (Kaupp and McLachlan, 1999). In a dry Mediterranean island Cyprus, PM₁₀ concentrations were noted to be 40.1 µg m⁻³ at traffic urban site, and 15.8 µg m⁻³ at rural site (Bari et al., 2005). PM₁₀ levels cause excess deaths and detrimental health effects (ARC, 1999).

The concentrations of carbonaceous particles (less than 8 µm in diameter, elemental C and organics) at Sapporo in Hokkaido island of Japan in 1982 were relatively high (12.7-16.0 µg m⁻³) during autumn and winter (October-February) as emission sources were mainly from domestic heating which comprised of 36 – 41% of the total aerosol mass (Ohta and Okita, 1990). In Hong Kong, one of the studies showed that the concentration of respirable particulate matter (PM₁₀), fine particulate matter (PM₂.₅) and nitrogen oxide (NO₂) pollutants had a high correlation between these parameters (Lam et al., 1999). In particular, those mineral aerosol particles, which are characterized by large surface area, can strongly absorb the short-wave solar radiation, influencing the radiative forcing of climate (Dickerson et al., 1997) or causing reduction in photolysis rate thus inhibits ozone production. In fact, mineral aerosol may strongly influence the balance of atmospheric trace gases in the lower atmosphere including ozone (Dentener and Crutzen, 1993;
Zang et al., 1994; Prospero et al., 1995; Dickerson et al., 1997). Source wise contribution of black carbon showed 20% black carbon is emitted from burning biofuels, 40% from fossil fuels and 40% from open biomass burning (Ramanathan and Carmichael, 2008). The presence of black carbon over highly reflective surfaces such as snow and ice or clouds may cause emission from biomass burning, which usually have a negative forcing (Hansen et al., 2005) and have a positive forcing over snow fields in the ecologically sensitive areas such as the Himalayas (IPCC, 2007).

The fractions of mass size distribution in particulate pollution in one of the metropolitan cities at Toufan in China showed fine particle (<2.5 µm) mass loading in the dichotomous samplers from 150 to 780 µg sample⁻¹; whereas the coarse particles (2.5-10 µm) from 70 to 450 µg sample⁻¹ indicate increasing adverse impacts on the natural environment (Wang et al., 1993). BC aerosols strongly absorb solar radiation over a wide spectral range. It is reported that the absorption by BC aerosols can greatly offset the direct radiative impact of sulphate aerosols (IPCC, 2001) and can even surpass the green house gas effect of some atmospheric trace gas species (Jacobson, 2001). In addition, BC mixed with other hydrophilic particles, can act as cloud condensation nuclei, leading to changes in the size distribution, optical properties and rainfall potential of the clouds (Ackerman et al., 2000). Being chemically inert and in the fine size range, the only effective removal mechanism of BC from the atmosphere is by wet deposition and as such BC particles have a long lifetime (>~1 week in the lower troposphere (Babu and Moorthy, 2001) and hence it remains available with the airmasses through long range transport from one place to another. Even though chemically inert, BC is an effective adsorbent for vapour phase species because of its porosity and thus it can act as a catalyst for many chemical reactions. BC also poses serious health problems, because of its fine sub-micrometer size and ability to get easily deposited into the respiratory system through inhalation (Horvath, 1993). A significant amount of BC, if present in rain clouds, can lead to increased absorption of solar radiation, resulting in heating and eventually burn off the clouds (Ackerman et al., 2000). The characterization of BC is attracting considerable interest in recent years due to its environmental and climatic significance as well as anthropogenic nature of its origin (Hansen et al., 2000). The atmospheric BC directly accounts for the reduction of the incoming solar radiation, leading to the heating of the incoming shortwave solar radiation and the atmosphere. BC aerosols play an important role in tropospheric chemistry due to their porous characteristics and adsorptive properties that aid in some of the chemical transformations like oxidation of SO₂ to SO₄, and conversion of HNO₃ vapour to NO and NO₂.
(Disselkamp et al., 2000) and destruction of O\textsubscript{3} and formation of CO (Fendel et al., 1995; Latha et al., 2004). BC showed negative correlation with ozone, especially during pollution peaks of certain species like NO\textsubscript{x} (NO and NO\textsubscript{2}). PM\textsubscript{10} particles also showed negative correlation with ozone, after the destruction of ozone during peak hours at 7 a.m. and 8 a.m. when NO\textsubscript{x} and PM\textsubscript{10} concentrations exhibit maximum value. Black carbon (~650 ng m\textsuperscript{-3}), surface ozone (15 ppbv) and NO\textsubscript{x} measured at La Reunion University in sub-urban site of Saint-Denis, a locally polluted island in the Southern tropics, showed straightforward negative correlation with ozone, especially during pollution peaks (Bhugwant and Bremaud, 2001).

In India, surface ozone and its precursors are widely being measured under ISRO-GBP. AT-CTM is one of the programmes under the ISRO-GBP of ISRO being executed at national level by PRL, Ahmedabad. In India, various groups have been involved to carry out long-term measurements of surface O\textsubscript{3} and its various precursors from different parts of India (e.g., Varshney and Aggarwal, 1992; Khemani et al., 1995; Lal et al., 2000; Naja and Lal 2002; Nair et al., 2002; Naja et al., 2003b; Jain et al., 2005; Beig et al., 2007; Ghude et al., 2008; Reddy et al., 2008; Kumar et al., 2010; David and Nair 2011; Singla et al., 2011, Ojha et al., 2012). Ozone levels at a high altitude site, e.g. Mt. Abu (India), were measured to be 33.4±13.3 ppbv for the period 1993-2000.

It is found that TSP and respirable suspended particulate matter (RSPM) exceed National Ambient Air Quality Standards (NAAQS) in most of the cities/towns, but SO\textsubscript{2} and NO\textsubscript{2} are within the NAAQS prescribed limits (Badhwar et al., 2006). PM\textsubscript{10} and its sources like soil-road dust and inorganic secondary particles like SO\textsubscript{4}, NH\textsubscript{4} and NO\textsubscript{3} were studied to know the cause-effect relationship of particles (PM\textsubscript{10}) in Kanpur city (Shukla and Sharma, 2008). Inhalation of PM\textsubscript{2.5} causes pulmonary inflammation and oxidative stress (Brook et al., 2004). The seasonal distribution of PM\textsubscript{10} and its ionic components (Fl\textsuperscript{-}, Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+}) during summer due to greater particles release and lower atmospheric levels during the rainy season due to washout effect in Tirupati were studied in detail (Mouli, 2006). The major proportion of PM\textsubscript{10} and PM\textsubscript{2.5} concentration levels in mega cities like Kolkata was produced by vehicular emissions (Das et al., 2006).

The dominance of SO\textsubscript{4}\textsuperscript{2-}, NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} in PM\textsubscript{10} was noticed in the Bay of Bengal and Arabian Sea during ICARB campaign (Reddy et al., 2008). Presence of ammonium, sulphate and ammonium nitrate in PM\textsubscript{10} as the major water soluble particles play also a very important role in the radiation budget (Reddy et al., 2008). In general, the spatial variation of aerosol mass
concentration in the peninsular India during winter time showed generally high values ranging from 50 to 80 μg m\(^{-3}\) along the coastal regions and low in the interior continental regions <30 μg m\(^{-3}\) (Moorthy et al., 2005). The mass concentration of sea salt aerosols from oceanic origin increases with increasing wind speed, whereas non-sea salt aerosols are mainly of continental or anthropogenic decreases with increasing wind speed (Nair et al., 2005). Biomass burning for agricultural and domestic purposes from the Indo-Gangetic Plain region has been reported to be a major source for BC emissions (Venkatraman et al., 2005). However, there are very few data available on BC aerosols from the Indian region except very few studies (Latha and Badrinath, 2003; Latha et al., 2004; Tripathi et al., 2005; Ramachandran and Rajesh, 2007; Safai et al., 2007; Sreekanth et al., 2007).

Surface ozone and NO\(_x\) concentrations in the tropical coastal site were measured at a rural site at Kanur University and Kanur town- an urban site, in Kerala during winter months of 2009 and 2010, negative correlation is observed for ozone and NO\(_x\) (Nishanth and Satheesh, 2010). Simultaneous measurements of surface ozone, NO\(_x\) (NO+NO\(_2\)) and meteorological parameters were carried out at a tropical coastal location of Trivandrum from November 2007 to May 2009 (David and Nair, 2011). Measurements of O\(_3\) and selected meteorological parameters have been made at Joharapur (19.3° N, 75.2°E, 474 m above sea level), a tropical rural site in India since March 2002. Bhopal, Lucknow, etc. due to a recent introduction of various control measures like reduction of sulphur in diesel and use of liquefied petroleum gas (LPG) in place of coal as a domestic fuel have brought about a change from the earlier days. Decrease in NO\(_2\) concentration has become possible due to use of domestic fuel in place of coal. This decrease in nitrogen dioxide levels in the residential areas of Bhopal and Madurai has been noticed where other factors such as stricter vehicular norms were adopted to bring down vehicular pollution (Badhwar et al., 2006).

The towns mainly the hill spots located in the Himalayan region have also been observed for TSP concentrations that sometimes either crossed the permissible limit or sometimes remained close to permissible limit. In Himachal Pradesh particularly where the present study is carried out showed these values in the background locations of hill spots in the Kullu valley where tourism and other developmental activities are commonly known anthropogenic interferences. The hill spots in the Kullu valley such as Mohal (Kullu) (158.5 ± 29.2 μg m\(^{-3}\)) in April 2005 and Kothi (Manali) (100.7 ± 15.5 μg m\(^{-3}\)) in March 2004 have been one of the best examples for increasing
TSP concentrations (Gajananda et al., 2005; Kuniyal et al., 2005; Kuniyal and Bhomick, 2005; Kuniyal and Vishvakarma, 2006; Kuniyal et al., 2007). In addition to peak tourist season, there are certain important cultural events such as the Kullu Dussehra festival when the TSP values crossed its permitted limit indicating two times more compared to without some such event days (Kuniyal et al., 2003). The holy Himalaya having high tourism potential has also started to face air pollution due to ever increasing smoke from vehicles and other bio-fuels from the hotels and biomass burning in the forests during May, June (the peak months of tourist influx), December and January (winter season). Increase in suspended particulate matter (SPM) and respirable particulate matter above the permissible limit in these months alarm the future. Many studies on tourism in the Himalayas have also been conducted focusing either on tourism and the environment or on the impact of tourism on natural components (Kaur, 1985; Singh, 1989 a and b; Ram and Kuniyal, 1994; Kuniyal et al., 1995). But there are rare studies incorporating these parameters mainly solid waste problems and air pollution in hill spots or urban towns (Kuniyal et al., 2003).

The maximum SO$_2$ concentration was 16.5 μg m$^{-3}$ at Mohal and 24.2 μg m$^{-3}$ at Kothi between April 2004 and March 2005 (Kuniyal and Vishvakarma, 2006). With the increase in vehicular emissions, incidents of forest fires, and biomass burning in this region, these pollutants are going to increase. The plying vehicles are considered to be the main sources of VOCs, SPM, SO$_x$, NO$_x$ and CO in the Himalaya (Safai et al., 2000; Ingle et al., 2005).

1.10 Objectives

Based on the background discussion of the problem, the major objectives of the present study are as under:

1. To obtain the concentrations of gaseous (O$_3$ and NOx) and particulate pollutants (PM$_{2.5}$, PM$_{10}$ and BC) within the ambient environment of the Kullu Valley.
2. To observe the behaviour of ozone precursors, analyze the impact of PM$_{2.5}$, PM$_{10}$ and black carbon (BC) on surface O$_3$.
3. To analyze the chemical components from the exposed particulate samples such as cation, anion and transition metals.
4. To investigate the behaviour of physio-chemical studies of surface ozone and particulate pollutants in relation to climate change under local meteorological conditions.
5. To identify external transported pollution sources using the Hybrid Single Particle
Lagrangian Integrated Trajectory and satellite imageries.

1.11 Experimental site

The present experimental site Mohal (31.54°N latitude and 77.07°E longitude, 1154 m
above mean sea level (amsl)) is located in the Kullu valley of the northwestern part of the Indian
Himalayas (Fig. 1). The sampling site is located in the campus of Govind Ballabh Pant Institute
of Himalayan Environment and Development (GBPIHED), Himachal Unit, Mohal-Kullu
(Himachal Pradesh), India. The distance of the sampling site from the National Highway (NH)21
is about 228 m. Mohal is about 5 km south of Kullu town. The famous River Beas flows in the
Kullu valley. This valley extends up to 80 km long from south to north and is 0.5 to 2 km wide,
which begins from Largi (957 m amsl) in the lower Beas basin and stretches up to the Rohtang
Crest (4,038 m amsl) in the upper Beas basin. The surrounding mountains of the Kullu valley have
considerable height in the range of 3,000-5,000 m (Sharma et al., 2009). This part of the Indian
Himalaya is topographically very fragile and ecologically very delicate. The Kullu valley
experienced a tremendous growth in tourism over a last decade, hosted 2.12 million tourists in
2008 (Sharma et al., 2009) and their numbers every year are continuously increasing. Due to
rapidly growing urbanization in the recent years, the surrounding environment in the immediate
vicinity of the experimental site is dominated by tourism and agri-horticultural activities (Kuniyal
et al., 2007) and is characterized with semi-urban settlement
(by converting arable land into house constructions for dwelling) (Kuniyal et al., 2007). The Kullu
valley experienced a tremendous tourism growth over the last decade. The population of Mohal
is 18,306 and has a floating population of about 24,000 visitors per day during the peak of summer
season (Kuniyal et al., 2009).
The high altitude with extreme diurnal variation in solar radiation leads to formation of inversion layer that can last for several days, particularly during winter season. The valley is a bowl shaped which during winter, traps cold air from higher peaks and/or produced by substantial nighttime cooling. The cold dense air settles to the valley floor and suppresses the vertical exchange of low level air. The suppression leads to a build up of pollutants. Solar heating destabilizes the surface air and the resulting vertical motion disperses the trapped pollutants.

1.12 Meteorology at Mohal

The climate of the Kullu valley is classified into four local seasons, namely, summer (April-July), rainy (August-September), autumn (October-November) and winter (DecemberMarch).
Winter season is a peculiar season from a viewpoint of the aerosols study because during this time the maximum aerosols are transported with the air masses. It is therefore associated with rain and heavy snowfall from the western disturbances. The westerly air-mass flow significantly influences the aerosol properties and trace gas concentration during pre-monsoon season (Kuniyal et al., 2009, Sharma et al., 2010, Guleria et al., 2011a, 2011b, 2011c). The observation site remains very hot in pre-monsoon or summer with intermediate spells of rainfall. In general, in most of the days in the present study site, sky during morning was cloud free, followed by partly cloudy in the afternoon. The monthly variations in meteorological parameters are shown in Figure 1.3. The wind speed was found in the range from 0.44 to 0.98
ms$^{-1}$ with an average speed of 0.71 ms$^{-1}$. However, the average values of wind speed were found to be slightly smaller during post-monsoon period. The predominant surface wind direction over Mohal is generally from the south-west west direction. The maximum relative humidity during the rainy season was around 76% followed by winter 63%, autumn 61% and summer 58%. The monthly average temperature varied between 5.8°C and 26.6°C. On a daily average basis, the temperature rose from 20°C in March to 26.6°C in July and then decreased gradually up to 5.8°C in January. On average, the temperature continuously increased from January to July every year and thereafter it starts to decrease continuously. Figure 1.3 (a) indicates that the maximum rainfall occurs during rainy months which amounted to be about 49% of the total rainfall while minimum rainfall was recorded about 2% of the total rainfall.