Chapter 2

Measurement Techniques and Data Analysis

In last few years, the use of techniques for the measurement of trace gases such CO, NOx and ozone have been improved significantly [e.g. Heard, 2006], with the improvement of the accuracy also. Atmospheric ozone has been measured using different techniques depending upon the objectives and the observational platform such as ground-based, balloon-borne, LIDAR, aircrafts and satellites. The most popular method for ground-based ozone measurements is based on the UV light absorption by ozone molecules present in the ambient air. This technique has been used globally for the surface monitoring [Poulida et al., 1991; Kleinman et al., 1994; Kajii et al., 1998; Lal et al., 2000; Naja and Lal, 2002].

CO measurements have been conducted using spectroscopic method [Migotte and Neven, 1952], mercuric oxidation reduction [Robbins et al., 1968; Seiler and Junge, 1970] and solar spectroscopic methods [Rinsland and Levine,
The tunable diode laser absorption [Ku et al., 1975; Sachse et al., 1987; Fried et al., 1992] and gas filter correlation, non-dispersive infrared absorption (NDIR) techniques are popular techniques for CO measurements [Parrish et al., 1990; Naja, 1997]. NO\textsubscript{y} measurements are generally carried out by first converting all reactive nitrogen compounds to NO by passing air sample over a Molybdenum or Gold converters [Bollinger et al., 1983; Dickerson, 1984; Fehsenfeld et al., 1987]. The measurements of hydrocarbons are still made through gas chromatography, which is a traditional technique. The measurements of radicals (HO\textsubscript{2} and RO\textsubscript{2}) are started since few years back in India, with an improved measurement technique, called ‘chemical ionization mass spectrometry’.

2.1. Measurement of Surface Ozone

Ozone was first discovered by Schonbein in 1839 using a paper covered in a paste of starch and Potassium Iodide (KI), which turned blue due to exposure of ozone [Schonbein, 1840]. However, this method had poor standardization in addition to the influences of humidity and wind speed on its sensitivity [e.g. Kley et al., 1988; Volz and Kley, 1988]. The commonly used measurement techniques are spectroscopic absorption, chemiluminescence, and electrochemical method. The electro-chemical method [Komhyr, 1969] is particularly suitable for balloon-borne measurements due to very fast time resolution (1-2 seconds) as compared with the spectroscopic absorption technique (10-20 seconds).

In the present work, the surface ozone measurements have been conducted using the ozone instrument based on the UV light absorption technique. The ozone analyzer from the Thermo Electron Corporation (TECO), USA (model 49i) is
employed. In this instrument, the ozone molecules present in the ambient air sample are exposed to UV light wavelength centred at 253.7 nm where the peak of ozone absorption spectrum also lies. The sample flow rate is about 1-3 litres per minute and the Lower Detectable Limit (LDL) of the instrument is about 1 ppbv. The instrument can operate over a temperature range of 0-45 °C. The zero drift of the analyzer is less than 2 ppbv and the span drift is less than 1% per month. The response time of the analyzer is about 20 seconds. The absolute accuracy of these instruments is reported to be about 5% [Kleinman et al., 1994].

2.1.1. Operating Principle

A simplified block diagram of the ozone analyzer is shown in the Figure 2.1. The principle of this method is based on the absorption of UV light by ozone molecules at 253.7 nm. The main principle of UV absorption technique is based on the Beer Lambert’s Law, given by:

\[ I = I_0 \exp \left[ - \int_0^t \left( \sigma_{O_3} n_{O_3} + \sigma_r n_{air} + \sum \sigma_i' n_i' \right) dt \right] \]  

(2.1)

\[ I' = I_0 \exp \left[ - \int_0^t \left( \sigma_r n_{air} + \sum \sigma_i' n_i' \right) dt \right] \]  

(2.2)
Where,

\[ I = \text{Attenuated intensity due to ozone and other species} \]
\[ I' = \text{Attenuated intensity due to other species} \]
\[ I_o = \text{Unattenuated intensity (intensity of UV source)} \]
\[ \sigma_{O_3} = \text{Absorption cross section of ozone in cm}^2 \]
\[ n_{O_3} = \text{Ozone number density in cm}^3 \]
\[ \sigma_r = \text{Rayleigh scattering cross section of air in cm}^2 \]
\[ n_{air} = \text{Air number density in cm}^3 \]
\[ \sigma_{i_i}' = \text{Absorption cross section of other (i^{th}) species in cm}^2 \]
\[ n_{i_i}' = \text{Number density of other (i^{th}) species in cm}^3 \]
\[ l = \text{Length of the absorption cell in cm} \]

The ratio of the two signals gives the ozone number density:

\[ \frac{I}{I'} = \exp \left[ -\int_0^l \left( \sigma_{O_3} n_{O_3} \right) dl \right] \] (2.3)

The analyzer takes ambient air through a Sample Hood System (SHS), which is made of Teflon to minimize the depositional loss of ozone in the inlet system. The ambient air is taken from a height of about 5 m above ground level to minimize the depositional loss of ozone in the air due to direct contact with the ground. After passing through the Teflon filter, ambient air is divided into two gas streams: sample/measurement gas and the reference gas. The gas stream which goes directly to the absorption cell provides the sample/measurement signal, while gas stream which flows through the ozone scrubber (MnO_2), before reaching to the absorption cell, provides the reference signal. In the absorption cell, these two gas streams are
exposed to UV light to measure the measurement (I) and reference (I’) signals. Solenoid valve switches these two streams one by one into the absorption cell.

![Figure 2.1: A simplified block diagram demonstrating the operating principle of the ozone analyzer. The reduction in the thickness of arrows originating from UV source represents the attenuation of UV light in the absorption cell.](image)

The measurement and reference signals represent the attenuation of UV radiation in the presence and absence of ozone in ambient air and ozone mixing ratios are determined using the Beer-Lambert’s law as mentioned above.

The UV light intensities of each cell are measured by the detectors, namely photodiodes are used. There are two detectors in Thermo ozone analyzer whereas the Teledyne ozone analyzer (another company) has one detector, for the detection of UV light intensity. In Thermo ozone analyzer two detectors are used to compensate for the drift in the instrument. When the solenoid valve switches the
reference and sample gas streams to opposite cells, the light intensities are ignored for few seconds to allow the cells to be flushed. The attenuation in the signals due to absorption or scattering by the other trace species gets eliminated due to the differential nature of the equation 2.1. The analyzer used here also incorporates the corrections due to changes in the temperature, pressure/flow rate and drifts in the lamp intensity.

2.1.2. Span and Zero Check

Periodic zero and span check of the ozone analyzer is performed. Zero air for the calibration is obtained from scrubbed ambient air. Zero air generator (*Thermo Electron, Model 1160*) is used to obtain zero air supply. In case of using the ambient air, the following compounds like; ozone, nitric oxide, nitrogen dioxide, sulfur dioxide and hydrocarbons, must be removed. By passing the air through Purafil, it oxidizes nitric oxide to nitrogen dioxide and scrubs nitrogen dioxide. Again, the air passes through another scrubber, activated charcoal to remove residual ozone, nitrogen dioxide, sulfur dioxide and hydrocarbons. Silica gel is also used to remove moisture from the air. Finally, the air passes through particulate filter to remove particulates which originate in scrubbing columns. In this way zero air is generated which is impurity free and further used for calibration purpose.

For the span check, the ozone analyzer has an in-built ozone generator. Here, an ozone concentration standard of ~80% of the upper range limit of the ozone analyzer is generated. The instrument is allowed to sample this ozone concentration standard until a stable response is obtained. After that, record the ozone concentration as determined by the calibration photometer and the corresponding
analyzer response. The ozone span coefficient is usually calculated during the calibration procedure.

![Zero and span test](image)

**Figure 2.2:** (a) Zero and span tests of Thermo Ozone analyzer during 2 Dec 2011 and (b) the correlation between the ozone observations by two ozone analyzers (Teledyne M400E and TECO) using common inlet system during 11-14 March 2011.

An example of zero and span tests performed during the thesis work are shown in the Figure 2.2. The sample mode of the instrument, that is before zero mode is also shown for clarity. In addition to the zero and span tests of the individual instruments, inter-comparison of two ozone analyzers are also made by running them side by side and using a common inlet system. Both the instruments are in strong positive correlation ($r^2 = 0.99$) with each other (Figure 2.2 b), for ozone observations.

### 2.2. Measurement of Carbon Monoxide (CO)

The first measurement of atmospheric carbon monoxide (CO) was made using spectroscopic method [Migotte and Neven, 1952]. It has also been measured using
mercuric oxidation reduction technique \cite{Robbins1968, Seiler1970}. Solar spectroscopic methods were used to evaluate trends in column CO abundance \cite{Rinsland1985, Zander1989}. CO has been also determined using tunable diode laser absorption \cite{Ku1975, Sachse1987, Fried1992}.

Surface CO measurements have been popularly conducted using a Gas Filter Correlation (GFC), non-dispersive infrared absorption (NDIR) techniques \cite{Parrish1990, Naja1997} due to its ease of operation. In the present work, a GFC based CO analyzer operating on the principle of Non Dispersive Infrared Technique (NDIR) employed from Thermo Electron Corporation (TECO Model 48i) has been used to measure CO.
2.2.1. Operating Principle

A simplified layout of the instrument components is shown in the Figure 2.3.

Figure 2.3: A simplified block diagram of carbon monoxide analyzer showing the working principle and different components of the system.

This instrument operates on the principle that carbon monoxide (CO) absorbs IR radiation at a wavelength of 4.6 µm. In this method, gas concentration is determined by measuring the absorption of Infrared (IR) radiation. The intensity of IR light that reaches the detector is inversely related to the concentration of target gas in the sample chamber. When the concentration in the chamber is zero, the detector will receive the full light intensity. As the concentration increases, the intensity of IR light striking the detector decreases. Beer’s Law describes the exact relationship between IR light intensity and gas concentration. The sample flow rate is 1 litre per...
minute and the analyzer has a lower detectable limit of 40 ppbv. This can operate over a temperature range of 0-45 °C. The zero drift of the analyzer is less than 0.1 ppmv and the span drift is ±1%. The response time of the analyzer is about 60 seconds. The precision of this instrument is about 1 ppbv.

The sample is drawn into the CO instrument through the sample bulkhead, which then flows through the optical bench. Radiation from an infrared source is chopped and then passed through a Gas Filter Correlation wheel (GFC) alternating between CO and N₂. The infrared radiation exits the optical bench and falls on the infrared detector. The CO gas filter produces a reference beam which cannot be further attenuated by CO in the sample cell. The N₂ side of the filter wheel is transparent to the IR radiation and thus produces a measurement beam which can be absorbed by CO in the cell. The IR signal from the source is usually chopped or modulated so that thermal background signals can be offset from the desired signal. The radiation then passes through a narrow band pass filter and enters the optical bench, where absorption by the sample gas occurs. This filter eliminates all light except the wavelength that the selected gas molecule can absorb. Other gas molecules do not absorb light at this wavelength (4.6 µm) and do not affect the amount of light reaching the detector, therefore, GFC responds specifically to CO.

Online measurement of CO using IR absorption (NDIR) method is a well-known technique and has been widely used. More details on this analyzer and calibration are available in previously published literature [Dickerson and Delany, 1988; Poulida et al., 1991; Naja, 1997].
2.2.2. Calibration

Calibration requires zero air that is free of contaminants which causes a detectable response of the CO analyzer. Ambient air which has been scrubbed of CO can be used as a zero air source. Since, the CO instruments, has much higher zero drifts its zero check have been conducted every day. Span calibrations were also conducted periodically to check the response of the instrument and apply the required calibrations in the span coefficients.

A cylinder of CO containing an appropriate concentration of CO suitable for the selected operating range of the analyzer is necessary. Multipoint calibration is done by diluting the cylinder concentration of 100 ppm to different levels in the observational range (100 ppb, 200 ppb, 500 ppb) by mixing it to zero air from the zero air generator using a dynamic gas calibrator employed from Thermo (Thermo Electron, Model 146i). The total flow for span calibration is set to be 3000 standard cubic centimeters per minute (sccm), while the flow rate is adjusted depending on the diluted concentrations of CO. It should be noted that the total flow should be greater than the instrument’s total flow demand, to ensure that no ambient air is pulled into the manifold vent. The CO concentrations in the range between 100-800 ppb are used for span calibrations. Primary span gas cylinders from Linde, UK, and secondary span gases from Ultra-Pure Gases, India, are used for multipoint calibrations of CO and NO. This also ensures the linearity of these instruments.
2.3. Measurement of the Oxides of Nitrogen (NO\textsubscript{y})

Reactive nitrogen is generally introduced into the atmosphere as NO, which is readily converted into NO\textsubscript{2} during the daytime. NO\textsubscript{x} represents the sum of NO and NO\textsubscript{2} and play an important role in the production of ozone in the troposphere. Further, oxidation gives rise to several other reactive nitrogen compounds classified as NO\textsubscript{y} which includes NO, NO\textsubscript{2}, NO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5}, H\textsubscript{2}NO\textsubscript{2}, HNO\textsubscript{3}, PAN, organic nitrates, etc. [Brasseur et al., 1999c]. The measurements of individual NO\textsubscript{y} species are very difficult due to their very low concentrations. The term NO\textsubscript{2} is defined as NO\textsubscript{y}-NO\textsubscript{x} [Pitts and Pitts, 2000]. The commonly used methods for the measurement of NO are chemiluminescence [Fontijn et al., 1970], two-photon laser-induced fluorescence (TP-LIF) technique [Bradshaw et al., 1985; Sandholm et al., 1990]. The detection of NO by chemiluminescence in turn enables the detection of other reactive nitrogen compounds, which can be converted to NO.

Several studies have been performed for the determination of NO\textsubscript{y} using molybdenum or carbon converters [Winer et al., 1974]. They found that, PAN was converted efficiently, while HNO\textsubscript{3} converted less efficiently but to a significant extent. This showed that measurements from such a converter are difficult to analyze, but they concluded that, it yields a measure of total oxides of nitrogen (NO\textsubscript{y}), rather than NO+NO\textsubscript{2}. Others such as Matthews et al., [1977] performed similar study for stainless steel converter with significant conversion of HCN and incomplete conversion of NH\textsubscript{3}. Kley and his co-workers [Kley et al., 1981] used the photolytic technique which has a greater specificity for NO\textsubscript{2} conversion. A comparison of photolytic technique with catalytic conversion technique has been made in a ground based study by Fehsenfeld et al., 1987, in which he found the
photolytic technique to be subject to significant interferences such as from PAN. For NO\textsubscript{y} measurement, it is required that all reactive nitrogen compounds be converted to NO, but not other nitrogen-containing species (e.g. NH\textsubscript{3}, N\textsubscript{2}O, HCN). The air sample containing NO and other oxides of nitrogen is passed over a catalyst (such as CO or H\textsubscript{2}), which converts all other oxides of nitrogen into NO and the resulting measurement is taken as the total oxides of nitrogen (NO\textsubscript{y}).

The most commonly used converters for the measurement for NO\textsubscript{y} are Molybdenum (Mo) and Gold (Au) converters. The Mo converter found applications in commercial instruments [Dickerson, 1984], to measure total reactive nitrogen in the free troposphere. The use of gold catalyst for the measurement of NO\textsubscript{y} was introduced by Bollinger et al., [1983]. These two converters are also compared and found that two gave similar estimates of NO\textsubscript{y} in ambient air over a wide range of mixing ratios [Fehsenfeld et al., 1987]. The details of NO\textsubscript{y} measurement by chemiluminescent method using Mo converter is described below.

### 2.3.1. Operating Principle

The NO\textsubscript{y} analyzer (Thermo Electron Corporation, USA (Model 42i)) used in the present study, works on the principle of chemiluminescence. Chemiluminescence is basically the emission of electromagnetic radiation after certain chemical reactions with intensity of the radiation being directly proportional to the mass flow rate [Heard, 2006]. Chemiluminescence is a widely used technique for the measurements of nitrogen oxides and also has been used in earlier studies [e.g. Ridley and Howlett, 1974; Dickerson, 1984].
Figure 2.4 shows a simplified layout of the NO\textsubscript{y} analyzer. The NO\textsubscript{y} analyzer is based on the chemiluminescence reaction of nitric oxide (NO) and ozone which produces a characteristic luminescence with intensity linearly proportional to the NO concentration. The sample flow rate is about 1 litre per minute and the analyzer has a lower detectable limit of 50 pptv. This can operate over a temperature range of 5-40 °C. The zero drift of the analyzer is very small (few pptv) and the span drift is ±1%. The response time of the analyzer is 300 seconds. The uncertainty in such NO\textsubscript{y} instruments varies from ±10% to ±20% [Williams et al., 1998]. Sample flows through the sample bulkhead which passes once directly to the ozonator (measuring NO) and alternatively through the Molybdenum (Mo) converter (measuring NO\textsubscript{y}). To minimize the loss of NO\textsubscript{y} prior to conversion and measurement, an external converter (Mo) module is used, that limits the sample transport time.

*Figure 2.4: A simplified block diagram of trace level nitrogen oxide analyzer showing the working principle and other important parts of the system.*
A bypass pump is used to rapidly draw the sample from the converter module, for both NO and NO\textsubscript{y} channels. First, when sample passes directly, bypassing the pump, ‘NO’ enters and simultaneously through the dry air port, dry air enters the ozonator, where it reacts to produce ozone. Fundamental to the principle of measurement of reactive nitrogen compounds is the chemiluminescent reaction of NO and O\textsubscript{3};

\[
NO + O_3 \rightarrow NO_2^* + O_2 \quad (2.4)
\]

Infrared light emissions occur when electronically excited NO\textsubscript{2} molecules decay to lower energy states.

\[
NO_2^* \rightarrow NO_2 + hv \quad (\lambda \text{ centred at 1200nm}) \quad (2.5)
\]

\[
NO_2^* + M \rightarrow NO_2 + M \quad (2.6)
\]

The transition of excited NO\textsubscript{2}* molecule to fundamental state gives luminous radiation in a spectrum covering red to infrareds region (\(\lambda = 580\text{-}2800\) nm). The temperature dependence of the chemiluminescence is due to the temperature dependence of NO\textsubscript{2}* production reaction. NO\textsubscript{y} is measured by converting it into NO by an external Mo converter [Williams et al., 1998; Wang et al., 2001].

When the sample passes through the Mo converter, heated to about 325 °C, all the NO\textsubscript{y} compounds are converted to NO. For example:

\[
3NO_2 + Mo \rightarrow 3NO + MoO_3 \quad (2.7)
\]

This externally used Mo converter is widely used due to low cost, sensitive detection and ease of operation [Xu et al., 2012]. The molybdenum converters are found to have higher sensitivity and higher conversion efficiency [Winer et al., 1974; Pitts and Pitts, 2000; Xu et al., 2012], however, some of the NO\textsubscript{y} species, in
particular HNO$_3$, were shown to suffer from incomplete conversion. Once this NO$_y$ is converted to NO these are measured again by the same principle. A photomultiplier tube (PMT) detects the luminescence generated following the reaction of NO with ozone. Further details on converter and technique can be seen in Steinbacher et al., [2007] and Heard [2006] and references therein.

2.3.2. Calibration

Calibration is normally done using first a zero gas and then using a span gas diluted from a span gas cylinder. The averaging time, in this case is taken to be 300 seconds. Dilution is done by mixing of known concentrations of span gas with zero air using a dynamic gas calibrator. A calibration cylinder of 1 ppm, NO flow of 10 sccm, and a total flow of 10,000 sccm, allows generation of span concentration of 1 ppb. Primary span gas cylinders from Linde, UK, and secondary span gases from Ultra-Pure Gases, India, are used for multipoint calibrations of CO and NO. This also ensures the linearity of these instruments.

2.4. Measurement of Hydrocarbons

The atmospheric hydrocarbons have been measured mainly using a Gas Chromatograph (GC) in conjunction with a Flame-Ionization Detector (FID) [Rudolph and Johnen, 1990; Parrish et al., 1992; Legreid et al., 2008; Honrath et al., 2008; Russo et al., 2010] or using a Mass Spectrometer (MS) [Wisthaler et al., 2002; de Gouw et al., 2003; Rinne et al., 2005; Jobson et al., 2010]. The short-lived and long-lived species that are of interest in atmospheric research, has led to the
development of many chromatographic techniques. Some atmospheric species such as organic acids, peroxides and aldehydes are measured using high performance liquid chromatography (HPLC) while the majority of organic species are analysed using gas chromatography (GC). The term chromatography applies to the separation technique in which separation of compounds is based upon the partition or distribution of analytes between two phases. One of these phases is stationary phase and the other is a mobile phase. When stationary phase is solid and mobile phase is gas, it is called ‘gas-chromatography (GC)’.

The main component of the gas-chromatograph is the column in which separation of the components takes place. Gas Chromatography requires a supply of carrier gas of sufficient pressure to achieve the desired separation. Carrier gas should be dry, inert and free of oxygen to prevent degradation of the column. The most common carrier gas used in GC is nitrogen, hydrogen and helium. Here, Helium (He) is used as a carrier gas for the measurement of hydrocarbons. The highest separation efficiencies are achieved using hydrogen gas, however, the choice of carrier gas is usually helium, due to more safety in handling and in-column hydrogenation of some unstable species associated with hydrogen. Various detectors can be coupled with GC depending upon the requirement. Flame Ionization Detector (FID) is one of the commonly used detectors for hydrocarbons.

2.4.1. Measurements of CH\textsubscript{4} and CO using GC

Air samples are analyzed for CH\textsubscript{4} and CO using the gas-chromatograph coupled with a Flame Ionization Detector (FID) (Thermo Trace Gas Ultra). Measurements of CO are made by converting it into CH\textsubscript{4} using a Ni catalyst heated to about 325 °C.
This conversion unit is also known as methanizer, and kept after column. A molecular sieve 13x, packed with a SS column of length 4m is used for the separation of CH₄ and CO. Figure 2.5 shows a schematic layout of the system.

![Schematic diagram of Gas Chromatograph.](image)

**Figure 2.5:** Schematic diagram of Gas Chromatograph.

Air samples were collected in pre-evacuated glass bottles of about 600 ml and were analyzed at PRL, Ahmedabad. Air samples were introduced into a sample loop of volume ~3 ml and subsequently injected into the GC column by eight port switching valve. Helium (He) gas was used as carrier gas, with flow rate of 35 ml/minute. The column temperature was kept constant at 75 °C. After the column, the separated gas sample passes through the methanizer with adequate supply of H₂, and CO is catalytically converted into CH₄ by the following reaction:
Calibrations of CH$_4$ and CO were performed by primary and secondary standards. High purity inter-gas cylinders obtained from NIST, USA for CH$_4$ (1.938 ppmv) and Linde, UK for CO (1150 ppbv) were used. A secondary standard was prepared at PRL which was also analysed at regular intervals during the sample analysis period.

A typical chromatogram of CH$_4$ and CO analyses is shown in Figure 2.6. The flow rates used for the flame gases like H$_2$ and zero air are 30 ml/min and 300 ml/min respectively. The bigger peak around 2.4 min is the CH$_4$ peak and the last smaller peak is the CO peak.

![Figure 2.6: A typical chromatogram, showing separation of CH$_4$ and CO.](image)
2.4.2. Measurement of Light (C₂-C₅) NMHCs using GC

Air samples were analyzed for light NMHCs using another GC (Hewlett-Packard 5890 series II) with a FID. The column is a 50m×0.32m i.d.; and a porous layer open tubular (PLOT) column of KCl/Al₂O₃ stationary phase is used. Here, Helium is used as a carrier gas with a flow rate of 8 ml/minute, while H₂ and zero-air is used as flame gas with flow rates of 30 and 300 ml/minute respectively. It is necessary to pre-concentrate the samples before the analysis, due to trace quantities of NMHCs in air samples. Air samples of ~1.5 L are preconcentrated using cryo-trapping procedure.

A simple method of pre-concentration is to place a sampling loop directly into the liquid nitrogen. The air to be analyzed is drawn through a so-called cold trap, consisting of a 1/8’’ stainless steel loop (packed with 75-100 micron size glass beads) submerged in liquid nitrogen. Since, the pre-concentration is done at such low temperatures; the majority of water vapor in the sample must be removed prior to analysis in order to stop blockage of lines with ice. The adsorbed NMHCs are thermally desorbed by submerging the loop into boiling water for the re-volatilization of hydrocarbons. The sample is then introduced into the column by flushing with helium gas through the loop using six port, dual-position-actuated valves (Valco Instruments, Inc.), which perform the gas line switching necessary for these pre-concentration steps. The column oven temperature was increased from 0 °C to 200 °C during the analysis, to separate the gases (Figure 2.7).
Figure 2.7: The oven temperature programming plot and how it varies with time is shown.

The temperature varies in step wise as shown in Figure 2.7. For a temperature of 0°C, there is a 3 minute hold, then for 40°C, there is 4 minute hold, when the temperature reached 110°C, there is 0 minute hold or no hold, after that, the temperature rises immediately to 200°C for 10 minutes.

Likewise, the system can resolve 9 identified light NMHC species. Identification of NMHCs was made by comparison with reference gas mixtures. Regular analyses of reference mixtures have also been performed to check the stability of the system. This GC-FID setup shows good stability for various analyzed NMHC species. Ultrahigh purity zero-air is used for dilution of calibration standard. Calibration mixture from Intergas (International Gases & Chemicals), UK traceable to National Physical Laboratory (NPL), UK, is used.
2.5. Observations of Meteorological Parameters

The standard meteorological parameters are measured continuously using Automatic Weather Station (AWS) obtained from Campbell Scientific Inc., Canada, Dynalab and Indian Meteorological Department (IMD), India. The observed meteorological parameters include air temperature, relative humidity, pressure, solar radiation, wind speed, wind direction and rainfall. Air temperature is measured using a thermistor which consists of a thermally sensitive resistor exhibiting the changes in electrical resistance with a change in the temperature. This change in the resistance is measured by passing a small direct current through it and measuring the voltage drop produced. The humidity sensor is a dielectric condenser hygroscopic polymer. As the dielectric constant for water is around 80, a strong variation of capacitance is obtained with the variation in the atmospheric humidity content. The advantages of this type of sensor are good linearity, insensitivity to temperature variations, brief response time and long life. The sensor has a temporary lack of precision if condensation forms on its surface. Both the air temperature and relative humidity sensors are packaged into a sensor housing to shield the sensors from direct sunlight.

Atmospheric pressure is measured using a silicon capacitive pressure sensor. The change in the atmospheric pressure bends the silicon diaphragm which in turn changes the height of the vacuum gap in the sensor as well as the capacitance of the sensor. The change in capacitance is measured and converted into a pressure reading. The incoming solar radiation is measured by a silicon photovoltaic detector. It is measured by relating the incident irradiance to the temperature difference between a radiation receiver and a shielded thermal reference. The wind speed is measured using the wind anemometer consisting of three rotating cups attached to a
rotating shaft. The angular speed of the rotating shaft is converted into pulses by a photo-detector. The wind direction sensor incorporates a precision wire-wound potentiometer that exhibit a variation in the voltage with change in wind direction. The rainfall measurements are carried out using a tipping bucket rain gauge with an internal siphon that causes the rain to flow to the measurement mechanism at a steady rate, regardless of its intensity. This approach reduces the typical rain bucket errors and produces more accurate measurements of rainfall.

2.6. Satellite Data

The ground based observations are highly sparse particularly over the remote mountains and oceanic regions. The satellite observations with global coverage provide a rich source of data to minimize this scarcity and can therefore be used in conjunction with the ground-based observation to improve our knowledge of the atmospheric state. Like ground-based instruments, the satellites do not observe the trace gases and meteorological parameters directly but they are designed to measure the radiation that is either the reflected solar radiation or emitted by the Earth’s surface. The satellite observations probe the atmosphere using the ultraviolet, visible, infrared and microwave radiations.

The geographical coverage of the satellites depends upon the orbit and the orientation of the instrument with respect to the orbital plane. The satellites flying at low altitude (about 700 km) are called polar orbiting satellites while the satellites at very high altitudes (about 35000 km) are called geostationary satellites. This study uses the space-borne observations from a variety of sensors including MODIS and AIRS. The following sections provide a brief description of these space-borne sensors.
2.6.1. Moderate Resolution Imaging Spectroradiometer (MODIS)

The MODIS instrument aboard the Terra and Aqua satellites of NASA’s Earth observing system (EOS) has been designed to improve the understanding of global dynamics and processes occurring over the land, oceans and the lower atmosphere. The MODIS measures the spectral radiances in 36 channels spanning the wavelengths from 0.4 to 14.4 µm with two channels representing the spatial resolution of 250m, five representing 500 m and the rest 29 representing 1 Km. The MODIS scans the Earth’s surface and atmosphere from an altitude of about 705 Km with a scanning pattern of ±55° to achieve an overall swath width of 2330 Km. In the present work, MODIS fire count data aboard Aqua and Terra satellites (http://modis-land.gsfc.nasa.gov/fire.html) are used. The retrievals of MODIS fire locations at the spatial resolution of 1 Km are based on the radiance measurements in the middle (4 µm) and long-wave (11 µm) infrared regions [Kaufman et al., 1998]. The MODIS fire channels are sensitive to the temperatures reaching about 450 and 400 K respectively. Further details regarding the design concepts, components and the specifications (e.g. orbit, scan rate, size, etc.) of MODIS instrument can be seen at its website http://modis.gsfc.nasa.gov.

2.6.2. Atmospheric Infrared Sounder (AIRS)

The Atmospheric Infrared Sounder (AIRS) is a high resolution infrared spectrometer onboard Earth Observing System (EOS)-Aqua Platform. It has a field of view of 1.1° and covers the IR spectrum from 650 to 2675 cm⁻¹ (3.74-4.61 µm, 6.20-8.22 µm and 8.8-15.4 µm infrared wavelengths) in 2378 channels at a nominal spectral resolving power of 1200. The measurement of infrared by AIRS allows high resolution retrievals of water vapor profiles for infrared cloud fraction of up to 70%
[Susskind et al., 2003]. The horizontal resolution of AIRS retrievals is about 45 Km and the vertical resolution is 2 Km for the water vapor in the troposphere. The standard products of AIRS retrieval include cloud top temperatures and pressures, vertical profiles of temperature, water vapor etc. The validation of AIRS retrievals have been successfully made against a variety of in situ and aircraft observations [e.g. Gettelman et al., 2004; Divakarla et al., 2006]. The standard products used in this study are AIRS version-5 Level-2 products. In this study, we have used the water vapor mixing ratio (dry air) as a tracer of stratospheric intrusion, for the analysis (Chapter-4).

2.7. Back Air Trajectory Simulations using HYSPLIT
Air trajectories represent the path of the air parcels and are one of key tools extensively used to study atmospheric transport climatology [e.g. Harris and Kahl, 1994], the identification of source regions of pollutants [e.g. Tsuang et al., 2002], the source-receptor relationships [e.g. Fiebig et al., 2009] and the regional fate of air pollutants [e.g. de Foy et al., 2009]. In light of these widespread applications, several air trajectory models like Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT; http://ready.arl.noaa.gov/HYSPLIT.php) model, Global Meteorological System (GMET) [Naja et al., 2003a] model, Meteorological Data Explorer [METEX; Zeng et al., 2003] model and FLEXPART [Stohl et al., 2005] model have been extensively used to simulate the history of air parcels.

In the present study, the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/HYSPLIT_info.php) has been used to simulate 5 particle ten days back air trajectories of the air parcel. This model has been developed collaboratively by NOAA and Australia’s Bureau of
Meteorology and other institutions. HYSPLIT model can be driven by standard meteorological forecast fields available from regional or global models. Generally, the meteorological datasets (NCEP/NCAR reanalysis) available at the spatial resolution of 2.5° x 2.5° at every 6 hours are used to run the HYSPLIT model. While in the present study, GDAS (Global Data Assimilation System) meteorological fields available at higher resolution (1° x 1°) available at every three hours have been used. There are uncertainties in the calculations of these trajectories mainly arising from errors in input meteorological fields as well as from the numerical methods. In order to reduce these uncertainties, in the present work, an ensemble of trajectories (5-particles) has been generated as discussed elsewhere [Naja et al., 2003a; Kumar et al., 2010]. The difference between the start and end positions of a forward-backward trajectory combination could represent the numerical errors. A measure of the errors in trajectory calculations is the absolute spherical distance or relative spherical distance (RSD) between two positions of particles, which is about 5% [Naja et al., 2003a]. It has been shown that trajectory accuracy mainly depends on the spatial and temporal resolution of the meteorological data used. More details of the back-air trajectory simulations using HYSPLIT model and obtaining meteorological parameters along the trajectory can be seen elsewhere [Draxler and Rolph, 2012; Draxler et al., 2012].

2.8. NCEP/NCAR Reanalysis Datasets
The NCEP/NCAR reanalysis datasets are generated by assimilating the meteorological observations from wide range of platforms including the ground stations, ships, radiosonde, radars, aircraft and satellites into a state-of-the-art global data assimilation system [Kalnay et al., 1996; Kistler et al., 2001]. All the observations are quality controlled before assimilation and the data assimilation
system has been kept unchanged over the decades to reduce the effects of modeling changes on climate statistics. These datasets are freely available since 1948 with three temporal resolutions of 6 hour, daily and monthly from the website http://www.esrl.noaa.gov/. The NCEP/NCAR reanalysis datasets have been widely used over the decades by the atmospheric research community for providing input to several regional and global models, transport models and understanding various research problems of scientific interest. In this study, the NCEP/NCAR reanalysis U and V wind components have been used for evaluating the WRF model simulated U and V winds. These NCEP/NCAR wind components are available 4 times (00, 06, 12 and 18 GMT) daily at the spatial resolution of 2.5° and at 17 pressure levels between 1000 and 10 mb.

2.9. Weather Research and Forecasting (WRF) Model

This study uses the version 3.1.1 WRF-met model developed jointly at NOAA and some other research institutes (http://ruc.fsl.noaa.gov/wrf/WG11). The model contains several dynamical cores and allows the user to select between different physical parameterizations to represent the processes that cannot be resolved by the model [Grell et al., 2005]. The chemistry and meteorology components of WRF-Chem use same transport scheme, same horizontal and vertical grids, same time steps and the same physics schemes for the sub grid-scale transport. In addition, the WRF-Chem model may also include the feedbacks between the chemistry and meteorology.

In this study, the simulation domain is defined on the Mercator projection centered at 25° N and 80° E. The domain covers nearly entire South Asian region
with spatial resolution of 45 km and has 90 grid points in west-east and 85 grid points in north-south directions. More details of the WRF-chem model setup and its evaluations over the the South Asia can be seen in Kumar et al. [2012a] and Kumar et al. [2012b]. Here, we have used WRF meteorology to investigate the diurnal variability in vertical wind component (w) and seasonal variations in the boundary layer height at Nainital. WRF meteorology has also been used to calculate the potential vorticity (PV), a stratospheric intrusion tracer.