Trace gases over the Indian region

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Some of the main results related to atmospheric ozone, related trace gases and aerosols in India are reviewed in this paper. Variability in tropospheric ozone has been observed, while there are no observed changes in the stratospheric ozone. Surface measurements of these species are being carried out by various research groups. Even though pollution levels are higher, surface ozone rarely exceed 100 ppbv in India. Aerosols show large spatial and temporal variability. There is a need for detailed measurements of these trace gases covering different regions in India and vertical distributions in the troposphere. Satellite measurements of these constituents are needed to understand their long range transport.

Keywords: Trace gases, Ozone, Aerosols, Carbon dioxide, Methane, Nitrous oxide

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1 Introduction

The gaseous envelop surrounding the Earth is unique among the atmospheres of the planets of the solar system. It has a composition that supports life, maintains critical temperature and filters out biologically harmful solar ultraviolet radiation. This tenuous atmosphere contains N$_2$, O$_2$ and Ar as major constituents. However, there are many other gases, which are in low quantities (down to parts per trillion level), but play important roles in its chemistry and radiation budget. These are divided in two different levels of concentrations, viz minor constituents and trace gases as they are popularly known (Table 1). The major gases are very long lived gases having natural sources but the other categories of gases have natural and or man made (anthropogenic) sources.

The thermal budget and chemistry of the atmosphere depends highly on some of the key trace gases like water vapour, O$_3$, CO$_2$, CH$_4$, N$_2$O, CFCs and other gases affecting their concentrations directly or indirectly. The abundance of many of these gases are also being affected by emissions of various gases by man made processes related to industry, agriculture, biomass and fossil fuel combustion, etc. Large depletion of ozone in the atmosphere over the Polar Regions has been found to be due to Cl and Br containing CFCs, which are released from refrigeration, foam making and many other industries. It is also clear now that the earth’s climate is changing due to emissions of greenhouse gases like CO$_2$, CH$_4$, N$_2$O, CFCs, etc. This paper reviews the research work being carried out in India and highlights some of the key observations mainly related to atmospheric chemistry.

2 Atmospheric ozone

Ozone is the most important trace gas, which has been talked about ever since it was discovered in the atmosphere. It absorbs the deadly ultraviolet (200-300 nm) radiation coming from the Sun. It is also an important greenhouse gas. The total amount of ozone is least (about 250 DU) in the tropics, where it is produced most. But it is highest (400 - 460 DU) in the polar region, where it gets transported from the tropics and where photochemical losses are a minimum. The first chemical scheme based on anthropogenically released nitrogen compounds for the loss of ozone was given by Crutzen$^1$. He suggested that the N$_2$O released from the agricultural fields and NO-NO$_2$ from the exhaust of the aeroplanes could deplete ozone in the stratosphere. Later, Rowland and Molina$^2$ suggested that chlorofluorocarbons (CFCs) released from the ground could also deplete the thin layer of ozone in the atmosphere. Large depletion of ozone is observed in the polar regions especially over the South Pole, but there is no any kind of long term change observed over the tropical regions$^{3,5}$.

Vertical distribution of ozone is being measured by the India Meteorological Department (IMD) regularly, from three stations – Trivandrum, Pune and Delhi using balloon borne sensors. The total column is also being monitored by them at several stations including now at the Indian station at Antarctica using Dobson
instruments. These data have been used to study changes in ozone due to eclipse and volcanic eruptions and long-term changes\(^5,8\). An increasing trend of columnar ozone in the range of 0.7-2.3% per decade has been observed at Kodaikanal, Ahmedabad, Delhi and Srinagar from the Dobson data. However, a decreasing trend of about 1% per decade has been observed at Varanasi\(^7\). However, mixed trends are observed in the total columnar ozone as well as in the tropospheric ozone. Long-term changes in the vertical distribution of tropospheric ozone over Trivandrum, Pune and Delhi have been studied for the period 1972-2001 by Saraf and Beig\(^9\). They found no significant trends over Trivandrum but positive trends are found to occur in the lower troposphere over Pune and throughout the entire troposphere over Delhi. However, during the last decade, no significant trend is observed even over Delhi, a polluted city\(^9\). Climatological seasonal values of tropospheric ozone residual based on satellite data show higher levels over the Indo-Gangetic Plain (IGP) in all seasons\(^10\). Similar model results show higher levels of ozone and its precursors in the boundary region over the same IGP\(^11\).

Measurements of vertical distribution of ozone have also been made from Thumba using rocket borne optical sensors to study chemical and dynamical processes during 1970s-1980s by Physical Research Laboratory (PRL), Ahmedabad. These data have been used to study changes in the vertical distribution of ozone during day and night hours and during eclipse of 1980.

A large number of rocket flights have been made from Thumba for ozone profile measurements at different times of the day as well as night time period and during different seasons during 1979-1990. These data have been used to construct a reference ozone profile for the equatorial region. Even though the data sets are available for the altitude region of 10-70 km, at altitudes below about 20 km, these data are subject to large source of errors due to both-instrument as well as atmospheric scattering. Hence, rocket data are used from 20 km onward while the IMD balloon ozonesonde data are used below 20 km. Also, this reference profile is restricted to 60 km height, as the number of observations was limited above this height. The composite profile is shown in Fig. 1. Ozone concentration within 4-5 km from the ground is about

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**Table 1 — Minor constituents and trace gases in the Earth’s atmosphere related to atmospheric chemistry and radiation budget**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical Formula</th>
<th>Volume Mixing Ratio</th>
<th>Major Sources/ Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Minor Constituents</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water vapour</td>
<td>H(_2)O</td>
<td>10,000-2 ppmv(^*)</td>
<td>Variable</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO(_2)</td>
<td>360 ppmv</td>
<td>Combustion &amp; Biosphere</td>
</tr>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
<td>1.7 ppmv</td>
<td>Biogenic</td>
</tr>
<tr>
<td><strong>Trace Gases</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N(_2)O</td>
<td>310 ppbv(^*)</td>
<td>Biogenic &amp; Anthropogenic</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>10-200 ppbv</td>
<td>Anthropogenic &amp; Photochemical</td>
</tr>
<tr>
<td>Ozone</td>
<td>O(_3)</td>
<td>10 ppbv - 10 ppmv</td>
<td>Photochemical</td>
</tr>
<tr>
<td>Non-methane hydrocarbons</td>
<td>NMHCs</td>
<td>5-20 ppbv</td>
<td>Biogenic &amp; Anthropogenic</td>
</tr>
<tr>
<td>Halocarbons</td>
<td></td>
<td>1-600 pptv(^*)</td>
<td>Anthropogenic</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>SO(_2),</td>
<td>10 pptv - 1 ppbv</td>
<td>Photochemical, Volcanic &amp; Anthropogenic</td>
</tr>
</tbody>
</table>

\(^*\)ppmv: parts per million by volume; ppbv: parts per billion by volume and pptv: parts per trillion by volume
6 × 10^{11} \text{ mol cc}^{-1} \text{ corresponding to mixing ratio of 25-30 ppbv. Further higher the number density decreases and reach to a minimum value of about } 1 \times 10^{11} \text{ mol cc}^{-1} \text{ at around 12 km height. The peak of ozone concentration occurs around 26-28 km height with a value of about } 4 \times 10^{12} \text{ mol cc}^{-1} \text{. There is a continuous decrease above this peak. Above about 50 km and below about 20 km, there is large variability in ozone profile due to chemistry and dynamics\textsuperscript{12,13}. Higher ozone concentrations have been observed during night and during an eclipse above about 45 km height\textsuperscript{14}.}

These measurements were events or campaign based only. Recently, PRL has initiated balloon borne measurements of ozone being conducted fortnightly since June 2003 at Ahmedabad. The results show that in the boundary layer ozone is maximum during winter season (DLF) and minimum during rainy season (JJAS), while in the middle troposphere ozone is maximum during rainy season and minimum during post-monsoon season (ON). Peak ozone concentration in the stratosphere has been observed to be highest during rainy season (JJAS) and minimum during winter (DJF). Enhanced ozone mixing ratios in the upper troposphere have been observed due to intrusion of stratospheric air on a strong foggy day at Kanpur during a land campaign\textsuperscript{15} in December 2004.

### 3 Vertical distributions of trace gases

Vertical distributions of various trace gases related to ozone depletion (CFCs, etc.) and greenhouse warming (CH\textsubscript{4}, N\textsubscript{2}O, SF\textsubscript{6}, etc.) has been made from Hyderabad using cryogenic air sampling on high altitude balloons. The air samples collected were analysed for a host of trace gases using gas chromatographic techniques. A total of six balloon flights have been conducted since 1985. These profiles have been used to study effects of dynamics and chemistry and to estimate total Cl loading, ‘age of the air’ and changes in their abundances. These profiles (Figs 2 and 3) show clear effect of stronger upwelling in the tropical atmosphere\textsuperscript{16-19}.

### 4 Tropospheric ozone

About 90% of the atmospheric ozone is present in the stratosphere (16-50 km height region) and only about 10% resides in the troposphere (below 16 km). Despite this relatively small fraction, tropospheric ozone governs the chemistry of the atmosphere. Tropospheric ozone is a greenhouse gas and it is the precursor of highly reactive hydroxyl radical. Higher concentrations of ozone in the boundary layer have deleterious effects on biological life and vegetation. Ozone in the lower troposphere is mainly produced by photochemistry involving pollutants that are released from various industrial and other anthropogenic activities. Tropospheric ozone concentrations and growth rates exhibit large spatial and temporal variabilities. Importance of ozone in different atmospheric processes and its budget are given below in detail.

#### 4.1 Role in atmospheric chemistry

The earth’s troposphere acts like a chemical chamber, in which huge quantities of trace species are transformed from one form to another, where ozone
can be considered as the principal product of this reactor. Most of the OH radicals are produced by ozone in daytime by the following reactions:

\[
\text{O}_3 + h\nu \rightarrow \text{O}^1\text{D}) + \text{O}_2 \quad \ldots (1)
\]

\[
\text{O}^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \ldots (2)
\]

The photo-dissociation of ozone in the wavelength range 290-315 nm (UVB radiation) gives rise to the electronically excited O(1D), which further reacts with the water vapour to produce the most reactive radical (OH) in the atmosphere. The hydroxyl radical is the dominant oxidizing agent in the atmosphere and thus acts as a tropospheric detergent. Due to large solar flux and water vapour, OH concentrations are found to be higher in the tropics than in the mid- and higher latitudes.

Tropospheric ozone is a potential greenhouse gas and contributes to global warming by absorbing the terrestrial radiation at 9.6 µm. Each additional mole of ozone produced in the atmosphere is 1200-2000 times more effective in global warming than an additional CO₂ molecule and 22 and 217 times higher²⁰ compared to CH₄ and N₂O. Recent studies indicate that it can be the second largest contributor to net heating after CO₂. Further, observations over the tropical troposphere show substantial radiative forcing of 0.5-1.0 Wm⁻² and globally averaged radiative forcing of 0.1-0.4 Wm⁻² for most of the times of the year²¹.

Surface concentrations of O₃ at some places have increased by a factor of 5 since the beginning of the 20th century, corresponding to an increase of 1.6% per year and even higher (2.4%) since last few decades. Ozone concentrations are observed to be increasing at the rate of 1-2% in many parts of the globe in northern hemisphere²²,²³. However, in Canada and at South Pole, a decreasing trend in ozone concentration is observed for the time period of 1980-1993 at many observational sites²²,²⁴.

### 4.2 Impact on crop yields and human health

Elevated concentrations of ozone at ground level are known to cause adverse effects on the human health, ecosystems and materials. Due to its deleterious effects, photochemical air pollution is given a high priority in scientific investigations and environmental policies. High ozone concentrations are not confined to the urban environments, but are also spreading to the relatively cleaner areas in remote locations. Most of this pollution spreads are observed in the downwind side of the urban/industrial areas²⁵. Chameides et al.²⁶ have shown that elevated ozone in a developing country like China can significantly reduce the crop yield of winter wheat. Experiments under controlled conditions confirm that O₃ is a pollutant and is affecting the health of both human and plants.

#### 4.3 Budget of the tropospheric ozone and its precursors

##### 4.3.1 Ozone (O₃)

While ozone in the stratosphere is decreasing due to man-made CFCs and other halogen containing gases, ozone in the troposphere is observed to be increasing. The increasing concentrations of CO, CH₄, NMHCs and NOₓ from various sources are causing ozone production in the lower troposphere.

Since about 90% of the atmospheric ozone is present in the stratosphere, traditionally, it was assumed that tropospheric ozone is controlled by stratospheric-tropospheric exchange (STE) across the extratropical tropopause. This first analysis was based on the observed O₃ gradient with altitude and suggested a source at the tropopause and a sink at the surface. The in situ O₃ formation is catalyzed by nitrogen oxides which are often emitted simultaneously with hydrocarbons (RH) and carbon monoxide (CO), in particular by man made sources²⁷. In daytime, oxidation of CO, CH₄ and RH lead to ozone production or loss depending upon the critical concentration of NO. A simple example of ozone production by CO oxidation is as follows:

\[
\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2 \quad \ldots (3)
\]

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad \ldots (4)
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad \ldots (5)
\]

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \ldots (6)
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \ldots (7)
\]

\[
\text{Net} \quad \text{CO} + 2\text{O}_2 + h\nu \rightarrow \frac{2}{3} \text{CO}_2 + \text{O}_3 \quad \ldots (8)
\]

Similarly, oxidation of CH₄ and NMHCs leads to ozone production. The reaction mechanisms for the oxidation of these gases are more complex, and lead to production of many other trace gases including ozone precursors. However, if the levels of NOₓ are lower (< 20 pptv), loss of ozone may take place.

The budgets of the tropospheric ozone calculated in different models are given in Table 2. The large variability in the two main sources of ozone, viz. the
intrusion from the stratosphere and *in situ* photochemical production is due to poor understanding of the dynamical parameters like advection, enroute transformation of ozone and other short lived trace species, boundary layer process and also lack of knowledge of the budgets of ozone precursors.

Ozone precursors are the trace gases such as NO$_x$, CO, CH$_4$ and NMHCs, which are responsible for ozone formation through photochemical reactions as shown by set of reactions given by Eqs (3)-(7) and similar other sets. Ozone precursors have both anthropogenic as well as natural sources, though there are large uncertainties in their budgets. The main common anthropogenic sources for all these gases are fossil fuel combustion and biomass burning.

### 4.3.2 Nitrogen oxides (NO$_x$)

Nitrogen oxides (NO and NO$_2$) play a central role in photochemical production of ozone in the troposphere, as mentioned earlier. In the troposphere, NO$_x$ (NO + NO$_2$) can have both anthropogenic as well as natural sources, but the major contribution is from the anthropogenic sources. The dominant source of NO$_x$ to the atmosphere is fossil fuel combustion for energy production (Table 3). Other major sources are biomass burning, emission from soils and by lightning activity. Biomass burning constitutes an important anthropogenic NO$_x$ source in the tropics and sub tropics of America, Africa and South Asia. Due to larger population and higher economical growth rates, emission of these gases are increasing in Asia and more so in the central and South Asia$^{32}$. The largest contribution to the Asian countries is from China where increase in NO$_x$ growth rate$^5$ is found to be about 7% per year from 1990 to 1994. Large increase is also projected for India$^28$. The total emission of NO$_x$ in India is in the range of 3.4-4.6 Tg yr$^{-1}$ (Table 4). Due to scarce measurements in India further details are not available.

### 4.3.3 Carbon monoxide (CO)

The major surface sources of CO are biomass burning and fossil fuel combustion (Table 5). In addition to this, a significant amount of CO is produced through oxidation of methane and NMHCs. Anthropogenic contribution of atmospheric carbon monoxide$^5$ is about 87%. Reaction with OH accounts for 80-90% loss of CO in troposphere and the remaining part is lost in the stratosphere and/or via biological processes in soil. Long term trends in CO are uncertain. The total emission of CO in India is about 63-69 Tg yr$^{-1}$ (Table 3).

### 4.3.4 Methane (CH$_4$) and non-methane hydrocarbons (NMHCs)

Atmospheric CH$_4$ has about 50% of anthropogenic sources (Table 6). The burden of the tropospheric methane continues to increase, but the rate of growth of this burden is declining. Recent measurements indicate a growth rate of 3-4 ppb (parts per billion) per year in the 1996-1997 period$^{33}$. Measurements of methane flux from paddy fields have been made in India by various groups. Measurements made from paddy fields in South India show large variability during the cropping seasons, type and amount of fertilizers used and duration and amount of water used$^{34,35}$. Methane flux measurements from India have helped to understand

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**Table 2 — Budgets of various processes contributing to the tropospheric ozone as given in some of the global chemistry-transport models (Tg O$_3$ yr$^{-1}$)**

<table>
<thead>
<tr>
<th>Source / Sink</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratospheric input</td>
<td>400-1400</td>
</tr>
<tr>
<td>Net Photochemistry</td>
<td>800-500</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>500-1200</td>
</tr>
</tbody>
</table>

**Table 3 — Contribution of various emission sources of NO$_x$ and SO$_2$ in India (in %)**

<table>
<thead>
<tr>
<th>Sectors</th>
<th>NO$_x$</th>
<th>SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power generation</td>
<td>27.9</td>
<td>46.1</td>
</tr>
<tr>
<td>Transport</td>
<td>32.0</td>
<td>7.8</td>
</tr>
<tr>
<td>Industry</td>
<td>19.2</td>
<td>34.4</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>18.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Other sectors</td>
<td>1.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Non-energy sources</td>
<td>0.3</td>
<td>2.7</td>
</tr>
</tbody>
</table>

**Table 4 — Total emission of various trace gases in India (Tg year$^{-1}$)**

<table>
<thead>
<tr>
<th>Sectors</th>
<th>NO$_x$</th>
<th>CO</th>
<th>CH$_4$</th>
<th>NMHCs</th>
<th>SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power generation</td>
<td>4.6</td>
<td>63.3</td>
<td>32.8</td>
<td>10.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Transport</td>
<td>(Ref. 28)</td>
<td>(Ref. 28)</td>
<td>(Ref. 28)</td>
<td>(Ref. 28)</td>
<td>(Ref. 28)</td>
</tr>
<tr>
<td>Industry</td>
<td>3.5</td>
<td>69.4</td>
<td>18.1</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>(Ref. 30)</td>
<td>(Ref. 31)</td>
<td>(Ref. 29)</td>
<td>(Ref. 30)</td>
<td></td>
</tr>
<tr>
<td>Other sectors</td>
<td>1.9</td>
<td>3.8</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-energy sources</td>
<td>0.3</td>
<td>2.7</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5 — Contribution of various emission sources of CO in India (in Tg yr$^{-1}$)**

<table>
<thead>
<tr>
<th>Sources</th>
<th>Total CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-fuel</td>
<td>34.2</td>
</tr>
<tr>
<td>Coal sector</td>
<td>16.8</td>
</tr>
<tr>
<td>Crop residues</td>
<td>12.0</td>
</tr>
<tr>
<td>Fossil fuel</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Table 6 — Estimates of the global methane budget 
[in Tg(CH\textsubscript{4} yr\textsuperscript{-1})]

<table>
<thead>
<tr>
<th>Sources</th>
<th>Emissions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands</td>
<td>120-230</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>75-110</td>
<td></td>
</tr>
<tr>
<td>Ruminants</td>
<td>80-115</td>
<td></td>
</tr>
<tr>
<td>Rice Agriculture</td>
<td>50-80</td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>40-50</td>
<td></td>
</tr>
<tr>
<td>Landfills</td>
<td>40-70</td>
<td></td>
</tr>
<tr>
<td>Total Source</td>
<td>~ 600</td>
<td></td>
</tr>
<tr>
<td>Loss</td>
<td>450-510</td>
<td></td>
</tr>
<tr>
<td>OH reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soils and Stratospheric loss</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

their large range of variability and to make total budget estimates from the Indian region. The campaign of methane flux measurements conducted by NPL, Delhi has been useful to estimate the total emission from the Indian paddy fields\textsuperscript{36}. There is a large difference in the estimation of total emission of CH\textsubscript{4} in India (Table 3).

Most of the NMHCs are emitted from the natural sources and vegetation is the major source among them. The relative contribution of natural sources (vegetation and oceans) and anthropogenic sources (fossil fuel combustion and biomass burning) are about 80% and 20%, respectively\textsuperscript{5}. A global source inventory\textsuperscript{37} of NMHCs included contribution from isoprene (44%), mono-tarpenes (11%) and other reactive (22.5%) and less reactive (22.5%) NMHCs. The total emission of NMHCs from India is about 10.8Tg year\textsuperscript{-1} (Table 3). Despite having large ozone production efficiency, detailed measurements of NMHCs in India are not available.

4.3.5 Sulphur dioxide

About 20\% of the sulphate precursor emission is from natural sources (biogenic and volcanic), and 80\% is anthropogenic. Less than half of the SO\textsubscript{2} entering the atmosphere contributes to the sulphate production, the rest being removed by dry and wet depositions. Total emission of SO\textsubscript{2} from India is about 4.6-5.5 Tg yr\textsuperscript{-1} (Table 3). Power generation and industries are the two main emission sources (Table 4).

5 Observation of tropospheric ozone and related trace gases

Surface measurements of ozone are being monitored by IMD at many locations since a long time. However, no trend analysis exists for this data set. PRL has also been monitoring ozone and some of its precursors at several sites in India, representing since 1992. These data have been analyzed and some of the results are detailed below.

5.1 General meteorology over India

Figure 4 shows the average wind fields at 925 hPa from NCEP during different seasons. These plots show the general meteorology in winter, when north-east wind pattern dominates and in summer, when south-west wind pattern dominates over this region. Such changes in wind patterns are observed each year. The wind pattern changes dramatically from south-westerly to north-easterly after September, which continues till January-February with some dominance of northerly winds over the central and southern region. Wind pattern is north-westerly in early spring (March), which changes gradually to south-westerly in late spring (May) and it is dominated during the entire summer period (June, July and August).

5.2 Surface ozone and precursors

Measurements of surface ozone and its precursors are being made at Ahmedabad, Mt. Abu, Gadanki by Physical Research Laboratory (PRL). The site is situated at the western edge of the city. Ahmedabad is an urbanized city having numerous industries and a thermal power station. The monsoon season extends from late June to early September. Similar measurements are being made at Delhi and Darjeeling by National Physical Laboratory (NPL), Delhi and at Pune by Indian Institute for Tropical Meteorology (IITM), Pune. There are several other groups – Space Physics Laboratory (SPL) Trivandrum, Center for Earth Sciences, Trivandrum, Jawarharlal Nehru University, Delhi; S.K.University, Anantpur also, making such measurements. However this paper will be restricted to measurements at Delhi, Ahmedabad, Pune, Mt. Abu and Darjeeling only.

5.2.1 Diurnal variations in ozone and precursors

Average diurnal variations of ozone observed at Delhi, Ahmedabad and Pune are shown in Fig. 5. During the day, ozone concentration starts increasing gradually after sunrise, attains maximum value during noon time and then decreases. The day time increase in ozone concentration, which is a pronounced feature of an urban polluted site, is basically due to the photooxidation of the precursor gases such as CO, CH\textsubscript{4} and NMHCs in presence of sufficient amount of NO\textsubscript{x}. Being urban sites, NO concentrations at these sites are generally found to be well above the threshold level (about 10 pptv) for ozone production.
Boundary layer processes and meteorological parameters also play important roles in $O_3$ variabilities. After sunrise, boundary layer height increases gradually from 200-300 m to 1500-2000 m during noon hours, due to convective heating. During this period, air in the lower heights, which has low amounts of ozone, mixes with the air of higher heights, which is relatively rich in ozone. Ozone levels are observed to be low during night time.\(^{38-40}\)

Such a diurnal pattern in ozone is observed throughout the year, except during the cloudy-rainy days. Non-availability of sufficient solar radiation and washout of pollutants result in near absence of photochemical ozone production during this period. During monsoon months the diurnal amplitude of ozone is found to be small. The minimum ozone concentrations are observed during early morning hours, near the sunrise time.

It is very interesting to note that the diurnal variation is sharper at Delhi as compared to that at Ahmedabad. But at Pune, the afternoon net decrease is slowest of all the three sites. The noontime ozone is highest and nighttime is lowest at Delhi as compared to the other two sites. The production as well as loss
of ozone depends on NO\textsubscript{x} also. Delhi, which is a bigger city as compared to Ahmedabad and Pune, has higher level of NO\textsubscript{x}. On the contrary, Pune has the lowest NO\textsubscript{x} concentration. This makes afternoon decrease slower at Pune. Similarly, Gadanki and Thumba show lower afternoon decrease rates as compared to Ahmedabad\textsuperscript{41,42}.

Average diurnal variations of CO and NO\textsubscript{x} observed at Ahmedabad and Pune are shown in Fig. 6. Both, NO\textsubscript{x} and CO show buildup during morning (0700-0900 hrs IST) and late evening/night hours (1900-2400 hrs IST), which are different from the variations in ozone. The lowest values for both the species (NO\textsubscript{x}, 5-10 ppbv; CO, 100-200 ppbv) are observed during 1400-1700 hrs IST in all the months. In order to sustain high levels of ozone during noon period, large amounts of precursors (like CO, NO\textsubscript{x}, etc.) are needed. This leads to very low levels of these precursors during noon period. Diurnal amplitudes of NO\textsubscript{x} and CO during different months exhibit similar seasonal trends as that of ozone. Increase in the average levels of NO\textsubscript{x} and CO are observed during October. During winter months, higher levels of NO\textsubscript{x} and CO are observed to be more regular and intense due to frequent temperature inversions and lower boundary layer heights.

Higher levels of NO\textsubscript{x} and CO during morning and late evening hours at Ahmedabad are due to the combinations of anthropogenic emissions, boundary layer processes, chemistry as well as local surface wind patterns. During night hours, the boundary layer descends and remains low till early morning, thereby resisting the mixing of the anthropogenic emissions with the upper layer. During these hours of maximum concentrations of NO\textsubscript{x} and CO, anthropogenic emissions are also prominent due to rush hours. It is important to note that the major anthropogenic source for CO and NO\textsubscript{x} (mainly NO) is fossil fuel burning (combustion in motor vehicles). Where as during noon time the higher height of the boundary layer provides a larger mixing region and hence the pollutants get diluted. However, NO\textsubscript{x} observed at
Pune only shows pronounced morning peak. For the chemical loss of NO\textsubscript{x} (NO + NO\textsubscript{2}) during noon time, the major loss of NO is due to titration with O\textsubscript{3} and for NO\textsubscript{2}, photo-dissociation. The major chemical loss of CO is by reaction with OH radical during day time, producing ozone.

5.2.2 Seasonal variations in ozone and precursors

There is a very clear and systematic seasonal variation in the surface ozone concentration at all the three sites (Fig. 7). Higher ozone concentrations have been found during autumn/winter months and lowest concentrations are found during summer (which includes monsoon period).

During summer season, particularly in the monsoon period, minimum ozone levels are observed. During this period insufficient sunshine for photochemical ozone production and rain washout of the pollutants cause very low ozone levels. During July and August these sites experience about 500-800 mm rainfall.

Change in wind circulation over the Indian region, takes place during autumn, it becomes north-easterly from generally south-westerly during summer period. The north-easterly wind flow bring the air, rich in pollutants to the observational sites, causing higher levels of O\textsubscript{3} and its precursor gases. During June, July and August the wind pattern is mainly south-westerly, which brings cleaner air from the Arabian Sea and the Indian Ocean.

Similar to O\textsubscript{3}, NO\textsubscript{x} and CO attain higher levels during autumn/winter seasons, as they get transported through north-easterly wind flow from the polluted regions. Also in winter months, the pollutants emitted from various anthropogenic and natural sources are trapped in the boundary layer due to frequent temperature inversions, while in the summer months this polluted air mixes well with the free tropospheric air, causing dilution of the pollutants.

5.2.3 Variations of ozone at Mount Abu and Darjeeling

Measurements are made at a remote mountaintop called Guru Shikhar at Mt Abu (hereafter, only Mt Abu). This region comes under the southern end of Aravali range of mountains and is the highest in the entire western-central Indian region. The main town of Mt Abu (about 10 km from Guru Shikhar) is situated at a height of 1220 m. Nearest urban city (Ahmedabad) is about 200 km towards south.

Surface ozone measurements were carried out at Bose Institute, Darjeeling since 2004. It may represent the background value of the Darjeeling town. The nearest major town is Kolkata. During June-September period (rainy season) the sky is normally overcast. Dry periods are observed from November to May.

Average diurnal variations in ozone over Mt. Abu and Darjeeling are shown in Figs 8(a) and (b). The Mount Abu data show a dip around noon hours. The nighttime and early morning values are around 42-43 ppbv. The noon values are lower around 39-40 ppbv during 1100-1200 hrs IST. The day time maximum (~ 45 ppbv) ozone occurs around 4 pm. This is a typical mountain type of diurnal variation. There are mainly two processes, viz. mountain–valley induced wind system and chemical ozone loss in low NO environments, which generally explain lower ozone values during daytime at a high altitude site\textsuperscript{43}. Solar heating warms the air near the mountain surfaces and causes warm upslope wind after the sunrise. This induces the ozone loss by surface deposition during this period. Further details are given in Naja et al.\textsuperscript{44}
The Darjeeling data, on the contrary, show little diurnal variation and maintains rather large concentrations throughout the day. A low value of 34 ppbv is observed around 6 am. The day time maximum is around 42 ppbv and occurs in the late afternoon around 4 pm. This is a typical pattern of a semi-urban site. Further details are given in Singh et al.\textsuperscript{45} During daytime up slope winds blow, which enhance the vertical mixing. Whenever non-precipitating white clouds are passing through the inlet tube of analyzer, O\textsubscript{3} concentrations were observed to increase, suggesting that O\textsubscript{3} is being transported by clouds vertically. The ozone concentrations showed increasing behaviour during nighttime hours with a distinct preference for midnight. This may be attributed to cooling of mountain causing down slope flow, which draws more ozone rich air from aloft\textsuperscript{45}.

The monthly average ozone values are shown in Fig. 9 for both the sites. The Mount Abu data show 40-43 ppbv during January-May and July months. June and August values are low around 33 ppbv. These values increase in September onwards. Highest average ozone (56 ppbv) is obtained in October. All the four months show higher ozone values. These variations are due to changes in the wind pattern. The monsoon months (JJA) bring cleaner marine air and due to cloud cover, photochemical production may not occur. In September month the wind flows from south-west to north-east. It brings the continental polluted air over this site.

The Darjeeling data are again different. The highest ozone values (in the range of 50-65 ppbv) are observed in March-May months. The lowest of about 20 ppbv is observed in August. There is an increase from September and continue till January. These variations are again related to the wind patterns. The August is again the monsoon month.

### 6 Atmospheric aerosols

Atmospheric aerosols affect the radiation budget of the atmosphere. Some of the aerosols (e.g. sulphate aerosols) can scatter back the solar radiation and cool
the earth’s surface, thus nullifying the warming being caused by greenhouse gases to a certain extent. Some other types of aerosols (like black carbon) can absorb the solar radiation and warm the lower part of the atmosphere. Measurements of physical as well as chemical properties of aerosols are very important to understand changes in the radiation balance. Measurements of total atmospheric aerosols are being made by many groups in the country. The first vertical distributions of aerosols in India were made by PRL, measuring scattering of solar radiation using rocket sensors and later using balloon borne sensors$^{30,47}$. The IITM, Pune initiated measurements of vertical distribution of aerosols using a lidar at Pune$^{8,49}$. Ground based measurements of aerosol optical depth were initiated by SPL, Trivandrum$^{50,51}$. There are now a chain of stations in India for such measurements. Some of the measurements show increasing trend in aerosol column content$^{49}$. It is beyond the scope of this paper to review the enormous work related to atmospheric aerosols being carried out in India.

Measurements of chemical composition of aerosols were initiated at IITM, Pune by Khemani et al.$^{52}$ Now there are several research groups in India making such measurements. Table 7 shows average chemical composition of aerosols at Ahmedabad, Hyderabad, and Mumbai.

Long-term measurements carried out on the chemical composition of bulk-aerosols, collected from an urban site (Ahmedabad) of a semi-arid region in western India. The average total suspended particulates (TSP) are found to be about 125 μg m$^{-3}$. Concentrations of various species are found in the order of $\text{SO}_4^{2-} > \text{Ca}^{2+} > \text{Cl}^- > \text{NO}_3^- > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{2+}$ at Ahmedabad$^{53}$. The mineral dust particles (accounting for 60-80% of the total aerosol mass exhibit extensive reactivity with the acidic species ($\text{NO}_3^- + \text{SO}_4^{2-}$)$^{34}$. The TSP concentration ranging from 65 to 400 μg m$^{-3}$ (Average = 180 μg m$^{-3}$) were observed during December 2004 at Hissar a semi-urban site north of Delhi. Water-soluble species follow the mass abundances pattern as: $\text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+$. The abundances of carbonaceous species exhibit large variations; OC: 15-120 μg m$^{-3}$ and EC: 2-10 μg m$^{-3}$ with OC/EC ratios ranging from 5 to 18 (Average = 8.5$^{55}$).

At Hyderabad, the concentration of various constituents of total suspended particulates (TSP) followed the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+ > < \text{Na}^+ > \text{Mg}^{2+}$ indicating abundance of $\text{SO}_4$ and $\text{NO}_3$ aerosols. It is slightly different than that observed at Ahmedabad. The contribution of these aerosols may be due to oxidation of gases $\text{SO}_2$ and $\text{NO}_x$ which are emitted by vehicular and industrial sources in Hyderabad. It also revealed that $\text{Ca}$ and $\text{NH}_4$ act as countering agents for these anionic aerosol species at this site. The presence of ($\text{NH}_4$)$_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$ indicate the anthropogenic influence, while $\text{Ca}$ aerosols are contributed by re-suspension of soil dust (present as $\text{CaCO}_3$) which react with atmospheric $\text{SO}_2$ forming $\text{CaSO}_4$. One of the reasons why most of the Indian sites show alkaline nature of rain water is the presence of $\text{CaSO}_4$ in the atmosphere, which is removed by below cloud scavenging process during rain. Calcium acts as buffering agent against the acidity contributed by $\text{SO}_4$ aerosols$^{36}$. Mumbai, a coastal site, Kanpur in central India as well as other sites in India show different chemical compositions$^{57,58}$.

### 7 Summary and discussions

Atmospheric ozone and trace gases as well as aerosols play important roles in the chemistry and radiation budget. Emissions of many of these constituents are increasing due to rapid industrialization, agricultural practices and urbanization. These can lead to environmental and climatic changes. There have been some efforts in estimating budgets of $\text{NO}_x$, $\text{CO}$, $\text{CO}_2$, $\text{SO}_2$ and NMHC, but detailed measurements of emissions of these trace gases are lacking in India. Methane flux from paddy fields have been measured by many groups now, but the campaign in 1990s by NPL gave useful results$^{36}$.

The IMD is regularly monitoring vertical distribution of ozone as well as total columnar ozone at several sites in India. There is no evidence of stratospheric ozone change over the tropical region including that over India. However, mixed trends are

<table>
<thead>
<tr>
<th>Component</th>
<th>Ahmedabad</th>
<th>Hyderabad</th>
<th>Mumbai</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>1.98</td>
<td>4.0</td>
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</tr>
<tr>
<td>NO$^+_3$</td>
<td>1.69</td>
<td>25.3</td>
<td>6</td>
</tr>
<tr>
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<td>26.6</td>
<td>6.2</td>
</tr>
<tr>
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<td>2.8</td>
<td>2.2</td>
</tr>
<tr>
<td>NH$^+_4$</td>
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<td>10.1</td>
<td>--</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.58</td>
<td>3.9</td>
<td>8.9</td>
</tr>
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<td>6.2</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.29</td>
<td>1.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>
observed in the total columnar ozone as well as in the tropospheric ozone. Saraf and Beig\textsuperscript{9} found positive trends to occur in the lower troposphere over Pune and throughout the entire troposphere over Delhi. However, during the last decade, no significant trend is observed even over Delhi, a polluted city\textsuperscript{9}.

Surface measurements of ozone and some of its precursors are being measured at several sites in India but not very regularly. Except at some remote mountain sites like Mount Abu, daytime buildup of ozone has been observed due to higher levels of pollutants. However, in spite of higher levels of precursors, high levels of ozone, exceeding 80 ppbv, are rarely observed. Ozone concentration is highest during noon time, mainly due to photochemical production\textsuperscript{38-40}. Diurnal variations in NO\textsubscript{x} and CO are a manifestation of combined effects of local emissions, boundary layer processes, chemistry and local wind pattern, causing higher levels during morning and late evening hours. Recently distributions of light NMHCs, which are important precursors for tropospheric O\textsubscript{3} chemistry, have also been made at Ahmedabad and Mt. Abu. These also show strong diurnal and seasonal variations as observed\textsuperscript{59} in CO and NO\textsubscript{x}.

Monthly average surface ozone values observed at Delhi, Ahmedabad and Pune are listed in Table 8. Generally higher levels of ozone are observed in winter and spring months and lower during the monsoon period. Seasonally, maximum concentration of ozone is supported by similar variations in its precursor gases, such as CO, NO\textsubscript{x} and CH\textsubscript{4}. On the other hand, ozone shows different diurnal variation than observed in CO and NO\textsubscript{x}, exhibiting anti-correlation.

A comparison of ozone measured during 1954-55 with that during 1992-95 shows higher amplitude of diurnal variation as well as higher levels throughout the year. The approximate linear increase between these years is 0.5% per year\textsuperscript{23}.

A poor correlation of about 0.3 is found between ozone and NO\textsubscript{x} at Gadanki. Correlation between ozone and CO measured at Mt. Abu gives ozone production efficiency (slope) of about 0.13, which is similar to those of other studies over the Asian region. However, studies made over North America show higher slope value (about 0.3). Lower ozone production efficiency and lower correlations are indications of incomplete photochemical processes over the Asian region. It has been shown that biomass and fossil fuel burning emissions occur simultaneously over Asia unlike over North America and Europe or Africa\textsuperscript{60} and carbon to NO\textsubscript{x} emission ratio is much higher over India and China than over North America\textsuperscript{32}.

Measurements of surface level ozone and its precursors have also been made over the marine regions of the Indian Ocean, the Arabian Sea and the Bay of Bengal. Higher levels of ozone have been observed over the Arabian Sea and the Bay of Bengal especially during the winter season due to transport of ozone as well as its precursors from the surrounding continental regions. Also, the Bay of Bengal is found to be more polluted than the Arabian Sea due to transport from the Indo-Gangetic plain in winter\textsuperscript{26,61-63}. The ISRO GBP has conducted three major campaigns, two over the Indian continental region during 2004 and one over the marine regions surrounding India in 2006, to study levels and transport of trace gases and aerosols.

Table 8 — Average monthly surface ozone (ppbv) observed at Delhi, Ahmedabad and Pune [These values are taken from Jain et al.\textsuperscript{38}, Sahu et al.\textsuperscript{59}, and Beig et al.\textsuperscript{60}, respectively.]

<table>
<thead>
<tr>
<th>Months</th>
<th>Delhi</th>
<th>Ahmedabad</th>
<th>Pune</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>17.0</td>
<td>38.4</td>
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</tr>
<tr>
<td>Feb</td>
<td>22.7</td>
<td>43.2</td>
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<tr>
<td>Mar</td>
<td>29.7</td>
<td>40.8</td>
<td>52.6</td>
</tr>
<tr>
<td>Apr</td>
<td>34.0</td>
<td>25.5</td>
<td>40.9</td>
</tr>
<tr>
<td>May</td>
<td>37.0</td>
<td>16.0</td>
<td>24.6</td>
</tr>
<tr>
<td>Jun</td>
<td>27.4</td>
<td>13.2</td>
<td>20.7</td>
</tr>
<tr>
<td>Jul</td>
<td>17.7</td>
<td>16.8</td>
<td>16.5</td>
</tr>
<tr>
<td>Aug</td>
<td>15.4</td>
<td>19.0</td>
<td>13.7</td>
</tr>
<tr>
<td>Sep</td>
<td>17.5</td>
<td>17.9</td>
<td>18.3</td>
</tr>
<tr>
<td>Oct</td>
<td>24.6</td>
<td>26.0</td>
<td>24.0</td>
</tr>
<tr>
<td>Nov</td>
<td>23.2</td>
<td>30.5</td>
<td>26.3</td>
</tr>
<tr>
<td>Dec</td>
<td>20.0</td>
<td>28.0</td>
<td>34.3</td>
</tr>
</tbody>
</table>
ozone in the Asian region by the end of this century due to increased emissions of ozone precursor gases. More concentrated measurements are needed to delineate natural variations and changes due to anthropogenic sources over the Indian region. In particular, vertical distributions of these trace gases and aerosols are needed to study their impact on chemistry and climate. Simultaneous measurements of trace gases, aerosols, clouds and radiation will help to understand coupling between these parameters. Satellite measurements of these constituents are needed to understand their long range transport and transformation. There is also a need to enhance modeling activity to support the observations and to estimate their contributions in environmental and climatic changes.

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