Latest seasonal trend of aerosol, particulate matter and ozone in Delhi

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ABSTRACT. In this work, latest seasonal variation of aerosol, particulate matter and ozone in Delhi has been studied. Observations show that during winter, concentration of surface O3 is low and that of PM 2.5 and PM 10 is high. Aerosol size and aerosol content increases during winter. Decrease in surface ozone is explainable by gas phase and heterogeneous chemistry. An interesting feature is, along with surface ozone, total ozone also shows a low value during winter. This is a characteristic of ozone in Indo-Gangetic plain. Indo-Gangetic plain is covered by mild to heavy fog during most of the days in winter. It is possible that increase in size and content of aerosol and PM particles coupled with low temperature, low solar flux and high humidity is the cause of fog formation during winter in Indo-Gangetic plain.

Key words – Aerosol, Ozone, PM2.5 and PM10.

1. Introduction

National Green Tribunal has recently said “It is undisputed and unquestionable that air pollution in Delhi is getting worse with each passing day”. Air pollution is indeed a serious health problem in Delhi with levels of tiny particles that carry toxins and go deep inside lungs is 3-4 times above the safe standards. In winter, foul air coupled with fall in temperature, increases wheezing, chest constriction, shortness of breath, bronchitis and severe asthma. Surface ozone, a secondary pollutant, if not in right amount, can cause vegetation injury, visible injury, pulmonary damage, asthma attacks and hazardous episodes to environment (Prather et al., 2003; Molina and Molina, 2002). Stratospheric ozone has impact on radiative balance, global warming and climate change. Due to population growth and industrial expansion, the pollution level in Delhi has been increasing over the years. Beig et al. (2013) have studied pollution level of Delhi during Commonwealth game for only 20 days of October 2010. Earlier, Sharma et al. (2010), Ali et al. (2004) and Goyal and Sidharth (2003) have studied seasonal variation of some pollutants over Delhi. Sharma et al. (2010) measured mixing ratio of NO and NO2 in Delhi for different seasons. They reported that NO value was low (12.18 ppb) and NO2 value was high (10.70 ppb) during winter compared to other seasons. Ali et al. (2004) reported a summer value of SO2 over Delhi 25 μg/m3. SO2 values were also studied by Sharma et al. (2010) in Delhi for different seasons. They found SO2 values high (1.97 ppb) during winter compared to other seasons. Goyal and Sidharth (2003) also reported higher SO2 values during winter over Delhi. In this paper, we have presented the latest picture of seasonal behavior of aerosols, particulate matter and O3 in Delhi.

2. Experimental sites

The site is Delhi (28.38° N, 77.12° E) which is the capital city of India. Its population is ~14 million covering an area of ~1483 km². It is surrounded by four satellite towns, Faridabad, Gurgaon, Noida and Ghaziabad.
and is called National capital region. The whole region is highly polluted by a large number of vehicular traffic and small & big industries. A river, Jamuna, encompasses the eastern side of Delhi.

3. Measuring instruments

Aerosol characteristics have been measured by sun tracking sky radiometer. Surface ozone has been measured by electrochemical sonde and column ozone has been measured by Dobson spectrophotometer.

4. Results and discussion

4.1. Aerosol

The sources of aerosol are vehicle, industry, power plant, soot, soil, dust etc. Aerosol optical depth (AOD), a characteristic of aerosol has been reviewed for the Indian region by Moorthy et al. (2013) using the measured values since 1985. They report a long-term variation of AOD ~2.3-4% per decade. India Meteorological Department has measured aerosol optical depth in Delhi in 7 wavelengths ranging from 340 nm to 1020 nm for the year 2012 (Soni et al., 2014). These are shown in Fig. 1(a). A decrease in AOD with an increase in wavelength is seen. When wavelength dependence of AOD is determined using the following equation:

$$AOD \propto \lambda^{-n}$$

(1)

The value of $n$ comes to 1.2. The profile calculated with $n = 1.2$ is also shown in Fig. 1(a). There is good match between the observed and calculated AOD. According to Chung et al. (2005) a value of $n$ higher than 1 and close to 1.3 signifies that the aerosol is black carbon.

Fig. 1(b) shows the seasonal variation of AOD for 2012 in Delhi for wavelengths 870 and 1020 nm. The trend is the same for both the wavelengths, i.e., AOD is maximum during summer ~0.8 and minimum during winter ~0.4. This actually shows an increase in aerosol density during winter which will be clear from the following when AOD is further analyzed using Angstrom power law:

$$AOD(\lambda) = \beta \lambda^{-\alpha}$$

(2)
where, $\alpha$ and $\beta$ are Angstrom parameters commonly used to describe the columnar distribution of aerosols. The wavelength exponent, $\alpha$ describes the size parameter of aerosol and $\beta$ is directly proportional to the amount of aerosol particles along the ray path. Higher the value of $\alpha$ smaller is the aerosol particles size and vice versa (Angstrom, 1961). The aerosol optical depth values when plotted with respect to wavelength on a log-log scale, then the slope of the fitted line yields the wavelength exponent $\alpha$. Fig. 1(c) shows the plot of log (AOD) vs log ($\lambda$) for December. The value of $\alpha$ comes to -1.048. Fig. 1(d) shows the plot of log (AOD) vs log ($\lambda$) for June. The value of $\alpha$ comes to -0.208. The decrease in the value of $\alpha$ indicates that aerosol size has increased during winter. The value of $\beta$ during December is 2.692 and during June is 0.553. The increase in the value of $\beta$ indicates that aerosol content has increased during winter. It may be noted that the wavelength dependence of AOD ‘$n$’ obtained from (1) is different from that ‘$\alpha$’ obtained from (2). This is because in (2) size parameter is being assumed constant for all the wavelengths where as in (1) it is calculated from the best fit curve of the data.

4.2. PM$_{2.5}$ and PM$_{10}$

The tiny particles known as PM$_{2.5}$ and PM$_{10}$ (particulate matter of radius 2.5 and 10 μm) influence the global climate system through direct radiative forcing. An indirect effect results from the activation of cloud condensation nuclei. These particles originate from a variety of natural and anthropogenic sources and are the result of chemical conversion in gas phase, heterogeneous and multiphase reactions (Mikkoness et al., 2011; Rollins et al., 2012). Spindler et al. (2013) have done a long-term characterization study of PM$_{10}$, PM$_{2.5}$ and PM$_{1}$ at Mel-pitz using data from November 1992 to April 2012. Measurements of PM$_{2.5}$ and PM$_{10}$ were initiated by India Meteorology Department since 2011. Fig. 2 shows the values of PM$_{2.5}$ and PM$_{10}$ in Delhi from January 2012 to October 2013. Trend is the same for both the PMs, low during monsoon season (particles are washed away by rain) and high throughout the winter. Also PM$_{10}$ values are about 50% higher than PM$_{2.5}$.

4.3. Surface ozone

Surface ozone is a secondary pollutant produced after a series of reaction from primary pollutants.
Fig. 3(a) shows the monthly averaged values of surface ozone for Delhi from November 2008 to December 2013 in µg/m³. It is seen in this figure that during November to February, in all the block years, 2008-09, 2009-2010, 2011-12 and 2012-13 ozone values are low compared to other months. Using the data of all the years, average monthly values have been calculated. These are shown in Fig. 3(b). Ozone value appears to be low in December-January, ~40 µg/m³ compared to other seasons. Also there is an increasing long term trend ~0.16 µg/m³/month as seen from Fig. 3(a).

For the sake of comparison with other stations, monthly averaged values of O₃ at Delhi are shown for all the seasons in Fig. 3(c) in ppbv (1 ppbv = 2.14 μg/m³) along with those at Kolkata, Haldia, Ahmedabad, Pune and Trivandrun. It can be clearly seen from this figure that in comparison to Ahmedabad, Pune and Trivandrum, ozone concentration at Delhi, Kolkata and Haldia is low during winter. It is to be remembered that Delhi, Kolkata and Haldia are situated in Indo-Gangetic plain while Ahmedabad, Pune and Trivandrum are located outside this plain.

Indo-Gangetic plain remains engulfed by heavy to moderate fog during most of the days in winter. As a result solar radiation reaching the earth’s surface is very low during this period. Tropospheric ozone or surface ozone is produced by photochemical oxidation of CO, CH₄, NMHCs etc. in the presence of sufficient amount of NO. An example is as follows:

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{O}_3^P + \text{NO} \\
\text{O}_3^P + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

Fig. 4. A simplified reaction scheme

Fig. 5. Seasonal variation of total ozone in Delhi

Nitrogen oxides are mainly the limiting species for ozone production in the troposphere. A simple reaction scheme is shown in Fig. 4. During winter, the intensity of solar radiation is low. As a result, loss of NO₂ through photo-dissociation (NO₂ + hv → NO + O³P) is less and hence [O³P] decreases. When [O³P] decreases, O₃ production decreases and hence [O₃] decreases. As O₃ is low, the production of NO₂ through the reaction O₃ + NO is less and since, solar intensity is also low, the channel O₃ + hv → O¹D + O₂ followed by O¹D + H₂O → 2OH will be slow even though [H₂O] is high. Since [OH] is low, therefore, production of NO₂ through OH will be less which will further decrease [NO₂]. Since, however, the loss of NO₂ through the reaction NO₂ + hv → NO + O³P is less, NO₂ should build up. But this does not happen. The build-up of [NO₂] is possible either due to high value of its production rate or low value of loss rate. It can be seen from Fig. 4 that the production rate of NO₂ is unlikely to have increased during winter. It appears therefore that there should be additional loss processes of NO₂ other than shown above. Since solar radiation is low during winter, NO₂ is likely to be lost, as in nighttime or during eclipse, through the following reactions (Chakrabarty and Peshin, 2011) to form aqua HNO₃:

\[
\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_2 + \text{NO}_3 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} \\
\text{N}_2\text{O}_5 \text{ (g)} + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 \text{ (aq)}
\end{align*}
\]

This will further decrease [O₃].

4.4. Total ozone

Interestingly, not only surface ozone, total ozone also has similar behaviour, i.e., minimum during winter.
Total ozone is being measured in Delhi by Dobson spectrophotometer by India Meteorological Department since 1957. (It may be mentioned here that Delhi Dobson instrument is internationally calibrated and is the standard Dobson instrument for the Asian region). The average value of all the months from 1957 to 2012 has been calculated and has been shown in Fig. 5. Low value is clearly seen during winter.

In total ozone, 85% is in the stratosphere. Therefore low value of total ozone during winter is due to the low value of ozone in the stratosphere. Stratospheric ozone is produced through the following reactions:

\[ \text{O}_2 + h\nu \rightarrow \text{O}^1(\text{D}) + \text{O}^1(\text{D}) \quad \lambda < 2400 \text{ Å} \]

\[ \text{O}^1(\text{D}) + \text{M} \rightarrow \text{O}^3(\text{P}) + \text{M} \quad (\text{M} = \text{O}_2 \text{ and } \text{N}_2) \]

\[ \text{O}^3(\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

and lost through:

\[ \text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2 (\text{Jo}_3) \quad \lambda < 2950-3500, 4500-8000\text{Å} \]

Loss also takes place by catalytic reactions with NOx, HOx, ClOx. During winter, solar intensity is low as a result the production of ozone is less. This is one of the reasons for low value of total ozone during winter. Also, downward transport of stratospheric ozone through free troposphere to near ground level and then lost as tropospheric ozone is another possibility.

5. Conclusions

In this work, seasonal variation of aerosol, particulate matter and ozone in Delhi, a station situated in Indo-Gangetic plain has been studied. This plain is covered by light to heavy fog during most of the days in winter. During fog, solar radiation and temperature are low and H2O concentration is high near the surface of the earth. Observations show that during winter, surface concentration of O3 is low. This is due to the low density of [NO3] caused by non-availability/less-availability of solar radiation. The concentration of PM1.5 and PM10 is also high during winter. Aerosol size and aerosol content also increases during winter. Decrease in surface ozone is explainable by gas phase and heterogeneous chemistry. An interesting feature is, along with surface ozone, total ozone also shows a low value during winter. This is a characteristic of ozone in Indo-Gangetic plain. It is possible that increase in size and content of aerosol and PM particles coupled with low temperature, low solar flux and high humidity is the cause of fog formation during winter in Indo-Gangetic plain. However, certain features like low value of total ozone and surface ozone need 2-D model study and behavior of NO2 need to be examined by more measurements. Our study will help the authorities and the public to keep the air pollution level below the safe standard.

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