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

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सार – इस शोध पत्र में अभी हाल ही में दिल्ली में वायुविलयों के मौसमी परिवर्तन, पर्टिकुलेट मैटर और ओज़ोन के बारे में अध्ययन किया गया है। इस विषय में किए गए प्रेक्षणों से यह पता चला है कि शीत ऋतु के दौरान सतह O_3 की सांद्रता कम और $PM_{2.5}$ और PM_{10} अधिक है। सतह ओजोन में कमी को गैस अवस्था और हीट्रोजेनेस रसायन द्वारा समझाया गया है। सतह ओजोन कुल ओज़ोन की विशेषता सर्दियों के मौसम में कम मान भी दर्शाती है। भारतीय गांगेय मैदानी क्षेत्रों में ओजोन की यह विशेषता है। भारतीय गांगेय मैदानी क्षेत्र में सर्दियों के मौसम में अधिकांश दिनों में हल्के से भारी कोहरा छाता है। वायु विलय के आकार और कंटेंट में बढ़ोतरी और PM कण के साथ निम्न तापमान निम्न सौर प्रवाह और अधिक नमी भारतीय गांगेय मैदानी क्षेत्रों में सर्दियों के दौरान कोहरे के बनने की वजह से है।

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 O_3 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.

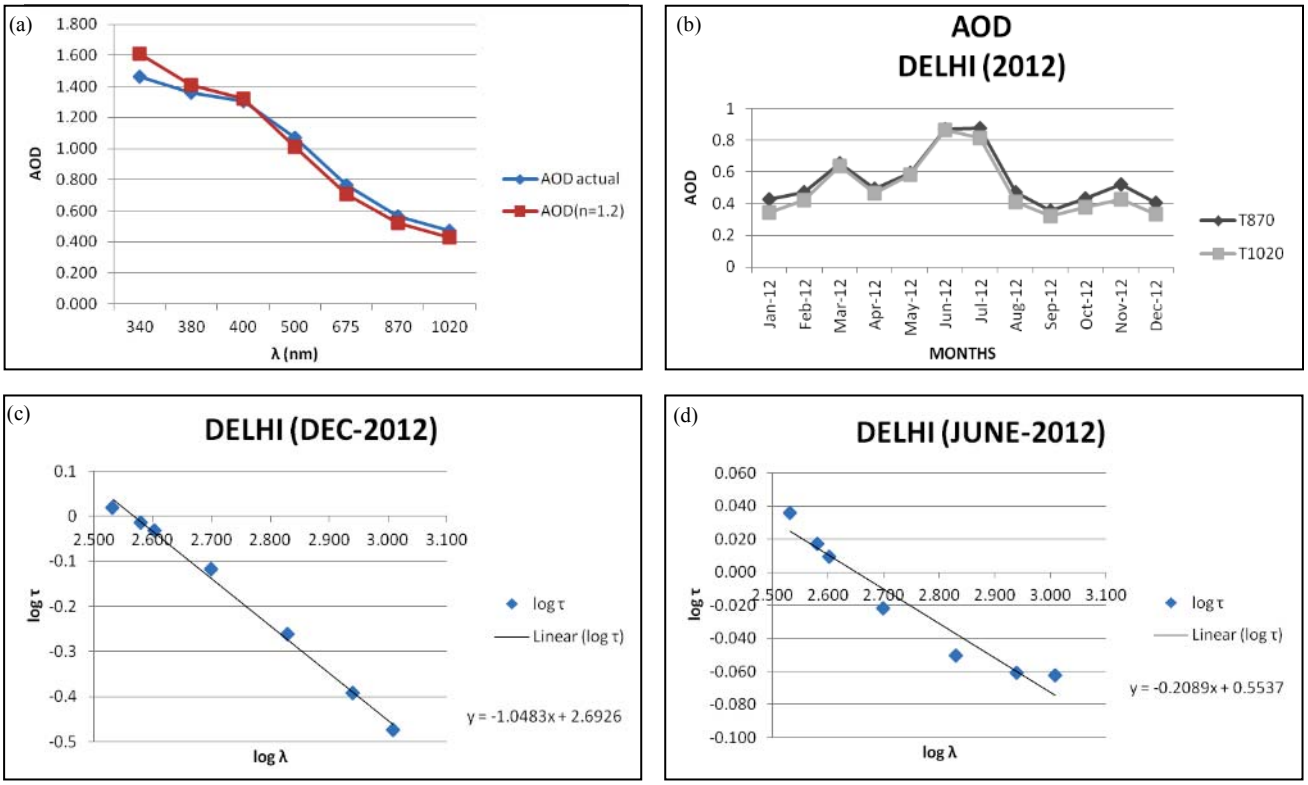
Key words – Aerosol, Ozone, $PM_{2.5}$ and PM_{10}.

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 toxin 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 NO_2 in Delhi for different seasons. They reported that NO value was low (12.18 ppb) and NO_2 value was high (10.70 ppb) during winter compared to other seasons. Ali *et al.* (2004) reported a summer value of SO_2 over Delhi 25 $\mu g/m^3$. SO_2 values were also studied by Sharma *et al*. (2010) in Delhi for different seasons. They found SO_2 values high (1.97 ppb) during winter compared to other seasons. Goyal and Sidharth (2003) also reported higher SO_2 values during winter over Delhi. In this paper, we have presented the latest picture of seasonal behavior of aerosols, particulate matter and O_3 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 km^2. It is surrounded by four satellite towns, Faridabad, Gurgaon, Noida and Ghaziabad



Figs. 1(a-d). (a) Measured and calculated AOD values for wavelengths 340 to 1020 nm (b) Seasonal variation of AOD for wavelengths 870 and 1020 nm (c) Plot of log (AOD) *vs* log (λ) at Delhi for December and (d) Plot of log (AOD) *vs* log (λ) at Delhi for June

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:

$$AOD \propto \lambda^{-n} \quad (1)$$

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:

$$AOD\ (\lambda) = \beta.\lambda^{-\alpha} \quad (2)$$

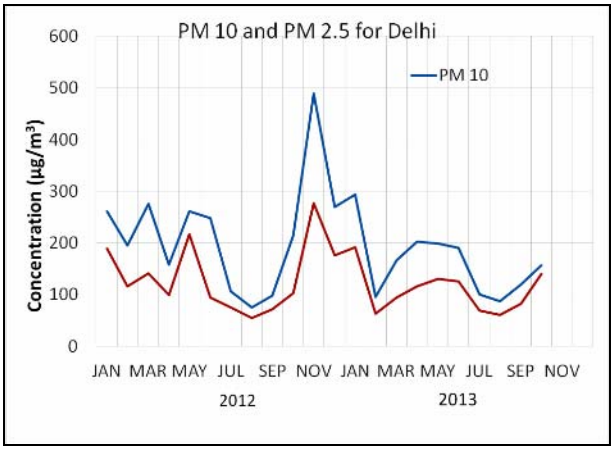
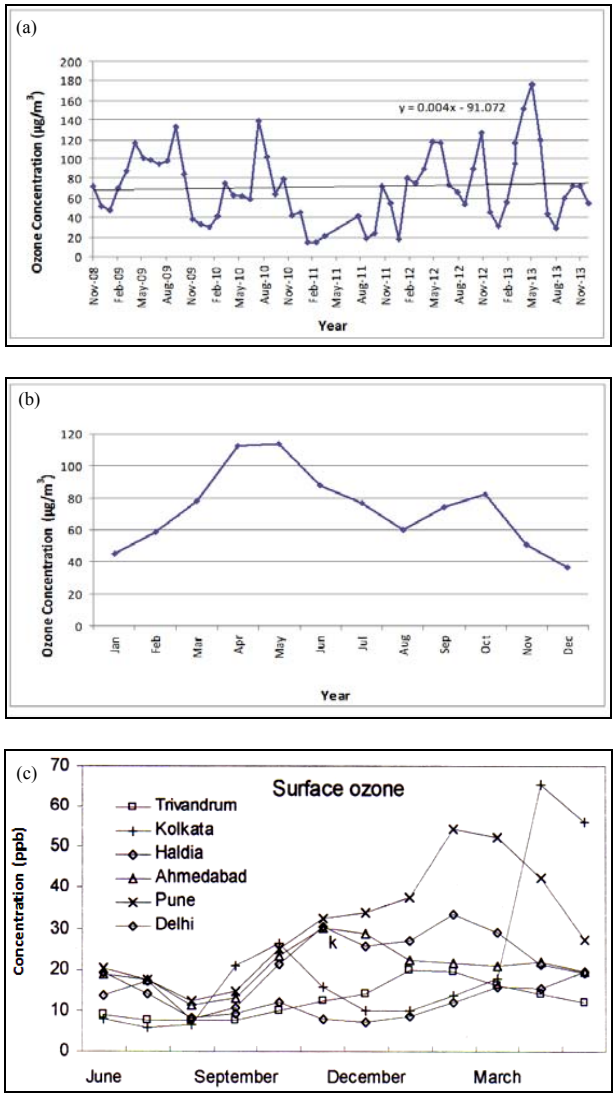


Fig. 2. Seasonal concentration of $PM_{2.5}$ and PM_{10} in Delhi

where, β and α are Angstrom parameters commonly used to describe the columnar distribution of aerosols. The wavelength exponent, α describes the size parameter of aerosol and β is directly proportional to the amount of aerosol particles along the ray path. Higher the value of α 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 α. Fig. 1(c) shows the plot of log (AOD) *vs* log (λ) for December. The value of α comes to -1.048. Fig. 1(d) shows the plot of log (AOD) *vs* log (λ) for June. The value of α comes to -0.208. The decrease in the value of α indicates that aerosol size has increased during winter. The value of β during December is 2.692 and during June is 0.553. The increase in the value of β 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 'α' 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 $PM_{2.5}$.



Figs. 3(a-c). (a) Monthly averaged surface ozone values for each month from November 2008 to December 2013 at Delhi, (b) Monthly averaged surface ozone values in Delhi at µg/m^3 and (c) Monthly averaged values of O_3 mixing ratio in ppbv at Delhi, Kolkata, Haldia, Ahmedabad, Pune and Trivandrum

4.3. *Surface ozone*

Surface ozone is a secondary pollutant produced after a series of reaction from primary pollutants.

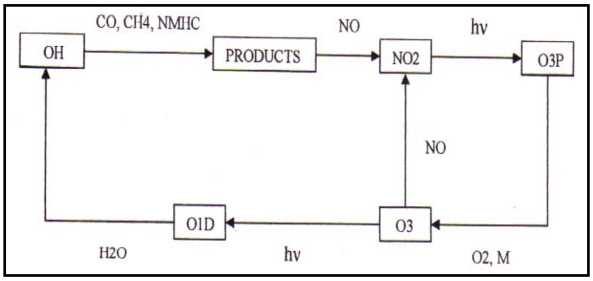


Fig. 4. A simplified reaction scheme

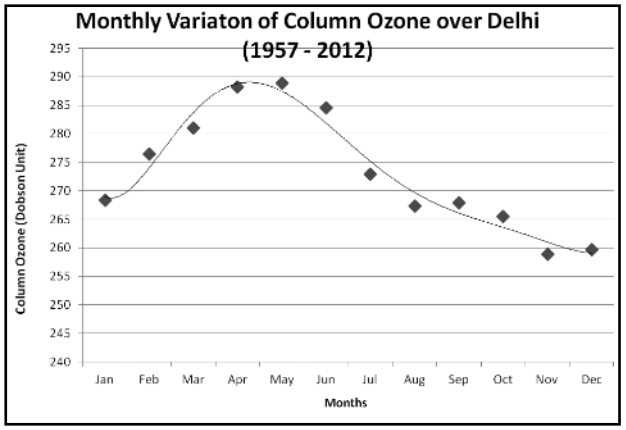


Fig. 5. Seasonal variation of total ozone in Delhi

Fig. 3(a) shows the monthly averaged values of surface ozone for Delhi from November 2008 to December 2013 in $\mu g/m^3$. 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 $\mu g/m^3$ compared to other seasons. Also there is an increasing long term trend ~0.16 $\mu g/m^3$/month as seen from Fig. 3(a).

For the sake of comparison with other stations, monthly averaged values of O_3 at Delhi are shown for all the seasons in Fig. 3(c) in ppbv (1 ppbv = 2.14 $\mu g/m^3$) 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 Trivandrun 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, CH_4 NMHCs etc. in the presence of sufficient amount of NO. An example is as follows:

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow O^3P + NO$$

$$O^3P + O_2 + M \rightarrow O_3 + M$$

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 NO_2 through photo-dissociation ($NO_2 + h\nu \rightarrow NO + O^3P$) is less and hence $[O^3P]$ decreases. When $[O^3P]$ decreases, O_3 production decreases and hence $[O_3]$ decreases. As O_3 is low, the production of NO_2 through the reaction $O_3 + NO$ is less and since, solar intensity is also low, the channel $O_3 + h\nu \rightarrow O^1D + O_2$ followed by $O^1D + H_2O \rightarrow 2OH$ will be slow even though $[H_2O]$ is high. Since [OH] is low, therefore, production of NO_2 through OH will be less which will further decrease $[NO_2]$. Since, however, the loss of NO_2 through the reaction $NO_2 + h\nu \rightarrow NO + O^3P$ is less, NO_2 should build up. But this does not happen. The build-up of $[NO_2]$ 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 NO_2 is unlikely to have increased during winter. It appears therefore that there should be additional loss processes of NO_2 other than shown above. Since solar radiation is low during winter, NO_2 is likely to be lost, as in nighttime or during eclipse, through the following reactions (Chakrabarty and Peshin, 2011) to form aqua HNO_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$

$$N_2O_5\,(g) + H_2O \rightarrow 2HNO_3\,(aq)$$

This will further decrease $[O_3]$.

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:

$$O_2 + h\nu \rightarrow O(^1D) + O(^1D) \quad \lambda < 2400 \text{ Å}$$

$$O(^1D) + M \rightarrow O(^3P) + M \quad (M = O_2 \text{ and } N_2)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

and lost through:

$$O_3 + h\nu \rightarrow O + O_2 \; (Jo_3) \; \lambda < 2950\text{-}3500, 4500\text{-}8000\text{Å}$$

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 H_2O concentration is high near the surface of the earth. Observations show that during winter, surface concentration of O_3 is low. This is due to the low density of [NO_2] caused by non-availability/less-availability of solar radiation. The concentration of $PM_{2.5}$ and PM_{10} 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 NO_2 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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