Variation in the concentration of ground level ozone at selected sites in Delhi

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ABSTRACT

To improve the quality of air in a city like Delhi which is mainly affected by vehicular exhaust, from 2002 onwards, CNG has been introduced, which shows remarkable change in the concentration of pollutants, but even then there are some pollutants like NOx, O₃ which are still either crossing their permissible limits or at the margin of their crossing. Objective of the present study is to compare the variation in concentration of ground level ozone at three selected sites in Delhi which are distinct in vegetation and traffic densities and to monitor, if the prevailing meteorological conditions are responsible for spatial variation of pollution in Delhi. For this, the sampling was carried out during two seasons i.e. monsoon (Aug.-Sept.'06) and winter season (Nov.-Dec.'06) at three sites - Site I (Inter State Bus Terminus - ISBT), a high density traffic intersection area with low vegetation, Site II (Yamuna Biodiversity Park - YBP, Wazirabad), away from traffic intersection with high vegetation, and Site III (University of Delhi - DU, North Campus), an institutional area which is near to traffic intersection i.e. with moderate traffic density and high vegetation. The overall result shows that highest concentration of ground level ozone was found at Site II (YBP) followed by Site III (DU) and Site I (ISBT) in the month of monsoon (Sept’06) whereas interestingly, in the month of winter (Nov’06), the highest ozone concentration was found at Site III followed by Site II and then Site I. This is might be due to the reason, at Site II in the month of September due to favourable meteorological conditions like less relative humidity which is negatively and highly significant to ozone concentration whereas, at Site III, in the month of November, this site is highly dense in vegetation and also near to traffic intersection so might be acting as an accumulation ozone of pollutants and moreover, with favourable meteorological conditions like increase in temperature which is positively correlated and highly significant with ozone concentration along with less relative humidity and wind speed which are negatively correlated with ozone concentration. Therefore, it was concluded that the site which is highly dense in vegetation and also have impact of vehicular emission exhibits high ozone concentration level than less vegetative area.

Keywords: Ground level ozone, VOCs, Nitrogen Oxides, Vegetation, Traffic intersection

1. Introduction

Air is considered as the most important constituent of our life and its quality is affected by anthropogenic activities, regional weather and topographical variance. Cleaner air means fewer respiratory diseases among adults, fewer asthma attacks among children, fewer hospital admissions and fewer premature deaths. In India, about 65% of the total air pollution is caused by vehicular emissions especially in metropolitan cities and the rest is due to rapid urbanization and industrialization (CSE, 2004). The available data shows that in Delhi, every day vehicular emissions form close to two-third (66%) of total air pollution, in Mumbai, this
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2. Materials and Method

Ground level ozone measurements were carried out with the help of a UV based ozone analyzer (Model O₃ 42M, Environment S.A., France). The instrument was kept at a height of about 10 meters above the ground. A 5 meter long Teflon tube (12mm dia.) was used as the intake tube for air sampling. An inverted Teflon funnel was fitted at the entrance of the tube to prevent dust and rain water going directly into the tube and the system. The data was generated every day at three sites during monsoon season (Aug & Sept’06) and winter season (Nov & Dec’06). At each site, sampling was done for consecutive 15 days. Simultaneously, the hourly meteorological parameters viz. relative humidity, air temperature and wind speed were also recorded using Pocket Weather Monitor (Kestrel, USA). The study was carried out at three selected sites (Figure 1), viz. Site I (Inter State Bus Terminus - ISBT), a very high density traffic intersection with low vegetation, is situated in the Northern part of Delhi with latitude of 28°33’27 N, longitude of 077°08’49 E and an altitude of 295 m, Site II (Yamuna Biodiversity Park - YBP, Wazirabad), a very low density traffic intersection with high vegetation is situated 1 km away from the bank of river Yamuna near Wazirabad in the...
northern region of Delhi with latitude of $23^033'27''$ N, longitude of $077^008'49''$ E and an altitude of 216 m and Site III (University of Delhi - DU, North Campus), an institutional area with moderate traffic density and high vegetation, is situated in the Northern Ridge area inside the north campus of University of Delhi with $28^037'11''$ N latitude, $27^040'10''$ E longitude and an altitude of 126 m.

**Figure 1:** Map of Delhi Showing Sites

### 3. Result and Discussion

As per the EPA guidelines/ National Crop Loss Area Network (NCLAN), the critical value of ground level ozone concentration is 40ppb/8hr (for plant species) and this threshold value was compared with the generated ozone concentration at the selected sites. The general trend of hourly ozone variation at Site I (ISBT) during monitoring period is represented in Figure 2.

**Figure 2:** Hourly Average Ozone variation (2006) at Site I- ISBT
In the month of August, the ozone concentration was $8.85 \pm 1.70^{b}$ and highest concentration (13.70 ppb) was recorded at 15:00 hours, whereas in the month of September, the ozone concentration was $13.35 \pm 2.11^{ab}$ and peak concentration of ozone was reported to be 19.12 ppb at 11:00 hours. However, in the month of November, ozone concentration was $18.72 \pm 9.75^{a}$ and highest concentration of ozone was observed to be 30.65 ppb at 13:00 hours. The data followed by different letters in a column are significantly different at $P \leq 0.05$ which clearly predicts that ozone concentration are different and was highest in November month followed by September and August (Table 1).

Table 1: Variation in Ozone Concentration in different months (Aug, Sept & Nov) 2006 at Site 1 (ISBT). The values indicate mean ± standard error

<table>
<thead>
<tr>
<th>Months</th>
<th>Ozone concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August</td>
<td>$8.85 \pm 1.70^{b}$</td>
</tr>
<tr>
<td>September</td>
<td>$13.35 \pm 2.11^{ab}$</td>
</tr>
<tr>
<td>November</td>
<td>$18.72 \pm 9.75^{a}$</td>
</tr>
</tbody>
</table>

Each value represents mean of 7 replicates ± standard error. Data followed by different letters in a column are significantly different at $P \leq 0.05$.

It may be due to low mixing height and higher accumulation rate of ozone in the atmosphere during winter months (Tiwari and Peshin, 1995). Figure 3 shows the distribution of hourly day variation of surface ozone in different months (Aug, Sept & Nov, 2006).

![Figure 3 (i): Hourly average day variation at ISBT](image1)

![Figure 3 (ii): Hourly average night variation at ISBT](image2)

**Figure 3 (i-ii):** Hourly average day & night variation at ISBT in 2006

The diurnal trend evident in Figure 3 indicates the daytime in situ photochemical production of $O_3$ throughout the seasons with an increase in ozone concentration during daytime and decline at nighttime. The maximum ozone concentrations were observed between 12 and 14 h. The decrease in nighttime $O_3$ concentration was mainly due to the titration of $O_3$ by surface emission of NO and the ground level destruction of $O_3$ in a shallow boundary-layer (Stillman et al., 2003, Subbaraya et al., 2000). The highest ozone concentration of 30.5 ppb was reported at 13:00 hrs in the month of November as compared with September of 23.8 ppb at...
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11:00 hrs and August of 10.1 ppb at 15:00 hrs. On most of the days, the nighttime surface O₃ concentration was found to be highest in the month of November of 4.20 ppb at 21:00 hrs followed by September of 2.01 ppb at 2:00 hrs and in the month of August of 1.01 ppb at 20:00 hrs. Variation of ozone concentration, in the recorded months, has also been studied in relation to meteorological parameters in Figure 4 (i-iii).

“The general trend shows (in all the reported months) that with the increase in ambient temperature favours the increase of ozone concentration through photochemical reaction which can be substantiated with the report of Hauglustaine et al. (2001)”. Relative humidity has a great role in the production of ozone because it begins with the photolysis of ozone and produces excited oxygen atom \( \text{O} \left( \text{^1D} \right) \) which leads to the formation of hydroxyl radical. The hydroxyl radical undergoes further reactions, and some of which eventually lead to the formation of ozone (Pandey and Chasta, 2005). Observing the correlation matrix Table 2, ozone was significantly positively correlated with temperature at 0.01 level in the month of November which shows that with the increase in temperature there is increase in ozone concentration. At Site I, ozone concentration showed low correlation coefficient with meteorological parameters.

Table 2: Pearson correlation matrix for measured ozone concentration (ppb) at Site 1 (ISBT).

<table>
<thead>
<tr>
<th></th>
<th>August</th>
<th>September</th>
<th>November</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Temperature</td>
<td>0.287</td>
<td>0.051</td>
<td>0.366**</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>-0.158</td>
<td>0.032</td>
<td>-0.148</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>0.049</td>
<td>0.236</td>
<td>0.375**</td>
</tr>
</tbody>
</table>

The general trend of ozone concentration at Site II (YBP) which can be observed during experimental period is depicted in Figure 5.
In the month of September, the ozone concentration was $42.79 \pm 6.88\text{ppb}$ and highest was recorded $(51.01 \text{ppb})$ at 15:00 hours. Besides, major consistent peaks were also observed between 11:00 hours - 15:00 hours. In the month of November, the ozone concentration was $40.23 \pm 1.24\text{ppb}$ and highest was recorded $(42.30 \text{ppb})$ at 16:00 hrs and major consistent peaks were also observed between 13:00 – 16:00 hrs. In the month of December, the ozone concentration was $41.23 \pm 1.84\text{ppb}$ and highest $(48.10 \text{ppb})$ was recorded at 14:00 hours with other peak ozone values between 13:00 hours-17:00 hours. The data followed by same letters in a column are non-significant at $P \leq 0.05$ which clearly predicts that ozone concentration shows no significant difference (Table 3).

Table 3: Variation in Ozone Concentration in different months (Sept & Dec) 2006 at Site II (YBP). The values indicate mean ± standard error.

<table>
<thead>
<tr>
<th>Months</th>
<th>Ozone concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>September</td>
<td>$42.79 \pm 6.88\text{ppb}$</td>
</tr>
<tr>
<td>November</td>
<td>$40.23 \pm 1.24\text{ppb}$</td>
</tr>
<tr>
<td>December</td>
<td>$41.23 \pm 1.84\text{ppb}$</td>
</tr>
</tbody>
</table>

Each value represents mean of 7 replicates ± standard error. Data followed by same letters in a column are non-significant at $P \leq 0.05$.

Figure 6 (i-ii) shows the distribution of hourly day variation of surface ozone in different months (Sept, Nov & Dec, 2006).

The highest ozone concentration $(44.2 \text{ppb})$ was recorded at 16:00 hrs in the month of September, in the month of November, the highest ozone concentration $(42.30 \text{ppb})$ at 16:00 hrs and in December, the highest ozone concentration was reported to be $44.1 \text{ppb}$ at 15:00 hrs. as shown in Figure 6 (i). Similarly in Figure 6(ii), with respect to hourly night variation in the month of September, the highest ozone concentration was found to be $16.31 \text{ppb}$ at 21:00 hours, in the month of November, the highest ozone concentration $(5.77 \text{ppb})$ at 20:00 hours and in December, the highest ozone concentration was found to be $8.73 \text{ppb}$ at 2:00 hrs. Interestingly, it was observed that ozone concentration in the month of September was quite high at YBP (Site II) as compared to ISBT (Site I), both during day as well as night time. It
may be because YBP is a highly dense vegetative area and closer to outer ring road and hence acting like an accumulatory zone.

The highly dense vegetation may be responsible for the emission of biogenic VOCs (isoprenes and terpenes) which are precursors for the formation of ozone. One more interesting thing was noted that, during night time, the ozone level never becomes zero but has shown consistently higher values. In this regard, “Naja et al. (2003) have reported that during night time, when earth cools, a new boundary layer forms above its surface, separating some pollutants that were emitted during the previous day from the fresh emissions occurring at the surface. These fresh emissions of pollutants trapped below the boundary layer and near the surface of the earth can be recorded and are responsible for ozone level not becoming zero even during night time”. This seasonal variation of ozone profile can be attributed to the variation in the meteorological variables which is depicted in Figure 7 (i-iii).

**Figure 6 (i):** Hourly average day variation at YBP

**Figure 6 (ii):** Hourly average night variation at YBP

**Figure 6 (i-ii):** Hourly average day & night variation at YBP in 2006

**Figure 7(i):** Variation in Sept., 2006

**Figure 7(ii):** Variation in Nov., 2006

**Figure 7(iii):** Variation in Dec., 2006

**Figure 7 (i-iii):** Variation in ozone concentration with meteorological parameters at YBP
The general trend shows (in all the recorded months) with the increase in temperature and relative humidity favoured the formation of ozone concentration (Chan and Kwok, 2001; Eshel and Joseph, 2006). Observing the correlation matrix Table 4, ozone was significantly negatively correlated with relative humidity at 0.01 level in all three months of September, November and December which shows that with the increase in relative humidity there is decrease in ozone concentration. At Site II, ozone concentration showed low correlation coefficient with meteorological parameters.

**Table 4:** Pearson correlation matrix for measured ozone concentration (ppb) at Site II (YBP).

<table>
<thead>
<tr>
<th></th>
<th>September</th>
<th>November</th>
<th>December</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Temperature</td>
<td>0.135</td>
<td>0.154</td>
<td>0.168</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>-0.345**</td>
<td>-0.352**</td>
<td>-0.336**</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>-0.062</td>
<td>-0.074</td>
<td>0.091</td>
</tr>
</tbody>
</table>

The profile of ozone variation at Site III (DU) in the recorded months is given in Figure 8.

**Figure 8:** Hourly Average Ozone variation (2006) at Site III- DU

In the month of August, the ozone concentration was 40.11 ± 2.88b and highest was found to be 50.33 ppb at 16:00 hours and the relative peak was accompanied with other shorter peaks from 14:00-19:00 hours. In the month of September, the ozone concentration was 39.72 ± 3.03b and highest was recorded 43.48 ppb at 16:00 hours and similarly other peaks were observed between 12:00-16:00 hours. In the month of November ozone concentration was 41.06 ± 4.76a at 14:00 hours and highest (56.91 ppb) and other accompanying peaks of ozone were recorded from 12:00-15:00 hours. In the month of December, ozone concentration was 30.80 ± 4.39a and highest 36.98ppb at 12:00noon. The data followed by different letters in a column are significantly different at P≤0.05 which clearly predicts that ozone concentration are different and was highest in November followed by August, September and December (Table 5).

**Table 5:** Variation in Ozone Concentration in different months (Aug, Sept and Nov- Dec) 2006 at Site III (DU). The values indicate mean ± standard error.
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<table>
<thead>
<tr>
<th>Month</th>
<th>Mean Concentration (ppb) ± Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>August</td>
<td>40.11 ± 2.88b</td>
</tr>
<tr>
<td>September</td>
<td>39.72 ± 3.03b</td>
</tr>
<tr>
<td>November</td>
<td>41.06 ± 4.76c</td>
</tr>
<tr>
<td>December</td>
<td>30.80 ± 4.39a</td>
</tr>
</tbody>
</table>

Each value represents mean of 7 replicates ± standard error. Data followed by different letters in a column are significantly different at P≤0.05.

It is also alarming to notice that in all the reported months at this site, the ozone concentration also exceeding the permissible limit (40 ppb), it can be interpreted that as it is an institutional area, presence of large number of two wheelers (a great source of NOx emission) and the presence of biogenic VOCs (due to local dense vegetation) accelerates the process of ground level ozone formation. Figure 9 shows the distribution of hourly day variation of surface ozone in different months (Aug, Sept, Nov & Dec, 2006).

In case of hourly day variation, the highest ozone concentration (50.2ppb) was recorded at 11:00 hrs in the month of August, in September the highest concentration was 43.3 ppb at 16:00 hrs, in November, it was 58.2ppb at 14:00 hrs and in December, it was 39.9 ppb at 14:00 hrs as shown in Figure 9(i). “According to Tiwari et al. (1995) this may be due to increase in temperature inversions, lower mixing depths and increase in moisture content”. But hourly night variation (as shown in Figure 9(ii)) shows the highest concentration of 19.2 ppb at 3:00 hrs in the month of September as compared to other months. This might be due to higher accumulation of ozone concentration from near emission sources. The ozone concentration is also high at this site as compared to ISBT (Site I) & YBP (Site II) during day as well as night probably because DU (Site III) is a dense vegetative area (source of biogenic VOCs), adjacent to ring road (pollution accumulation rate is high). Figure 10 (i-iv) has been interpreted the variation of ozone concentration in the recorded months with the meteorological variables.
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Figure 10(i): Variation in Aug., 2006
Figure 10(ii): Variation in Sept., 2006
Figure 10(iii): Variation in Nov., 2006
Figure 10(iv): Variation in Dec., 2006

Figure 10 (i-iv): Variation in ozone concentration with meteorological parameters at DU

It also shows (in all the recorded months) that increase in temperature favours the formation of ozone. The declining trend of relative humidity was also showcasing the increase in the production of ozone after the production of hydroxyl radical (Salve et al., 2005; Lal et al., 2000 and Walcek and Yuan, 1995). Observing the correlation matrix Table 6, ozone was significantly positively correlated with temperature and negatively correlated with wind speed in the month of November at 0.01 level. This clearly shows that at Site III with increase in temperature there is increase in ozone concentration and moreover, the highest ozone concentration was reported in the month of November due to favourable meteorological factor wind speed which represents that when there is low wind speed there is high ozone concentration. Moreover, it may be due to low mixing height and higher accumulation rate of ozone in the atmosphere during winter months (Tiwari and Peshin, 1995).

Table 6: Pearson correlation matrix for measured ozone concentration (ppb) at Site III (DU).

<table>
<thead>
<tr>
<th></th>
<th>August</th>
<th>September</th>
<th>November</th>
<th>December</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Temperature</td>
<td>0.440**</td>
<td>0.388**</td>
<td>0.496**</td>
<td>0.270</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>0.041</td>
<td>0.451**</td>
<td>-0.062</td>
<td>-0.576**</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>-0.235</td>
<td>0.491**</td>
<td>-0.185</td>
<td>0.306*</td>
</tr>
</tbody>
</table>
A comparison of hourly ozone variation among three different sites has also been presented in Figure 11 (i&ii) for the month of September and November. According to the profile, in the month of September (Fig11 (i)), Site II shows higher peak values (48.07 ppb) followed by Site III (43.48 ppb) and Site I (17.33 ppb) and interestingly, in the month of November (Fig11 (ii)), Site III shows high ozone concentration (56.91 ppb) followed by Site II (42.30 ppb) and Site I (30.65 ppb). Overall, in one of the month of monsoon (Sept’06) Site II (YBP) shows highest ozone concentration profile in all reported months compared to other sites due to favourable meteorological conditions like less relative humidity which is negatively and highly significant at 0.01 level to ozone concentration whereas, conversely, in one of the month of winter season (Nov’06), Site III (DU) exhibits highest ozone concentration as compared to other selected sites, which may be due to, this site is highly dense in vegetation and also near to traffic intersection so might be acting as an accumulation ozone of pollutants and moreover, with favourable meteorological conditions like increase in temperature which is positively correlated and highly significant with ozone concentration along with less relative humidity and wind speed which are negatively correlated with ozone concentration.

Figure 11 (i): ISBT, YBP & DU in Sept

Figure 11 (ii): ISBT, YBP & DU in Nov

Figure 11 (i-ii): Comparison of hourly ozone variation at ISBT, YBP & DU in 2006

4. Conclusion / Suggestions/ Findings

From the overall detailed study at all the three distinct sites, it was concluded that the site which is highly dense in vegetation and also have impact of vehicular emission exhibits high ozone concentration level than less vegetative area. So, our monitoring programme in new areas (where pollution exposures are expected) and reporting of results is an effort to make public aware of the present dangers they are exposed to. Once more we have to initiate our thought process on how we can get rid off the harmful secondary pollutants everyday and also to force the government to make stricter norms for the control of these secondary pollutants immediately.

Acknowledgement

The author would pay sincere thanks to Mr. J.K. Bassin, Scientist Head, National Environmental Engineering Research Institute (NEERI), Delhi for providing opportunity to use their institute’s facilities in carrying out the research work at ISBT and grateful to Dr. Anupam Joshi, Scientist Incharge, Yamuna Biodiversity Park, Wazirabad, for facilitating support in regard to this study.
5. References


