SEASONAL VARIATION OF PHOTOCHEMICAL SMOG POLLUTION IN METROPOLITAN CITY OF INDIA IN RELATION TO OZONE PRECURSOR CONCENTRATIONS AND METEOROLOGICAL CONDITIONS

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The Third Workshop on Atmospheric Composition and the Asian Monsoon (ACAM) and Second ACAM Training School
Common Aim:

- Photochemical Pollutants status during 2009-10 by taking different seasons in Delhi, India.

Complementary research questions???

- Why Photochemical Pollutants?
- How meteorological parameters affect photochemical smog pollution?
- Why it is an important topic for photochemical smog modellers?
Diurnal variations of photochemical pollution precursors, NO, NO$_2$, CO, NMHC, and CH$_4$, and O$_3$ for the selected stations (6, 7, 8 and 10) for each month were analyzed at Bangkok, Thailand. January (with high O$_3$) and August (with minimum O$_3$) data for the stations are presented. Source: Zhang and Oanh, 2002, Atmos. Env. 36: 4211-4222.
Average diurnal variations of O\textsubscript{3}, NO, NO\textsubscript{2}, CO, CH\textsubscript{4} and NMHC in different seasons for the period from January 2000 to February 2003 in Nanjing.

The amplitude, which is the difference in O\textsubscript{3} concentration between daytime and nighttime, is the highest in spring, the second highest in summer, the third highest in autumn, and the lowest in winter.

The diurnal variations of the precursors for the four seasons show a similar pattern; however, the hourly concentrations and/or amplitudes of the diurnal variations show significant differences among seasons (p<0.001). Source: Tu et al., 2007, Atmos. Res. 85: 310-337.
Strong diurnal variation is observed in all the four seasons viz. winter, summer, monsoon and post-monsoon with the daytime values almost 3 times the nocturnal values except in the monsoon season at Agra. Source: Singhla et al. 2011, Atmos. Res. 101: 373-385.
The concentrations of ozone increased to a significant extent. This is consistent with the increase in the number of vehicles on road, which corresponds to the increasing levels of NOx and VOCs as a result of increasing vehicular emissions in Delhi.

Ozone concentrations fall rapidly at higher NOx concentrations, whereas the concentrations of NO and NO₂ rise with increasing NOx levels.
• NO dominates over NO₂ and O₃ at higher NOx concentrations.
O₃ and NO curves crossover at 54 ppb NOx. Source: Tiwari et al. 2015, Atmos. Res. 157: 119-126.
RATIONALE OF STUDY

- Lack of systematic monitoring data of ozone and its precursors mostly in Asian countries.
- Very less studies have been reported so far on photochemical pollutants in most of the developing Asian countries.
- Studies related to monitoring data of photochemical pollutants sets up a platform for photochemical smog modellers.
OBJECTIVES

- Ozone pollution status and trend in New Delhi, India during three different seasons viz. summer, monsoon and winter from year 2009-2010.
- Average monthly and diurnal variations of ozone are analyzed in connection with O₃ precursors i.e. photochemical pollutants and meteorological conditions.
- To estimate the effective NOx/NMHC ratio for production of O₃, and seasonal variations in NOx/NMHC ratios are analyzed to assess the seasonal photochemical smog potentials.
Sampling Sites

1. ISBT, Kashmere Gate
2. Yamuna Biodiversity Park, Wazirabad
3. University of Delhi, North Campus
4. Shalimar Bagh
Parameters Under Study

A. Measurement of pollutant concentration:
   - \( \text{NO}_2 \): using NOx analyzer, Thermofischer
   - \( \text{O}_3 \): using \( \text{O}_3 \) analyzer, Environment S.A.
   - NMHCs: THC analyzer, Thermofischer

B. Meteorological Parameters:
   Secondary data from IMD.

Sampling Pattern

Sampling Pattern: Samples were collected during three seasons viz. summer (Apr-Jun), monsoon (July-Sept) and winter (Nov-Feb).

Data Matrix: 4 sites x 3 seasons x 3 parameters

Statistical Analysis

• Pearson’s Correlation

Software Package Used: SPSS (19.0 version)
High O₃ concentrations were found at away from traffic intersection site (YBP) reflect the dispersion of O₃ and its precursors as compared to other sites.

Interestingly, near to traffic intersection site (ISBT), relatively low O₃ was found as compared to away from traffic intersection site (YBP) may be due to O₃ destruction by NO in the NO₂ photolytic cycle.
O₃ levels generally increasing from 13:00 till 15:00 and showed decreasing levels from 18:00 hrs at all the sites due to its high photochemical activity during that time and also the influence of meteorological parameters like comparatively high temperature and low wind speed during the time period of 13:00 – 15:00.

Highest hourly concentration of O₃ was found to be 69.93 ppb which is crossing the permissible limit 40 ppb for O₃ in case of plants by NCLAN and nearby to NAAQS CPCB permissible limit.
- Lowest percentage contribution of ozone was found in monsoon. Aqueous reactions in clouds consume radicals or effects of vertical mixing, wet deposition of soluble O₃ precursors, decrease in solar radiation and decrease in temperature.
- Highest O₃ average of hours of O₃ exceeding 40 ppb was found to at all the sites except residential site.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Total Hours</th>
<th>Total Days</th>
<th>Max. O₃ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>3</td>
<td>78.65</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2</td>
<td>58.89</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>48.87</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
## Comparison of Monthly Mean Meteorological Data of Delhi (Source: IMD, Delhi)

<table>
<thead>
<tr>
<th>Months</th>
<th>Temp. (°C)</th>
<th>Rel. Humidity (%)</th>
<th>Wind Speed (m/s)</th>
<th>Solar Radiation (MJ/m²)</th>
<th>Rainfall (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April</td>
<td>39</td>
<td>43</td>
<td>1.3</td>
<td>23.67</td>
<td>2.0</td>
</tr>
<tr>
<td>May</td>
<td>43</td>
<td>40</td>
<td>1.2</td>
<td>28.76</td>
<td>4.3</td>
</tr>
<tr>
<td>June</td>
<td>40</td>
<td>47</td>
<td>2.5</td>
<td>24.11</td>
<td>5.4</td>
</tr>
<tr>
<td>July</td>
<td>37</td>
<td>74</td>
<td>4.2</td>
<td>19.5</td>
<td>124.2</td>
</tr>
<tr>
<td>August</td>
<td>33</td>
<td>81</td>
<td>7.8</td>
<td>17.5</td>
<td>188.6</td>
</tr>
<tr>
<td>September</td>
<td>32</td>
<td>78</td>
<td>6.1</td>
<td>14.8</td>
<td>201.9</td>
</tr>
<tr>
<td>October</td>
<td>28</td>
<td>60</td>
<td>3.4</td>
<td>15.9</td>
<td>0.3</td>
</tr>
<tr>
<td>November</td>
<td>23</td>
<td>62</td>
<td>2.3</td>
<td>12.76</td>
<td>14.2</td>
</tr>
<tr>
<td>December</td>
<td>14</td>
<td>64</td>
<td>1.8</td>
<td>11.65</td>
<td>1.0</td>
</tr>
<tr>
<td>January</td>
<td>11</td>
<td>68</td>
<td>1.4</td>
<td>10.65</td>
<td>0.0</td>
</tr>
<tr>
<td>February</td>
<td>20</td>
<td>65</td>
<td>3.6</td>
<td>13.87</td>
<td>14.2</td>
</tr>
</tbody>
</table>
# Correlation between O₃ and meteorological variables

<table>
<thead>
<tr>
<th>Meteorological Variables</th>
<th>Karl Pearson’s Correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Summer (n = 730)</td>
</tr>
<tr>
<td><strong>T_{max}</strong></td>
<td>0.764**</td>
</tr>
<tr>
<td><strong>DP_{avg}</strong></td>
<td>-0.067</td>
</tr>
<tr>
<td><strong>RH_{avg}</strong></td>
<td>-0.608**</td>
</tr>
<tr>
<td><strong>SR_{avg}</strong></td>
<td>0.692*</td>
</tr>
<tr>
<td><strong>WS_{avg}</strong></td>
<td>-0.465</td>
</tr>
<tr>
<td><strong>NMHCs avg.</strong></td>
<td>-0.690**</td>
</tr>
<tr>
<td><strong>NO₂ avg.</strong></td>
<td>-0.566*</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).  
* Correlation is significant at the 0.05 level (2-tailed).
Site 1: ISBT

- In the early morning rush hours (around 7:00-8:00 a.m.) the NMHCs concentrations were found to be high.
- NO₂ peaks at around 9:00 a.m. starts increasing which reflects the time taken for conversion of NO to NO₂ involving HC.
- O₃ concentration also starts increasing after sunrise i.e. around 8:00 am. Onwards and reached to its peak in between 13:00 – 15:00 hrs.
Site 2: YBP

- Among all the months of selected seasons i.e. summer, monsoon and winter, May had reported highest and August lowest O₃ hourly averaged concentrations at all sites.
- Photochemical destruction of O₃ by NO in the NO₂ photolytic cycle and also high OH radical activity during the month of August.
Site 3: DU

- No significant change has been observed in near to traffic intersection (ISBT) and institutional site (DU) in case of especially O₃. This is due to DU is also surrounded by commercial places, traffic congestion especially of two-wheelers and one traffic intersection area.
- O₃ found to be minimum in early morning may be due to high NO concentrations and lower solar radiation and temperature as compared to afternoon.
Site 4: SB

- NMHCs concentrations were found to be low both in summer as well as monsoon months i.e. May and August because May is a summer month in which volatility rate is high which leads to evaporation.
\[ y = 0.7945x + 30.506 \quad R^2 = 0.6307 \]  
**Summer**

\[ y = 0.272x + 25.885 \quad R^2 = 0.0877 \]  
**Monsoon**

\[ y = 0.379x + 17.323 \quad R^2 = 0.2594 \]  
**Winter**

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]
\[ \text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]
CONCLUSION

- Ozone formation and accumulation in Delhi reflects the interaction of local emission and photochemistry as well as the urban and regional transport of the pollutant and its precursors to study area.

- Photochemical smog potential in Delhi is high due to the high local emission of O$_3$ precursors and the favourable meteorological conditions like high temperature and low wind speed.

- The Asian monsoon with associated typical local meteorological conditions and the regional transport is the main factor causing the seasonal variations of O$_3$.

- Seasonal variations of NOx/NMHC ratios are showing more effective O$_3$ production in summer (0.79), followed by winter (0.37), and the lowest in monsoon season (0.27).
Interactions of local emission and regional meteorological conditions in the formation and accumulation of $O_3$ are important for development of efficient and cost-effective $O_3$ pollution management strategies.

Further studies are necessary to better understand the synoptic meteorological transport processes especially for high ozone days.
ACKNOWLEDGEMENT

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