Annual and seasonal variations in tropospheric ozone concentrations around Varanasi

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Annual and seasonal variations in tropospheric ozone concentrations around Varanasi

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This study examines the annual, seasonal and diurnal variations in the ambient concentrations of ozone at a suburban site of Varanasi, India, during 2002–2006. Prominent seasonal variations in ozone concentrations were recorded. Ozone concentrations were higher during the warmer months. Daytime 12-hourly mean monthly ozone concentrations varied from 45.18 to 62.35 ppb during summer, from 28.55 to 44.25 ppb during winter and from 24 to 43.85 ppb during the rainy season from 2002 to 2006. Distinct diurnal variations in ozone concentrations were also observed. Daytime maxima in ozone concentration were recorded between 1200 and 1400 h, whereas morning and evening hours showed lower concentrations of ozone. Ozone concentrations in the atmosphere depended on several meteorological factors. Monthly average ozone concentration was significantly correlated with maximum temperature \((p<0.001)\) and mean monthly temperature \((p<0.05)\), maximum relative humidity \((p<0.001)\), minimum relative humidity \((p<0.001)\) and mean monthly relative humidity \((p<0.001)\), and sunshine hours \((p<0.001)\). Ozone concentrations in the ambient air have shown an increase in the past decade that was more in the winter and rainy seasons than in the summer. This study suggests that ozone concentrations around Varanasi were sufficiently high to cause significant damage to agricultural production. The present work can be extended to a regional level by incorporating modelling studies using recent remote sensing tools.

1. Introduction

Tropospheric ozone \((O_3)\) is considered to be the most widespread and damaging air pollutant to which living organisms are exposed (Fuhrer et al. 1997, Musselman and Massman 1999, Ollerenshaw et al. 1999, Smidt and Herman 2004). It occurs naturally at low concentrations ranging from 5 to 15 ppb (Marenco et al. 1994). However, in the past few decades, anthropogenic activities have led to an increase in the level of tropospheric \(O_3\) beyond the critical limit throughout the world (Ashmore 2005, Karnosky et al. 2005).

The current level of \(O_3\) is high enough to exceed the tolerance threshold of many plants, thus impairing plant growth, reducing crop yields and altering the composition of plant community (Davison and Barnes 1998). Background concentration of \(O_3\) in the troposphere has doubled in the past decade and there is also evidence of an increase in annual mean values ranging from 0.1 to 1 ppb per year (Coyle et al. 2003).

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Ozone concentration builds up in the atmosphere by several natural and anthropogenic sources. These include (1) downward transport of stratospheric O₃ through the free troposphere to near ground level, (2) in situ O₃ production from methane emitted from swamps and wetlands reacting with natural nitrogen oxides (NOₓ), (3) production of O₃ from reaction of volatile organic compounds (VOCs) with NOₓ and (4) long-range transport of O₃ from distant pollution sources (EPA 1993, Kondratyev and Varotsos 2001a,b, Varotsos et al. 2004). Ozone is a secondary air pollutant that is formed by the transformation reactions of primary air pollutants, especially nitrogen dioxide (NO₂). Over the past decades, motor vehicles have emerged as a crucial source of air pollutants emitting hydrocarbons and nitrogen oxides (Faiz 2000, Kondratyev and Varotsos 2002). Nitrogen oxides are rapidly oxidized to NO₂ in the atmosphere and act as a precursor to O₃, thus increasing its concentration (Dibbs et al. 2003). High temperature and sunlight intensity found in tropical countries are ideal conditions for O₃ formation (Varotsos et al. 2001a, 2005).

In India, despite the favourable tropical conditions for O₃ formation, very few systematic simultaneous measurements of surface O₃ have been performed. Pandey and Agrawal (1992) recorded O₃ concentrations (24 h annual mean) ranging from 6.12 to 10.2 ppb during 1989–1990 around Varanasi. During the same period O₃ concentrations (daytime 9 h mean) were reported to vary from 9.4 to 128.31 ppb at an urban site in Delhi (Varshney and Aggarwal 1992). Singh et al. (1997) observed that 10 h ground level mean O₃ concentrations in Delhi varied between 34 and 126 ppb during the winter season in 1993. An annual average daytime O₃ concentration of 27 ppb and hourly concentrations of 2–69 ppb at Pune during August 1991 to July 1992 were reported by Khemani et al. (1995). Lal et al. (2000) studied the patterns of O₃ concentration from 1991 to 1995 at an urban site at Ahmedabad and reported that daytime mean O₃ concentrations exceeding 80 ppb were rarely observed. A more detailed monitoring result from Delhi was reported by Jain et al. (2005). Increasing O₃ concentrations have been implicated as leading to severe losses in agricultural yields. Ozone affects several physiological and biochemical processes in plants, including reduction in photosynthesis (Fangmeier et al. 1993) and alteration in carbon and nitrogen metabolism (Agrawal and Agrawal 1990, Soja and Soja 1995), which ultimately leads to a reduction in yield (Fumagalli et al. 2001, 2003, Fuhrer and Booker 2003, Ishii et al. 2004, van Tienhoven et al. 2006). Field experiments conducted under the National Crop Loss Assessment Network (NCLAN) in the USA in the early 1980s and the European Open Top Chamber (EOTC) studies during 1987–1991 showed that elevated surface O₃ concentrations can substantially reduce grain yield (EPA 1996, EEA 1999). Based on the NCLAN results, yield losses of 10% were calculated for about one-third of crop species in the USA at ambient O₃ concentrations by the US Environmental Protection Agency (EPA 1996). MOZART-2 model simulation studies have predicted that because of increased levels of O₃, grain yield loss may increase from 1990 to 2020 by 2–16% for wheat, rice and corn and 28–35% for soybean in China, Japan and South Korea (Wang and Mauzerall 2004). A Community Multiscale Air Quality model has calculated highest O₃ concentrations ranging from 55 to 70 ppb during May and June in the boundary layer over East China and Japan (Yamaji et al. 2006). Ozone monitoring conducted in Pakistan showed that average (8 h) O₃ concentrations were 72 ppb during December 2003 to April 2004 (Wahid 2006a) and 71 ppb during December 2004 to April 2004 (Wahid
Ozone concentrations were investigated using the Urban Airshed Model in the Kanto area of Tokyo, Japan during 1978–1994 and the highest hourly \( O_3 \) concentration during this period was 223 ppb in 1994 (Wakamatsu et al. 1999). In Hong Kong, when \( O_3 \) concentrations were monitored during 1994–1999, the Hong Kong Air Quality objective for \( O_3 \) (122 ppb) was violated six times, with the highest \( O_3 \) concentration being 170 ppb during August 1999 (Lee et al. 2002). Average summer \( O_3 \) concentrations at 28 locations in the south of the Spanish Mediterranean basin ranged from 40.8 ppb to 51 ppb depending on the distance from the urban centre (Caballero et al. 2007).

The European approach to determining the impact of \( O_3 \) on crops has centred around the concept of a ‘critical level’ (CL), which is based on a cumulative exposure above a cutoff concentration, below which only an acceptable level of harm is incurred. Based on the experimental results of the EOTC, the yield reductions were found to be highly correlated with cumulative exposure to \( O_3 \) above a threshold of 30–40 ppb during daylight hours (Fuhrer 1994). A cumulative indicator of \( O_3 \) exposure above a 40 ppb threshold (AOT40) was therefore established. AOT40 was set at 3000 ppbh accumulated during daylight hours for three months (May, June and July) when clear-sky radiation is greater than 50 W/m² (Fuhrer et al. 1997). Currently, the AOT40 parameter exceeds 3000 ppbh in most of the European Union (EU), with the exception of northern Scandinavia and the UK (Fuhrer et al. 1997).

Apart from phytotoxic effects, \( O_3 \) has important climatic implications because it acts as a greenhouse gas, and also has an important role in the radiative and chemical balance in the atmosphere. The development of remote sensing techniques to measure \( O_3 \) and its precursors from the Earth’s surface to the tropopause is an important achievement in measuring tropospheric \( O_3 \) (TROZ) variability. It has now become possible to analyse global scale TrOZ dynamics as well as specific features of the \( O_3 \) concentration vertical profile. Several modelling studies using remote sensing as a monitoring device have predicted an increase in TROZ concentrations (Kondratyev and Varotsos 2001a,b, 2002). Saraf and Beig (2004) analysed tropospheric column ozone (TCO) data derived from an ozonesonde and the Nimbus 7 Earth Probe TOMS over three different tropical stations in India from 1972 to 2001. The average surface volume mixing ratios of \( O_3 \) during 1972–2001 were 5–100 ppb over Delhi, 5–80 ppb over Pune and 5–60 ppb over Trivandrum (Saraf and Beig 2004). To validate the modelling results, however, ground level monitoring of \( O_3 \) is also required. The present work was therefore an attempt to analyse the increasing trends in ozone concentrations over an area in the Gangetic plains of India for more than three years.

India is an agricultural country and its economy is dependent on agricultural production. A survey conducted by the Ministry of Agriculture reported that the total foodgrain production showed an increment of 12% during 1993–2005 (Indian Statistical Data 2005). However, data from the Indian Census Board reported an increase of 21.24% in the population during 1991–2001. Thus the increase in foodgrain production does not match the demands of the increasing population. Increasing air pollution is one of the factors responsible for the poor agricultural production. Ozone has emerged as the most damaging air pollutant in recent years, with plants exposed to elevated \( O_3 \) concentrations showing severe yield reductions in various crops (Wahid et al. 1995a,b, Reinert et al. 1997, Zheng et al. 1998, Ollerenshaw et al. 1999, Agrawal et al. 2003, Tiwari et al. 2006). Transect studies
conducted by Agrawal et al. (2003) along varying pollution load showed significant reductions in yield of mung at a suburban site of Varanasi experiencing high seasonal mean O₃ concentrations (55.7 ppb) during summer. At the same site, during winter, the yield of wheat and mustard did not vary significantly as compared to the reference site when the O₃ concentration was low (15.4 ppb).

In view of the reports of the negative impact of O₃ on crop productivity from different parts of the world and the lack of O₃ monitoring data from suburban and rural areas supporting agriculture, the present study was undertaken with the objective of long-term assessment of O₃ concentrations in the ambient environment of an agricultural area situated in the lower Gangetic plains of India experiencing a tropical monsoonic climate. Annual, seasonal and diurnal variations in O₃ concentrations were monitored from November 2002 to May 2006. Correlation of O₃ concentrations with different meteorological parameters such as temperature, relative humidity, sunshine hours and wind speed were also computed to understand their role in O₃ formation.

2. Study area

Varanasi is situated in the eastern Gangetic alluvial plains on the bank of river Ganga at 25°78’ N latitude and 83°1’ E longitude at an elevation of 76.19 m above mean sea level. The weather in Varanasi is characterized by a dry tropical monsoonic climate with three distinct seasons: summer (March–June), the rainy season (July–August) and winter (November–February). The summer season is dry, associated with strong hot winds, high temperature during the day and infrequent premonsoon rains during the late summer months. During the study period from November 2002 to May 2006, the mean monthly maximum temperature during the summer season varied from 30.25°C to 42°C and the mean minimum was between 15.75°C and 28.57°C. The mean monthly maximum relative humidity varied from 40.8% to 77% and the minimum from 20.20% to 56.75%. The rainy season starts with the onset of heavy monsoons towards the end of June and continues to mid-October, with 90% of the annual rainfall falling within four months. During this season, the mean monthly maximum temperature varied from 30.9°C to 33.66°C and the mean minimum from 19.3°C to 26.7°C. The mean monthly maximum relative humidity varied from 88.6% to 93.4% and the mean minimum from 59.4% to 74.6%. During winter, the mean monthly maximum temperature ranged from 17°C to 28.8°C and the mean minimum from 7.7°C to 15.72°C. During this season, the mean maximum relative humidity varied from 84.25% to 90% and the mean minimum from 40% to 67%. Occasional light rains result from the retreating western monsoon. Table 1 shows the meteorological conditions during the study period. The wind direction shifts from predominantly westerly and northwesterly in October to April to easterly and northwesterly in the remaining months.

In the present study, the monitoring site Susuwahi was selected in the southern region of Varanasi, about 5.8 km from the city (figure 1). Susuwahi is a suburban area characterized by large agricultural lands and lies about 3 km away from the Allahabad–Howrah highway. As such, there is no specific source of pollution except transport of primary pollutants from the city and highway. Earlier studies have shown that during most of the year, the wind flows in the direction from north to south and thus accumulation of O₃ precursors leads to higher O₃ formation at this site (Rajput and Agrawal 2004). Most of the population of this area depends on farming as their main source of livelihood.
Table 1. Meteorological parameters recorded in different seasons during the study period.

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<tr>
<td></td>
<td>S</td>
<td>W</td>
<td>R</td>
<td>S</td>
</tr>
<tr>
<td>Total rainfall (mm)</td>
<td>218.88</td>
<td>104.8</td>
<td>859.4</td>
<td>184</td>
</tr>
<tr>
<td>Mean maximum temperature (°C)</td>
<td>36.88</td>
<td>24.31</td>
<td>32.13</td>
<td>36.77</td>
</tr>
<tr>
<td>Mean minimum temperature (°C)</td>
<td>22.81</td>
<td>11.50</td>
<td>25.12</td>
<td>23.47</td>
</tr>
<tr>
<td>Mean maximum relative humidity (%)</td>
<td>70.17</td>
<td>82.56</td>
<td>88.60</td>
<td>63.25</td>
</tr>
<tr>
<td>Mean minimum relative humidity (%)</td>
<td>31.38</td>
<td>52.11</td>
<td>71.06</td>
<td>34.05</td>
</tr>
<tr>
<td>Mean monthly sunshine (h)</td>
<td>8.92</td>
<td>5.44</td>
<td>6.01</td>
<td>9.13</td>
</tr>
<tr>
<td>Average wind speed (km h⁻¹)</td>
<td>5.11</td>
<td>1.79</td>
<td>3.39</td>
<td>5.30</td>
</tr>
</tbody>
</table>

S, summer; W, winter; R, rainy season.
3. Methodology

Air quality monitoring for O$_3$ was carried out using a Photometric Ozone Analyzer (Model 400A, API, Inc., USA). The detection of O$_3$ molecules in this instrument is based on absorption of 254 nm UV light due to the internal electronic resonance of the O$_3$ molecule. The Model 400A uses a mercury lamp constructed so that most of the light emitted is at 254 nm. Light from the lamp passes down a hollow quartz tube that is alternately filled with the sample gas and then the gas scrubbed to remove O$_3$. The ratio of the intensity of light passing through the scrubbed gas to that of the
sample ($I/I_0$) forms the basis for the calculation of the O$_3$ concentrations using the Beer–Lambert law.

Air quality monitoring was conducted for 12 h from 0700 to 1900 h. During this time period the O$_3$ concentration reaches its daytime maxima because of favourable meteorological conditions. Furthermore, at this time the plants are metabolically most active. High O$_3$ concentrations during this time adversely affect various physiological and biochemical processes and ultimately the productivity of plants. Twenty-four-hour monitoring of O$_3$ was also conducted on selected days in 2003.

4. Results and discussion

Seasonal variations in O$_3$ concentration from 2002 to 2006 are shown in figure 2. Elevated O$_3$ concentrations ranging from 45.18 to 62.35 ppb have frequently been observed during the summer months between 0700 and 1900 h. However, O$_3$ concentrations were lower during the winter (28.55–44.25 ppb) and rainy (24.09–43.85 ppb) seasons. The formation of O$_3$ in the troposphere depends upon several meteorological factors such as temperature, sunshine hours, wind velocity and relative humidity. Elevated O$_3$ levels during the summer months can be attributed to high temperature, which favours photochemical production of O$_3$. During the monsoon periods, minimum O$_3$ levels were observed. This may be due to non-availability of sufficient solar radiations and washout of primary pollutants. Relatively low levels of O$_3$ during the winter might be due to greater atmospheric stability and an increased incidence of nocturnal inversions, which might enhance the chemical scavenging of O$_3$ and dry deposition (Stephens 1969). During the summer season, the 12-h mean seasonal O$_3$ concentration was much higher than 40 ppb (the critical level for O$_3$ set by the EU), which proves to be harmful to plant growth and development. Hourly O$_3$ concentrations during the summer months were often in excess of 100 ppb and reached as much as 142 ppb in the year 2005. High temperature favours O$_3$ formation, and peak O$_3$ concentrations were recorded

![Figure 2. Seasonal and annual variations in ozone concentration in 2003–2006 (mean ± 1 standard error).](image-url)
During the summer months, Figure 3 shows the monthly variations in O$_3$ concentrations, and clearly indicates the effect of the different meteorological factors on O$_3$ concentration. The mean temperature remains low (8.9–20.5°C) during January and February but rises rapidly in March, reaching maxima of more than 33°C in May and June. A significant positive correlation was observed between maximum temperature ($R=0.55$) and mean monthly temperature ($R=0.32$) with mean monthly O$_3$ concentrations (figure 4). This indicates a temperature-dependent O$_3$ formation resulting in high O$_3$ maxima during the summer season as compared to the winter months. Besides temperature, O$_3$ concentrations also depend upon relative humidity. A significant negative correlation was found between mean relative humidity ($R=-0.85$) and mean monthly O$_3$ concentration (figure 5). O$_3$ concentrations were also significantly correlated with maximum relative humidity ($R=-0.79$) and minimum relative humidity ($R=-0.81$). Relative humidity was lowest during the summer months. The high temperature and low humidity observed during the dry summer months are favourable for O$_3$ formation. The
Figure 4. Correlation between mean minimum, maximum and monthly temperature and mean monthly ozone concentration during the study period. NS, not significant.

Figure 5. Correlation between mean monthly relative humidity and mean monthly ozone concentration during the study period.
condition is reversed during the winter and rainy seasons. The relative humidity is high and the temperature and sunshine hours are reduced, which explains the low O₃ concentrations during these seasons.

A similar seasonal dependence of O₃ has been reported in several other studies conducted in the USA (Cooper and Peterson 2000, Vingarzan 2004), Europe (Varotsos et al. 2001b, 2003), Canada (Monks 2000, Vingarzan 2004) and Korea (Ghim and Chang 2000, Kim et al. 2006). In Bulgaria, the average O₃ concentration during the summer was recorded in the range 46–50 ppb (Dovnev et al. 2002), which was slightly less than the average value of O₃ concentrations in the present study. In India, several studies have also recorded seasonal variations in O₃ concentrations (Pandey and Agrawal 1992, Varshney and Aggarwal 1992, Agrawal et al. 2003, Jain et al. 2005). Jain et al. (2005) observed that, in Delhi, the average monthly O₃ concentrations during the summers of 1997–2003 were in the range 62–95 ppb whereas they varied between 50 and 82 ppb in autumn (October–November) during the same time period. These values were higher than those recorded in the present study. Agrawal et al. (2003) reported that daytime mean O₃ concentration (6 h) was 15.44 ppb during winter and 55.70 ppb during summer of 1989 to 2000 at a suburban site of Varanasi, similar to the site selected in the present study.

The present study has also shown distinct diurnal variations in O₃ concentrations. Daytime O₃ concentrations were much higher than night-time O₃ concentrations. The hourly maxima were observed between 1200 and 1400 h whereas the evening and morning hours showed lower O₃ concentrations (figure 6). A positive correlation (R=0.76) between sunshine hours and mean monthly O₃ concentrations recorded in the present study explains the high O₃ concentrations during the daytime (figure 7). The daytime maxima were much higher during the summer months than the winter months (figures 8 and 9). During May, the hottest month of the year, hourly maxima reached as high as 131 ppb in 2003, 139 ppb in 2004, 142 ppb in 2005 and 150.9 ppb in 2006, whereas in January, which is the coolest month of the year, the O₃ concentration maxima were recorded to be 47.7 ppb in 2003, 49 ppb in 2004 and 47 ppb in 2005. Hourly O₃ levels often exceeded 100 ppb in
the Mediterranean region (Cartalis and Varotsos 1994, Danalatos and Glaves 1996). The maximum urban O₃ concentrations in Bulgaria during summer 2000 were reported to be 212 ppb and 248 ppb for May and June, respectively (PTL/AQ 2000). Khemani et al. (1995) observed that, at an urban site in Pune, the hourly O₃ concentrations during the winter period increased from a minimum value of 8 ppb to a value of 49 ppb. However, in summer the minimum O₃ value was 11 ppb, rising to

Figure 7. Correlation between mean monthly sunshine hours and mean monthly ozone concentration during the study period.

Figure 8. Daytime variation in ozone concentration on 22 May, during 2003–2006.
a maximum value of 40 ppb. These results are not in accordance with the results of the present study as the highest O₃ concentrations were recorded in the winter and not in the summer season. Similar observations were reported at Ahmedabad, where during the winter period surface O₃ concentrations increased from 18 ppb in the early morning to 55–60 ppb during noontime, whereas during the summer period they increased from 11 ppb to 30–33 ppb (Subbaraya et al. 1994). The higher concentration of hourly O₃ during the winter season represents characteristics of a polluted region as well as a region with high dynamical activity of the atmosphere, such as an increase in wind speed and in convective mixing height (Khemani et al. 1995). There is also the possibility of enhanced transport from the stratosphere, which is most effective during the winter season (Levy et al. 1985, Danielsen and Mohnen 1997).

This study found that the concentrations of O₃ showed an increasing trend during the course of monitoring from 2002 to 2006. The increase, however, is more in the winter and rainy seasons than in the summer season.

5. Conclusions

The mean monthly O₃ concentrations in Varanasi exceeded the limit that has been shown to cause significant damage to plant life. Maximum O₃ concentrations are found during the summer followed by the winter and rainy seasons. The O₃ concentration reached its maximum during hot and sunny days. Hourly maxima were recorded near noontime, which was found to be higher during the summer months as compared to the winter months. Ozone concentrations have shown an increasing trend in the past few years. Most crops in the developed countries are grown in summer when the O₃ concentrations are elevated and are frequently sufficiently high to reduce yields.
The present work was an attempt to assess the variations in tropospheric O₃ concentrations on a local scale. However, the monitoring network may be expanded to study the variability in O₃ concentrations over a regional scale. Remote sensing techniques need to be used to model O₃ concentrations over wider areas to predict climatic change and its impact on plant and human life.

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References


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PTL/AQ, 2000, Phare Topic Link on Air Quality (PTL/AQ) Ozone Exceedances Summary Table, Summer Season 2000, Available online at: www.chmi.ez/uoco/isko/ptl/about.html.


