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Ozone in ambient air at a tropical megacity, Delhi: characteristics, trends and cumulative ozone exposure indices

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Abstract Seven year data of hourly surface ozone concentration is analyzed to study diurnal cycle, trends, excess of ozone levels above threshold value and cumulative ozone exposure indices at a tropical megacity, Delhi. The ozone levels clearly exhibit a diurnal cycle, similar to what has been found in other urban places. A sharp increase in the ozone levels during forenoon and a sharp decrease in the early afternoon can be observed. The average rate of increase in ozone concentration between 09 and 12 h has been observed to be 7.1 ppb h^{-1}. We find that the daily maximum and daytime 8-h (10–17 h) ozone levels are increasing at a rate of about 1.7 (± 0.7) and 1.3 (± 0.56) ppb y^{-1}, respectively. The directives on ozone pollution in ambient air provided by United Nations Economic Commission for Europe and World Health Organization for vegetation (AOT40) and human health protection were used to assess the air quality. The present surface ozone levels in the city are high enough to exceed "Critical Levels" which are considered to be safe for human health, vegetation and forest. The human health threshold was exceeded for up to ~45 days per year. The AOT40 (Accumulated exposure Over a Threshold of 40 ppb) threshold was exceeded significantly during winter (D-J-F) and pre-monsoon (M-A-M) (Rabi crop growing season) season in India. Translating AOT40 exceedances during pre-monsoon into relative yield loss we estimate yield loss of 22.7%, 22.5%, 16.3% and 5.5% for wheat, cotton, soybean and rice, respectively.

Keywords Surface ozone · Megacity air quality · Ozone pollution · Ozone trends · AOT40

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1 Introduction

Megacities and other major population centers represent important and concentrated sources of anthropogenic pollutants in the atmosphere (Chow 2004). This raises serious concern for both, local air quality and regional and global atmospheric chemistry. Air in the megacities has become highly polluted and pollutant concentrations exceed the limit considered safe by the World Health Organization (WHO). High amounts of volatile organic compounds (VOCs) and NO_X from industrial and traffic emissions lead to a fairly high concentration of surface ozone in the boundary layer of industrial cities (Sillman et al. 1990). This further deteriorates air quality in the industrial cities (Jacob et al. 1999). Rapid urbanization and industrialization have made Delhi one of the most polluted cities in the world (Gurjar et al. 2008). Power stations, road transport, industries, use of coal for domestic purposes and burning of fossil fuels are the major sources of air pollution in Delhi (MOEF 1997; Gurjar et al. 2004). These anthropogenic activities lead to emission of NOx, CO, and a wide range of VOCs in Delhi, which participate in the photochemical reactions leading to ozone enhancement (Jain and Arya 2001; Ghude et al. 2006). Badhwar et al. (2006) observed that surface NOx concentration in Delhi is growing at a rate of ~3.8% per year and vehicular population is increasing by ~5.7% per year.

A significant part of the population of megacities is regularly exposed to peak level air pollution. Epidemiological and toxicological evidence indicate that ozone levels above the threshold (8-h>60 ppb, 1-h>90 ppb and 1-h>120 ppb) value during summer smog episodes have lead to associated health problems (Avol et al. 1998; Delfno et al. 1998), particularly, inflammatory responses and impaired lung function. Long-term exposure to high concentrations of ozone may lead to decrements in the lung function of children. Apart from causing health problems, ozone is also know to damage vegetation with possible relevant reductions in agricultural crop yields (Chameides et al. 1994; Emberson et al. 2001; Agrawal et al. 2003; Wang et al. 2005; Mills et al. 2007).

While these studies show the potential importance of the photochemical process on human health and vegetation, there exist only sporadic observational studies (Naja and lal 2002; Jain et al. 2005; Ahammed et al. 2006; Beig et al. 2007; Engardt 2008 and references therein) over the Indian region. All these studies (except more recently by Beig et al. 2008) rarely describe the events of excess in ozone levels above the threshold values (human health), cumulative ozone exposure indices (vegetation protection threshold) and trends in the surface ozone levels. In view of all these factors, the present study is aimed at assessing and evaluating ozone pollution in ambient air at the tropical megacity, Delhi using surface ozone measurements from 1997–2004, which in turn will help to develop adaptation and mitigation strategies to minimize the ozone impact on human health and agriculture productivity.

2 Method

2.1 Site overview

Measurements are carried out at Delhi (28° 65′ N, 77° 27′ E), an industrialized megacity in the northern part of India. The observational site, National Physical Laboratory (NPL), is situated in the residential area of western part of Delhi (Fig. 1). However, a good number of commuter traffic is observed in the surrounding areas. The nearest traffic juncture is located around 1.5 km from the observation site. Delhi is one of the most polluted megacities in

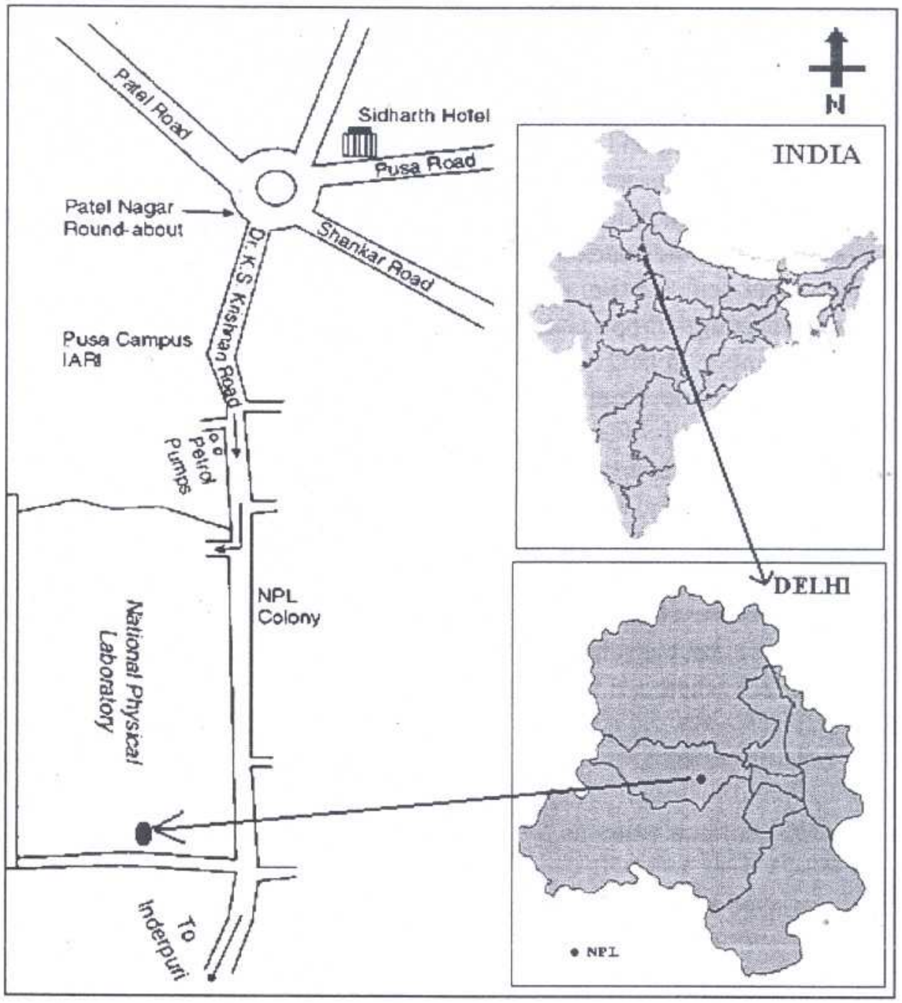


Fig. 1 Observational site and surroundings, showing the position of National physical Laboratory

tropics (population>10 million). Numerous industries are present within the city and the city itself is surrounded by an industrial area. The total number of vehicles has increased from about 3.03 million to about 4 million during the period 1997–2004. Generally, the temperature varies from 45°C in summer (maximum during day) to 1°C in winter (minimum in night). The winters are marked by mist and fog in the mornings. The cold wave from the Himalayan region makes winters very chilly. Dry summer season starts from late March to June, monsoon from late June to September, autumn (post-monsoon) from October to November and winter from December to February. In the monsoon season, precipitation, high humidity and occasional spells of heavy rainfall are commonly prevalent throughout the country. After mid September the shift of the Southwest monsoon to the Northeast monsoon generally occurs, which brings air masses from Northern and Northeast part.

2.2 Evaluation of surface ozone concentration

Surface ozone concentrations were measured using a Dasibi-make ozone analyzer. All the observed ozone mixing ratios are volume based. The details of the analyzer are given elsewhere (Jain and Arya 2001). The main air inlet was situated approximately 2.5 m above the ground. The Teflon tube between the inlet and the instrument was approximately 2 m long, and the flow rate was maintained at 2.5 l/m. The ozone analyzer was calibrated regularly (once a month) using a built-in ozone generator. The calibration was done at various levels of ozone concentration by diluting it with a zero gas in the range of 10 to 250 ppb. Daily mean (24-h) and daily maximum ozone concentration is calculated based on the hourly values. In the present study, we have used data with coverage of more than 80% of the time to compute monthly mean values and cumulative ozone exposure index. A cumulative ozone exposure index, AOT40 (Accumulated exposure Over a Threshold of 40 ppb), is calculated as the sum of the differences between the hourly ozone concentrations exceeding 40 ppb and 40 ppb using the hourly values measured for daylight hours between 07 and 19 h. AOT40 is an exposure-plant response index function set by the United Nations Economic Commission for Europe (UNECE). The AOT40 values of 3,000 ppb*h accumulated over a 3 months growing season, and 10,000 ppb*h over 6 months, correspond to the critical levels (5% yield loss) for the protection of agricultural crops and forest respectively, whereas, 8-h mean of 60 ppb corresponds to the critical level consider safe for human health (World Health Organization 2000). Percentage of hours in each month with a valid hourly ozone measurement over the period 1997-2004 is given in Table 1. Ozone measurements are only available for the month of January and November in 2000. Therefore, we have excluded the year 2000 in most of the subsequent analysis, except in section 3.3 where we studied the temporal evolution in surface ozone.

2.3 Satellite measurements

Tropospheric NO_2 column amounts derived from the space based measurements of GOME (on board ERS-2) from 1997-2002 and SCIAMACHY (on board ENVISAT) from 2003–2004 have been used to observe the temporal evolution in NO_2 concentration over Delhi during the study period. This data is available at http://www.temis.nl/airpollution/no2.html. The local overpass time of GOME (10:30 AM) and SCIAMACHY (10:00 AM) is close enough to avoid systematic differences in their time series (Van der et al. 2006). For data retrieval, error estimates and averaging kernel information see, Van der A et al. (Van der et al. 2006) and Boersma et al. (2004).

Table 1 Percentage of hours in each month with a valid hourly ozone measurement, for the site at New Delhi over the period 1997–2004

Months	1997	1998	1999	2000	2001	2002	2003	2004
Jan	–	100	100	95	74	99	36	59
Feb	–	100	38	–	100	63	59	95
Mar	–	100	88	–	100	–	98	94
Apr	–	100	99	–	100	45	98	99
May	97	100	100	–	100	51	99	87
Jun	89	100	90	–	100	83	78	99
Jul	85	100	33	–	100	93	20	80
Aug	100	100	–	–	100	67	04	18
Sep	73	100	–	–	100	81	81	81
Oct	100	100	–	–	100	97	08	58
Nov	100	100	–	73	100	98	–	88
Dec	100	100	–	–	98	96	–	97

3 Result and discussion

3.1 Diurnal variation and rate of change of surface ozone mixing ratios

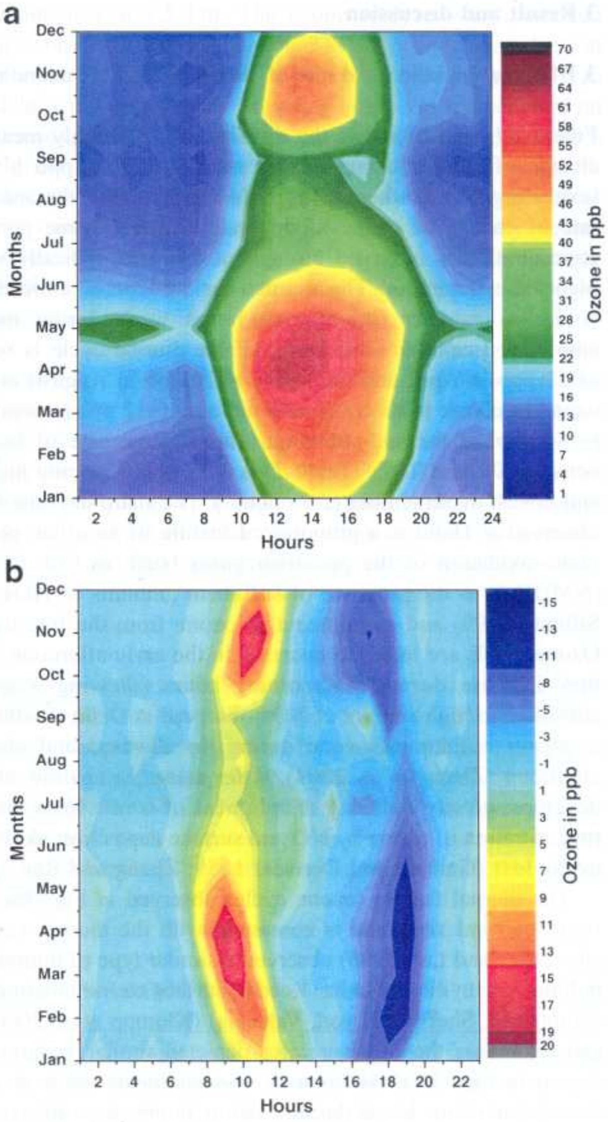
Figure 2 (a and b) shows the distribution of monthly mean diurnal variation and rates of change of surface ozone mixing ratios ($d(O_3)/dt$ ppb h^{-1}) at Delhi during 1997–2004 (excluding 2000), whereas Fig. 3 (a and b) shows the annual mean diurnal cycle and the rate of change of ozone mixing ratios for the same period. A diurnal cycle in ozone concentration is observed throughout the year, typically with a mid-afternoon peak and night-time minimum. The diurnal cycle becomes more distinct during the period from winter to summer (pre-monsoon) and weak during monsoon months. The average amplitude (maximum-minimum) of the diurnal cycle is ~37 ±10 ppb (with a maximum of 51 ppb in April and minimum of 20 ppb in August) at Delhi (Table 2). Annual mean ozone levels are low during early morning (~12 ppb (around 6 AM)) and reach a maximum (~ 44 ppb) in the mid-afternoon. The average rate of increase of ozone concentration between 08 and 12 h (Table 2) is ~7.1 ppbh^{-1}, being highest in November (~9 ppbh^{-1}) and lowest in September (2.5 ppbh^{-1}). The sharp daytime increase in ozone concentration observed at Delhi is a pronounced feature of an urban polluted site. It is mostly due to photo-oxidation of the precursor gases (such as CO, CH_4, non-methane hydrocarbons (NMHCs)) in the presence of sufficient amounts of NOx (Crutzen 1988; Penkett 1998; Sillman 1999) and entrainment of ozone from the free troposphere (Coyle et al. 2002). Ozone levels are found to decrease in the early afternoon hours with almost same rate as they increase during the morning hours (showing a symmetric cycle). This can be attributed to high amount of NOx observed in Delhi (Badhwar et al. 2006), which leads to a greater buildup of ozone during the daytime and also faster titration in the early afternoon (Zhang et al. 2004). After sunset, a shallow stable nocturnal inversion layer develops, greatly reducing entrainment of ozone from the free troposphere. During this time, titration of ozone by NO and surface deposition likely becomes the main process for ozone loss (Garland and Derwent 1979; Zhang and Rao 1999; Coyle et al. 2002).

The diurnal feature (ozone cycle) observed in Fig. 3(a and b) distinguishes the urban from the rural sites, and is consistent with the diurnal variation observed in other urban sites. Naja and Lal (1996) observed a similar type of diurnal cycle at Ahmadabad, a highly polluted urban city in India. Recent, surface ozone measurements at urban sites in Europe (Edinburgh, Sheffield, Lyon, Valencia) (Klumpp et al. 2006) and U.S. (Zhang et al. 2004, and references therein) have also depicted similar features of the diurnal ozone cycle as shown in Fig. 3(a). By contrast, measurements made at rural sites in India show slow decrease in ozone levels during evening hours, showing asymmetric ozone cycle (Naja and Lal 2002; Ahammed et al. 2006; Debaje et al. 2003). This type of diurnal variation in ozone has also been observed at the rural sites in southern U.S (Georgia) and Europe (Kleinman et al. 1994; Klumpp et al. 2006).

3.2 Seasonal variation in observed data at Delhi

Figure 4(a) shows the seasonal variation in surface ozone mixing ratios for the period 1997–2004 (excluding 2000) at Delhi. Annual average ozone concentration is found to be ~24 (±3.4) ppb. The monthly mean ozone value was found to be maximum (35.4 (±3.5) ppb) during May and minimum (14.3 (±3.05) ppb) in the month of August. Higher ozone concentrations have been found during summer months and lowest concentrations are found during monsoon months, which can be attributed to influence of meteorological

Fig. 2 (**a**) Diurnal variations of average surface ozone mixing rations in different months and (**b**) Rates of change of average surface ozone mixing ratios for each hour in different months for the period 1997–2004 (excluding 2000) at Delhi. (*Rate*= $d(O_3)/dt$ *ppb* h^{-1})



parameters and nature of the air masses arriving at the monitoring site. Lal et al. (2000) and Pochanart et al. (1999) reported similar type of seasonal variation in ozone concentration from tropical urban sites and attributed them to changing meteorological parameters and variation in concentrations of precursors gases due to local emissions and transport from regional sources. The general climatology (Fig. 4(b), (c) and (d)) over Delhi region shows that the air masses arriving at the site during monsoon season originate over the ocean (either over Indian Ocean, Arabian Sea or Bay of Bengal) and mix with continental air. The influx of marine boundary layer air reduces the possible presence of large amount of ozone as well as ozone precursors. Thus, these air masses (after mixing with the continental air) bring relatively less polluted air at the observational site. Moreover, there is also less solar

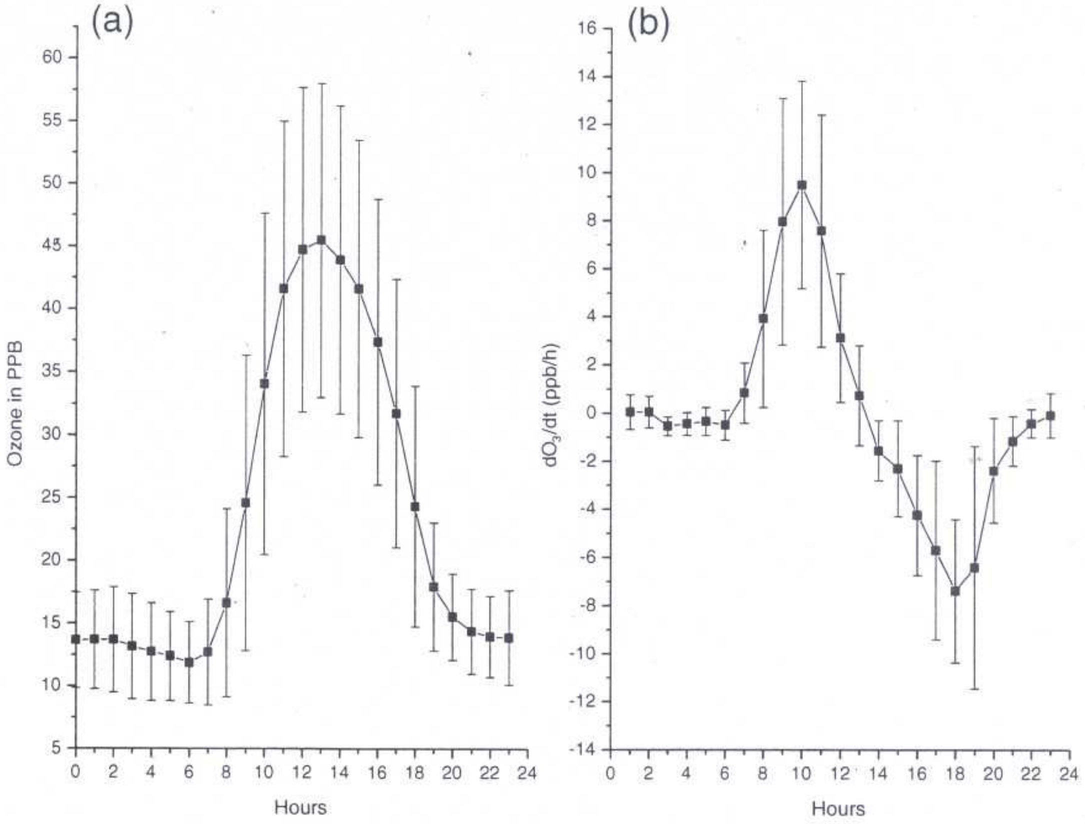


Fig. 3 (**a**) Diurnal variations of average surface ozone mixing ratio and (**b**) Rates of change of surface ozone mixing ratios averaged for each hour during 1997–2004 (excluding 2000) at Delhi. (*Rate*= $d(O_3)/dt$ *ppb* h^{-1})

Table 2 Monthly distribution of mean, daytime 8–hr (10–17 h) mean, maximum and minimum ozone concentration, and its amplitude, rate (*Rate*= $d(O_3)/dt$ *ppb* h^{-1}) of increase (between 8–12 h) and maximum rate of increase at Delhi for the period 1997 –2004 (without 2000)

Months	Mean Ozone in ppb	8 Hr (11–18) Ozone in ppb	Max Ozone in ppb	Min Ozone in ppb	Amplitude in ppb	Rate (8-12 h) ppb/h
Jan	19.3	32.2	40.7	10	30.7	5.5
Feb	25.3	45.9	55.7	10.9	44.8	8.2
Mar	29.7	49.5	58	13.8	44.3	7.2
Apr	33	54.8	64.3	13.7	50.6	6.8
May	35.4	55.2	62	19.8	42.2	5.6
Jun	25.6	40.7	46.4	12.8	33.6	4.7
Jul	19.1	30.3	37.1	9.4	27.7	3.7
Aug	14.3	24.2	29.5	9.7	19.8	2.8
Sep	17.7	29.8	37.7	7.7	29.9	2.5
Oct	21.7	39.7	56.9	9	47.9	7.6
Nov	22.6	40.8	55.1	9	46	8.7
Dec	20.2	33.9	40.3	9.1	31.2	5.8

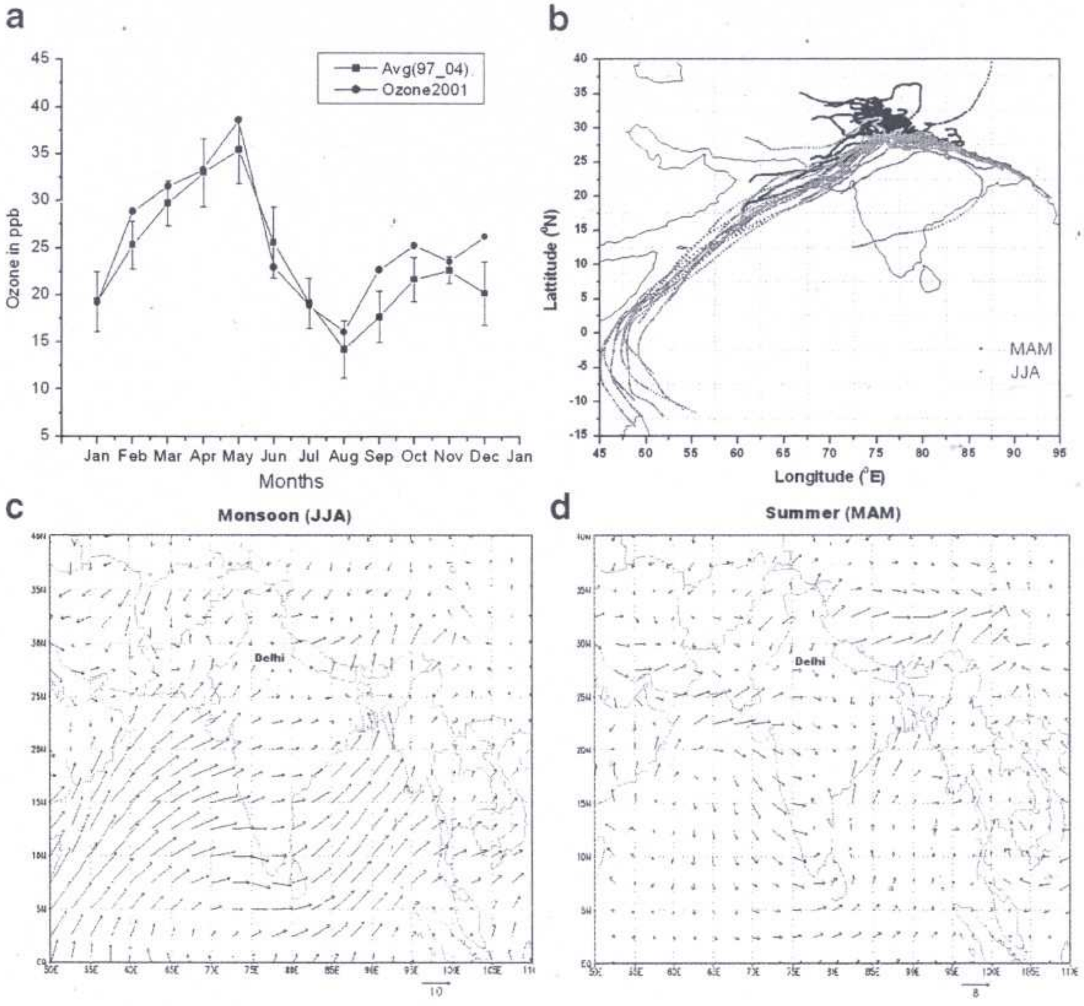


Fig. 4 (**a**) Seasonal variation of monthly average O_3 mixing ratios for the whole period (1997–2004 (excluding 2000)) and single year (2001) (**b**) map of biweekly 7-day backward air trajectory (NCEP data) at Delhi for monsoon (gray) and summer (Black) seasons. Bottom part of the figure shows the distribution of winds at surface level over Indian region during (**c**) monsoon and (**d**) summer seasons (*Wind vectors are plotted using NCEP Reanalysis derived data product*)

radiation for photochemical reactions on cloudy days and washout of the precursor pollutants during monsoon months. The combination of these factors results in the low ozone levels during monsoon (Ahammed et al. 2006; Beig and Brasseur 2006; Beig et al. 2008). Enhanced surface ozone concentration during summer can be explained by larger photochemical formation due to favorable meteorological conditions and presence of elevated precursor pollutants. During summer months, most of the air trajectories originate from the northern plain (Indo-Gangetic (IG) plain, which is a source of precursor pollutants) and either travel across IG region or confined mostly to the local region (Fig. 4(b)). This results in trapping of precursor pollutants and photo-chemically produced ozone. The general meteorological conditions prevailing over Delhi show warm weather, higher solar radiation, low humidity and stagnant wind pattern (Jain et al. 2005) during summer period. This is found to be favorable for production of high ozone concentration (Crutzen 1995).

3.3 Multi-annual trend

Figure 5 shows the time-series of monthly mean of daily maximum, daily 8-h (10–17 h) average, daily (24-h) average and night-time (21-05 h) ozone concentration for the 1997–2004 period. Trend values along with standard error are mentioned in the respective figures. Long term surface level measurements of ozone precursors are not available at the measurement site, Delhi. Therefore, we have used tropospheric NO_2 column amounts retrieved from the combined GOME and SCIAMACHY measurements to examine the temporal evolution of ozone precursor (in this case NO_2) over Delhi over the same period (Fig. 5). Since the chemical lifetime of NO_2 is short (of the order of one day), the tropospheric NO_2 columns observed from space are dominated by the NO_2 amount in the boundary layer. For every time-series a linear regression is performed and resulting gradient is obtained. Trends are significant at the 95% confidence level (except for monthly mean of daily average ozone concentration). An increasing trend in daytime surface ozone levels has been observed. At the same time, night-time ozone levels show decreasing trend at Delhi. Daily maximum, daytime 8-h (10–17 h) and daily average (24-h mean) ozone levels are

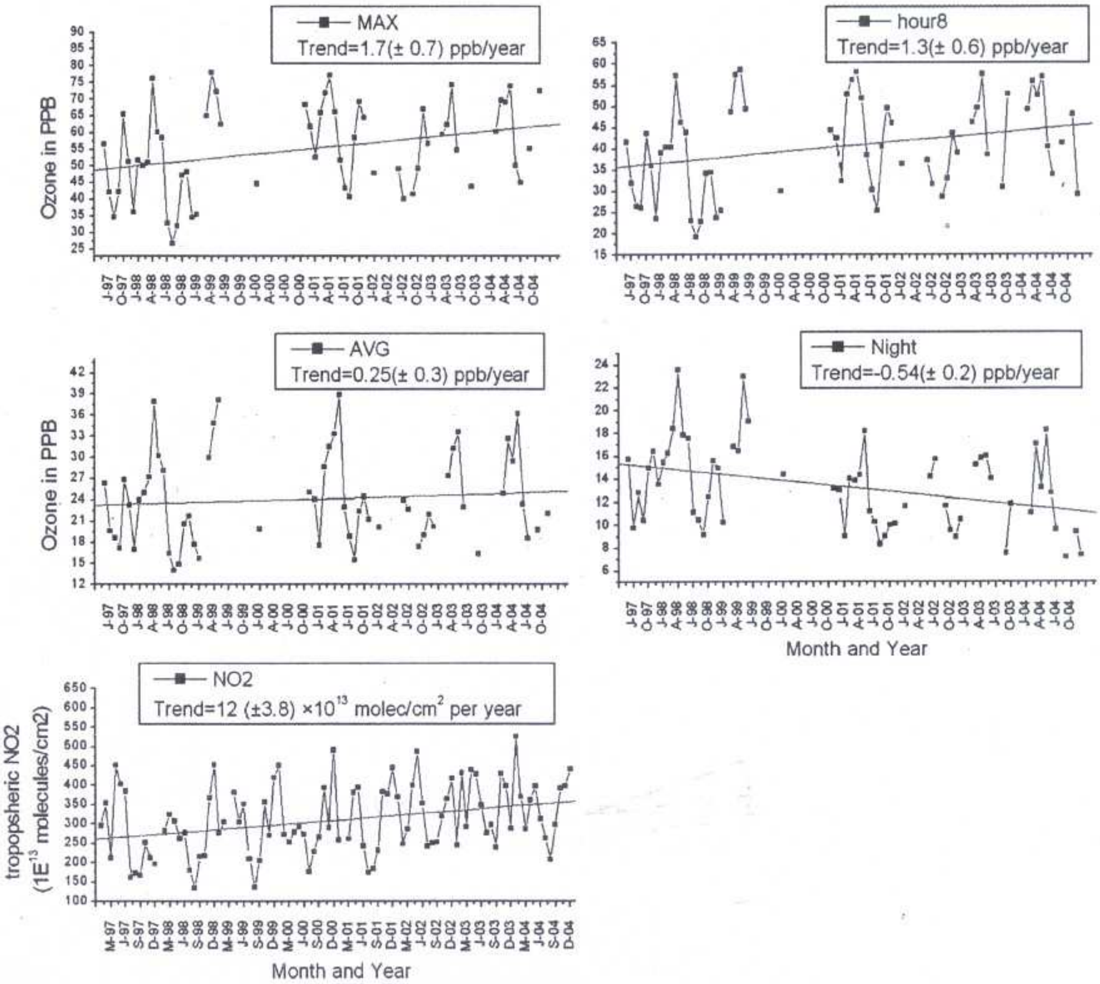


Fig. 5 Temporal evolution of daily maximum, daily 8-h (10-17 h) average, daily 24 h average and nighttime ozone (21-05 h) concentration, and SCIAMACHY tropospheric NO_2 column for the 1997–2004 period. Trend values along with standard error are mentioned in the center of the respective figures

found to be increasing at a rate of about 1.7 (± 0.7), 1.3 (± 0.6) and 0.25 (± 0.3) ppb y^{-1} respectively, whereas, night-time (21-05 h mean) ozone levels are found to be decreasing at a rate of about 0.54 (± 0.2) ppb y^{-1}. The combination of the positive daytime trend with the negative nighttime trend results in a small positive (non-significant) trend in the daily average. A plausible cause for the observed contrasting trend during day and night-time is the increasing level of NOx in Delhi. During daytime NOx catalyze the photochemical oxidation of VOCs and other species to form ozone. During night-time NOx remove ozone through titration reaction, in which NO reacts with ozone to form NO_2. As can be seen from Fig. 5, tropospheric NO_2 levels show increasing trend ($12\ (\pm 3.8) \times 10^{13}$ molec/cm^2 per year) over Delhi during the period 1996-2004, caused by rapid industrialization and vehicular growth during the past decade (Badhwar et al. 2006; Ghude et al. 2008). Contrasting trend during day and night-time (positive in day and negative in night) and resulting small positive trend in daily average suggests that exposure indices based on daytime threshold values and on peak values will show increasing trend, whereas indices based on daytime average or daily average will hide trend significantly. Thus, it illustrates the importance of the indicator chosen for regulatory purpose.

3.4 Exceedance of critical levels

Since an ozone pollution directive is not yet established for the Indian region, we have here used United Nations Economic Commission for Europe (UNECE) and World Health Organization (WHO) Directives on ozone pollution in ambient air. Accordingly, for the protection of human health, the daily 8-hour mean ozone concentration should not exceed 60 ppb on more than 25 days per calendar year, averaged over a 3-year period. Similarly, AOT40 (Accumulated exposure Over a Threshold of 40 ppb) values of 3,000 ppb*h for daylight hours over 3-month growing season and 10,000 ppb*h over a 6 months period is established as a critical level for protection of agricultural crops and forest respectively. We have evaluated the ozone exposure indices in excess of current limit values based on above UNECE and WHO guidelines for vegetation (AOT40) and human health protection.

3.4.1 Human health

The daily maximum, daily 8-h mean (over a fixed period of 10–17 h) and daily average surface ozone concentration during 1997–2004 are shown in (Fig. 6(a), (b) and (c)), respectively. Elevated ozone concentrations have been observed on a large number of days (generally during February-May and September-November) indicating prominent ozone pollution and systematic violation of health protection standard ((European Union, EU.: Directive, 2002) at Delhi. The annual number of days exceeding various threshold values is given in Table 3. In the table we report the number of ecxeedances actually observed during actual measurements days; the values given below are the number of exceedances extrapolated to 100% data coverage. In the case of Delhi the EU standard for human health protection (8-h>60 ppb) is exceeded during ~45 days per year (13% of measured days, average over the 7 years measurement period). One hour average exceedances of 80 ppb (defined as high ozone days) are occurring during ~45 days (~137 hours) per year, mostly during February-May and September-November. The information and alert threshold (1-h> 90 ppb and 1-h>120 ppb respectively), are violated during ~28 and ~5 days per year, respectively (~69 and ~17 hours per year respectively), averaged over the measurement period. This means that there is significant ozone pollution at the monitoring site and is of serious concern for human health.

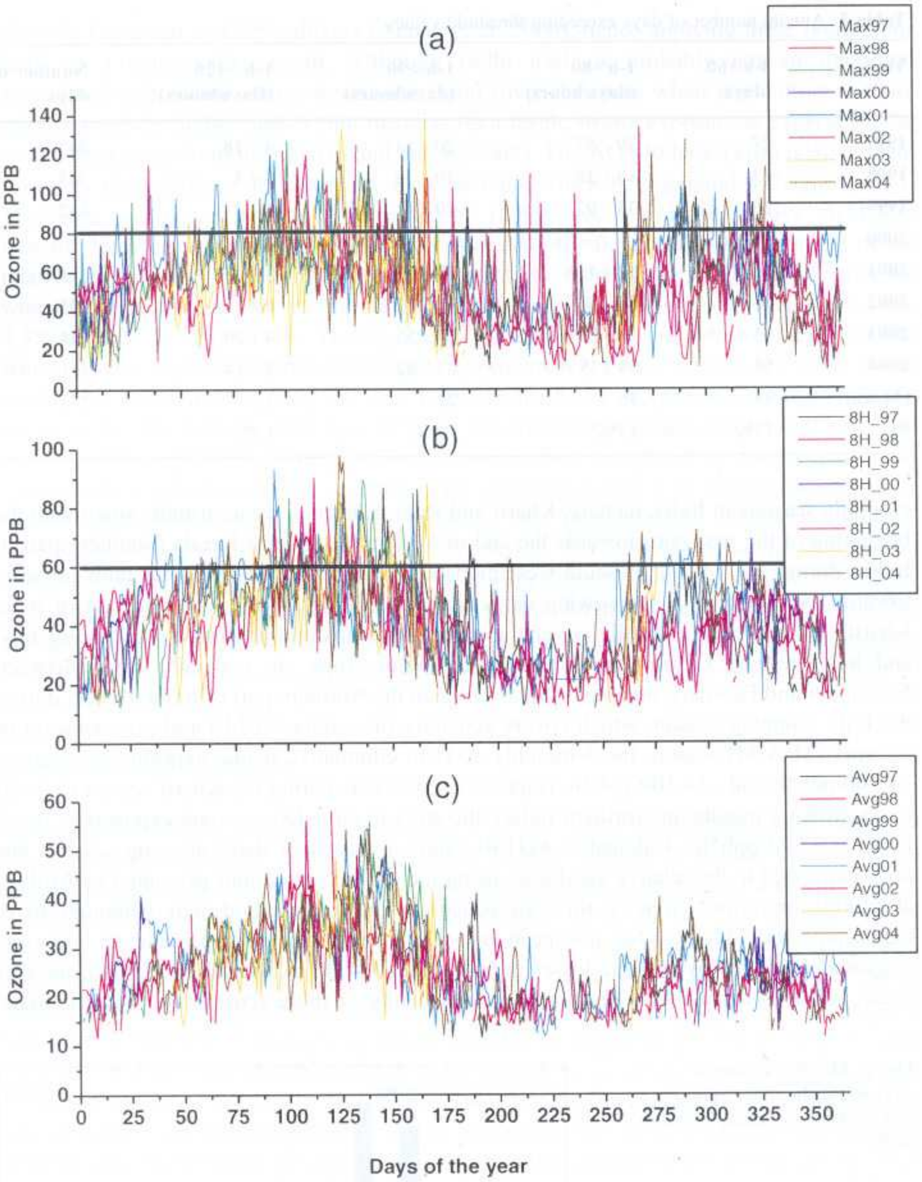


Fig. 6 (**a**) Daily maximum; (**b**) daily 8-h mean and (**c**) daily average surface ozone concentration (in ppb) during 1997–2004 at Delhi. Black horizontal grid line through 80 ppb (Fig. 6a), and 60 ppb (in Fig. 6b) is poor air quality threshold and health protection threshold, respectively

3.4.2 Vegetation and forest

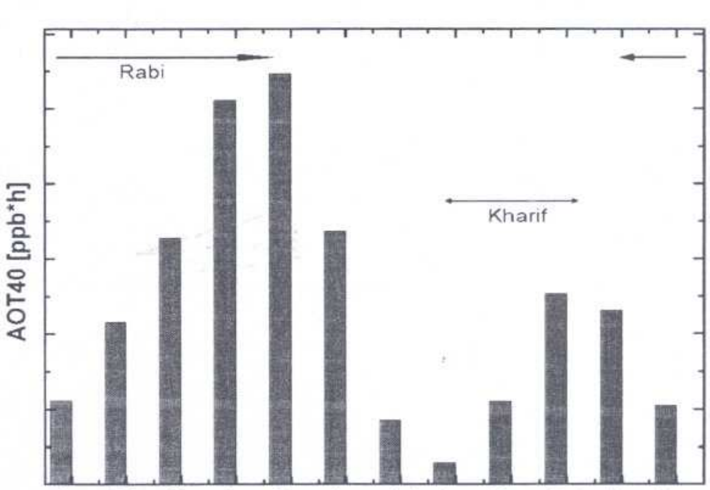
Monthly distribution of AOT40 cumulative ozone exposure averaged over the period 1997-2004 (excluding 2000) is shown in Fig. 7. Figure 7 show that monthly AOT40 values varied approximately between 300 (August) to 5,470 (May) ppb*h. There are two major

Table 3 Annual number of days exceeding threshold values

Year	8-h>60 (days)	1-h>80 (days/hours)	1-h >90 (days/hours)	1-h >120 (Days/hours)	Number of days
1997	27	29 / 87	20 / 51	4 / 18	243
1998	13	18 / 38	10 / 18	1 / 3	365
1999	36	33 / 93	20 / 41	1 / 4	162
2000	–	–	–	–	–
2001	55	52 / 158	31 / 73	3 / 15	356
2002	23	35 / 78	18 / 42	6 / 15	293
2003	33	28 / 91	14 / 55	4 / 20	194
2004	53	59/175	33 / 82	3 / 14	311
(Mean)	35	36	21	3.7	275
%	13%	13%	7.6%	1.3%	

cropping seasons in India, namely, Kharif and Rabi. Kharif crops are usually sown with the beginning of the first rains towards the end of May in the state of Kerala (Southern part of India) during the advent of south-west monsoon season. As the monsoon rains advance towards the North India the sowing dates vary accordingly. In the Northern part of India Kharif season would generally cover the months of rains and autumn (sown during July, and harvested by October end /November). Rabi crops are generally sown between November and February, and harvested by June in the Northern part of India. Hence, during the Rabi cropping season, which covers generally the winter (D-J-F) and pre-monsoon or summer (M-A-M) season, the 3-monthly AOT40 cumulative ozone exposure amounts to ~4,700 ppb*h and ~14,100 ppb*h, respectively, whereas during the Kharif season (A-S-O) (crop growing months in Northern India), the AOT40 cumulative ozone exposure is much lower (~3,700 ppb*h). Calculated AOT40 values for each of these growing seasons has been converted to the relative yield loss, using the simple regressions presented by Mills et al. (2007) for various crops (in this case wheat, cotton, soybean and rice). Although, these regressions are obtained for European and US crops, they may provide an order-of-magnitude estimate of possible losses in India. Small scale individual studies indicate that Asian cultivars for winter wheat and rice are equally or more sensitive to ozone damage

Fig. 7 Monthly observed AOT40 for the mean period 1997–2004 (excluding 2000) at Delhi



than the European and US cultivars (Aunan et al. 2000), hence applying these regressions leads to a conservative result. Although Delhi itself is probably not an important agricultural site, ozone values downwind Delhi (over the areas where agriculture is more relevant) will be higher than within the city. As a result, ozone exposure is expected to be even higher away from the city (Chand and lal 2004). The AOT40 based crop relative yield functions from Mills et al. (2007) have an intercept which is in general different from 1. Therefore, as suggest in Van Dingenen et al. (2009), we scaled the relative yield loss function by Mills et al. (2007) to their values at AOT40=0, such that the intercept of the relative yield equals 1. From these calculations it is observed that relative yield loss for wheat, cotton, soybean and rice during Kharif season (A-S-O) was approximately 6%, 6%, 4.3% and 1.5%, respectively. During Rabi crop growing season relative yield loss for wheat, cotton, soybean and rice increased to approximately 7.5%, 7.5%, 5.4% and 1.8% in winter (D-J-F), and 22.7%, 22.5%, 16.3% and 5.5% in pre-monsoon (M-A-M), respectively. The relative yield loss for most sensitive crops (wheat, cotton and soybean) is not really significant during Kharif seasons when compared to the critical limit considered (5%) to be safe for vegetation. By contrast, during Rabi crop growing season relative yield loss is significant both in winter and pre-monsoon, however it is more pronounced in pre-monsoon. Over a six month period, AOT40 cumulative ozone exposure exceeded up to ~10,500 and 18,700 ppb*h during June-November and December-May period, respectively. It is to be mentioned that the AOT40 limit values in the EU Directive are defined as 5-year mean in order to compensate for annual variations, while the present analysis is based on an average value between 1997 and 2004 (7-year excluding 2000).

4 Summary and conclusion

In this study, we have presented an analysis of surface ozone measurement (1997-2004) at tropical megacity, Delhi. The ozone levels clearly exhibit a typical diurnal cycle characterized by a sharp increase in the ozone levels during forenoon and a sharp decrease in the early afternoon (Naja and Lal 1996; Klumpp et al. 2006). The average rate of increase in ozone concentration between 09 and 12 h has been observed to be 7.1 ppb h^{-1}. Relatively high levels of ozone are observed during summer (MAM) whereas low ozone levels are noticed during monsoon. Over the 7 year observations period, daily maximum and daytime 8-h (10–17 h) ozone levels are found to be increasing (1.7 (± 0.7) ppb y^{-1} and 1.3 (± 0.56) ppb y^{-1}, respectively), while night-time ozone levels are found to be decreasing (0.54 (± 0.2) ppb y^{-1}) at Delhi. A possible explanation for the positive trend during daytime and negative trend during night-time is the increasing NO_2 levels in Delhi. According to UNECE and WHO ozone directives, the current surface ozone levels in this city are high enough to exceed "Critical Levels" considered safe for human health, vegetation and forest. The human health threshold was exceeded up to ~45 days per year, largely exceeding the 25 days target value per year permitted by the EU directive. One hour (1-h) threshold for information to the public and alert threshold is exceeded on ~28 (~69 hours) and ~5 (~17 hours) days per year respectively. Translating AOT40 exceedances during Kharif and Rabi seasons into crop relative yield it is observed that relative yield loss for most sensitive crops (wheat, cotton and soybean) is not really significant during Kharif season. By contrast, relative yield loss during Rabi season is observed significant of about 7.5%, 7.5%, 5.4% and 1.8% in winter (D-J-F) and 22.7%, 22.5%, 16.3% and 5.5% in pre-monsoon (M-A-M) for wheat, cotton, soybean and rice, respectively. The present study suggests that surface ozone in Delhi is much above critical levels and is a significant concern for human health.

Although Delhi is not an important agricultural site, transport of pollutants from major urban sites like Delhi can enhance ozone levels in their downwind rural sites (Chand and lal 2004). As a result, ozone exposure is expected to affect the food production in downwind areas where agriculture is more relevant. Therefore, these measurements give a broad picture of the likely levels of ozone exposure experienced in the surrounding region and have, to date, been useful for the assessment of ozone effects on vegetation and human health.

The present study shows the potential importance of photochemical process in the megacity, Delhi which highlights the need for continued monitoring by establishing a network of stations over the surrounding region. This will be helpful to develop adaptation and mitigation strategies to minimize the ozone impact on human health and agriculture productivity over this region. With continued economic development in India (Ghude et al. 2009), in any case, this region will have an increasingly large impact on human health and plant life. Therefore, attention should be drawn towards the impact of pollutants like surface ozone on human health and vegetation protection.

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