

A Photochemical Modelling Approach to Investigate O₃ Sensitivity to NO_x and VOCs in the Urban Atmosphere of Delhi

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Abstract

Ambient air pollutants data were used to evaluate whether O₃ formation at a specific site (Sirifort) in Delhi was limited by volatile organic compounds (VOCs) or oxides of nitrogen (NO_x). For this purpose, a photochemical model OZIPR (Ozone Isopleth Plotting Research) based on Lagrangian trajectory model was applied to 9 ozone episodes that occurred at Sirifort from August to October 2006. Emissions data were estimated using an area-source box model. The results show that the prediction for peak O₃ concentration agreed reasonably well with the observed data. O₃-isopleth plots clearly reveal that O₃ formation is more sensitive to VOC emissions for lower VOCs/NO_x ratio, while for higher VOCs/NO_x ratio, O₃ formation is more sensitive to NO_x emissions. However, for the purpose of practical O₃ control applications at the observation site, it is concluded that VOCs emissions should be reduced while keeping a lower VOCs/NO_x ratio.

Keywords: OZIPR; Photochemical modelling; Ozone; NO_x; VOCs.

INTRODUCTION

Tropospheric O₃, a well-known secondary pollutant is formed and sustained in the atmosphere due to a chain of complex reactions taking place among NO_x and VOCs in the presence of sunlight. To prepare a control strategy for O₃, it is crucial to investigate O₃ behavior in relation to its precursors (NO_x and VOCs), which are mostly

primary pollutants and which come from identifiable specific sources, such as vehicular traffic. This has led various researchers to employ different approaches in order to quantify this relationship.

For the Greater Athens Area, using an extended database of air pollution and meteorological parameters in an Urban Airshed Model (UAM), Ziomas *et al.* (1998) concluded that ozone abatement strategy should focus mostly on controlling VOC emissions rather than controlling NO_x (Blanchard and Stoeckenius, 2001) and compared O₃ predictions from six photochemical air-quality

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simulation models. For all simulations, peak ozone values increased following NO_x control in 95% (median over all simulations) of the high-ozone (> 80 ppbV hourly mixing ratio in the base-case) grid cells having mean afternoon O₃/NO_z ratios less than 5:1, O₃/NO_y less than 4:1. Peak ozone levels decreased in response to NO_x reductions in 95% (median over all simulations) of the grid cells having peak hourly ozone mixing ratios greater than 80 ppbV and where mean afternoon O₃/NO_z exceeded 10:1, O₃/NO_y was greater than 8:1. Arbilla *et al.* (2002) used an empirical kinetic modeling approach (EKMA) in order to simulate ozone concentrations for an urban downtown area with high vehicular traffic. The agreement between experimental and simulated results was quite good. The simulated ozone peak was obtained at 3:15 p.m. (23.0 ppb). A sensitivity-uncertainty analysis was performed and hypothetical scenarios were designed to illustrate the predictive potential of air quality models. Stein *et al.* (2005) examined the airborne measurements of sulphur dioxide (SO₂), total reactive oxides of nitrogen (NO_y), and O₃ taken from an instrumented aircraft to assess the governing photochemical processes of ozone formation. The sensitivity of ozone to changes in its primary sources was examined by simulating scenarios with varying rates of NO_x and VOC emissions. The study of Stein *et al.* (2003) show that for this particular case the measured and modeled upwind NO_x sources are more effective than VOCs emissions for lowering O₃. Cohan *et al.* (2006) applied nested grids of 36-, 12- and 4-km resolution to model an air

pollution episode in Georgia., USA. A direct sensitivity analysis method used to compute the O₃/NO_y ratios seems to identify a photochemical regime in which reductions in response of ozone to emissions of its precursors: nitrogen oxides (NO_x) and volatile organic compounds (VOCs). All three grids predict that ozone production is limited primarily by the availability of NO_x, and yield similar predictions of average ozone sensitivity to both regional and local emissions of NO_x. Toro *et al.* (2006) studied the relationship between VOC and NO_x emissions and the chemical production of tropospheric ozone through mathematical simulation for the Aburra Valley in the Columbian Andes. The model used for this application is the European modeling of atmospheric constituents (EUMAC) zooming model (EZM) which consists of a mesoscale prognostic model (MEMO, mesoscale meteorological model) and a chemical reaction model (MUSE, multiscale for the atmospheric dispersion of reactive species), coupled with the chemical mechanism EMEP (European Monitoring and Evaluation Programme). The analysis was performed for a real episode that was characterized by high ozone production. The sensitivity analysis showed that in order to keep current levels, the emphasis must be put to avoid increasing NO_x emissions, or alternatively, to augment VOC emissions to have a high VOC/NO_x ratio.

The present study employs the Lagrangian trajectory model (Seinfeld and Pandis, 1988; Jang, 1999) because it allows us to study the response of the photochemistry in isolation

from transport, which complicates the analysis in Eulerian grid model (Arbilla *et al.*, 2002). In this context, the Ozone Isopleth Plotting Research (OZIPR) (Gery and Crouse, 1990) model of the United States Environmental Protection Agency (USEPA) is a convenient tool to explore O₃ response for a large range of VOCs and NO_x emission levels. The hourly data of O₃, NO_x (NO and NO₂) and VOCs (benzene, ethylnezene, m,p-xylene and toluene) at Sirifort used in the present study were obtained from the CPCB (Central Pollution Control Board, Delhi, <www.cpcb.nic.in>].

OZIPR

The OZIPR simulates complex chemical and physical processes of lower atmosphere through the use of Lagrangian trajectory model. The physical representation is a well-mixed column of air extending from the ground to the top of the mixed layer. This ideal air column moves with the wind (along the wind trajectory), but cannot expand horizontally. Emissions from the surface are included as the air column passes over different emission sources, and air from above the column is mixed in as the inversion rises during the day. Very complex chemical mechanisms may be input into OZIPR to describe the chemical processes that occur within the modeled air mass. OZIPR performs a specified set of simulations to calculate ozone levels at fixed intervals. This allows for the plotting of fixed ozone concentration lines (isolines) as a function of initial precursors.

INPUT REQUIREMENTS OF OZIPR

Following are the main inputs required for the OZIPR model:

- Sunlight Intensity
- Dilution
- Post-0800 Emissions
- Ozone Transport
- Precursor Transport
- Chemical Reactivity
- Temperature
- Water Vapor
- Biogenic Emissions

(i) *Sunlight Intensity*: The OZIPR program uses a city's latitude, longitude, time zone, and day of the year being modelled to generate the appropriate diurnal pattern of photolytic reaction rates. Usually no changes need be made for this set of model inputs.

(ii) *Dilution*: In OZIPR model, dilution occurs as a result of the rise in atmospheric mixing height that typically occurs between early morning and mid-afternoon. The mixing height can be viewed as the top of a surface-based layer of air which is well-mixed due to mechanical and thermal turbulence. Specific input to OZIPR includes the early morning mixing height, the maximum afternoon mixing height, the time that the mixing height rise begins, and the time at which mixing height is finally attained. Procedure for estimating the early morning mixing height and maximum afternoon mixing height from available radiosonde measurements are outlined in EPA

(1989). This was implemented using MATLAB[®] program codes in the present study. Radiosonde measurements pertaining to Safdarjang, New-Delhi, measured with the help of Rutherford Appleton Laboratory, Chilton, and compiled by the British Atmospheric Data Centre (BADC, 2006) were used in this study.

(iii) *Post-0800 Emissions*: Post-0800 emissions refer to emissions occurring along the trajectory subsequent to the start of the model simulation (usually 08:00 AM). The actual inputs are expressed as emission densities (kg/km²-hr) of NMOC, NO_x, and carbon monoxide (CO) concentrations that should be added each hour to the effect of fresh precursor emissions.

In the present study, Area-Source Box Model (Masters, 1998) was used to estimate mass emission rate (kg/km²-hr) from the available ambient concentration data (in µg/m³). The present study makes use of steady state solution of area-source model to estimate the mass emission rate from ambient pollutant concentration. The steady state solution of box model is given by

$$Q = \frac{CuH}{L}; \quad (1)(\text{Masters, 1998})$$

Where:

Q = mass emission rate per unit area (mg/m²-s);

u = average wind speed against one edge of the box, m/s;

H = mixing height, m;

L = length of airshed, m;

C = pollutant concentration in the airshed, mg/m³.

Fig. 1 shows the map of New Delhi. A 10 km² enclosed square area around the observation site (Sirifort) is shown by a grey square on the map. An air parcel box was assumed having this area as the base area. The height of this box is given by mixing height determined by prevailing meteorological conditions. Air was assumed to be uniformly mixed within this box. For this assumed box model, the hourly mass emission rate were estimated by using Eq. (1).

(iv) *Ozone Transport*: The two possible mechanisms by which ozone is transported into an urban area are:

- (1). Advection of ozone along the earth's surface, and
- (2). Advection of ozone aloft, typically at night and during early morning hours, with downward mixing when the mixing layer increases later in the day.

Ozone transported at the surface is subject to surface reactions and scavenging by other species (e.g., NO) emitted during the night. As a result of night time atmospheric stability, ozone transported aloft does not come into contact with scavengers emitted during the night. Thus, overnight advection of ozone aloft is the more significant mechanism of transport from one urban area to another (EPA, 1989).



Fig. 1. Map of New Delhi (Source: Microsoft Encarta 2004). Area enclosed by grey square shows 10 square km area around Sirifort.

This study mainly simulated the model for daytime only when the ozone aloft mechanism was less significant. As such, ignoring ozone aloft values does not change the final result significantly. This exercise was carried out for some of the well-tested US cities data as provided by EPA (2004). The change in simulated result is not more than $\pm 5\%$. Hence, only surface ozone values were used in the present study; this is partly due to lack of ozone aloft data.

(v) *Precursor Transport*: Just as for ozone, precursor pollutants (NO_x , VOCs) could be transported in both the surface layer and aloft. However, outside of urban areas, the surface layer is expected to be very shallow. Thus, long range transport of precursors in the surface layer may not be significant. Again, in

the present study, for the reasons mentioned above, only surface precursor values have been used.

(vi) *Chemical Reactivity*: CB-4 mechanism (EPA, 1989) was used in the present study. This study selects CB-4 mechanism as this mechanism uses a highly condensed method to represent reactions of VOCs, with the goal being to predict ozone from ambient mixtures as accurately as possible. It was evaluated against a large number of environmental chamber experiments (Gery et al., 1988).

For the purpose of carbon-fractionation, annual mean concentration data of VOCs for residential areas in Delhi pertaining to Srivastava (2005) have been employed. In the Srivastava (2005) study, the samples were collected in 2001 and analyzed to estimate a

number of VOCs. Although there is a significant time gap between Srivastava (2005) and the present study, it can be a good representative for the purpose of estimating carbon fractions as per EPA (1989) recommendation. We have also compared this carbon-fraction estimation with the available CPCB hourly VOCs data at Sirifort from August to October 2006, which consists of only 5 VOCs. Within the range of ± 0.05 , o-Xylene, m,p-Xylene, Toluene, Benzene and Ethyl-benzene show an agreement with the carbon-fraction estimation based on Srivastava (2005). The small discrepancy shown here may also be due to the lack of other VOC data at Sirifort. Hence, the present study preferably uses carbon-fraction estimation based on Srivastava (2005) which is also more representative of VOC variability in Delhi, owing to its extensive broad-based sampling, monitoring and analysis using GC-MS techniques.

(vii) Temperature: Hourly temperature data must be utilized in OZIPR. Use of hourly temperatures allows reaction rates to be increased or decreased according to the hourly temperature. In the present work, hourly temperature data pertaining to Safdarjang, New Delhi, thankfully provided by Nautica Editrice Srl (1995-2006), was used.

(viii) Water Vapor: Ozone predictions are also sensitive to the amount of atmospheric moisture content. OZIPR estimates atmospheric moisture content using relative humidity values and ambient pressure level.

Hourly values of relative humidity were used for Safdarjang, New Delhi (provided by Nautica Editrice Srl, 1995-2006).

(viii) Biogenic Emissions: OZIPR also provides an option for biogenic emissions, such as isoprene, α -pinene, monoterpenes, and unknowns. EPA has prepared a computer program to estimate biogenic emissions rates on a county basis for the USA. This program estimates biogenic emission on the basis of day-specific meteorological parameters. However, in the absence of such data and facilities, EPA (1989) recommends to set it simply to zero, which was followed in the present case.

OZONE EPISODES, NO_x, VOCs AND METEOROLOGICAL CONDITIONS

High ozone episode is a condition when the level of O₃ concentration exceeds a certain threshold and thereby posing threats to the human health. The World Health Organization has prescribed a standard of 100 $\mu\text{g}/\text{m}^3$ (8-hour average) (WHO, 2006) for ambient O₃ concentration. In the present study, those conditions were considered as high ozone episodes when the ambient O₃ concentration repeatedly exceeded 100 $\mu\text{g}/\text{m}^3$ level (Fig. 2). In Fig. 2, encircled conditions depict the ozone episodes that occurred at Sirifort, New Delhi on various occasions. A total of 9 episodes from August to October 2006 were identified for the purpose of the present study. The corresponding NO_x and VOCs concentrations

are shown in Figs. 3a & 3b. The observed meteorological conditions during the study period, such as temperature, relative humidity, and wind speed are shown in Figs. 4, 5 and 6.

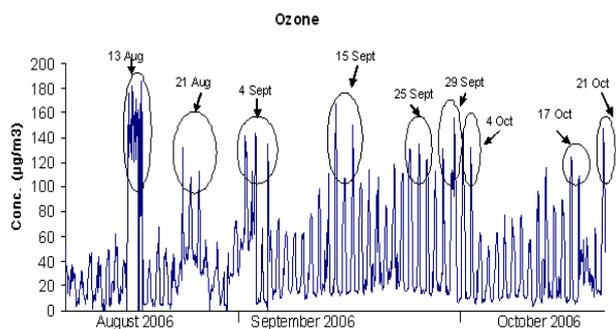


Fig. 2. Hourly average concentration of O₃ during the period of 3 August to 21 October 2006 at Sirifort.

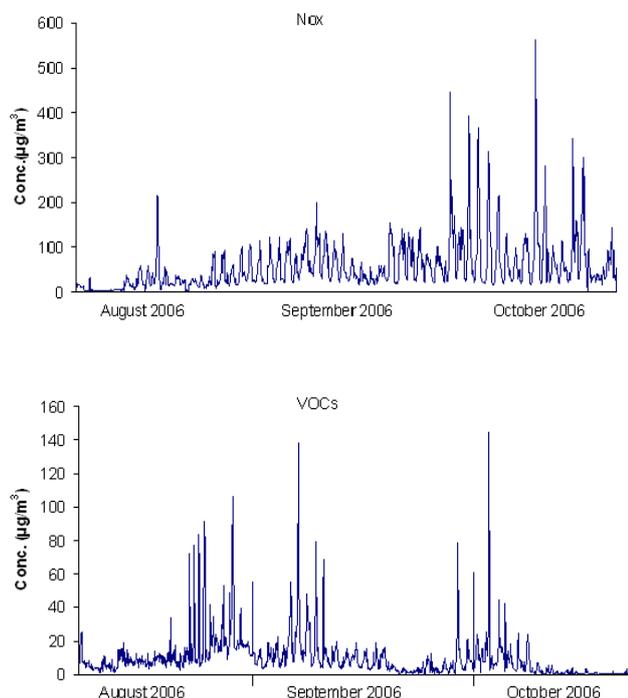


Fig. 3. Hourly average concentration of (a) NO_x, and (b) VOCs, during the period of 3 August to 21 October 2006 at Sirifort.

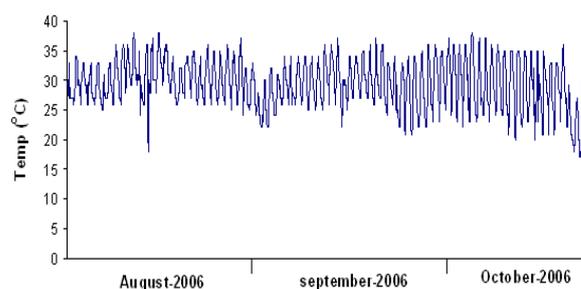


Fig. 4. Hourly variation of temperature (°C) from 3 August to 21 Oct 2006 at Sirifort.

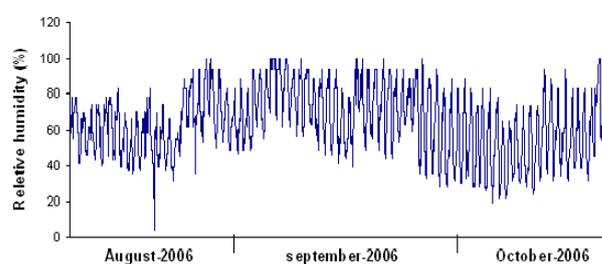


Fig. 5. Hourly variation of relative humidity (%) from 3 August to 21 Oct 2006 at Sirifort.

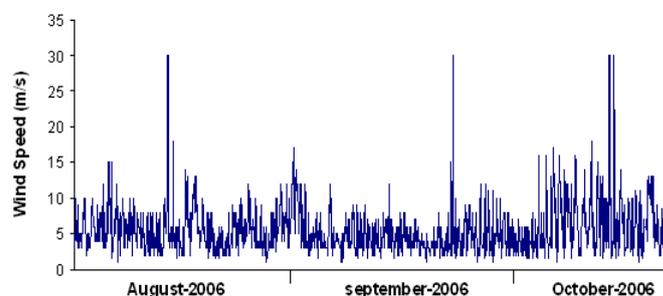


Fig. 6. Hourly variation of wind speed (m/s) from 3 August to 21 Oct 2006 at Sirifort.

MODEL AND SCENARIO CONDITIONS

For each of the ozone episodes, the inputs for OZIPR (section 3) were prepared. A series of simulations were carried out by using the prepared inputs for the various high-ozone

episodes that occurred on different occasions at Sirifort between August and October 2006. Initial VOC, NO_x and CO concentrations were specified at 8 a.m. for a day. The unit for the initial concentrations of NO_x and CO was ppmV (parts per million by volume), while the unit for initial VOC was ppmC (parts per million by carbon). Fresh emissions of VOC and NO_x were added from 8 a.m. to 7 p.m. on an hourly basis; and in each of the simulations, emissions of VOC and NO_x were scaled to be proportional to their initial concentrations. The growth of the daytime boundary layer was simulated by allowing the box to rise according to mixing height as obtained by applying EPA (1989) procedure to radiosonde data. Model simulations were run from 8 a.m. to 7 p.m. local time.

The models were evaluated by comparing the model predicted peak O₃ with the observed peak O₃ concentrations. The observed vs. simulated peak O₃ concentration for all the ozone episodes taken together is shown in Fig. 7. In general, peak O₃ concentration has either been over- or under predicted by the model. However, the mean absolute percentage error (MAPE) of observed vs. simulated peak O₃ concentration varied from 15.2% on one occasion to 26.7% on another occasion. The MAPE for all the ozone episodes taken together is 21.3%. These MAPE values are well within the prescribed limit of 30% by EPA (1989) for OZIPR. Hence, the models can be adjudged to be sufficient to proceed with control estimate calculation.

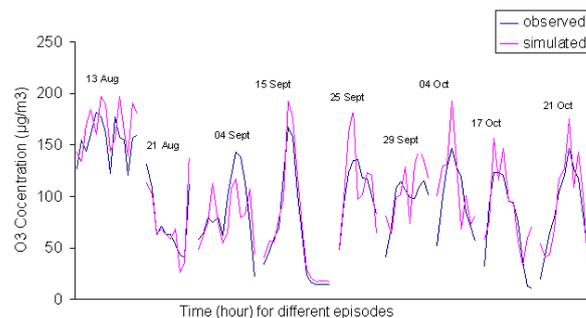


Fig. 7. Observed vs. simulated peak O₃ concentration for different episodes at Sirifort.

O₃ ISOPLETHS

Figs. 8 to 16 show the O₃ isopleths in the model simulations for all the 9 ozone-episodes. In each case, the straight line identifies a ridgeline of maximum O₃ defined as the level of NO_x emissions (E_{NO_x}) that maximize O₃ for a given level of VOC emissions (E_{VOC}); thus, on the O₃ ridgeline, $d[O_3]/d E_{NO_x} = 0$. The ridgeline separates the O₃ response surface into a region that is VOC-limited where VOC reductions are more effective for reducing O₃; and a region that is NO_x-limited where NO_x reductions are more effective for reducing O₃. Fig. 8 shows that for a NO_x-value (> 0.04 ppm), O₃ production is more sensitive to the amount of VOCs than to the amount of emitted NO_x (VOC limited regime). For a NO_x-value (< 0.04 ppm), O₃ production is more sensitive to the amount of NO_x-emission than to the amount of emitted VOCs (NO_x limited regime). An examination of Fig. 9 reveals that O₃ formation is more sensitive to NO_x for a higher VOC/NO_x ratio, while for lower VOC/NO_x ratio, O₃ formation is more sensitive to VOCs. Fig. 10 also exhibit the similar characteristics with a difference that isopleths are relatively

closer indicating a greater sensitivity. In Fig. 11, O₃-isopleths are much closer and for a NO_x value (> 0.04 ppm), O₃ production is more sensitive to the amount of VOCs than to the amount of emitted NO_x (VOC limited regime) while for a NO_x value (< 0.04 ppm) O₃ production is more sensitive to the amount of NO_x than to the amount of emitted VOCs (NO_x limited regime). The O₃-isopleths in Figs. 12, 13 and 14 show a marked similarity. The isopleths are shifted towards the relatively higher VOC range. In addition, O₃-isopleths in these cases are within the limited range of NO_x concentration (up to 0.10 or 0.15 ppm). Figs. 15 and 16 also show a greater sensitivity of O₃ formation to VOCs for lower VOCs/NO_x ratio, while higher VOC/NO_x ratio, O₃ formation is more sensitive to NO_x.

In all the cases except Fig. 8, it is remarkable to note that O₃ formation is relatively insensitive to VOC for a very high NO_x concentration (say, > 0.26-0.27 ppm). Normally, ambient NO_x concentration in Delhi varies within the range of 0.01-0.15 ppm and very rarely exceeds 0.20 ppm (www.cpcb.nic.in). Therefore, the study of O₃ sensitivity to NO_x, as well as to VOCs is important while delineating the conditions for controlling tropospheric ozone in the ambient environment of Delhi. In the present emission scenario, the analysis of the observed ozone episodes reveals that O₃ formation is more sensitive to VOC for lower VOC/NO_x ratio, while for higher VOC/NO_x ratio it is more sensitive to NO_x; although the range and threshold of NO_x or VOC concentration (for O₃ sensitivity to VOC/NO_x ratio) may vary from

one episode to the other. These ranges and thresholds seem to depend upon the meteorological conditions, as one may notice that O₃-isopleths of nearby days are more similar to each other than days which are further apart. For instance, O₃-isopleths for 25 Sept, 29 Sept and 4 Oct (Figs. 12, 13 and 14) are very similar in nature, as well as in terms of range and threshold of NO_x and VOCs concentration (for O₃ sensitivity to VOC/NO_x ratio). In the same way, O₃-isopleths for 17 Oct and 21 Oct (Fig. 15 and 16) are similar in these characteristic terms. The typical behavior of O₃-isopleths in Fig. 8 (13 Aug) shows that for lower VOC/NO_x, O₃ formation is greater, while a similar amount of O₃-formation required much higher VOC/NO_x ratio on the other days. This may be due to the fact that the early morning of 13th August witnessed several thunderstorms (Nautica Editrice Srl, 1995-2006) and consequently higher O₃ concentrations at the start of the day. This might be the reason that even for low VOC/NO_x ratio, O₃-production seems to be higher on that day.

Figs. 8 to 16 can be useful in the regulatory control of ozone. If VOC/NO_x ratio is relatively high (> 1) and NO_x-emission is within a certain range, the higher the VOC concentration, the higher the O₃ production. While for the similar VOC/NO_x ratio and NO_x emission below the lower threshold value of the range, the higher the NO_x emission, the higher the O₃ production. On the contrary, if the VOC/NO_x ratio is relatively low (< 1) and NO_x emission is above the lower threshold value of the range, O₃ production is sensitive to

VOC concentrations. While for the similar VOC/NO_x ratio and NO_x emission below the lower threshold value of the range, O₃ production is more sensitive to NO_x emission. Therefore, the most effective way to reduce the O₃ levels (or at least not to increase them) would be to reduce VOC emissions while keeping a relatively low VOC/NO_x ratio.

It is worth mentioning here that the studies on O₃, NO_x and VOCs variation in the ambient urban environment of Delhi have so far been rather limited (e.g., Varshney and Aggarwal, 1992; Singh *et al.*, 1997; Padhy and Varshney, 2000; Srivastava, 2005; Chelani and Devotta, 2006). Varshney and Aggarwal (1992) and Singh *et al.* (1997) deal with seasonal variation of O₃ in the Delhi's atmosphere, while the studies of Padhy and Varshney (2000) and Srivastava (2005) pertain to VOC variability. Chelani and Devotta (2006) forecasts NO₂ concentration using a hybrid model. However, so far no available reported studies deal with the interaction of O₃, NO_x and VOCs or O₃ sensitivity to NO_x and VOCs in the context of Delhi. We expect this study to provide an insight into the nature of ozone episodes, its sensitivity to NO_x and VOCs, and possible control measures in the urban atmosphere of Delhi.

CONCLUSIONS

A photochemical modeling approach was employed to examine the relationship between O₃ levels and concentration of NO_x and VOCs aimed at suggesting ozone abatement strategy in an urban area of Delhi. Ozone formation

was found to be more sensitive to VOCs emissions for lower VOC/NO_x ratio. For higher VOC/NO_x ratio, O₃ formation is more sensitive to NO_x-emissions. However, for the purpose of practical O₃ control applications, it is concluded that VOC emissions should be reduced while keeping a lower VOC/NO_x ratio in order to reduce the ambient O₃ levels at the observation site.

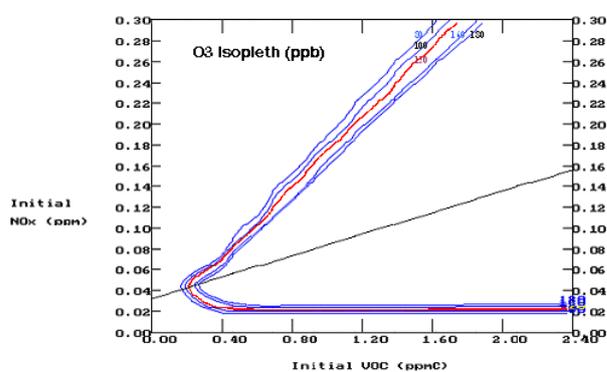


Fig. 8. O₃ isopleths for 13 August 2006 simulation at Sirifort.

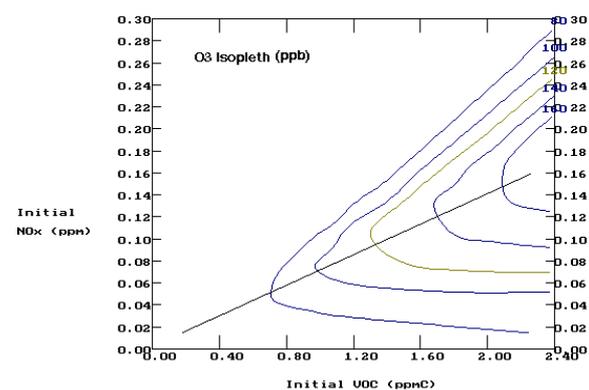


Fig. 9. O₃ isopleths for 21 August 2006 simulation at Sirifort.

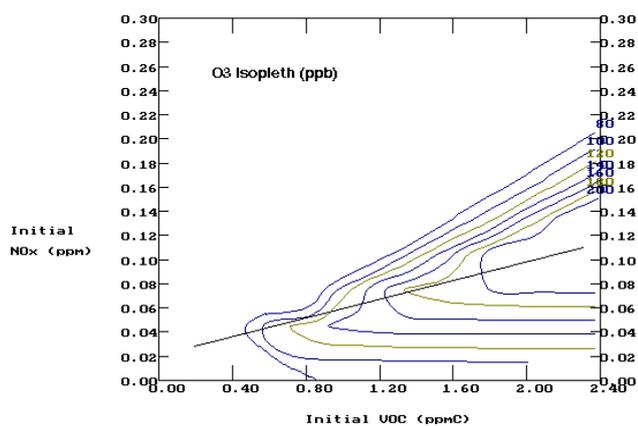


Fig. 10. O₃ isopleths for 4 September 2006 simulation at Sirifort.

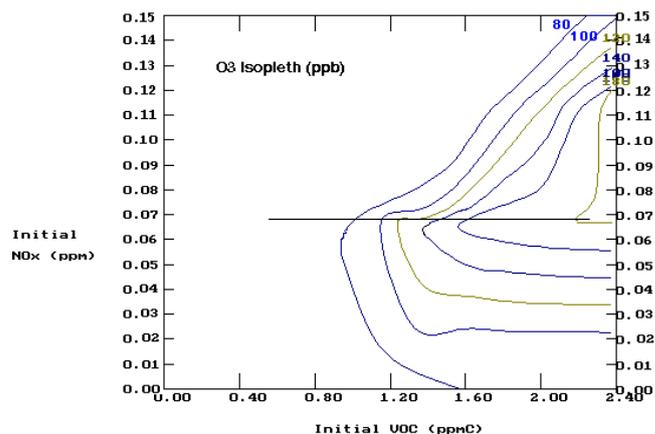


Fig. 13. O₃ isopleths for 29 September 2006 simulation at Sirifort.

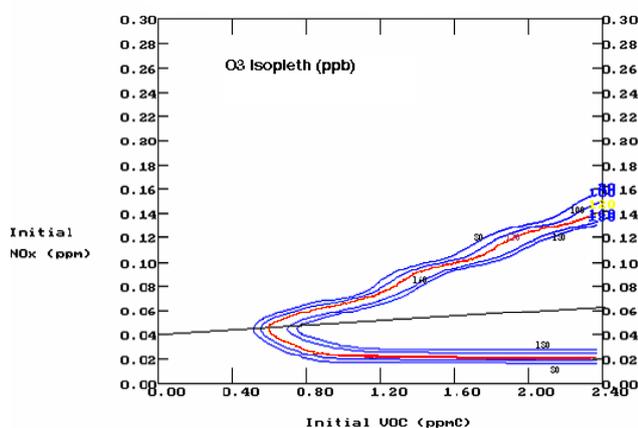


Fig. 11. O₃ isopleths for 15 September 2006 simulation at Sirifort.

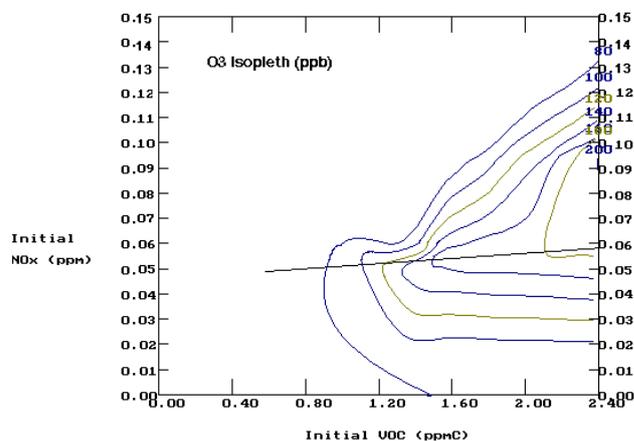


Fig. 14. O₃ isopleths for 4 October 2006 simulation at Sirifort.

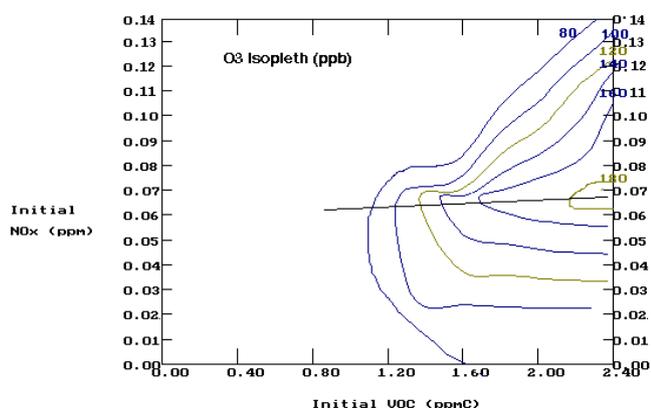


Fig. 12. O₃ isopleths for 25 September 2006 simulation at Sirifort.

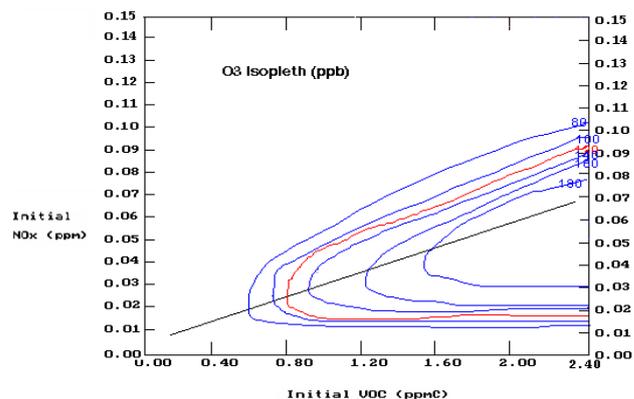


Fig. 15. O₃ isopleths for 17 October 2006 simulation at Sirifort.

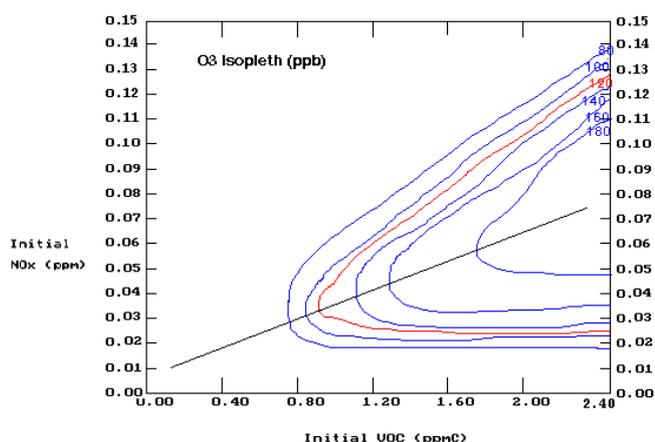


Fig. 16. O₃ isopleths for 21 October 2006 simulation at Sirifort.

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