An Eulerian photochemical model for tropospheric ozone over the tropics

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A time-dependent Eulerian photochemical model for the highly reactive tropospheric trace species is formulated to gain insight into the observed trace species (ozone, NOx, PAN, HOx, etc.) over the tropics. In the present study, the model is designed to simulate a diurnal variation of surface ozone and vertical profile of the tropospheric ozone up to 15 km by considering the chemical and physical processes. The basis for this model is the mass balance of the concerned species (for example, ozone in this study) and it is solved by using Euler’s numerical techniques assuming quasi steady state approximation (QSSA) as suggested by Hov\(^7\). The various terms like advection, turbulent diffusion, chemical transformations, emission and removal in mass balance equation can be solved independently. Therefore, in this study, emphasis is on the chemistry of the mass balance equation of tropospheric ozone. The model results are compared with ozone measurements made at Pune. The simulated ozone concentrations for clear sky agree within less than 20% differences except for monsoon season (cloudy days). The high tropospheric ozone observed usually in March (summer season) is shifted to monsoon season in model results. This shift in ozone is due to the neglect of the impact of cloud and aqueous phase processes on tropospheric ozone production in the model.

MATHEMATICAL models are needed to study the highly reactive tropospheric trace species as their data are sparse and difficult to measure. These increasing highly reactive trace species (for example, tropospheric ozone (O\(_3\)), nitrogen dioxide (NO\(_2\)), nitric oxide (NO), peroxyacetyl nitrate (PAN) and reactive hydrocarbons) are mainly responsible for adverse impact on our biosphere. Predictions from mathematical models provide the means to assess the response of these highly reactive tropospheric trace species on future changes in the environment. Models can also be used to study the effect of an increase or decrease in the emissions of the highly reactive species on photochemical processes.

The Eulerian photochemical model is designed to simulate the concentrations of chemically highly reactive tropospheric trace species by simulating the physical and chemical processes in the troposphere. The chemistry and transport parts of the mass balance equation can be solved independently\(^1\). Therefore, the main emphasis is on an accurate description of the chemistry of the mass balance equation in this study.

The development and validation of the model are presented in three parts: (i) Formulation of the model; (ii) Inventory of trace species emissions; and (iii) Evaluation of the model.

The formulation of a model for predicting the dynamic behaviour of a highly chemically reactive tropospheric trace species in an urban atmosphere is studied. The basis for the model is the mass balance equation of the concerned highly reactive tropospheric trace species. This equation represents a mass balance in which all of the relevant emissions, transport, diffusion, chemical transformations and removal processes are expressed in mathematical terms as follows:

\[
\frac{\delta c_i}{\delta t} = -\frac{\delta (uc_i)}{\delta x} - \frac{\delta (vc_i)}{\delta y} - \frac{\delta (wc_i)}{\delta z} + \frac{\delta K_H}{\delta x} \frac{\delta c_i}{\delta x} + \frac{\delta K_H}{\delta y} \frac{\delta c_i}{\delta y} + \frac{\delta K_V}{\delta z} \frac{\delta c_i}{\delta z} + R_i + S_i + L_i,
\]

where \(c_i\) represents the concentration of species \(i\) and is a function of space \((x, y, z)\) and time \(t\). Subscript \(i\) denotes the number of species \((i = 1, 2, \ldots, n)\); where \(n\) is the number of species to be studied) simulated in the model. For simplicity in the chemical scheme the single species (ozone) is studied by putting \(n = 1\) in the model eq. (1).

The other terms in eq. (1) are:
- \(u, v, w\) are meridional and zonal wind speed components;
- \(K_H, K_V\) are horizontal and vertical turbulent diffusion coefficients;
- \(R_i\) is rate of production of species \(i\) by chemical transformations;
- \(S_i\) is emission rate of species \(i\), and \(L_i\) is net rate of removal of species \(i\) by surface uptake processes (dry and wet deposition).

Equation (1) is integrated forward in time using an Euler numerical technique\(^1\). Numerical solution of eq. (1) requires specification of initial conditions, together with time- and space-resolved descriptions of meteorology and emissions at the grid point.

Equation (1) can be simplified, for the study of ozone initially by putting \(n = 1\) for a single cell and applying the following assumptions:
- (i) advection term is neglected;
- (ii) concentration of the species is uniform in the grid, i.e. turbulent diffusion is neglected;
- (iii) emission and deposition terms are neglected.

Then, eq. (1) reduces to

\[
\frac{\delta c_i}{\delta t} = R_i (\{P_K\}_i, T)
\]

where \(R_i\) is the net generation term of the ozone (balance of chemical production and destruction) and is a function of space and time. In eq. (2), \(\{P_K\}_i\) stands for a detailed photochemical mechanism, including all the relevant species participating in the \(O_3\) generation and destruction, and is a function of space, time, temperature \((T)\) and solar zenith angle \((\zeta)\).
The chemistry in eq. (2) is defined to be as simple as possible so that the number of equations (and hence number of species) could be kept at a minimum. Chemical transformation processes are known to be difficult to handle numerically. The set of reactions used is a simplified version of a chemical scheme for the investigation of a chemical transformation of species \( O_3 \) in the troposphere\(^5\). The condensed chemical scheme omits parallel chemical pathways and concentrates on generic aspects of the chemical interaction between the highly reactive trace species. The chemistry is driven by two forces, namely solar radiation and sources of highly reactive trace species. There are two major sunlight-induced photolytic processes in the troposphere, one is the photolysis of \( NO_2 \) and other is production of \( O_3 \). The former produces NO and \( O_3 \) in the troposphere. The chemical scheme used in eq. (2) is given in Table 1.

Equation (1) can be split into several parts (chemistry part, diffusion part, transport part, emission part and removal part) and each part is integrated separately at each time step\(^1\). The main principles that are applied in the integration of the chemical part are based on a quasi steady state approximation (QSSA). In QSSA, it is assumed that rate of production and destruction of species in eq. (2) are constant over a time step interval for a given species while integrating. The integration of eq. (2) is performed forward in time with a time step of 1 hour using Euler's numerical techniques.

The model requires hourly input data of \( NO \), \( NO_2 \), \( J_{NO_2} \) and temperature \((T)\) for simulation of \( O_3 \) concentration in eq. (2). The other species are kept constant while integrating eq. (2). The hourly averaged surface diurnal variations of \( NO_2 \) input data for diurnal \( O_3 \) simulation at Pune latitude are derived from Logan et al.\(^5\) and Subbaraya et al.\(^4\). The reaction rate constant \((k)\) and the \( NO_2 \) photodissociation rate \((J_{NO_2})\) are calculated by using diurnal variation in temperature and solar zenith angle, respectively at Pune latitude as per the chemical scheme used in Table 1. The diurnal variation in temperature data is used from Tiwari and Peshin\(^7\) and vertical temperature profile is taken from Mani and Sreedharan\(^6\) for Pune (19°N). The vertical NO and \( NO_2 \) profiles are derived from Logan et al.\(^5\) to simulate the vertical \( O_3 \) profile at Pune. The photodissociation rate of \( NO_2 \) is calculated at 19°N using solar zenith angle for local noon (1200 h) while simulating vertical \( O_3 \) profile in the troposphere. Annual variations of tropospheric ozone are simulated at an interval of 15 days by varying the photodissociation rate of \( NO_2 \) and using average vertical NO, \( NO_2 \) and temperature profiles at Pune.

The photodissociation rate of \( NO_2 \) is a function of altitude and it increases with altitude as actinic flux increases\(^9\).\(^10\). To consider this increase in \( J_{NO_2} \) with altitude, the troposphere is divided into three parts, surface-5 km, 5-10 km and 10-15 km. \( J_{NO_2} \) calculated at surface is kept constant for surface-5 km. \( J_{NO_2} \) is increased by 2.5% of surface value for 5-10 km and by 5% of surface value for 10-15 km as the actinic flux profile for a cloudless atmosphere linearly increases\(^10\). Input data to the model were adjusted to avoid the appearance of negative concentrations and as closely as possible to match the initial field conditions for the seasons at Pune. In view of the simplicity of the model, the contribution from natural and anthropogenic hydrocarbons in \( O_3 \) formation is not included. But it is possible to include natural hydrocarbons like isoprene and anthropogenic hydrocarbons which have high maximum incremental reactivity (MIR) value as suggested by Carter\(^11\) regarding ozone forming potential (for example, MIR of isoprene is 9.1 g \( O_3 \)/g isoprene).

The reliability of any model can be evaluated by comparisons of simulated results with measurements. The comparisons were carried out by using \( O_3 \) measurements made by Tiwari and Peshin\(^7\) (averaged on an hourly basis) on a time scale of one day with simulated \( O_3 \) by simulating the chemical scheme given in Table 1. Comparisons of simulated vertical \( O_3 \) profiles were carried out with measured vertical \( O_3 \) profile by Mani and Sreedharan\(^6\). In this study a primary attempt is made to simulate the chemistry part of the atmospheric processes in the mass balance model eq. (1). It is important to simulate diurnal and vertical profile variations of the highly reactive trace species that participate in a photochemical reaction in the troposphere. For example, it is essential to determine correctly daily maxima of surface ozone concentrations (hourly averaged permissible limit is 80 parts per billion

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**Table 1. Chemical scheme used in the eq. (2)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( NO_2 + h\nu \rightarrow NO + O_3 )</td>
<td>( J = 1.33 \times 10^{-2} \exp(-0.254 \sec(z)) )</td>
<td>Tremmel (1992)</td>
</tr>
<tr>
<td>( NO + O_3 \rightarrow NO_2 + O_3 )</td>
<td>( k = 2.0 \times 10^{-15} \exp(-1370/T) )</td>
<td>Atkinson (1992)</td>
</tr>
<tr>
<td>( O_3 + h\nu \rightarrow O(\Delta) + O )</td>
<td>( J = 8.58 \times 10^{-4} \exp(-2.55 \sec(z)) )</td>
<td>Tremmel (1992)</td>
</tr>
<tr>
<td>( O(\Delta) + O_3 \rightarrow O_2 + O_3 )</td>
<td>( k = 1.82 \times 10^{-18} \exp(110/T)^{0.78} )</td>
<td>DeMore et al. (1987)</td>
</tr>
<tr>
<td>( k = 3.2 \times 10^{-15} \exp(70/T)^{0.21} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O_3 + OH \rightarrow HO_2 + O_3 )</td>
<td>( k = 1.6 \times 10^{-12} \exp(-940/T) )</td>
<td>DeMore et al. (1987)</td>
</tr>
<tr>
<td>( O_3 + HO_2 \rightarrow OH + 2O_3 )</td>
<td>( k = 1.1 \times 10^{-11} \exp(-500/T) )</td>
<td>DeMore et al. (1987)</td>
</tr>
<tr>
<td>( NO + HO_2 \rightarrow NO_2 + OH )</td>
<td>( k = 3.7 \times 10^{-12} \exp(240/T) )</td>
<td>DeMore et al. (1987)</td>
</tr>
<tr>
<td>( NO_2 + OH + M \rightarrow HNO_3 + M )</td>
<td>( k = 6.0 \times 10^{-14} )</td>
<td>Atkinson et al. (1992)</td>
</tr>
</tbody>
</table>

\( \sec(z) = \sec(\cos(z) = \cos(LHA) \cos(LAT) \cos(DEC) + \sin(LAT) \sin(DEC), LHA = \text{local angle of hour, which is} 0^\circ \text{for local noon (1200 h) and increments by} 15^\circ \text{for each hour from noon; LAT = latitude at Pune; DEC = sun declination; } a \text{ is Planck's constant and } v \text{ is frequency of radiation; } k \text{ is the first-order reaction rate constant; } J \text{ is photolysis rate of the molecule in is} (s^{-1}) \text{unit. All reaction rate constants used are from Schmidt et al.} \)\(^3\). The cosine of the local solar zenith angle \((z)\) is given by Brasseur and Solomon\(^9\).
by volume (ppbv) as per World Health Organization (WHO) air quality guidelines) because ozone can have damaging effects on all living things. The model simulated results for diurnal ozone variation and vertical ozone profile concentrations are encouraging when compared with measurements made by Tiwari and Peshin and Mani and Sreedharan at Pune. All the results agree very well within less than 10 to 30% differences. These differences can be reduced sufficiently by choosing appropriate time steps to integrate eq. (2). In the present study a time step of 1 hour is taken for simulation of the model. To achieve good results, it is required to use accurate input data with high resolution, especially for NO and NO$_2$ which have very high ozone forming potential. In this sense the input data used in the model at present have less resolution. In spite of these difficulties, an attempt is made to simulate atmospheric processes (chemistry part) in the mathematical model eq. (2). The results can potentially be improved by refining the input data field (here, especially, the emission fields are important). Simulation for NO$_2$, NO, PAN and other trace species is also possible by adding appropriate chemical reactions which contribute in production and destruction of the species in the chemical scheme given in Table 1.

Figures 1 and 2 show the comparison of diurnal variation of ozone and vertical ozone profile concentration with measured ozone concentration in winter (January). The simulated results match very well with measurements. In Figure 1 simulated diurnal variation of ozone is compared with measurements made by Tiwari and Peshin and Khemani et al. at Pune. The diurnal variation of ozone in winter (January) shows maximum ozone concentration (more than 40 ppbv) around 1200 h and minimum concentration (less than 10 ppbv) before sunrise (0700 h) as observed by these workers. Simulated O$_3$ maxima follow O$_3$ measurements but simulated O$_3$ minima do not follow O$_3$ measurements. In Figure 1, O$_3$ values of Khemani et al. are more than the simulated values whereas O$_3$ values of Tiwari and Peshin are less than the simulated values. The important feature in our result is that simulated O$_3$ follows general diurnal features. This means that we are able to simulate diurnal variation pattern, maxima and minima of surface ozone up to a certain extent. The simulated surface ozone maxima around noon is better when compared with measurements than its minima in the morning. The morning minima of surface ozone is related to the complex night-time chemistry of nitrate radical (NO$_3$). The NO$_3$ chemistry strongly depends upon ambient temperature and aqueous phase reactions. The chemical reactions of night-time chemistry of NO$_3$ for surface ozone destruction are not included in the present chemical scheme in the Table 1. Hence morning minima of simulated surface ozone does not compare well with measurements. The differences in simulated O$_3$ with measured O$_3$ by Tiwari and Peshin and Khemani et al. may be due to different measurement locations and different O$_3$ measuring techniques. The simulated vertical profile of ozone is compared with measured ozone profile by Mani and Sreedharan in Figure 2. The simulated O$_3$ profile comes well with the measured profile. The simulated tropospheric O$_3$ maxima is at about 2 km whereas measured O$_3$ maxima is at the surface. The simulated and measured tropospheric O$_3$ minima are at about 15 km (below the local tropopause.

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**Figure 1.** Diurnal variation of surface ozone in winter at Pune.

**Figure 2.** Tropospheric vertical profile of ozone in winter at Pune.
level) as observed by Mani and Sreedharan. The ozone level starts increasing above 15 km in the stratosphere.

Figure 3 shows the contour map of annual (1 to 365 days) tropospheric ozone at Pune latitude simulated at an interval of 15 days (day number \( \times 15 = \) day of the year) by varying \( J_{NO_3} \) value. The maximum O\(_3\) concentration occurs at about 2 km and changes from day to day and from month to month. The highest tropospheric O\(_3\) concentration observed from surface to 7 km occurs in June and the lowest in December-January. At altitudes of about 2–3 km and 6–7 km gradients (distance between two contour lines are less) of tropospheric O\(_3\) are simulated and there after above 7 km the gradients are less (distance between two contour lines are more). During winter when temperatures fall, the thermal decomposition of ozone precursors (PAN and active hydrocarbons) decreases and their atmospheric lifetime increases. In this way more ozone precursors are accumulated as temperature decreases during winter. In March, temperatures start increasing due to high radiation and accumulated ozone precursors thermally decompose, producing more active radicals. This results in photochemical ozone processes which are more active producing more ozone in the month of March mostly when clear sky condition prevails. From April onwards, pre-monsoon cloud in the sky disturbs the photochemical ozone production processes in the troposphere resulting in less ozone production. This indicates that photochemical ozone production in the troposphere is active in March which is supported by measurements. Figure 3 shows that the maximum O\(_3\) concentration occurs at about 2–3 km during June instead of March.

Model eq. (2) is simulated for the vertical O\(_3\) profile without considering the cloud effect. The cloud plays a very important role in tropospheric O\(_3\) formation during the monsoon season. The photodissociation rate of NO\(_2\) (reaction R1 in Table 1) is proportional to the actinic flux and it is the only reaction which produces ozone in the troposphere. The actinic flux deals with the energy that is incident on a molecule. In the lowest parts of the troposphere the effect of the cloud on the actinic flux can be very strong. The actinic flux in-cloud, above and below clouds depends on the cloud optical thickness and solar zenith angle. The cloud optical thickness depends on origin of the cloud, (i.e. marine cloud or continental cloud). The marine cloud has high optical thickness due to the presence of more small particles than continental cloud. The winds are south-westerly in the monsoon season and cloud mainly transported to Pune originate from the Arabian Sea. These clouds have high optical thickness which reduces actinic flux considerably in the troposphere at Pune. This reduction in actinic flux decreases photodissociation rate of NO\(_2\) and results in less O\(_3\) production. Thus the cloud plays a dominant role in tropospheric O\(_3\) formation by dissociation of NO\(_2\) molecule.

In another study by Jonsson and Isaksen, the impact of cloud chemistry on tropospheric ozone chemistry has shown that the loss of ozone in an aqueous phase, with pronounced reduction in ozone levels by about 10 to 30% in the troposphere are due to these processes (Reaction R8 in Table 1). These processes affect ozone in two ways: they reduce the gas-phase concentration of the species involved (precursors) in ozone production, and they provide a source for compounds interacting with ozone in the aqueous phase. This fact supports the minimum ozone measurements in August by Mani and Sreedharan.

Equation (2) is simulated without cloud effect and aqueous phase reactions, hence the tropospheric O\(_3\) maxima in Figure 3 is seen at height of about 2–3 km during monsoon season (August) instead of in the summer season (March). If 10, 20 and 30% ozone are subtracted (as per the study of Jonsson and Isaksen) from simulated
Table 2. Comparison of simulated vertical ozone (ppbv) profile with and without cloud impact with the mean profiles of soundings made at Pune.

<table>
<thead>
<tr>
<th>Height (km)</th>
<th>Winter</th>
<th>Summer</th>
<th>Monsoon</th>
<th>Post-monsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M S</td>
<td>M S</td>
<td>M S ***</td>
<td>M S **</td>
</tr>
<tr>
<td>Surface</td>
<td>23 27 24</td>
<td>26 31 28</td>
<td>15 32 22</td>
<td>25 30 24</td>
</tr>
<tr>
<td>2</td>
<td>28 31 28</td>
<td>29 35 31</td>
<td>23 34 24</td>
<td>23 34 27</td>
</tr>
<tr>
<td>5</td>
<td>20 20 20</td>
<td>26 24 26</td>
<td>20 24 17</td>
<td>20 23 20</td>
</tr>
<tr>
<td>10</td>
<td>13 15 14</td>
<td>12 15 13</td>
<td>9 16 11</td>
<td>13 15 13</td>
</tr>
<tr>
<td>15</td>
<td>12 14 13</td>
<td>13 13 13</td>
<td>7 14 10</td>
<td>11 14 13</td>
</tr>
</tbody>
</table>

M, measured ozone value; and S, simulated ozone without cloud effect
* , simulated ozone with cloud effect for different seasons
** , simulated ozone value is reduced by 10% in winter and summer season
*** , simulated ozone value is reduced by 20% in post-monsoon season
The annual amount of cloud data are used from Nihgt15

Source: Nighut15.

Table 2 compares simulated vertical O3 profile with and without cloud impact for some selected heights (surface, 2, 5, 10, 15 km) with the mean profile of soundings made at Pune during the four main seasons, winter (November–February), summer (March–May), monsoon (June–August) and post-monsoon (September–October). For comparison it is considered that December 15 is representative of winter, March 15 is representative of summer, August 15 is representative of monsoon and October 15 is representative of post-monsoon season.

From Table 2 it is seen that measured O3 concentrations, simulated O3 without cloud impact for winter, summer and post-monsoon seasons are comparable within less than 10 to 30% differences whereas during monsoon season they are not comparable. The reason for this is that the cloud effect and removal processes are more pronounced in the monsoon season. After considering the cloud impact and aqueous phase processes, simulated results for tropospheric ozone agree well with measurements (Table 2 columns with * marks and Figure 4). If cloud effect is incorporated in the result then simulated ozone is comparable with measurements made by Mani and Sreedharan. Figure 4 shows that simulated maximum ozone in March and minimum in August compare well with measurements. It also reveals that ozone contour height increases in March whereas it decreases in August in the troposphere. These variations are expected in the troposphere considering the ozone formation and destruction mechanism. The present study helps to understand the mathematical modelling response of photo-chemical processes to tropospheric ozone and its precursor level in the troposphere over the Indian region. The proposed chemical scheme used in the model will also be tested for other highly reactive species like NO, NO2 and PAN in the Indian sub-continent in the near future.


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