Atmospheric photochemical modeling: 
Introduction and tutorial exercise 

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Introduction

Atmospheric chemistry models are used to determine the abundance of chemical species as a function of space and time as dictated by relevant chemical and physical processes.

Since the first generation models of the 60-70s there has been an exponential increase in model complexity closely linked to the availability of affordable processing

~$10^6$ fold increase over 30 years or ~doubling every 1.5 years
History of Atmospheric Chemistry & Model Development

1920s
Richardson (based on work of Bjerknes) develop first primitive weather forecast ‘model’

1930s
Chapman explanation of stratospheric ozone
Chemical box models employed based on Chapman mechanism

1940s
With advent of digital computers forecasting becomes feasible

1950s
Bates and Nicolet suggest oxides of hydrogen could catalytically destroy ozone
Sweden first to begin real-time forecasting
1960s

1965: Engleman identifies critical $\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{OH}$ reaction

1D vertical diffusion models

late 1960s: first 2D chemical transport models – applied to stratospheric ozone

1970s

1970: Crutzen suggests oxides of nitrogen another natural catalyst for ozone destruction

1971: Levy proposed $\text{O}_3$-$\text{H}_2\text{O}$-$\text{CO}$-$\text{CH}_4$-$\text{NO}_x$ photochemical mechanism

1974: Stolarski & Cicerone suggest chlorine released from space shuttle exhaust could destroy ozone

1974: Molina & Rowland (based on CFC measurements of Lovelock) propose CFCs as ambient source of reactive chlorine in the stratosphere
1970s (con’t)

First 3D general circulation models (GCMs) – complexity of chemistry follows computer power

1972: McElroy and Donohue successfully address problem of stability of CO₂ in Martian atmosphere using 1D diffusion model

late 1970s: ‘transformed Eulerian mean’ 2D chemical transport models (superior to previous 2D)

1980s

Antarctic ozone hole discovered
Montreal protocol and amendments
First generation 3D climate models
late 1980s: models beginning to correctly simulate ozone hole
History of Atmospheric Chemistry & Model Development

1990s
improved quantitative understanding of polar ozone depletion; models under-predict mid-latitude ozone depletion by factor of 2
merging of 3D stratospheric and tropospheric chemistry models
first air quality model forecasts

2000s
Operational use of high-resolution air quality forecast models
First ‘Earth system’ models linking atmosphere to land surface, ocean, and biosphere
THE TROPOSPHERE WAS VIEWED AS CHEMICALLY INERT UNTIL 1970

• “The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen…Methane and CO are chemically quite inert in the troposphere” [Cadle and Allen, Atmospheric Photochemistry, Science, 1970]

• Lifetime of CO estimated at 2.7 years (removal by soil) leads to concern about global CO pollution from increasing car emissions [Robbins and Robbins, Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants, SRI report, 1967]

FIRST BREAKTHROUGH:

• Measurements of cosmogenic $^{14}$CO place a constraint of ~ 0.1 yr on the tropospheric lifetime of CO [Weinstock, Science, 1969]

SECOND BREAKTHROUGH:

• Tropospheric OH $\sim$1x10$^6$ cm$^{-3}$ predicted from O(1D)+H$_2$O, results in tropospheric lifetimes of ~0.1 yr for CO and ~2 yr for CH$_4$ [Levy, Science, 1971, J. Geophys. Res. 1973]

THIRD BREAKTHROUGH:

• Methylchloform observations provide indirect evidence for OH at levels of 2-5x10$^5$ cm$^{-3}$ [Singh, Geophys. Res. Lett. 1977]

Atmospheric Chemistry Models

The atmospheric evolution of a species \((X)\) is described by the *continuity equation*:

\[
\frac{\partial [X]}{\partial t} = E_x - \nabla \cdot (U[X]) + P_x - L_x - D_x
\]

- **local change in concentration with time**
- **emission**
- **transport** (flux divergence; \(U\) is wind vector)
- **chemical production and loss** (depends on concentrations of other species)
- **deposition**

This equation is too complex to be solve analytically thus computer models are required.

Model types

Dimensionality often traded off again complexity of other processes such as chemistry or aerosol microphysics
Define lifetime ($\tau$) as average time molecule X remains in the box; where $m$ is the mass of X

$L, D, and F_{out}$ are the loss terms

Chemical lifetime:

$$\tau_{chem} = \frac{m}{L}$$

$$\tau = \frac{m}{L + D + F_{out}}$$
Model types: others

Two-box model
System described by pair of coupled ODEs

One-dimensional
Usually a series of boxes stacked in the vertical, with transport simulated using a diffusion-like process
Model types: puff model

In a puff model the air parcel follows the wind motion

\[ \frac{dX}{dt} = E + P - L - D \]

...no transport terms as they are implicit in the trajectory

Application to the chemical evolution of an isolated pollution plume:
Model types: three-dimensional

Most comprehensive, describes $X(t, x, y, z)$

Continuity equation solved for individual gridboxes

Computationally expensive

Can be run with $\sim 10^6$ gridboxes based on current computing power

For global simulation: $\sim 200$ km in the horizontal and $\sim 1$ km in the vertical

Terms in the continuity equation

**Emission**, \( E = \left. \frac{dX}{dt} \right|_{\text{emm}} \)

Release of substances into the atmosphere due to natural or anthropogenic processes.

**Transport**, \( F = \left. \frac{dX}{dt} \right|_{\text{trans}} \)

Primary transport processes are *advection* (transport of a species by the mean horizontal motion of air parcel), convection, and diffusion.
Terms in the continuity equation

Chemistry, \[ P - L = \frac{dX}{dt} \bigg|_{\text{chem}} \]

Production (\(P\)) and Loss (\(L\)) as a result of chemical reactions, including heterogeneous and photolysis reactions.

e.g., \( NO + HO_2 \rightarrow NO_2 + OH \quad k=3.5 \times 10^{-12} \text{ e}^{250/T} \text{ [cm}^3/\text{molecule/s]} \)

Deposition, \[ D = \frac{dX}{dt} \bigg|_{\text{deposition}} \]

Dry deposition describes the uptake of atmospheric species (gases or aerosol particles) at the surface of the Earth.

Wet deposition describes the scavenging of soluble gases and aerosol particles from the atmosphere by precipitation.
Applications

Atmospheric chemistry models are used to consolidate and test our understanding of atmospheric chemistry and to make predictions of its future state.

Problems being addressed include:
- acid rain
- ozone depletion
- photochemical smog
- greenhouse gases
- global warming
- carbon cycle
Applications – A stratospheric photochemical box model

The UCI (University of California, Irvine) box model developed originally by M. Prather and used in support of various satellite remote sensing missions:

**General:**
- Chemistry at a single location or point; no transport
- Pressure, temperature, and long-lived species need to be specified
- These can be constant (for a point at a fixed location) or be varied (as if point is following a trajectory).

**Applications:**
- to create look-up tables for first guess profiles of NO$_2$ and BrO in profile retrieval algorithms for the OSIRIS satellite instrument
- to calculate profile of short-lived species at measurement locations
  * model constrained with measured profiles of p, T, O$_3$, (possibly N$_2$O and NOy) as measured by the Atmospheric Chemistry Experiment or OSIRIS to better capture radicals
Applications – A stratospheric photochemical box model

Long-lived species (specified):
\( \text{O}_3, \text{N}_2\text{O}, \text{NO}_y, \text{CH}_4, \text{H}_2\text{O}, \text{Cl}_y, \text{Br}_y, \text{CFCs}, \text{H}_2, \text{NH}_3, \text{CH}_3\text{Cl}, \text{CH}_3\text{Br}, \text{a few others…} \)

Radicals (calculated in model):
\( \text{O}, \text{O}_3 \)
\( \text{H}, \text{OH}, \text{HO}_2, \text{H}_2\text{O}_2 \)
\( \text{NO}, \text{NO}_2, \text{NO}_3, \text{N}_2\text{O}_5, \text{HONO}, \text{HNO}_3, \text{HNO}_4 \)
\( \text{Cl}, \text{Cl}_2, \text{ClO}, \text{OCIO}, \text{HOCI}, \text{Cl}_2\text{O}_2, \text{ClONO}_2, \text{HCl} \)
\( \text{Br}, \text{BrO}, \text{BrCl}, \text{HBr}, \text{HOBr}, \text{BrONO}_2 \)
\( \text{HCHO}, \text{CH}_3\text{OO}, \text{CH}_3\text{OOH} \)

Reactions (210 total):
Gas phase – 159; Heterogeneous – 8; Photolysis – 43

\( \text{NO}_y, \text{Cly}, \text{and Bry} \) represent the total amounts of reactive nitrogen, chlorine, and bromine

\( \text{O}_3 \) may be either specified or allowed to evolve
Applications – A stratospheric photochemical box model

- JPL MkIV FTIR instrument

- Model-measurement study of the stratospheric nitrogen budget

- Sept. 21, 2005 35°N

- April 1, 2003 68°N

- Model Constraints: MkIV Measured p, T, O₃, N₂O, NOy

- Applications – A stratospheric photochemical box model

- Volume Mixing Ratio [ppb]

- NO, NO₂, HNO₃, N₂O₅, ClONO₂, NOy

- NO/NO₂ ratio

- JPL MkIV box model
Canadian Air Quality Forecast Suite
Operational Configuration: GEM-MACH15

- Meteorology from GEM (Global Multi-scale Environment Model)
- GEM-MACH (Modelling Air quality and Chemistry) options chosen to meet EC’s operational AQ forecast needs; key characteristics include:
  - limited-area (LAM) configuration where grid points are co-located with operational met-only GEM which supplies initial conditions and lateral boundary conditions for GEM-MACH15
  - 15-km horizontal grid spacing, 58 vertical levels to 0.1 hPa
  - 2-bin sectional representation of PM size distribution (i.e., 0-2.5 and 2.5-10 μm) with 9 chemical components
    - Some processes resolved with increased number of bins
  - Full process representation of oxidant and aerosol chemistry:
    - gas-, aqueous- & heterogeneous chemistry mechanisms
    - aerosol dynamics
    - dry and wet deposition (including in and below cloud scavenging)
Canadian Air Quality Forecast Suite: Operational Model

- 3D, continental-wide, hourly forecasts of PM$_{2.5}$, O$_3$ and NO$_2$, twice a day (00 and 12 UTC), for the next 48h
  - Publicly accessible at http://www.weatheroffice.gc.ca (Analyses & Modelling)
- Forecasts are based on GEM-MACH: multi-scale chemical weather forecast model composed of dynamics, physics, and in-line chemistry modules
Overview of the Canadian AQ forecast program

- Ten year old program that has evolved from an O\textsubscript{3}-only forecast in Eastern Canada to a Canada-wide O\textsubscript{3}, NO\textsubscript{2}, PM\textsubscript{2.5} forecast program
- Forecast is communicated in most areas as an *Air Quality Health Index* (AQHI)

\[
AQHI = \frac{10}{10.4} \times 100 \times [\exp(0.000871 \times NO_2) - 1] + \exp(0.000537 \times O_3 - 1) + \exp(0.000487 \times PM_{2.5} - 1)
\]

- 10 point scale that links air quality to the health risk associated with exposure to a 3 pollutant mixture
- Developed by Health Canada (Stieb et al., 2008, JA&WMA) from Canadian multi-city mortality/morbidity studies of short term health effects and AQ data from the Canadian National Air Pollution Surveillance Network (NAPS)
References

Texts:

Online Material:
Course notes and textbooks related to atmospheric chemistry and atmospheric chemistry modeling are available at:
http://acmg.seas.harvard.edu/education/
There is excellent material here at both the undergraduate and graduate level

* pdf available from ftp://exp-studies.tor.ec.gc.ca/pub/ftpcm/CREATE/
Two-box model

This atmospheric chemistry model makes use of simplified chemistry and transport to simulate the abundance of six chemical species in two boxes (troposphere and stratosphere).

There are six chemical “tracers” in the model:
- CH$_4$ (methane)
- CO (carbon monoxide)
- OH (hydroxyl radical)
- N$_2$O (nitrous oxide)
- NOy (sum of all reactive nitrogen species)
- O$_3$ (ozone)

The chemistry consists of 18 reactions (including emissions) and is designed to give “representative” values of each species (with the exception of OH).

The purpose of this model is to examine coupling between tropospheric methane chemistry (CH$_4$, CO, OH) and stratospheric ozone chemistry (N$_2$O, NOy, O$_3$).
Background

- Methane (CH₄) and Nitrous oxide (N₂O) are both greenhouse gases

- CH₄ has also has environmental impacts via chemistry that enhances the abundance of tropospheric ozone (O₃) and decreases that of hydroxyl radicals (OH) and hence alters the atmospheric lifetime of many other pollutants

- Likewise, N₂O is a known O₃-depleting substance

- Both CH₄ and N₂O interact directly in the chemistry of stratospheric O₃, where global CH₄ concentration increases drive proportional but much smaller N₂O increases

- The pathway of how N₂O affects global CH₄ is more complex, involving the coupling of stratospheric O₃ depletion with global tropospheric chemistry through OH, and consequently the lifetime of CH₄.

Two-box model chemical mechanism

*Tropospheric:*
R01: emission of CH$_4$ (3.1e13 moles/year)
R02: CH$_4$ + OH $\rightarrow$ CO + ...
R03: emission of CO (3.4e13 moles/year)
R04: CO + OH $\rightarrow$ ... (loss of CO)
R05: OH + X $\rightarrow$ ... (loss of OH to other gases, fixed freq)
R06: production of OH: O$_3$ + h$_v$ $\rightarrow$ ... OH (h$_v$ depends on strat-O3)
R07: emission of N$_2$O (5.5e11 moles/year)
R08: NOy $\rightarrow$ ... (first-order loss)
R09: O$_3$ $\rightarrow$ ... (first-order loss)

*Stratospheric:*
R10: CH$_4$ $\rightarrow$ ... loss of methane (e.g., Cl)
R11: CO $\rightarrow$ ... loss of CO, all channels
R12: OH $\rightarrow$ ... loss of OH
R13: N$_2$O + h$_v$ & N$_2$O + O(^1D) $\rightarrow$ ... (loss to null)
R14: N$_2$O + O(^1D) $\rightarrow$ NOy ... (loss producing NOy)
R15: production of O$_3$ (2.7e19 moles/yr)
R16: O$_3$ + O$_3$ $\rightarrow$ ... ozone loss via Chapman
R17: O$_3$ + NOy $\rightarrow$ ... (+ NOy) ozone loss via NOx
R18: O$_3$ + CH$_4$ $\rightarrow$ ... (+ CH$_4$) ozone loss via HOx

**Transport Mechanism**

$F_{\text{air}} = 7.5 \times 10^{18}$ moles/yr
$F_{12} = F_{\text{air}} (X_{\text{trop}} - X_{\text{strat}})$
$F_{21} = -F_{12}$
Two-box model chemical mechanism

Transport (STE)

CH$_4$ → loss

CO → loss

OH → loss

N$_2$O → loss

O$_3$ → loss [Ox cycle]

NOy → loss [NOx cycle]

OH → loss [HOx cycle]

O$_3$ → loss

Prod

CH$_4$, CO, OH, N$_2$O, NOy, O$_3$

Transport (STE)

E: CH$_4$

E: CO

E: N$_2$O

Stratosphere

Troposphere

Two-box model chemical mechanism
**twobox.exe** input file

*** Input parameters for the 2-box model ***
> species numbers 1=CH4-trop, 2=CO-trop, 3=OH-trop, 4=N2O-trop, 5=NOy-trop, 6=O3-trop,
> 7=CH4-strt, 8=CO-strt, 9=OH-strt, 10=N2O-strt, 11=NOy-strt, 12=O3-strt
> number of years to simulate
100
> initial conditions: use steady-state mixing ratios (0) or those below (1)
1
> mixing ratios in ppb (1-5,7-11) or DU (6,12)
  1, 1.6964E+03
  2, 1.0808E+02
  3, 3.6295E+00
  4, 3.2995E+02
  5, 1.4019E-02
  6, 3.0320E+01
  7, 1.2573E+03
  8, 7.4539E-01
  9, 2.7228E-03
 10, 2.3662E+02
 11, 9.2665E+00
 12, 3.0017E+02
> use constant surface emissions (0) or linearly ramp up over length of run (1)
0
> scaling factors for surface emissions (CH4, CO, N2O)
 1.0
 1.0
 1.0
> output filename (.dat added automatically)
out_2100
### twobox.exe output file

Columns 1 to 13:

<table>
<thead>
<tr>
<th>Time(yr)</th>
<th>CH4(t)</th>
<th>CO(t)</th>
<th>OH(t)</th>
<th>N2O(t)</th>
<th>NOy(t)</th>
<th>O3(t)</th>
<th>CH4(s)</th>
<th>CO(s)</th>
<th>OH(s)</th>
<th>N2O(s)</th>
<th>NOy(s)</th>
<th>O3(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.69E+3</td>
<td>1.08E+2</td>
<td>3.62E+0</td>
<td>3.09E+2</td>
<td>1.40E-2</td>
<td>3.03E+1</td>
<td>1.257E+3</td>
<td>7.4E+0</td>
<td>2.72E+3</td>
<td>2.36E+2</td>
<td>9.26E+0</td>
<td>3.00E+2</td>
</tr>
</tbody>
</table>

Values are in ppb
- e.g., \(CO(t) = 1.08e2 = 108\) ppb
- Except ozone which is in Dobson Units
  - e.g., \(O3(s) = 3.00e2 = 300\) DU

Columns 14 to 16:

<table>
<thead>
<tr>
<th>E(CH4)</th>
<th>E(CO)</th>
<th>E(N2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>372</td>
<td>40.8</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Values are Tg(C)/year or Tg(N)/year

Columns 17:22:

<table>
<thead>
<tr>
<th>m(CH4)</th>
<th>m(CO)</th>
<th>m(OH)</th>
<th>m(N2O)</th>
<th>m(NOy)</th>
<th>m(O3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Values are total of strat + trop (Tg) departures from steady-state
Thanks to

Felicia Kolonjari, Xiaoyi Zhao, Stephanie Conway

for their beta-testing efforts.
0. Test. Run the model executable (twobox.exe) and examine the output file, twobox.dat. Compare it to ‘twobox_reference.dat’ and confirm that they are identical.

1. The initial values of mixing ratio given in the input file (‘twobox.inp’) represent the steady-state values (when the emissions scaling factors are set to 1).

a) Calculate the total burden of N$_2$O, $N$, (in moles) using the formula

$$N = \chi_{trop} n_{trop} + \chi_{strat} n_{strat}$$

where $\chi$ is the mixing ratio of N$_2$O and $n$ represents the moles of air.

(b) Calculate the lifetime of N$_2$O, where lifetime is defined as the burden divided by the loss rate. [Hint: the system is in steady-state.]

(c) In the same way calculate the lifetime of CH$_4$ and CO.
Exercises

2. In the input file, increase the initial mixing ratio of tropospheric N\textsubscript{2}O (species 4) by 20 ppb (from 309.9 to 329.9) and run the model for 200 years. This represents a perturbation to the system. Plot the time series of the species (the ones mentioned in parts (i), (ii) and (iii), below) in the new output file.

a) Explain the behaviour of tropospheric N\textsubscript{2}O and stratospheric N\textsubscript{2}O. Why is there a delay in the increase in stratospheric N\textsubscript{2}O?

b) Explain the behaviour of stratospheric ozone.

c) Explain the behaviour of tropospheric OH, CH\textsubscript{4} and CO. What seems to be the key connection between CH\textsubscript{4} and N\textsubscript{2}O?

d) Using values from the last few years of the N\textsubscript{2}O time series, determine the time constant at which N\textsubscript{2}O is returning to its steady-state value. The time constant, $\tau$, can be calculated using:

$$\tau = (t_2-t_1) / \ln[\Delta \chi(t_1)/\Delta \chi(t_2)]$$

where $t_1$ and $t_2$ are two point in the time series (several years apart) and $\Delta \chi(t_1)$ and $\Delta \chi(t_2)$ are the mixing ratio perturbations (that is, the difference between the mixing ratio of N\textsubscript{2}O and the steady-state value; 309.95 ppb for tropospheric N\textsubscript{2}O).

e) How does $\tau$ compare with the lifetime of N\textsubscript{2}O from 1(ii)? Explain any difference.

f) Compute $\tau$ in a similar manner for any other species. Comment.