Outline

Goals - I

Introduce concepts of atmospheric chemistry

- Today it's all about ozone
- Primary/secondary pollutants
- Emission (briefly)
- Photochemistry (more detail)
- Box model exercise

Goals - II

Run first numerical simulation of a chemical system

- Simple photochemical system
- Conditions to produce ozone production

Code is available here

You can clone the code using git via

```
git clone git@gitlab.com:ptg21/LCLUC_presentation.git
```

Who is this course for?

My goal is to introduce atmospheric chemistry with a focus on tropospheric ozone and other secondary pollutants.

I won't discuss the chemistry in detail but will summarise the relevant reactions. It gets complex towards the end.

The goal is to use these reactions to study how ozone levels respond to other pollutants.

Our focus is on rates of production of ozone during the day.

For the purpose of this course, everything is a pollutant.

Tricks of the trade

Mostly think about processes in terms of their characteristic timescales

- How fast is ozone formed?
- How fast is transport out of the planetary boundary layer?
- How does this compare with transport times?

What are the important species?

- Ozone
- NO_2
- Aldehydes
- Oxidants such as OH, NO_3
- Key species such as O^1D

Air pollution is a global problem

Figure: loss of visibility

Biogenic emissions are also important

Figure: 'Trees cause more pollution than automobiles do' - Ronald Reagan, 1981

Typical levels of atmospheric constituents

Pollutant	Concentration	Lifetime / yr
CH_4	1700 ppbv	10
H_2	500 ppbv	4
CO	40-200 ppbv	0.2
O_3	20-120 ppbv	0.05
OH	0.1 pptv	0.1s

1 ppbv = 10^{-9}
1 pptv = 10^{-12}

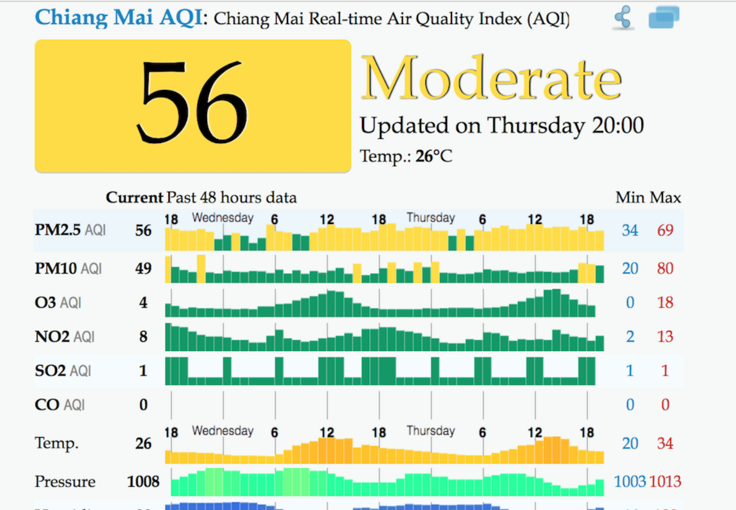
US EPA Air Quality Index levels of pollutants

Pollutant	Low	Moderate	UFSG	Unhealthy
Ozone	0-54	55-70	71-85	86-105
NO2	0-53	54-100	101-360	186-304
CO	0-4.4	4.5-9.4	9.5-12.4	12.5-15.4

Levels are in ppbv

Air quality index

$$I = \frac{(I_{high} - I_{low})}{(C_{high} - C_{low})}(C - C_{low}) + I_{low}$$



Primary and secondary pollutants

Primary Emitted directly into the atmosphere (usually at the surface)

- Nitric oxide, NO
- Volatile organic compounds such as methane, CO
  - Biogenic VOCs suc as isoprene, terpenes, formaldehyde (HCHO)
  - Anthropogenic VOCs such as benzene, gasoline
- Primary aerosol such as soot
- SO_2

Secondary Made in the atmosphere by oxidation

- Ozone, O_3
- NO_2
- Formaldehyde (HCHO)

Emission and loss - Timescales in atmospheric chemistry

Considering the atmosphere as a whole, or some air-mass within in it, we could write an equation describing the rate of change ('tendency') of a species.
Prognostic equation for species X, with concentration x

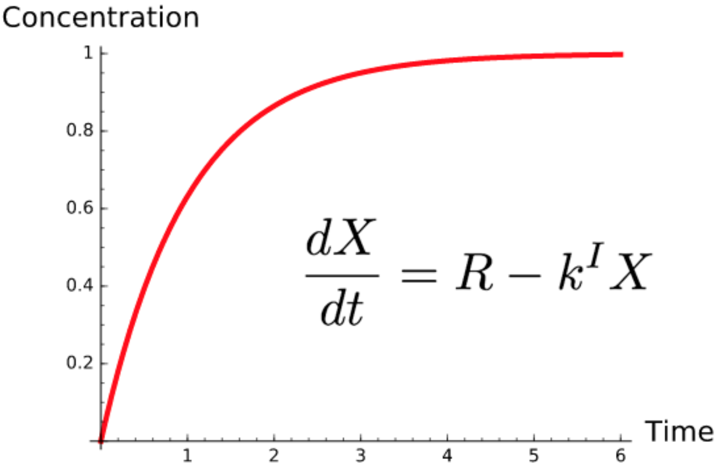
$$\frac{dx}{dt} = R - kx$$

where R is the (constant) rate of emission of X and k is a constant
We now have a first-order linear differential equation, which can be solved to give

$$x(t) = \frac{R}{k_1}\big(1 - \exp(-k_1 t)\big)$$

System has a characteristic time, $\tau = 1/k$

Time dependence of X



$$\frac{dX}{dt} = R - k^I X$$

Figure: Time dependence of concentration of chemical species X

Time dependence for constant emission rate and first-order loss.

The rate law

Basic points

- Rate is defined as change in concentration per unit time
- Natural unit of concentration in air quality modelling:
  - concentration: molecules per cm^3 gas so units are cm^{-3}
  - rate: cm^{-3} s^{-1}
- Law of Mass Action - Double the concentration = Double the rate

$NO + O_3 = NO_2 + O_2$

- The rate of change of NO can be expressed as

$$\frac{d[NO]}{dt} = -k_1[NO][O_3]$$

- Similarly, $\frac{d[NO_2]}{dt} = k_1[NO][O_3]$

Photochemistry

- Molecules absorb photons and the chemical bonds are broken - *photolysis*

$$NO_2 + hv \rightarrow NO + O$$

- Rate of photolysis depends on number of photons of the correct wavelength.

$$\frac{d[NO_2]}{dt} = -J[NO_2]$$

J depends on molecule and flux of photons (hence: time of day, lat, lon, cloud cover). Units of J are s^{-1}

Example: NO2

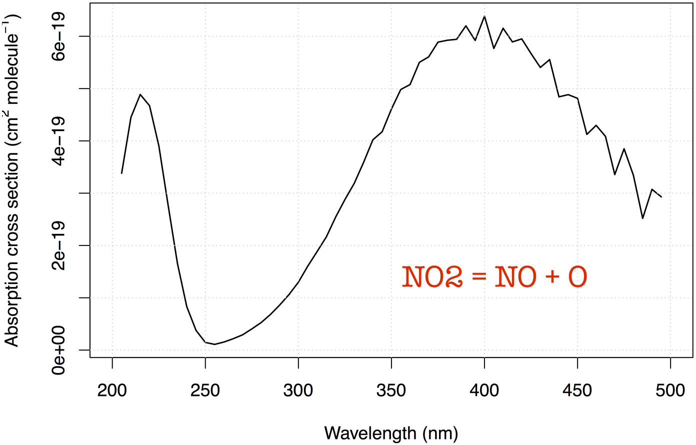


Figure: absorption cross-section of NO_2

Example: NO2

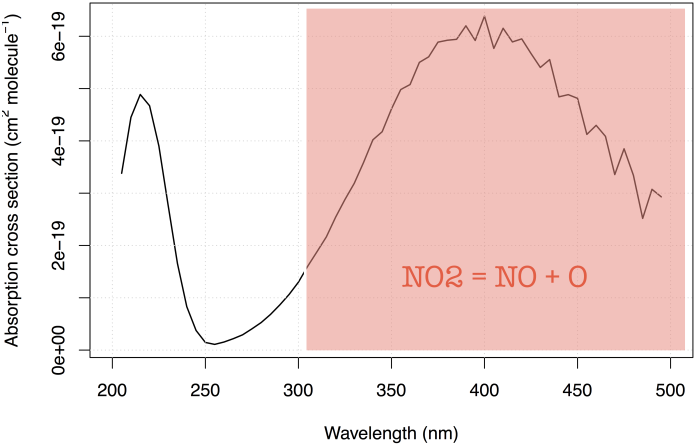


Figure: as before showing region of significant UV/VIS solar flux

NO_2/NO 'Photostationary state' - our first chemical model

Using the reactions already given,

$$\begin{aligned}
\mathrm{NO} + \mathrm{O_3} &\rightarrow \mathrm{NO_2} + \mathrm{O_2} \\
\mathrm{NO_2} + hv &\rightarrow \mathrm{NO} + \mathrm{O} \\
\mathrm{O_2} + \mathrm{O} &\rightarrow \mathrm{O_3}
\end{aligned}$$

we can write rates of change for each species

$$\begin{aligned}
\frac{d[\mathrm{NO_2}]}{dt} &= -J_1[\mathrm{NO_2}] + k_3[\mathrm{NO}][\mathrm{O_3}] \\
\frac{d[\mathrm{NO}]}{dt} &= J_1[\mathrm{NO_2}] - k_3[\mathrm{NO}][\mathrm{O_3}] \\
\frac{d[\mathrm{O}]}{dt} &= -k_2[\mathrm{O}][\mathrm{O_2}] + J_1[\mathrm{NO_2}] \\
\frac{d[\mathrm{O_3}]}{dt} &= k_2[\mathrm{O}][\mathrm{O_2}] - k_3[\mathrm{NO}][\mathrm{O_3}]
\end{aligned}$$

A set of coupled differential equations results!

How to proceed - I

What is our mechanism going to do?

- We can see that NO and ozone make NO2
- NO2 makes NO and O, and O makes O3
- so NO2 regenerates the NO and O3
- This is an active equilibrium - NO and NO2 interconvert, consuming/releasing ozone as they do so.

As we shall see in L2, this equilibrium is crucial.

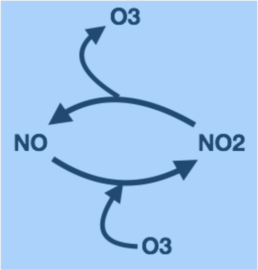


Figure: NO:NO2 interconversion and concomitant O3 consumption/production

How to proceed - II

- So we expect our equations to solve to an equilibrium with zero net rate of change
- There exists a wealth of literature on the solution of these stiff differential equations (lifetimes of each species vary by many orders of magnitude, resulting in small timesteps).
- In our example, the lifetime of O is very short, set by k_2[O2], while that of NO2 is determined by J and can be much longer.
- Step forward our numerical ('box') model...

Box models

- Box models represent a single representative area of the atmosphere.
- Notionally 1cmˆ3 in volume
- Can be connected to the ground via emission/deposition.
- Could also be chosen to represent the free troposphere.
- Need to supply photolysis rates, emissions

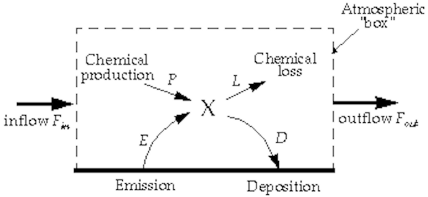
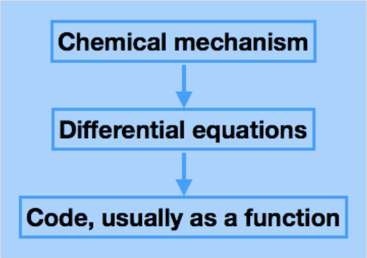


Figure: Box model (figure (c) Dan Jacob)

Anatomy of a box model - I

- Box models need a chemical mechanism.
- The literature can supply these, or you can write your own.
- You then code up the mechanism as a differential for each species, in terms of other species' concentrations and other inputs.



Anatomy of a box model - II

- Implementation in the language of your choice
- You need an integrator for the differential equations.
- There are good ones already implemented, so don't write your own!
- Typically you supply initial conditions, C0, functions for the tendency of each species, f, a timestep (dt) and an end point (tend).

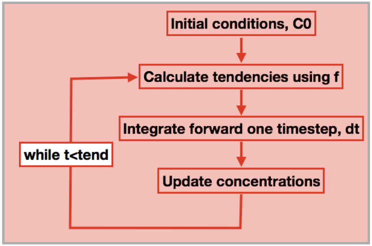


Figure: Box model (figure (c) Dan Jacob)

End of lecture 1

Getting started

- Open RStudio or R
- Look at `kinetics-box-model-pss.R`

in the src folder.

- What do equations describe?
- What do you expect to happen?

Any Pythonistas in the audience?

Anyone not got the software installed?

Practical one

Run the simulation

- `source("kinetics-box-model-pss.R")`

Do the results make sense?

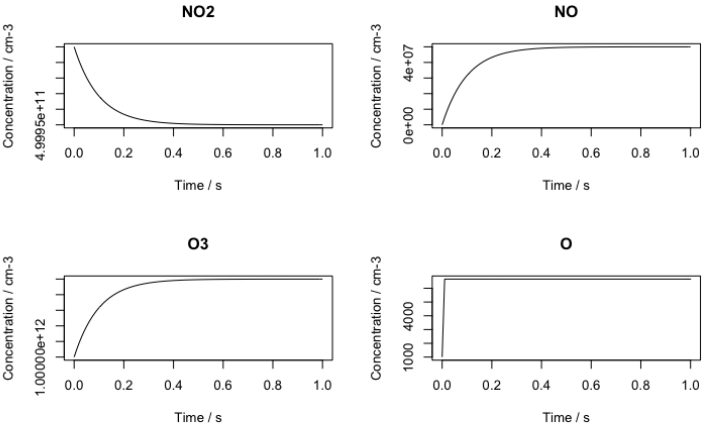
- If so: get a coffee!
- If not: shout out!

Coffee break

Recap of the first hour

Begun to think about putting together a chemical mechanism

First model looked at the NO / NO_2 / O_3 interconversion reactions



Box models in recent literature

Box models are great for process-based studies and the box can be as big as you like

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日本語要約

Isotopic constraints on marine and terrestrial N_2O emissions during the last deglaciation

Adrian Schilt Edward J. Brook Thomas K. Bauska Daniel Baggenstos Hubertus Fischer Fortunat Joos Vasilii V. Petrenko Hinrich Schaefer Jochen Schmitt Jeffrey P. Severinghaus Renato Spahni Thomas F. Stocker

and isotopic data for the last deglaciation, from 16,000 to 10,000 years before present, retrieved from air bubbles trapped in polar ice at Taylor Glacier, Antarctica. With the help of our data and a box model of the N_2O cycle, we find a 30 per cent increase in total N_2O emissions from the late glacial to the interglacial, with terrestrial and marine emissions contributing equally to the overall increase and generally evolving in parallel over the last

Figure: Box model used to constrain N_2O emissions

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日本語要約

High winter ozone pollution from carbonyl photolysis in an oil and gas basin

Peter M. Edwards Steven S. Brown James M. Roberts Ravan Ahmadov Robert M. Banta

producing basins in the western United States have identified ozone mixing ratios well in excess of present air quality standards, but only during winter[9, 10, 11, 12, 13]. Understanding winter ozone production in these regions is scientifically challenging. It occurs during cold periods of snow cover when meteorological inversions concentrate air pollutants from oil and gas activities, but when solar irradiance and absolute humidity, which are both required to initiate conventional photochemistry essential for ozone production, are at a minimum. Here, using data from a remote location in the oil and gas basin of northeastern Utah and a box model, we provide a quantitative assessment of the photochemistry that leads to these extreme winter ozone pollution events, and identify key

Figure: Box model used to study impact of fracking

Can focus on processes of interest, parameterize other processes (e.g. mixing), build up complexity as required.

Goals of lecture 2

Introduce ozone formation reactions

- Photochemical oxidant, OH, formation
- Peroxy radicals introduction

Run a box model describing ozone formation

- Conceptual overview of a box model
- Implementing air quality into a box model

Our mechanism

Our mechanism is rather complex - the CO and NO emissions interact with sunlight and water vapour

$$
\begin{aligned}
NO_2 + hv &\rightarrow NO + O \\
O_2 + O &\rightarrow O_3 \\
NO + O_3 &\rightarrow NO_2 + O_2 \\
O_3 + hv &\rightarrow O_2 + O1D \\
O1D + H_2O &\rightarrow 2OH \\
O1D + N_2/O_2 &\rightarrow O + N_2/O_2 \\
OH + \color{red}{CO} + O_2 &\rightarrow HO_2 + CO_2 \\
\color{red}{NO} + HO_2 &\rightarrow OH + NO_2
\end{aligned}
$$

Primary species coloured in red

Some general points

VOCs such as CO are degraded by reaction with OH

$$\mathrm{OH} + \mathrm{CO} + \mathrm{O_2} \quad \rightarrow \quad \mathrm{HO_2} + \mathrm{CO_2}$$

and HO_2 (a class of 'peroxy') radicals are produced.

NO2 is produced additionally via reaction of peroxy radicals with NO

$$\mathrm{NO} + \mathrm{HO_2} \quad \rightarrow \quad \mathrm{OH} + \mathrm{NO_2}$$

NO2 photolysis leads to O3

$$\begin{aligned} \mathrm{NO_2} + hv \quad &\rightarrow \quad \mathrm{NO} + \mathrm{O} \\ \mathrm{O_2} + \mathrm{O} \quad &\rightarrow \quad \mathrm{O_3} \end{aligned}$$

Implementation in a box model

As a series of tendencies

```
dNO2 = -J1*NO2   + k3*NO*O3 + k8*HO2*NO - k9*OH*NO2 +
k13*OH*HONO2

dNO  =  J1*NO2   - k3*O3*NO - k8*HO2*NO

dO3  =  k2*O     - k3*NO*O3 - J4*O3

dO   =  J1*NO2   - k2*O  + k5*O1D*M

dOH  =  2.k6*O1D*H2O - k7*OH*CO + k8*HO2*NO +
k11*HO2*O3 - k12*OH*O3 - k9*OH*NO2

dHO2 =  k7*OH*CO - k8*HO2*NO - k11*HO2*O3 +
k12*OH*O3 - k14*HO2*HO2

dCO  = -k7*OH*CO
```

Formation of OH from ozone and water vapour

The photochemical oxidant, OH, is formed from ozone and water vapour.

$$\begin{aligned} O_3 + hv &\rightarrow O_2 + O1D \\ O1D + H_2O &\rightarrow 2OH \\ O1D + N_2/O_2 &\rightarrow O + N_2/O_2 \end{aligned}$$

Via excited state oxygen atoms - the O1D species.

These are distinct from the ground state oxygen atoms, O, produced by NO2 photolysis.

The photochemical oxidant OH is reactive towards VOCs. This species initiates the photochemical degradation of VOCs and in the presence of NO will produce ozone.

Reaction of photochemical oxidant, OH, with VOCs

Able to react with CO and with other VOC via the H atoms, and so initiate photo-degradation.

$$OH + CO + O_2 \rightarrow HO_2 + CO_2$$

$$OH + CH_4 \rightarrow H_2O + CH_3O_2$$

Once produced, these peroxy radicals oxidize NO to NO2 and ozone is produced.

$$\begin{aligned} NO + HO_2 &\rightarrow OH + NO_2 \\ NO_2 + hv &\rightarrow NO + O \\ O_2 + O &\rightarrow O_3 \end{aligned}$$

Without the HO_2 the NO reacts with ozone to produce NO2, which recreates the ozone. No net ozone production!!

Conclusions

If you have an air mass with NO, VOC (here CO) and sunlight you can expect ozone formation.

The amount of ozone formed also depends on H_2O, number of photons (sunlight).

You can calculate the rate at which ozone is being formed.

Without these ozone will be destroyed

Ozone in model world

- There is significant **loss in the mid troposphere** (via HO2 + O3)
- Most global tropospheric ozone is produced in the NH and lost in the tropics

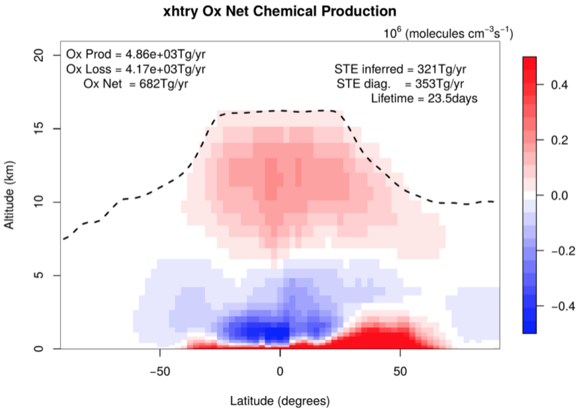

Figure: Zonal mean net ozone production/loss in the model world

Practical 2

- Open RStudio or R
- Look at `kinetics-box-model-ozone.R`

in the src folder.

- What do equations describe?
- What do you expect to happen?

Any Pythonistas in the audience?

Practical 2

Run the simulation

- `source("kinetics-box-model-ozone.R")`
- Can you shift the atmosphere from ozone destruction to ozone production?
- How?

Next steps

Hand coding the tendency functions gets tedious and can be error-prone.

- Automatic code generation is possible
- See KPP, the *Kinetic Pre-Processor*
- Generates F77, F90, C, Matlab code which you compile and run (or run within Matlab)
- This has been incorporated into DSMACC

This is an excellent model but its usage requires good Shell and compiler skills.

It's easy to show that J values are key to the chemistry

- Consider using a verifiable radiative transfer model such as TUV (Tropospheric Ultraviolet and Visible TUV model)

This is the end of the 'planned part'

Thank you for your attention

Any questions?

Any suggestions?

Emissions and deposition

Emission of primary pollutants

Emissions into a boundary layer - dimensional analysis

- Emissions per unit surface area:
  - Flux E has units of (molecules) per unit of surface area per unit time (cm^{-2} s^{-1})
- Into a well-mixed layer of height h (cm)

Rate equation

- A rate of change of E/h

$$\frac{d[NO]}{dt} = E_{NO}/h$$

has the correct dimensions (cm^{-3} s^{-1})

Dry deposition at the surface

- Flux depends on concentration in gas phase above surface and on the reactivity of the surface
- Flux has units of (molecules) per unit of surface area per unit time (cm^{-2} s^{-1})

$$\mathrm{Flux} \quad \propto \quad C[O_3]$$

- Units of C are therefore cm s^{-1}, a 'velocity', v, dependent on surface type

$$\frac{d[O_3]}{dt} \quad = \quad -\frac{v}{h}[O_3] = -k_1[O_3]$$