Outline

Introduce concepts of atmospheric chemistry

Run first numerical simulation of a chemical system

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

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)

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 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

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

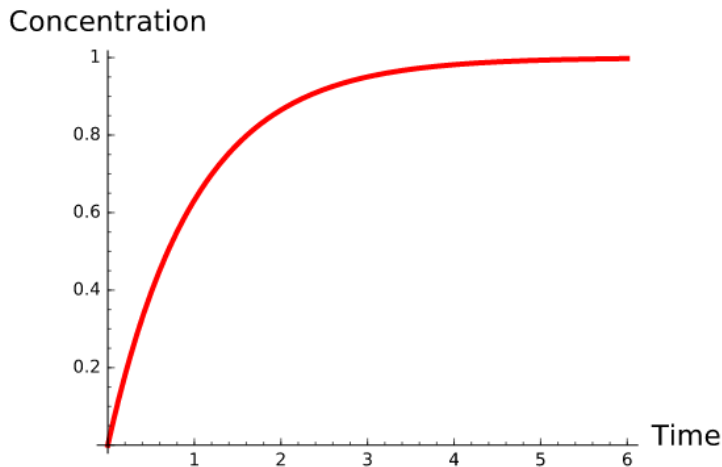System has a characteristic time, $\tau = 1/k$

Time dependence of X

Figure: Time dependence of concentration of chemical species X

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

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
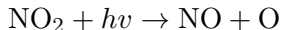- Flux has units of (molecules) per unit of surface area per unit time (cm^{-2} s^{-1})

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

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

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

Photochemistry

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

$$NO_2 + h\nu \rightarrow NO + O$$

- 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

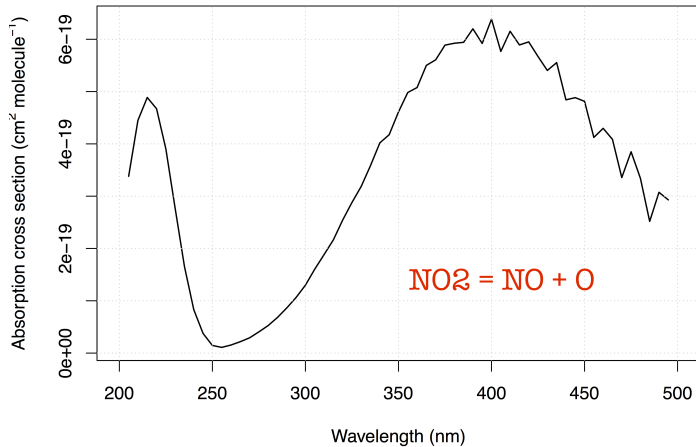Figure: absorption cross-section of NO_2

Example: NO2

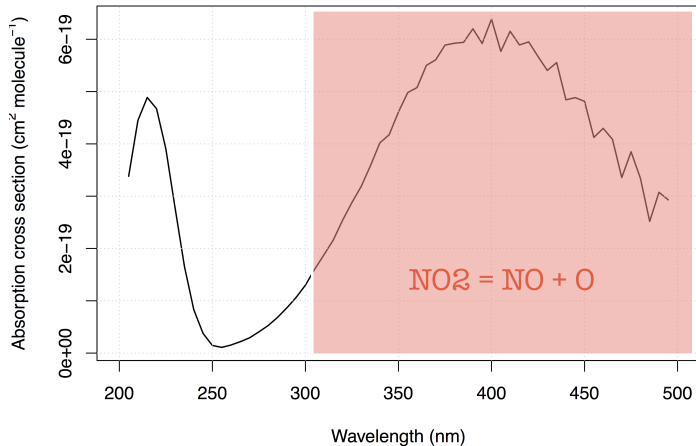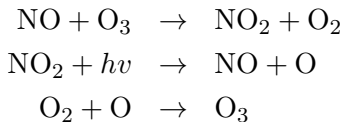Figure: as before showing region of significant UV/VIS solar flux

NO$_2$/NO 'Photostationary state'

Using the reactions already given,

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

we can write rates of change for each species

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

A set of coupled differential equations results!

- 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 model...

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?

Run the simulation
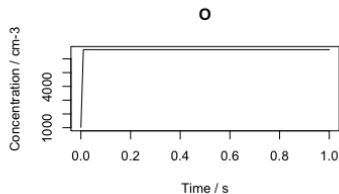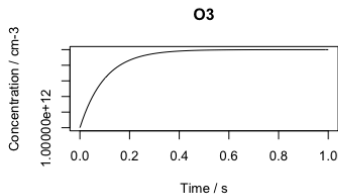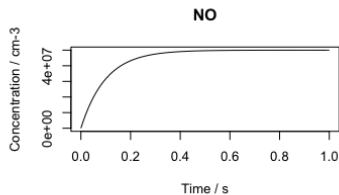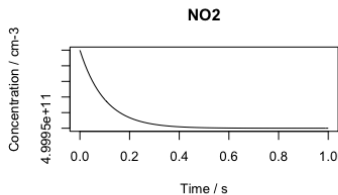
- ▶ `source("kinetics-box-model-pss.R")`

Do the results make sense?

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

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

Introduce ozone formation reactions

Run a box model describing ozone formation