

# Outline

## Lecture 1

General comments on atmospheric pollution

Quantitative treatment of chemical processes

Emissions and deposition

Photochemistry

Putting these together

first example: the  $\text{NO}/\text{NO}_2$  interconversion by ozone

Practical one

## Lecture 2

# Goals

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 <sub>4</sub>	1700 ppbv	10
H <sub>2</sub>	500 ppbv	4
CO	40-200 ppbv	0.2
O <sub>3</sub>	20-120 ppbv	0.05
OH	0.1 pptv	0.1s

$$1 \text{ ppbv} = 10^{-9}$$

$$1 \text{ pptv} = 10^{-12}$$

## US EPA Air Quality Index levels of pollutants

Pollutant	Low	Moderate	UFSG	Unhealthy
Ozone	0-54	55-70	71-85	86-105
NO <sub>2</sub>	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 such as isoprene, terpenes, formaldehyde (HCHO)
  - ▶ Anthropogenic VOCs such as benzene, gasoline
- ▶ Primary aerosol such as soot
- ▶ SO<sub>2</sub>

**Secondary** Made in the atmosphere by oxidation

- ▶ Ozone, O<sub>3</sub>
- ▶ NO<sub>2</sub>
- ▶ 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 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

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

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



## Time dependence of X

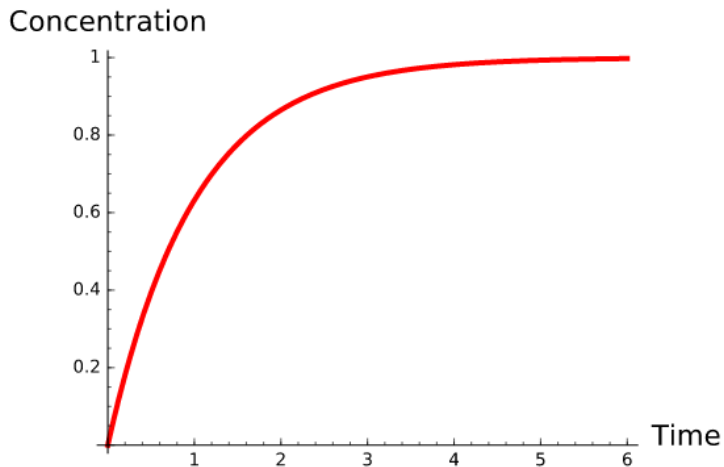


Figure: Time dependence of concentration of chemical species X

# 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<sup>3</sup> gas so units are cm<sup>-3</sup>
  - ▶ rate: cm<sup>-3</sup> s<sup>-1</sup>
- ▶ Law of Mass Action - Double the concentration = Double the rate



- ▶ The rate of change of NO can be expressed as

$$\frac{d[\text{NO}]}{dt} = -k_1[\text{NO}][\text{O}_3]$$

- ▶ Similarly,  $\frac{d[\text{NO}_2]}{dt} = k_1[\text{NO}][\text{O}_3]$

# 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 ( $\text{cm}^{-2} \text{s}^{-1}$ )
- ▶ Into a well-mixed layer of height  $h$  (cm)

## Rate equation

- ▶ A rate of change of  $E/h$

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

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

## 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 ( $\text{cm}^{-2} \text{s}^{-1}$ )

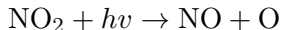
$$\text{Flux} \propto C[\text{O}_3]$$

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

$$\frac{d[\text{O}_3]}{dt} = -\frac{v}{h}[\text{O}_3] = -k_1[\text{O}_3]$$

# Photochemistry

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



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

$$\frac{d[\text{NO}_2]}{dt} = -J[\text{NO}_2]$$

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

## Example: NO<sub>2</sub>

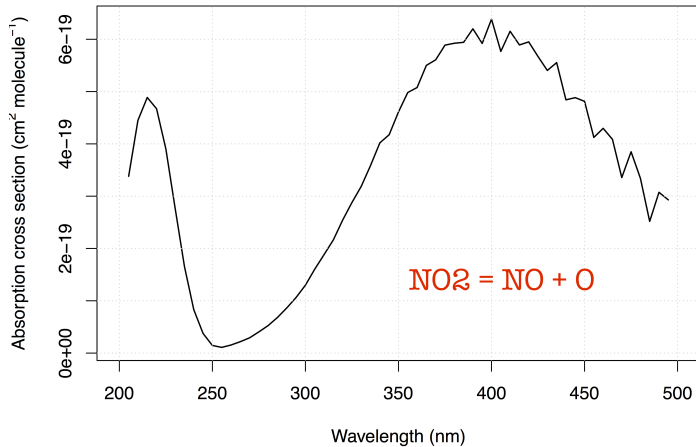


Figure: absorption cross-section of NO<sub>2</sub>

## Example: NO<sub>2</sub>

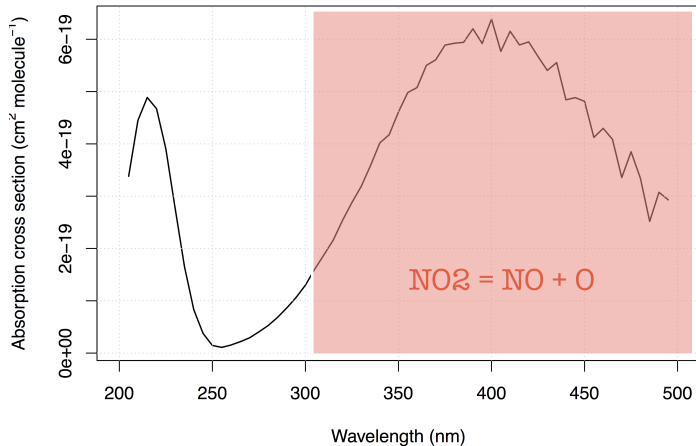
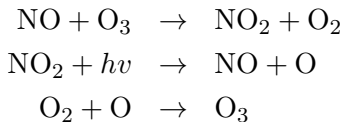


Figure: as before showing region of significant UV/VIS solar flux

## NO<sub>2</sub>/NO 'Photostationary state'

Using the reactions already given,



we can write rates of change for each species

$$\begin{aligned}\frac{d[\text{NO}_2]}{dt} &= -J_1[\text{NO}_2] + k_3[\text{NO}][\text{O}_3] \\ \frac{d[\text{NO}]}{dt} &= J_1[\text{NO}_2] - k_3[\text{NO}][\text{O}_3] \\ \frac{d[\text{O}]}{dt} &= -k_2[\text{O}][\text{O}_2] + J_1[\text{NO}_2] \\ \frac{d[\text{O}_3]}{dt} &= k_2[\text{O}][\text{O}_2] - k_3[\text{NO}][\text{O}_3]\end{aligned}$$

A set of coupled differential equations results!



## How to proceed

- ▶ There exists a wealth of literature on the solution of these stiff (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  $k_3[\text{O}_2]$ , while that of  $\text{NO}_2$  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!

## Goals of lecture 2

Introduce ozone formation reactions

Run a box model describing ozone formation