# Lecture 29. <u>Introduction to atmospheric chemical transport models. Part 1.</u>

Objectives:
1. **Model types**.
2. **Box models.**
3. **One-dimensional models.**
4. **Two-dimensional models.**
5. **Three-dimensional models.**

Readings: Graedel T. and P.Crutzen. "Atmospheric change: an earth system perspective". Chapter 15."Bulding environmental chemical models", 1992.

## 1. <u>Model types.</u>

**Mathematical models** provide the necessary framework for integration of our understanding of individual atmospheric processes and study of their interactions. Note, that atmosphere is a complex reactive system in which numerous physical and chemical processes occur simultaneously.

- Atmospheric chemical transport models are defined according to their spatial scale:

| Model | Typical domain scale | Typical resolution |
|---|---|---|
| Microscale | 200x200x100 m | 5 m |
| Mesoscale(urban) | 100x100x5 km | 2 km |
| Regional | 1000x1000x10 km | 20 km |
| Synoptic(continental) | 3000x3000x20 km | 80 km |
| Global | 65000x65000x20km | $5^0$x$5^0$ |

Figure 29.1 Components of a chemical transport model (Seinfeld and Pandis, 1998).
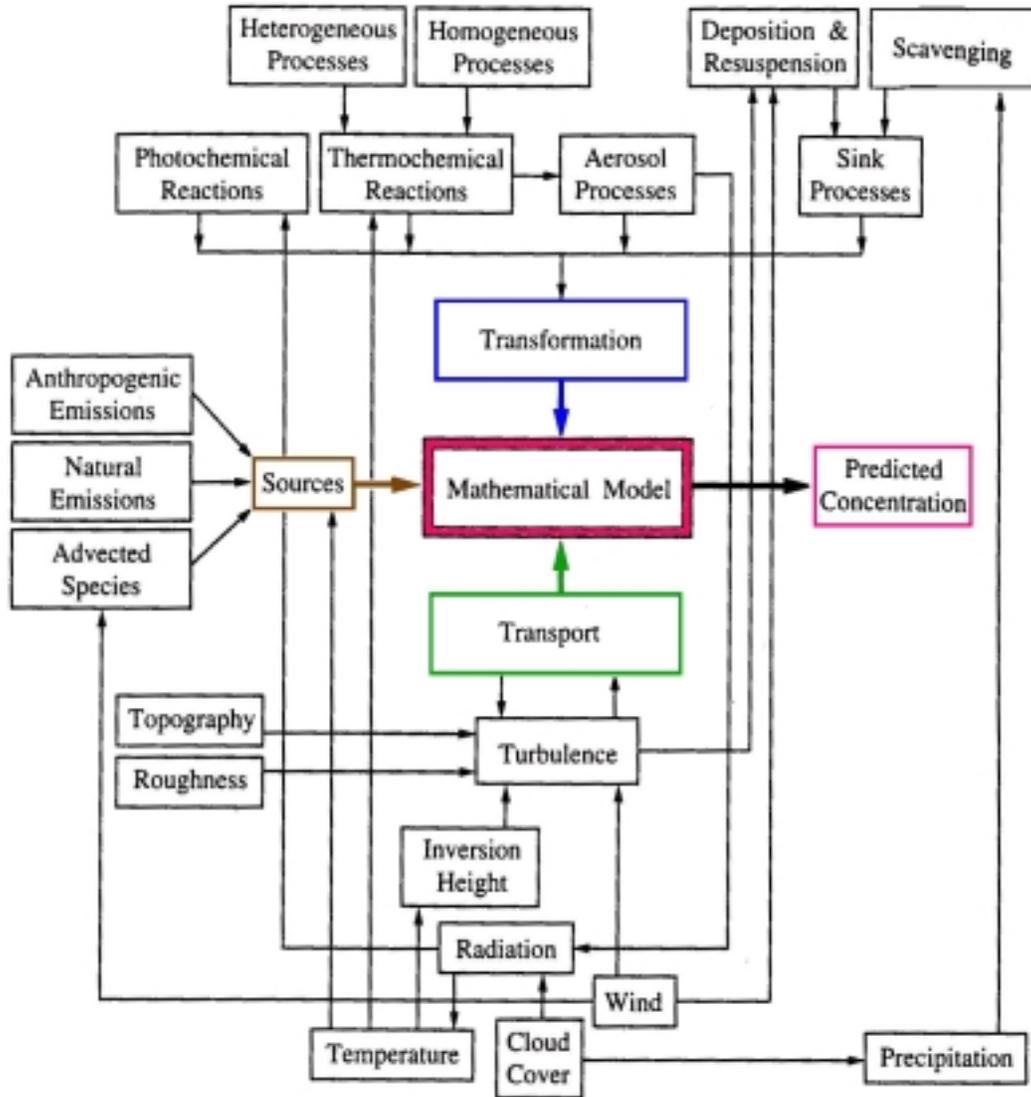
- **Domain** of the atmospheric model is the area that is simulated. The computation domain consists of an array of **computational cells**, each having uniform chemical composition. The size of cells determines the spatial resolution of the model.

- Atmospheric chemical transport models are also characterized by their dimensionality: **zero-dimensional (box) model; one-dimensional (column) model; two-dimensional model; and three-dimensional model.**

Box (0-D)

Column (1-D)

2-D

3-D
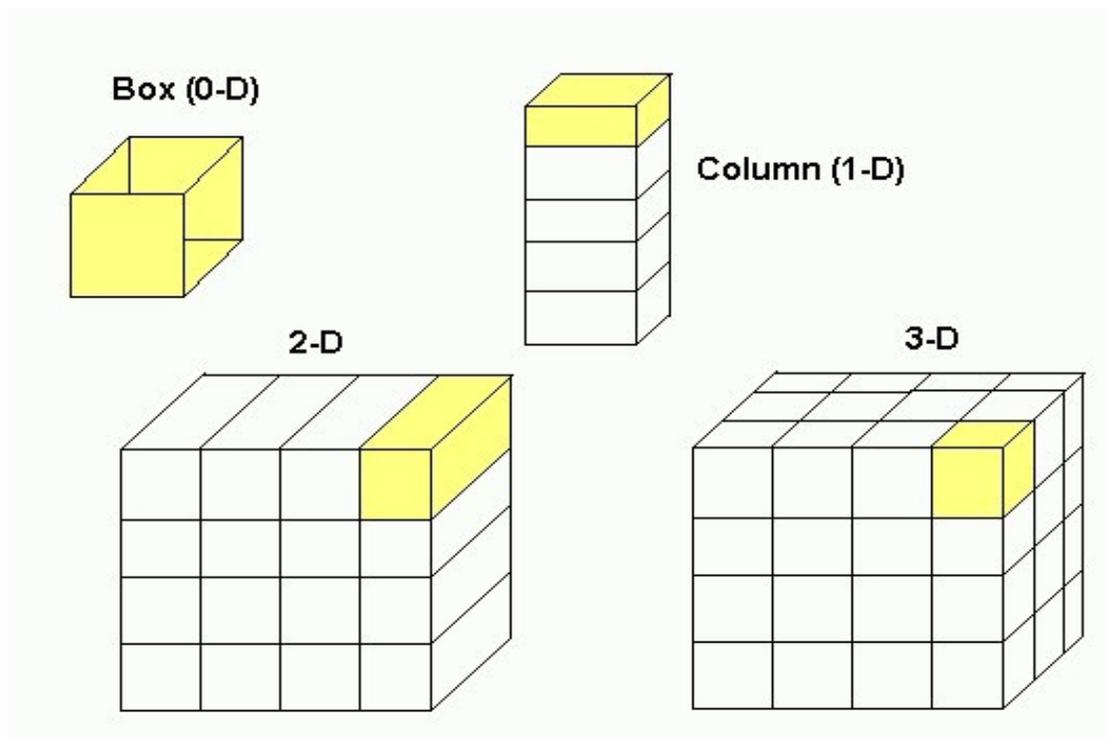
- Model time scale depends on a specific application varying from hours (e.g., air quality model) to hundreds of years (e.g., climate models)

<u>Two principal approaches to simulate changes in the chemical composition of a given air parcel:</u>

1) **Lagrangian approach:** air parcel moves with the local wind so that there is no mass exchange that is allowed to enter the air parcel and its surroundings (except of species emissions). The air parcel moves continuously, so the model simulates species concentrations at different locations at different time,

2) **Eulerian approach:** model simulates the species concentrations in an array of fixed computational cells.

Figure 29.2 Movement of the reactive air parcel in a Lagrangian model.
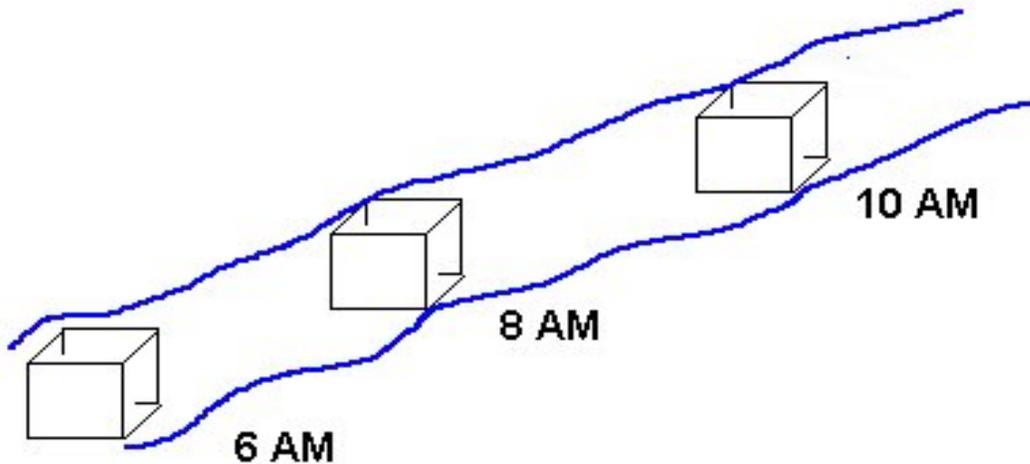


2. **<u>Box models (or 'zero dimensional', or 0-D models)</u>** are the simplest models, where the atmospheric domain is represented by only one box.

➢ In a box model concentrations are the same everywhere and therefore are functions of time only, $n_i(t)$.

Figure 29.3 A schematic diagram of 0-D model of atmospheric chemistry (Eulerian approach).
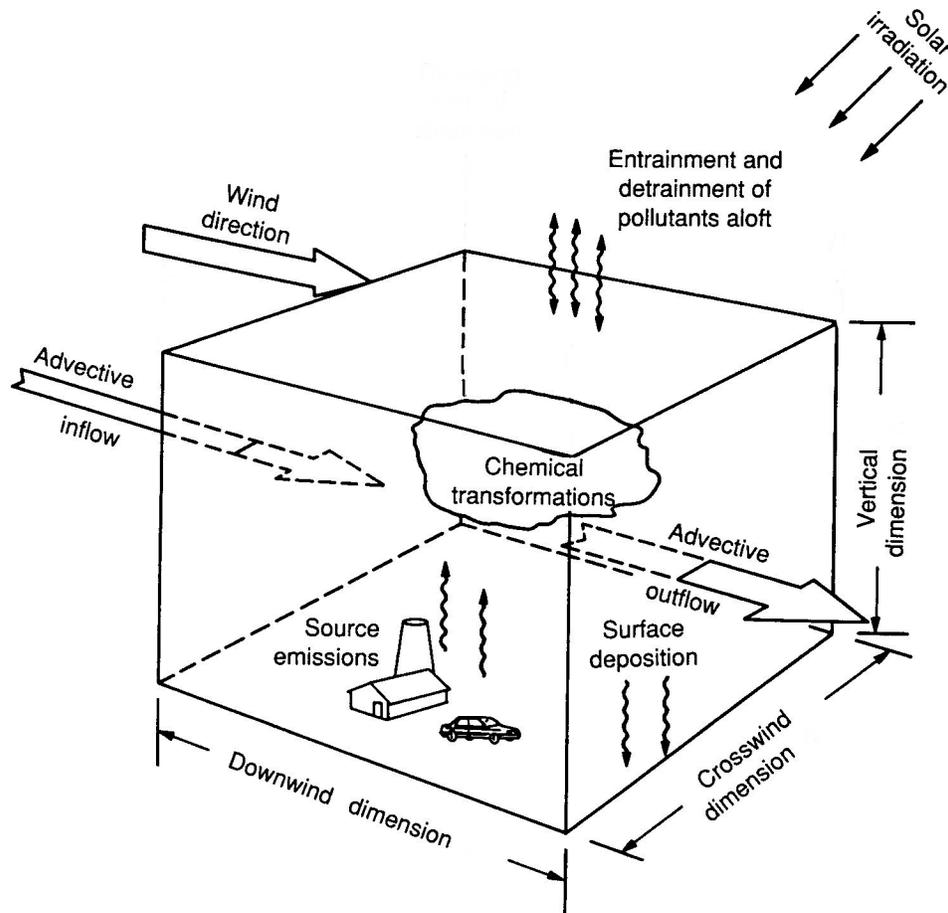


## Eulerian box model:

Chemical species enter a box in two ways:

1) source emissions;
2) transport: **advection** (the transport of a species by the mean horizontal motion of air parcel) and **entrainment** (the vertical movement of air parcels as a consequence of turbulent mixing)

Chemical species are removed from a box in three ways:

1) transport: **advection** out of the box and **detrainment** due to upwards motion;
2) chemical transformations;
3) removal processes: dry deposition on surface.

- In the Lagrangian box model: advection terms are eliminated, but source terms vary as the parcel moves over different source regions.

**Some features of the box models:**

- **The dimensions and placement of the box is dictated by the particular problem of interest.**

For instance, to study the influence of urban emissions on the chemical composition of air, the box may be design to cover the urban area.

- **Box models can be time dependent. In that case, any variations in time of the processes considered need to be accurately supplied to the model.**

For instance, if a box model is used to compute air quality for 24-hr day in an urban area, the model must include daily variations in traffic and other sources; diurnal wind speed patterns; variations in the height of the mixed layer; variation of solar radiation during the day; etc.

Limitations of a box model:

i)      assumes rapid vertical and horizontal mixing;
ii)     assumes uniformity of surface sources;

## Simplified mathematical formulation of a box model:

A separate equation is written for each chemical species of interest. For species **i**, present at concentration $n_i$, in a well-mixed box of length L and height H, the time dependence of the concentration of species **i** is given by

$$d n_i / dt = S_i + C_i + v_{ad} (n_i^0 - n_i)/L + v_v (n_i^{trop} - n_i)/H - v_{dep} n_i /H$$

where

$S_i$ is the emission source term;

$C_i$ is the chemical loss or production rate;

$v_{ad} (n_i^0 - n_i)/L$ is the advection term, here $v_{ad}$ is the advection wind velocity and $n_i^0$ is the upwind concentration of species **i**;

$v_v (n_i^{trop} - n_i)/H$ is the entrainment or detrainment term, here $v_v$ is the ventilation velocity that describes the exchange with air above the box, and $n_i^{trop}$ is the concentration of species **i** above the box (often in the free troposphere).
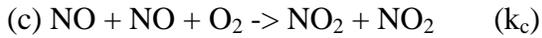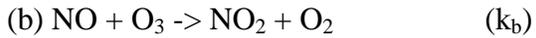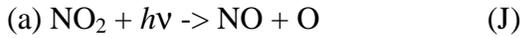
➢ The chemical loss or production rate $C_i$ is dependent on the number of chemical reactions included into the model, and it is given by

$$dn_i/dt = C_i = P_i - R_i$$

$P_i$ is the production term of species i; and $R_i$ is the loss term.

## Problem:

Find the rate of change of $NO_2$ concentration if nitrogen dioxide is involved in the following reactions with the rate coefficients J, $k_b$, and $k_c$:

(a) $NO_2 + h\nu \rightarrow NO + O$            (J)

(b) $NO + O_3 \rightarrow NO_2 + O_2$         ($k_b$)

(c) $NO + NO + O_2 \rightarrow NO_2 + NO_2$     ($k_c$)


## Solution:

The rates of these reactions are

$Rate_a = J\ [NO_2]$

$Rate_b = k_b\ [NO]\ [O_3]$

$Rate_c = k_c\ [NO]\ [NO][O_2]$

The rate of change of $NO_2$ concentration can be written as production minus loss terms. Thus,

$d\ [NO_2]\ /dt\ =\ P_{NO2} - R_{NO2}$

where $P_{NO2}$ and $R_{NO2}$ are total chemical production and loss terms, respectively:

$P_{NO2} = Rate_b + 2\ Rate_c = k_b\ [NO]\ [O_3] + 2\ k_c\ [NO]\ [NO][O_2]$

$R_{NO2} = Rate_a = J\ [NO_2]$

Therefore

$d\ [NO_2]\ /dt\ =\ P_{NO2} - R_{NO2} = k_b\ [NO]\ [O_3] + 2\ k_c\ [NO]\ [NO][O_2] - J\ [NO_2]$

3. **One-dimensional (1-D) models** assume that species concentrations are functions of height and time, $n_i(z, t)$.

Figure 29.4 A schematic diagram of 1-D model of atmospheric chemistry (Eulerian approach).
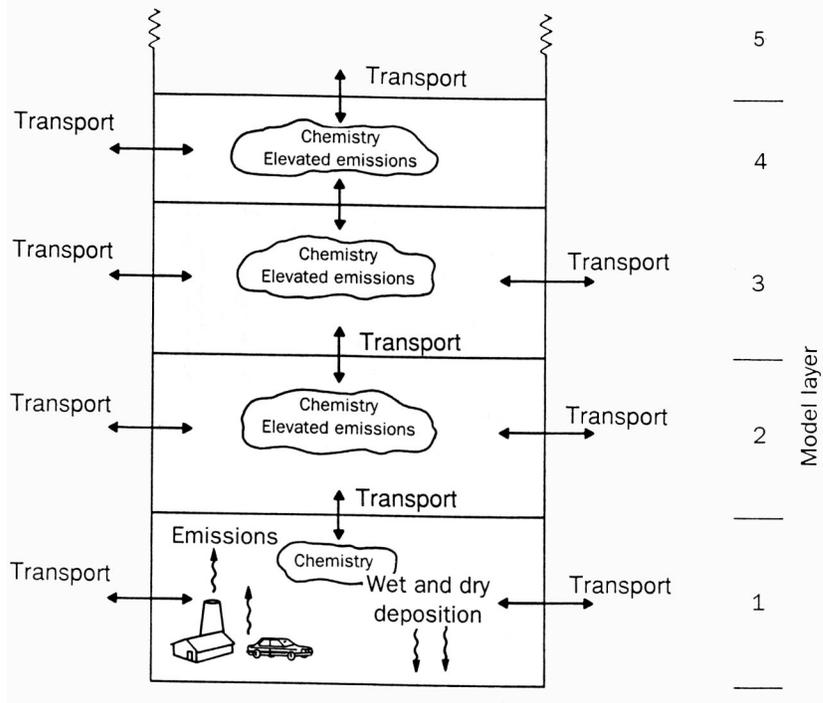


4. **Two-dimensional (2-D) models** assume that species concentrations are uniform along one dimension and depend on the other two and time, for example $n_i(x, z, t)$.

- 2-D models are often used in description of global atmospheric chemistry, assuming that concentrations are functions of latitude and altitude but do not depend on longitude.

- 2-D models have mainly been used for stratospheric studies, because in troposphere there is essential longitudinal variations.

NOTE: Application of a 2-D model will be discussed in Lecture 30.

Figure 29.5 The computational cells of 2-D model.
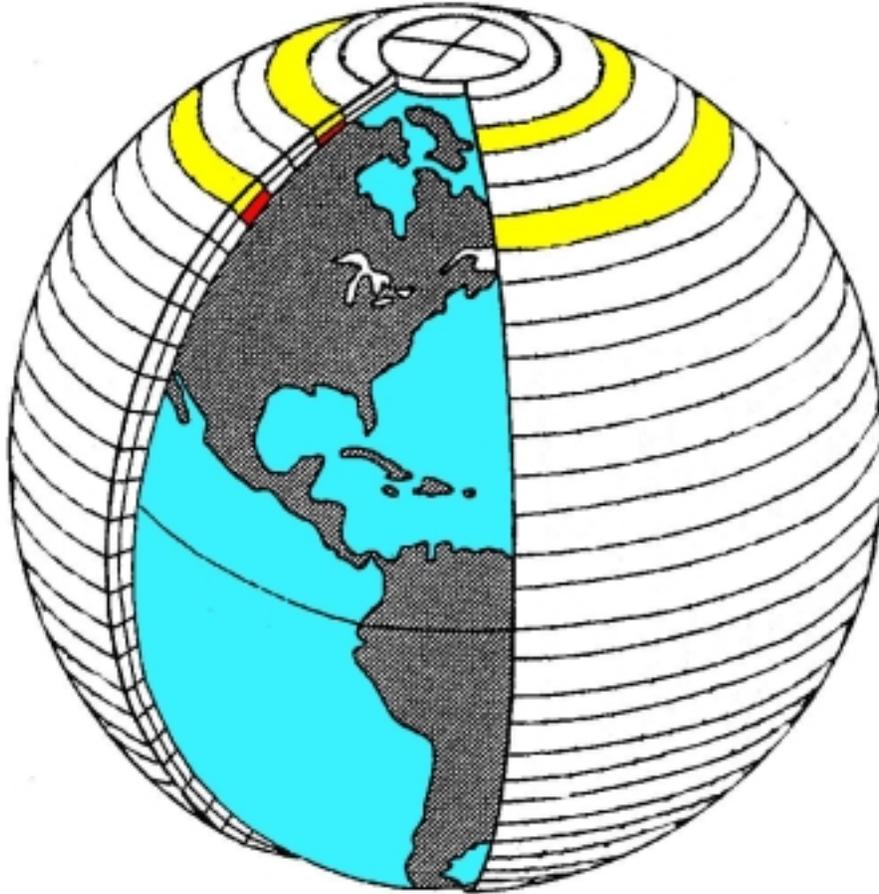
5. **<u>Three-dimensional (3-D) models</u>** simulate the full concentration field

$n_i(x, y, z, t)$.

Figure 29.6 The computational cells of 3-D model.



- **3-D models** require simultaneous calculations of the meteorological field and chemistry. The chemistry is often very simplified, because of computational complexities of the meteorological field.

<u>Decoupled (or off-line) 3-D chemical model:</u>

first meteorological model is run to for chosen time period and for a geographical location (or entire globe), and the calculated wind field, temperature, water vapor, cloud, etc. are stored to be used as input variable in 3-D chemical model.

Advantage of decoupled 3-D model: treats photochemical processes with more details.

- 3-D chemical transport model seeks a solution **of the continuity (or mass conservation) equation** for each species (gas or aerosols) included in the model.

General form of the continuity equation:

$$d n_i/dt = (d n_i/dt)_{tran} + (d n_i/dt)_{cloud} + (d n_i/dt)_{rem} + (d n_i/dt)_{aeros} + (d n_i/dt)_{chem} + S_i$$

where $n_i$ is the concentration of a species $i$;

$(d n_i/dt)_{tran}$ is the rate of change of $n_i$ due to transport (advection, diffusion, etc.);

$(d n_i/dt)_{cloud}$ is the rate of change of $n_i$ due to cloud processes (cloud scavenging, evaporation of cloud droplets, aqueous-phase reactions, wet deposition, etc.);

$(d n_i/dt)_{aeros}$ is the rate of change of $n_i$ due to aerosol processes (transport between gas and aerosol phases, aerosol microphysical transformations, etc.);

$(d n_i/dt)_{chem}$ is the rate of change of $n_i$ due to gas-phase reactions;

$S_i$ is the emission rate.

Which models are used for which applications:

**0-D and 1-D models** are used when one knows very little about a problem or when data are not available to validate model performance;

**2-D models** are used when a horizontal dimension is important.

**3-D models** are used when the most complete answers are required, but computer resources and model building still severely limit their use.