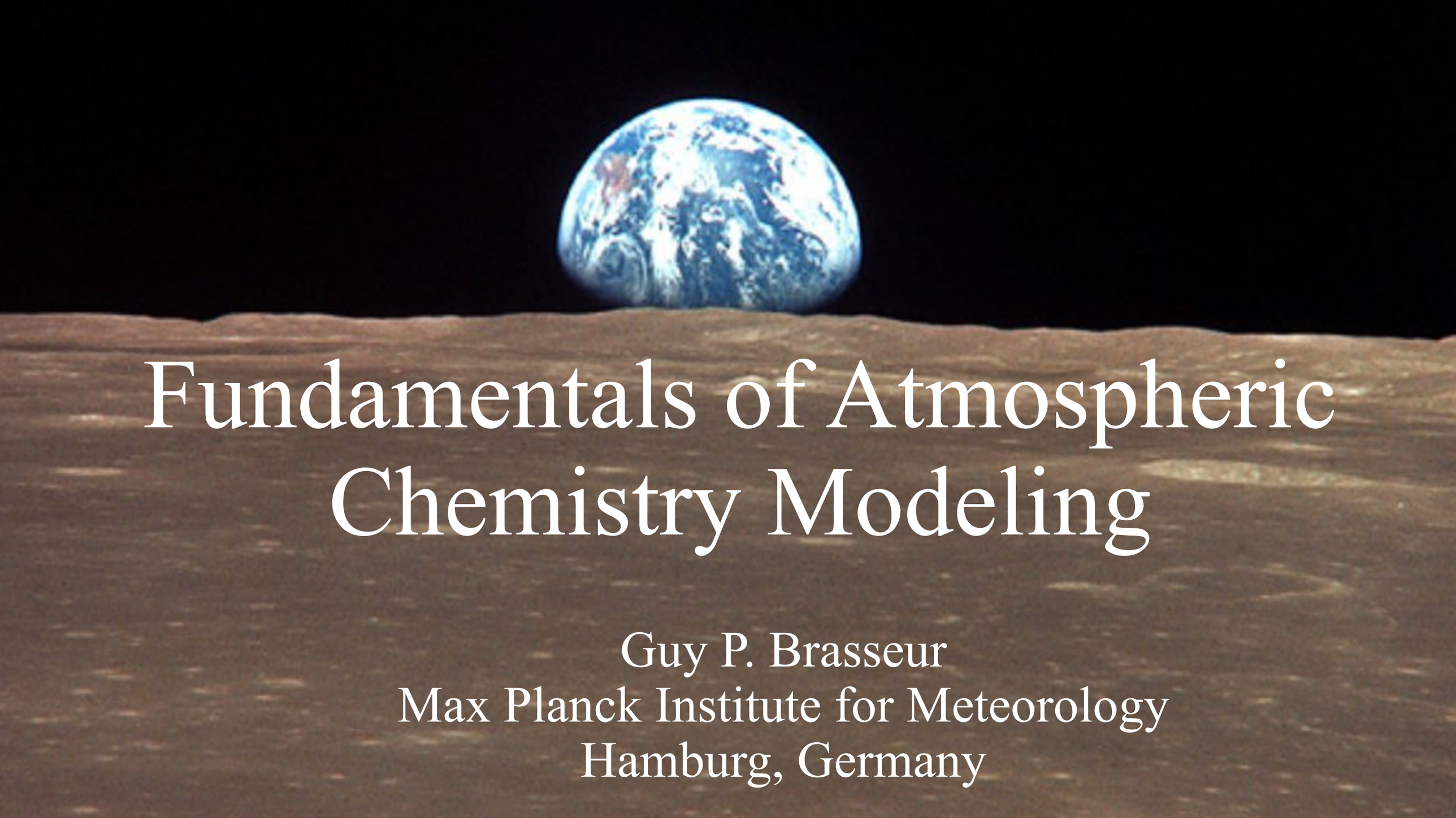
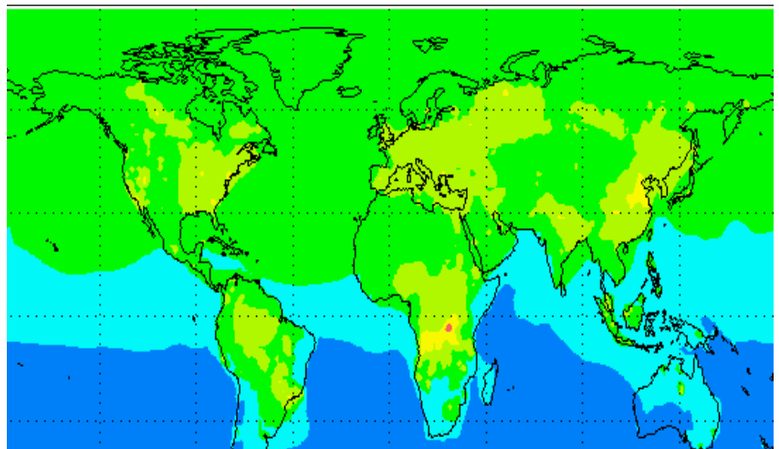
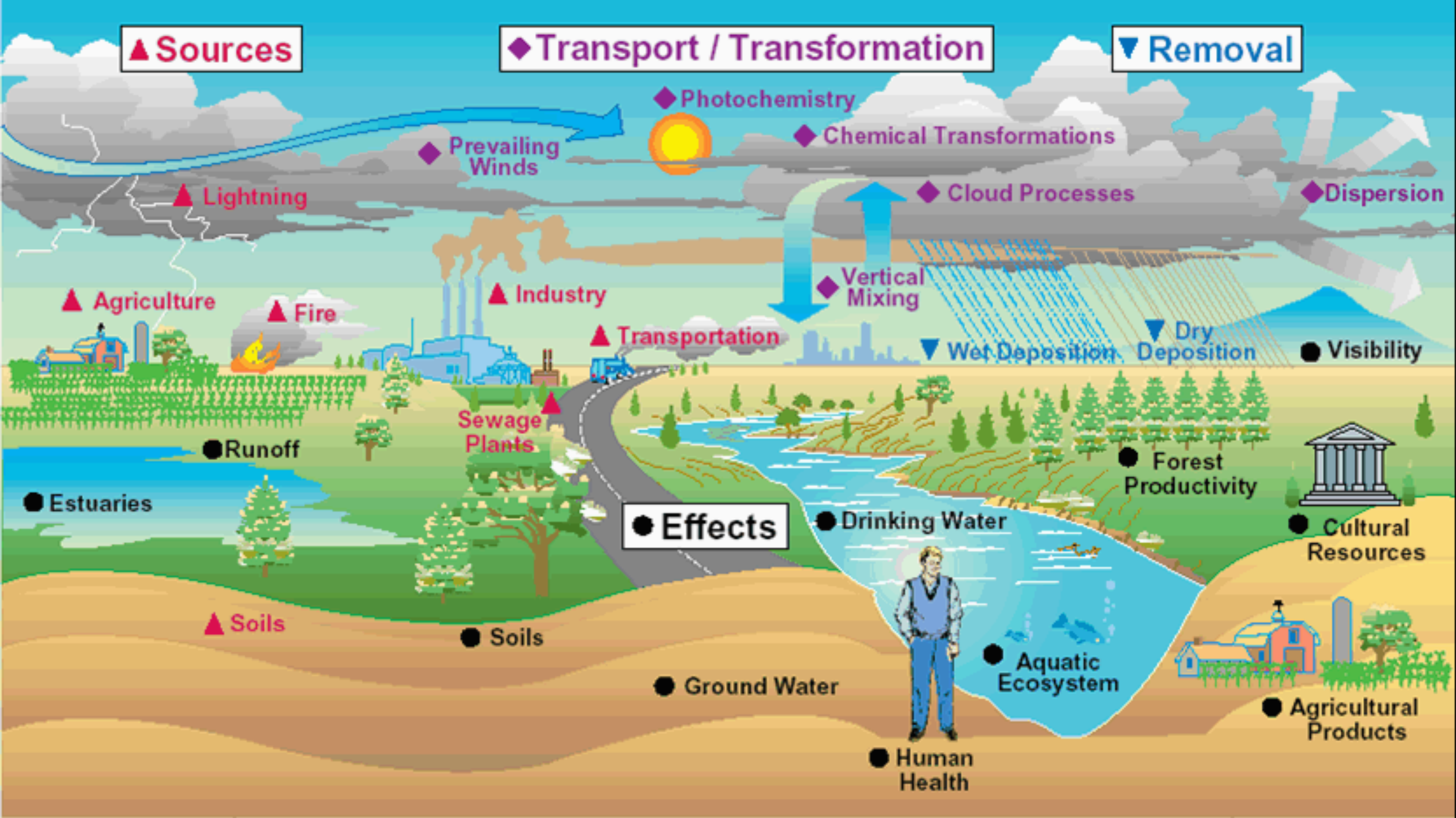


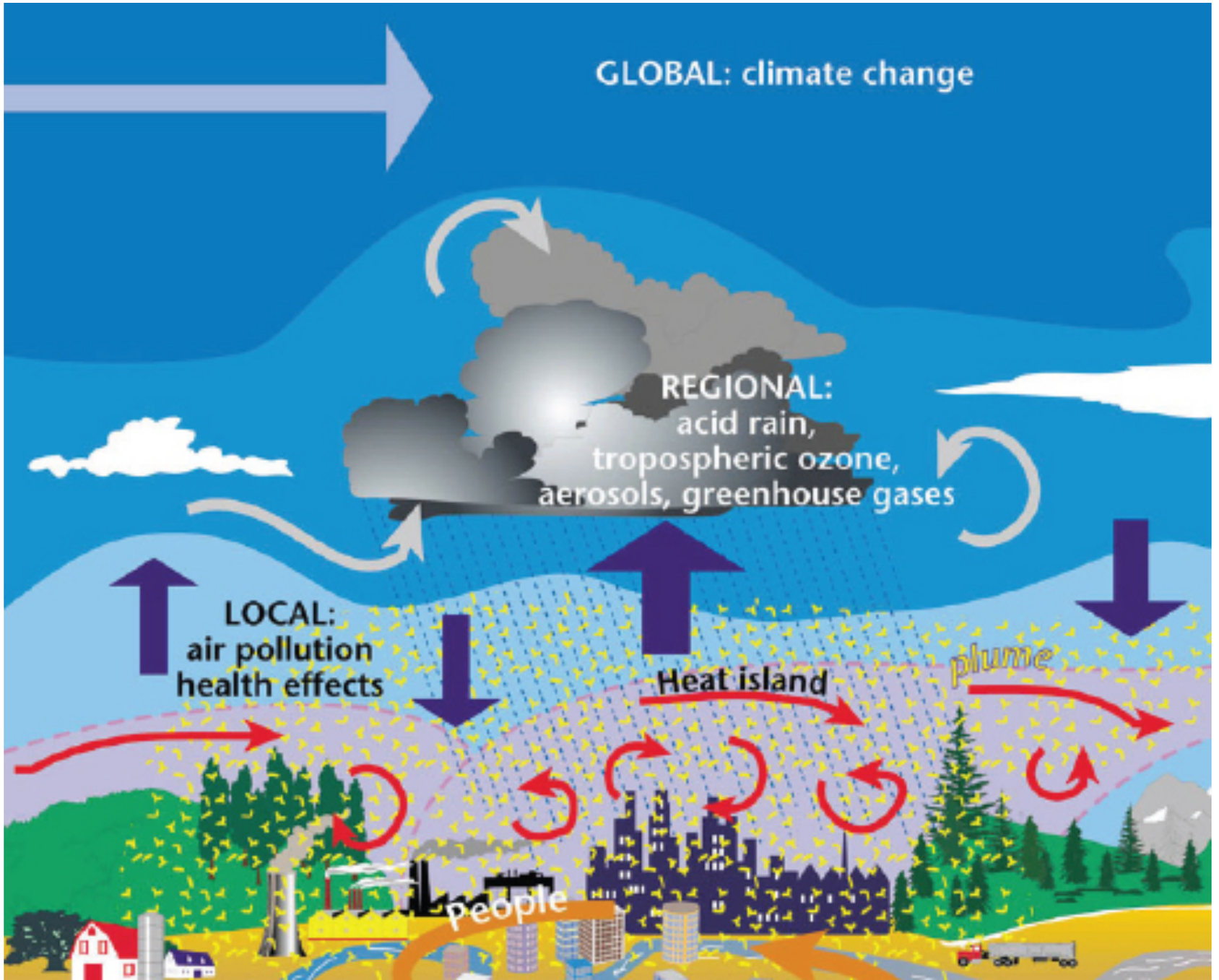
Fundamentals of Atmospheric Chemistry Modeling

Guy P. Brasseur
Max Planck Institute for Meteorology
Hamburg, Germany

Part 1. Introduction

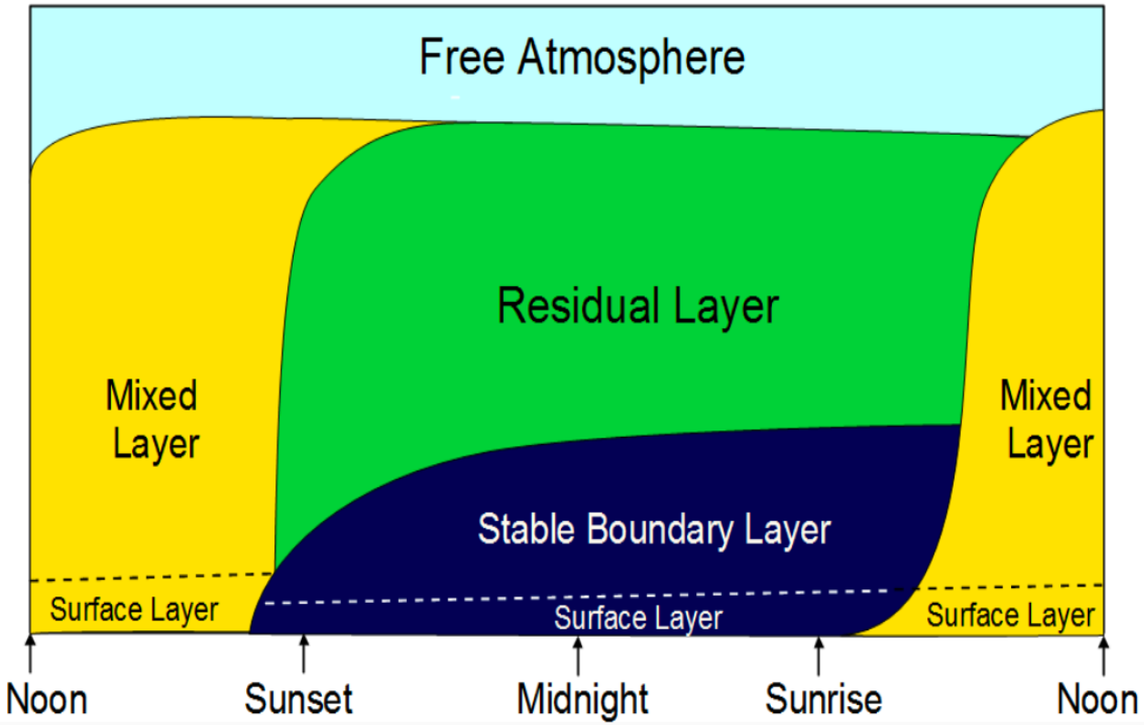



Sources
Transport / Transformation
Removal
Photochemistry
Chemical Transformations
Prevailing Winds
Lightning
Cloud Processes
Dispersion
Vertical Mixing
Agriculture
Fire
Industry
Transportation
Wet Deposition
Dry Deposition
Visibility
Sewage Plants
Runoff
Forest Productivity
Estuaries
Effects
Drinking Water
Cultural Resources
Soils
Soils
Ground Water
Aquatic Ecosystem
Agricultural Products
Human Health


GLOBAL: climate change
REGIONAL:
acid rain,
tropospheric ozone,
aerosols, greenhouse gases
LOCAL:
air pollution
health effects
Heat island
plume
people

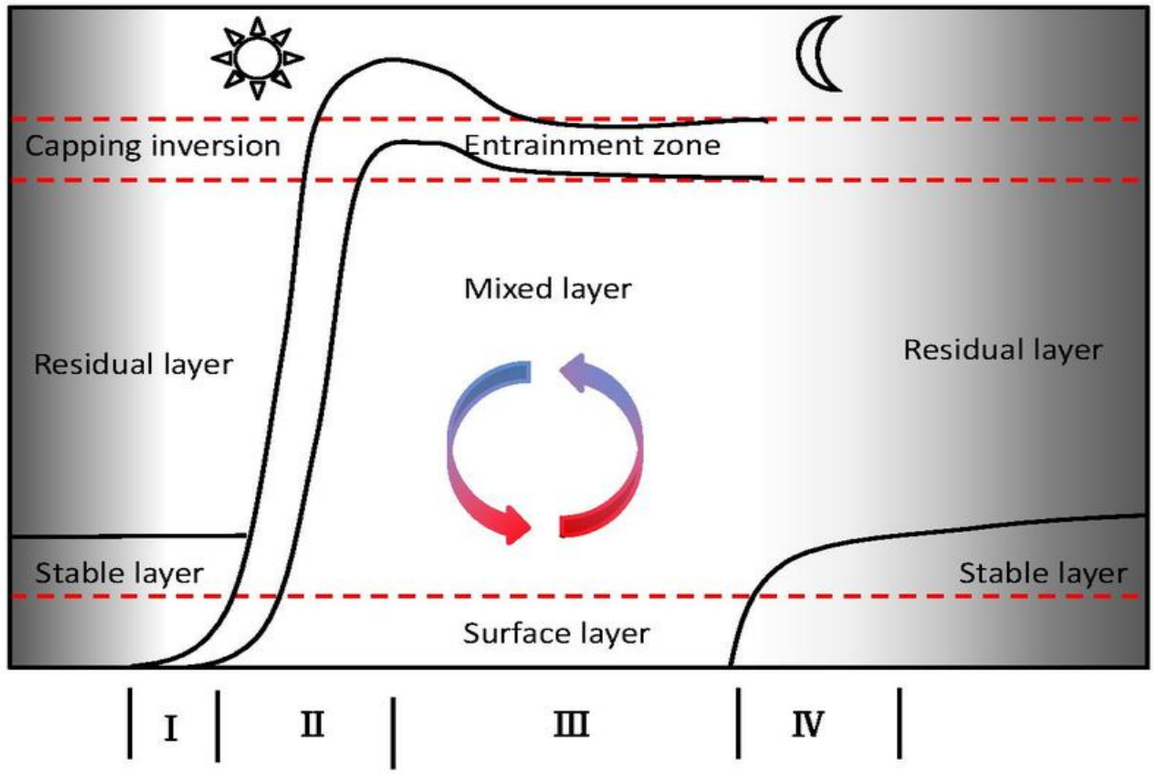
Atmospheric Boundary Layer Structure

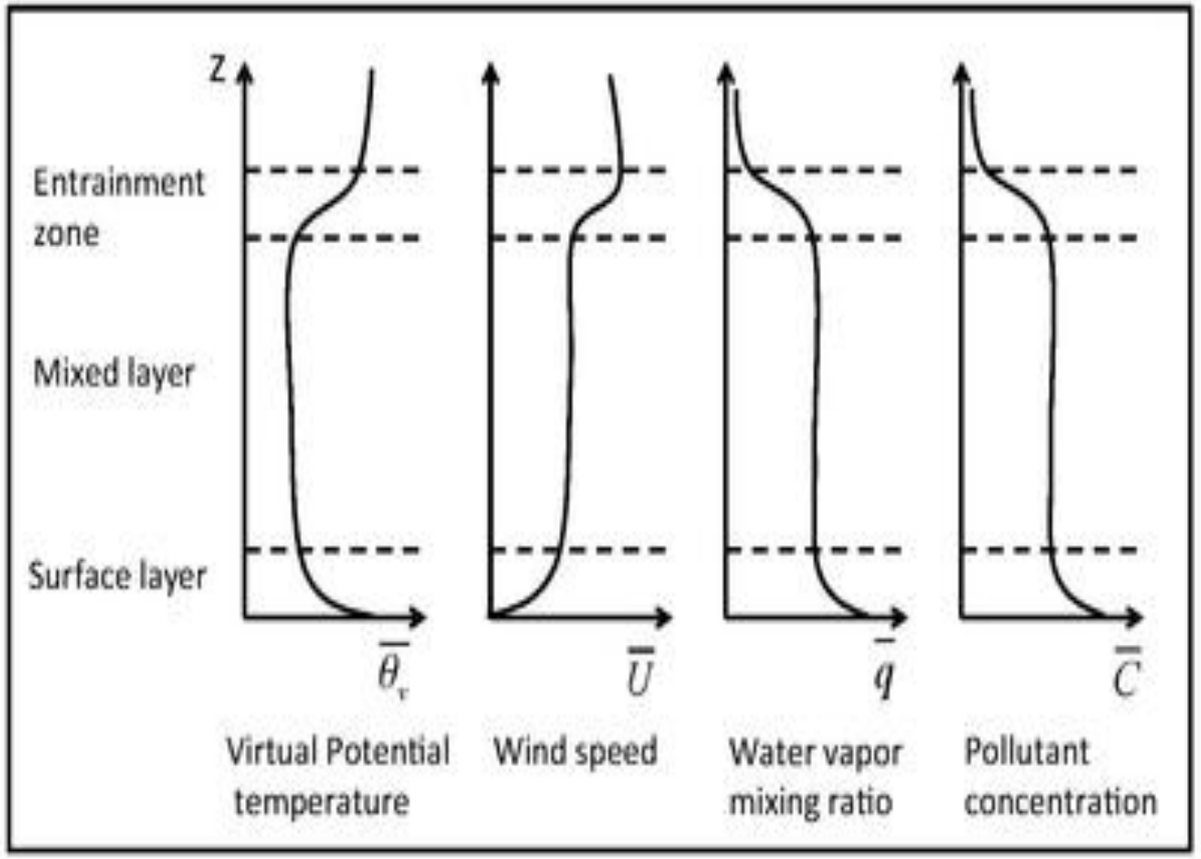
- Atmospheric boundary layers are usually classified into three types: **neutral**, **convective** and **stable**, based on atmospheric stability (buoyancy effects) and production of turbulence by wind shear.
- Turbulence in the **stable boundary layer (SBL)** is generated by shear and destroyed by negative buoyancy and viscosity. The strength of turbulence in the SBL is much weaker and it is much shallower in comparison to the neutral and convective boundary layers.

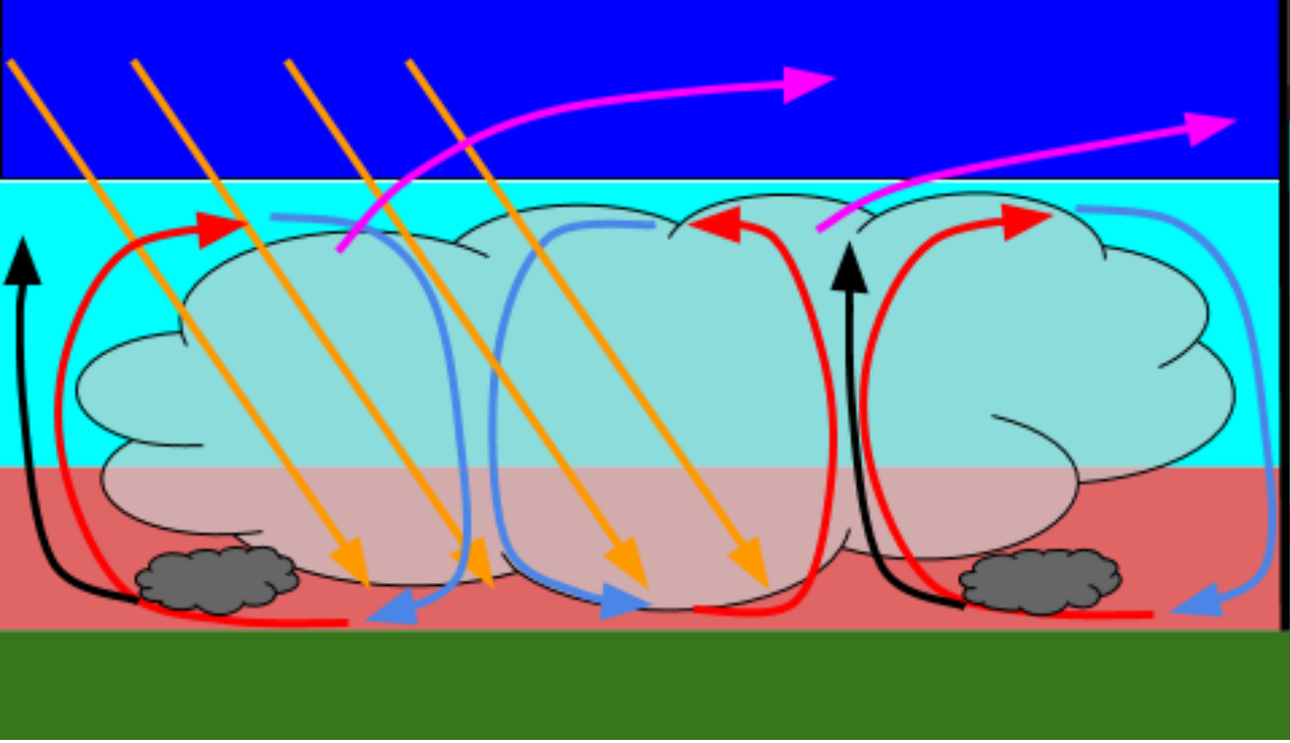


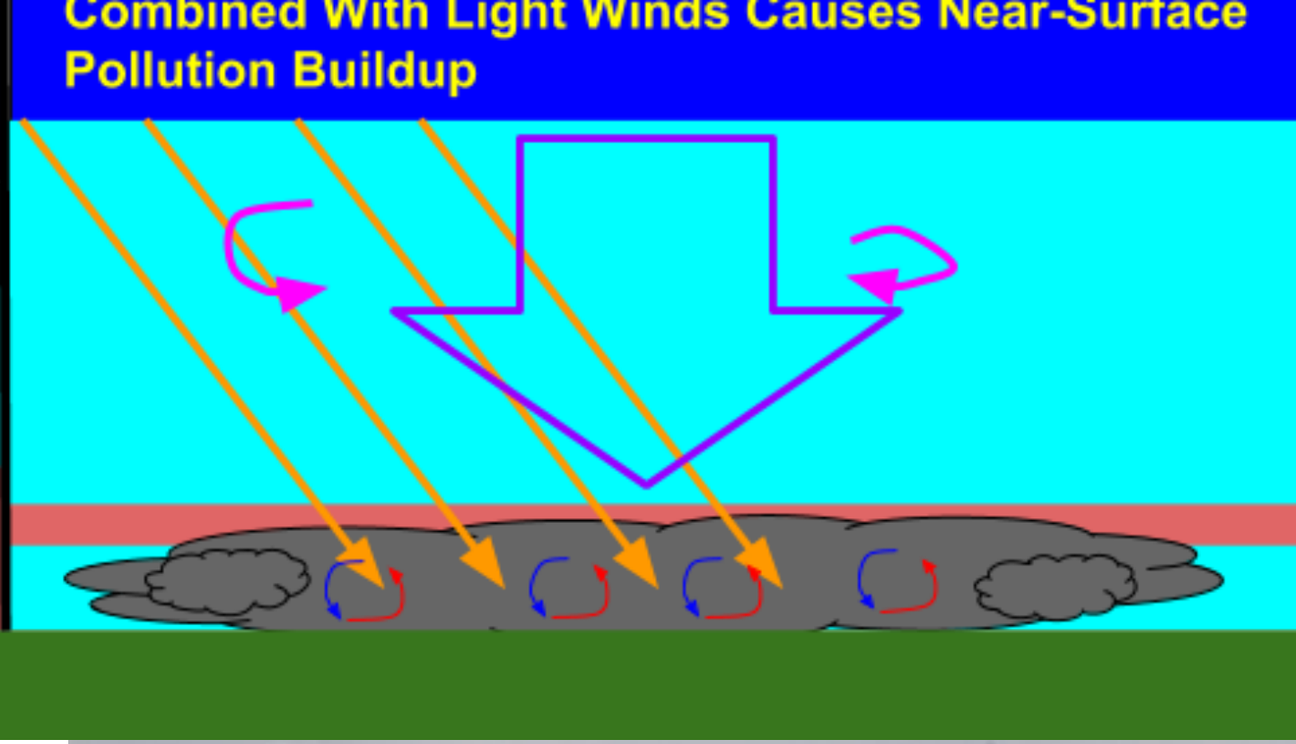
A typical daily cycle of the atmospheric boundary layer in fair weather (after Stull, 1988).

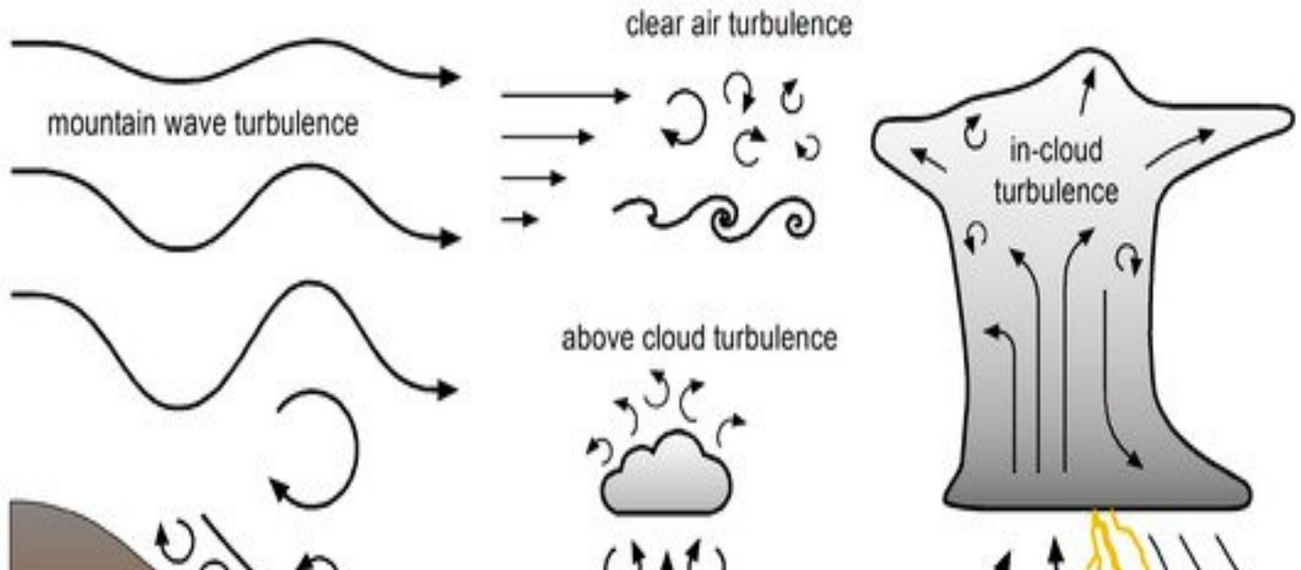
The Convective Boundary Layer

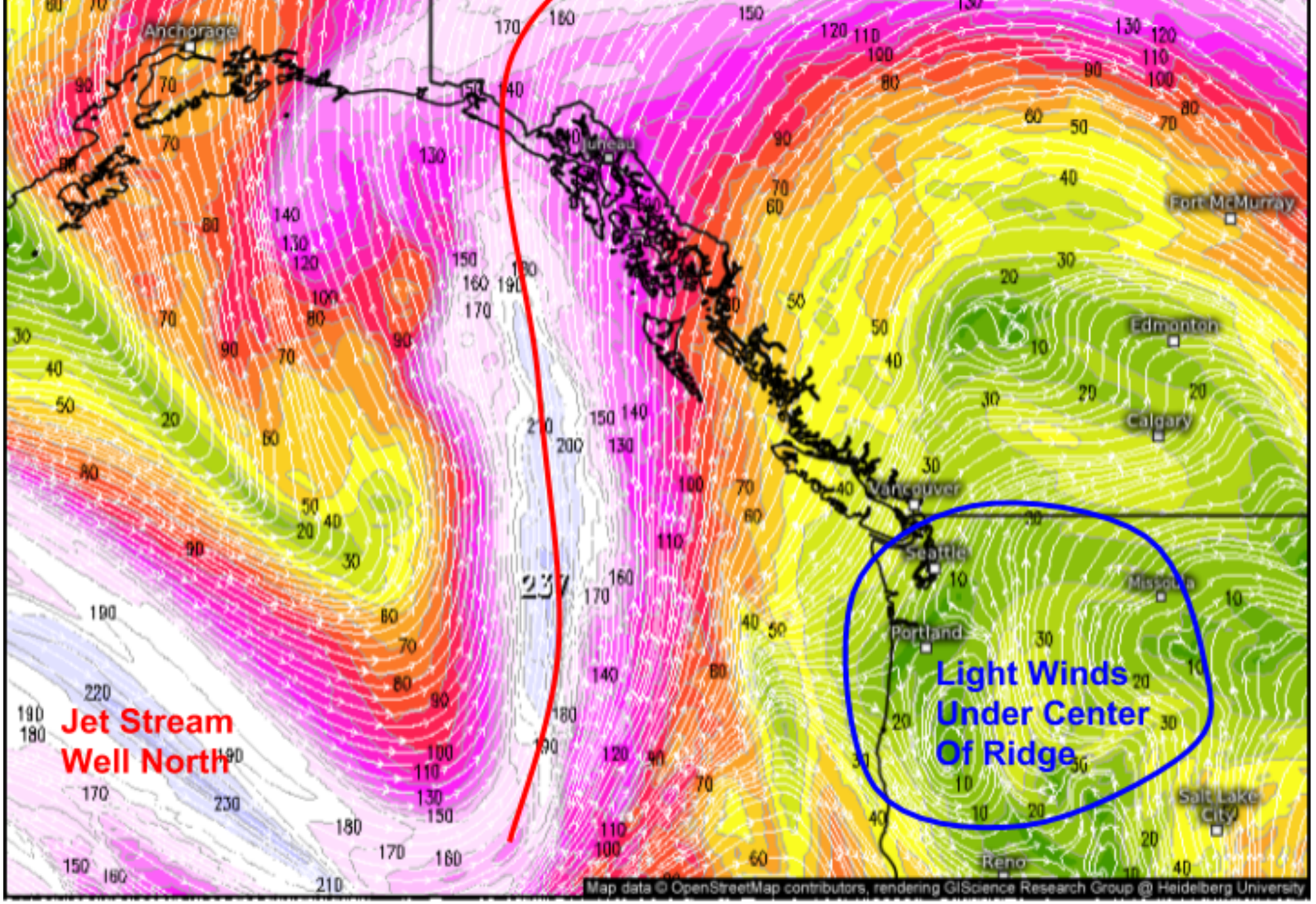







Combined With Light Winds Causes Near-Surface
Pollution Buildup

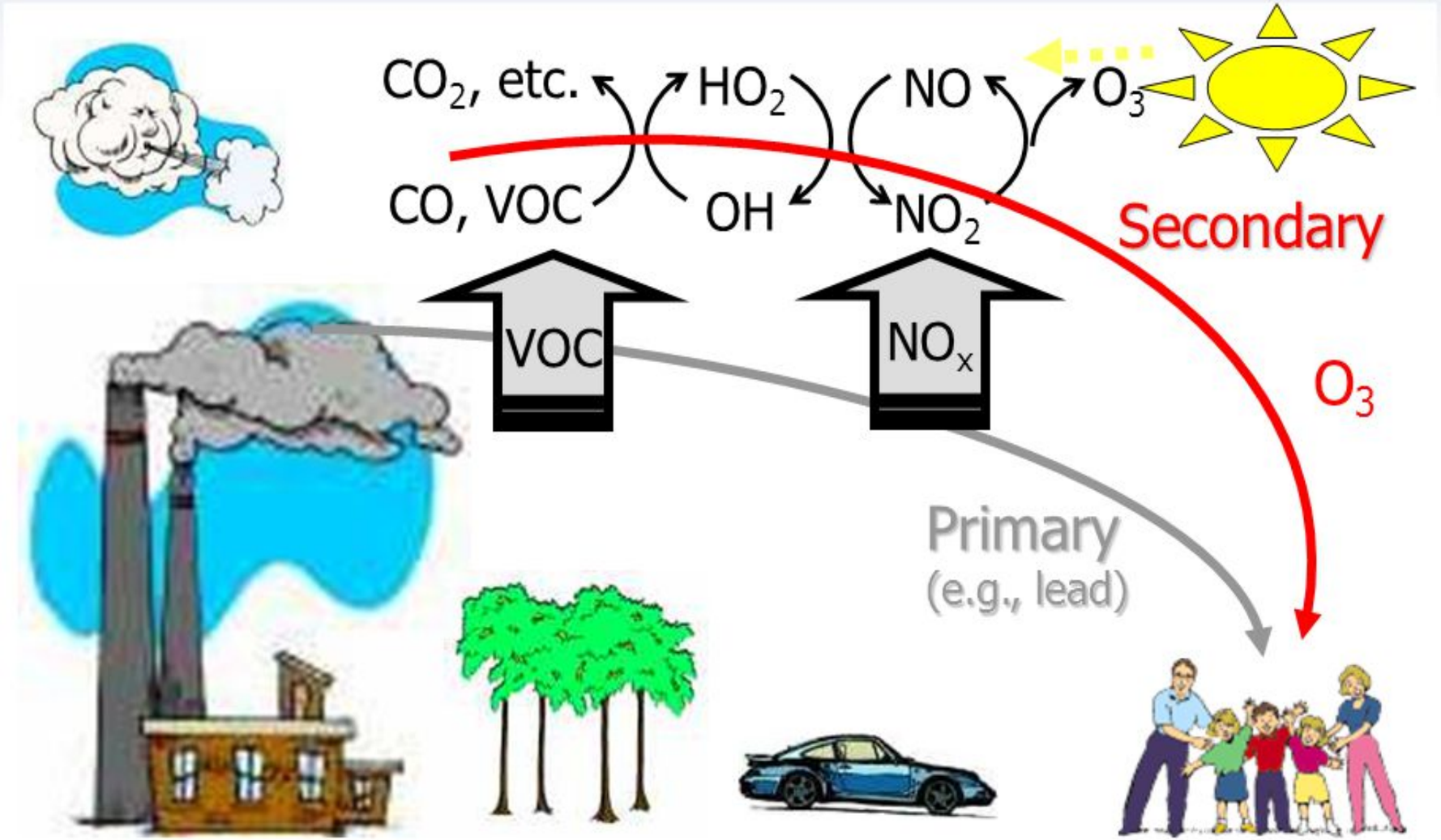

clear air turbulence
mountain wave turbulence
in-cloud
turbulence
above cloud turbulence



Wind speed and streamlines, 300mbar (kph)

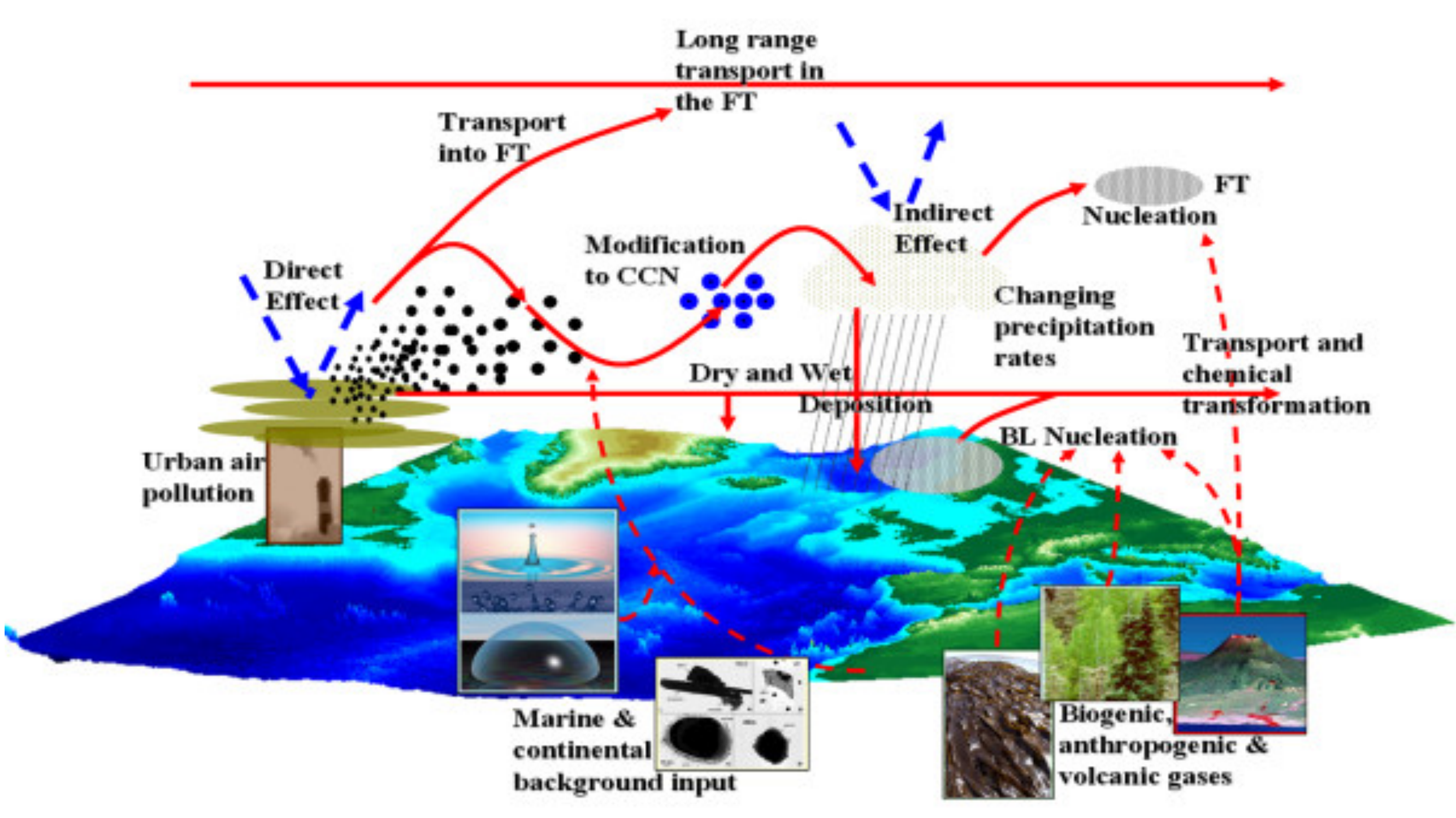
Valid for
10/22/2018, 08:00pm EDT

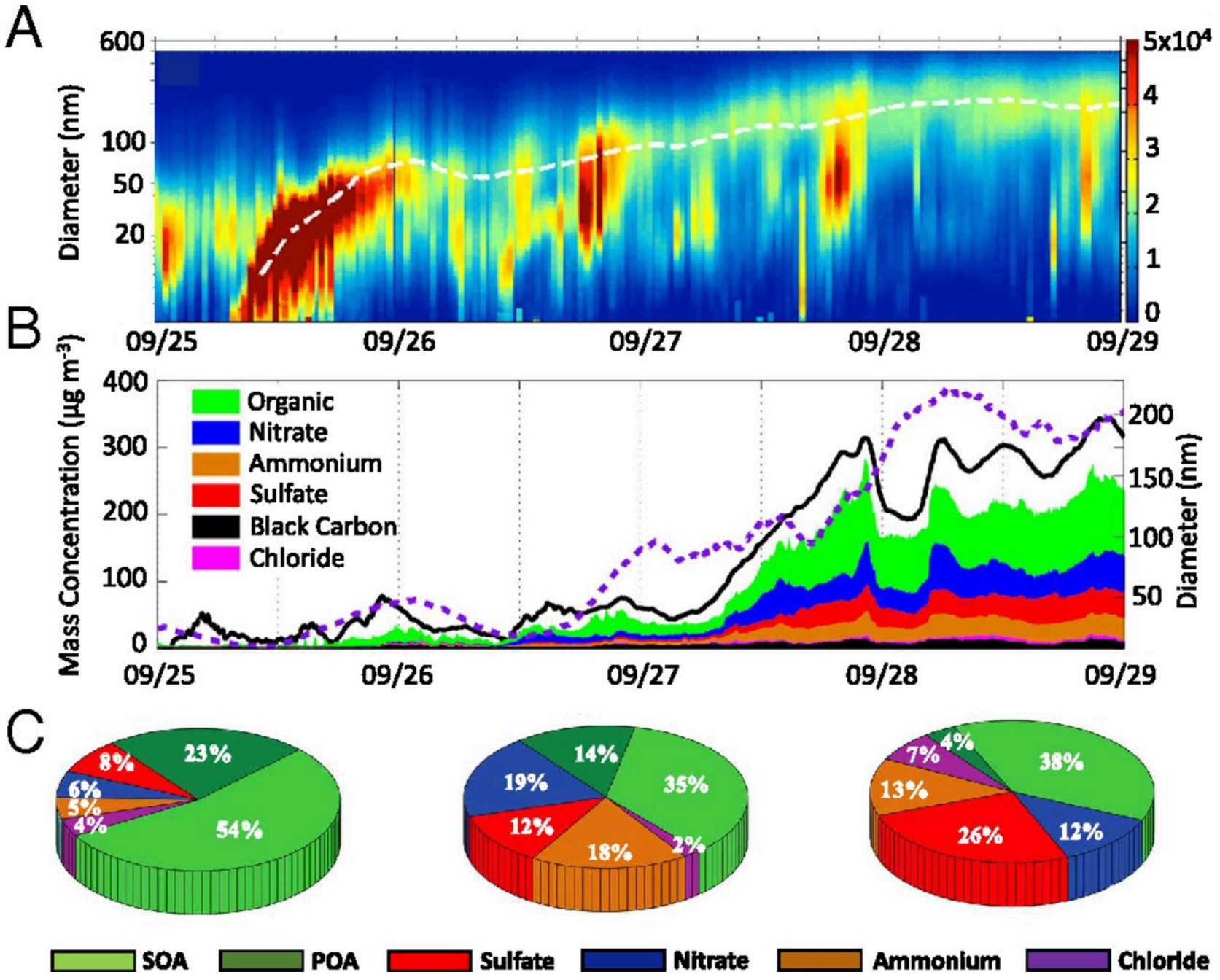
Primary & secondary pollutants

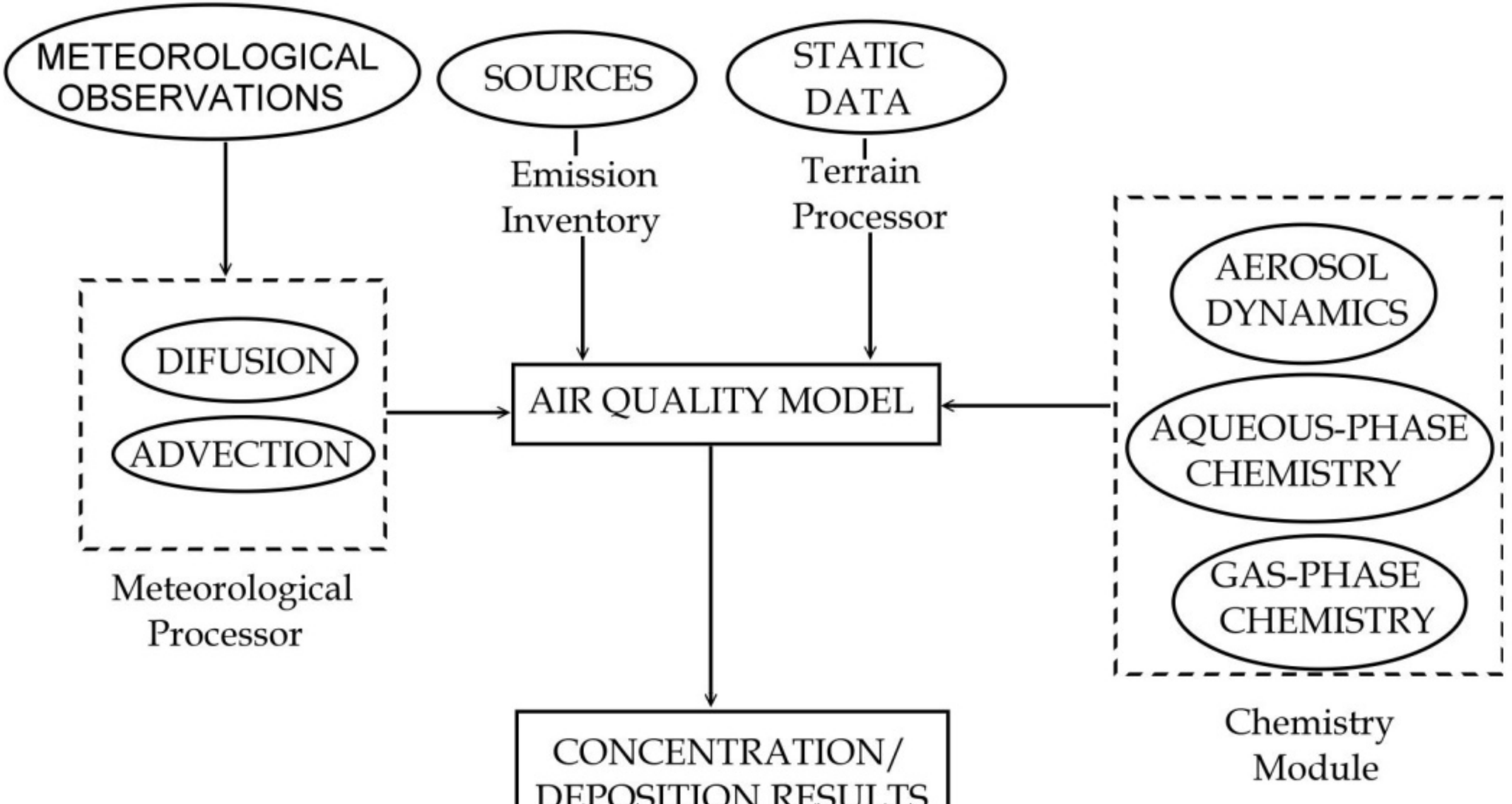


Primary: Emitted directly to the atmosphere

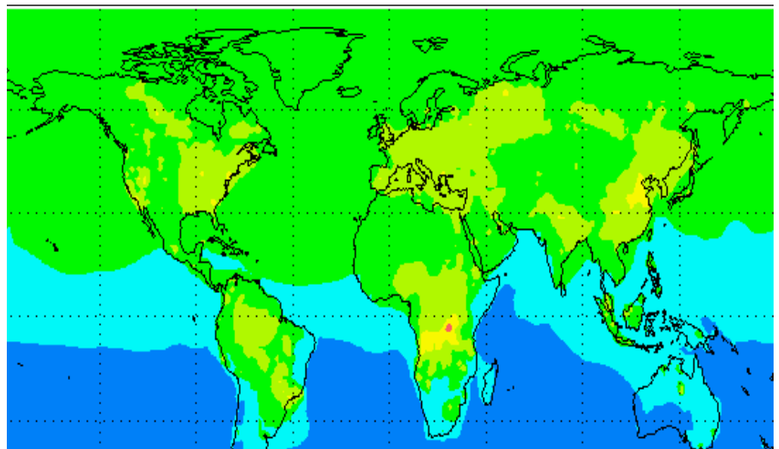
Secondary: Forms in the atmosphere


Long range transport in the FT
Transport into FT
Indirect Effect
FT Nucleation
Modification to CCN
Direct Effect
Changing precipitation rates
Transport and chemical transformation
Dry and Wet Deposition
BL Nucleation
Urban air pollution
Marine & continental background input
Biogenic, anthropogenic & volcanic gases


A
600
100
50
20
Diameter (nm)
5x10⁴
4
3
2
1
0
09/25
09/26
09/27
09/28
09/29
B
Mass Concentration (μg m⁻³)
400
300
200
100
0
Organic
Nitrate
Ammonium
Sulfate
Black Carbon
Chloride
200
150
100
50
Diameter (nm)
09/25
09/26
09/27
09/28
09/29
C
23%
8%
6%
5%
4%
54%
14%
19%
35%
12%
18%
2%
4%
7%
38%
13%
26%
12%
SOA
POA
Sulfate
Nitrate
Ammonium
Chloride


METEOROLOGICAL OBSERVATIONS
SOURCES
STATIC DATA
Emission Inventory
Terrain Processor
DIFUSION
ADVECTION
Meteorological Processor
AIR QUALITY MODEL
AEROSOL DYNAMICS
AQUEOUS-PHASE CHEMISTRY
GAS-PHASE CHEMISTRY
Chemistry Module
CONCENTRATION/

Part 2. Fundamental Equations



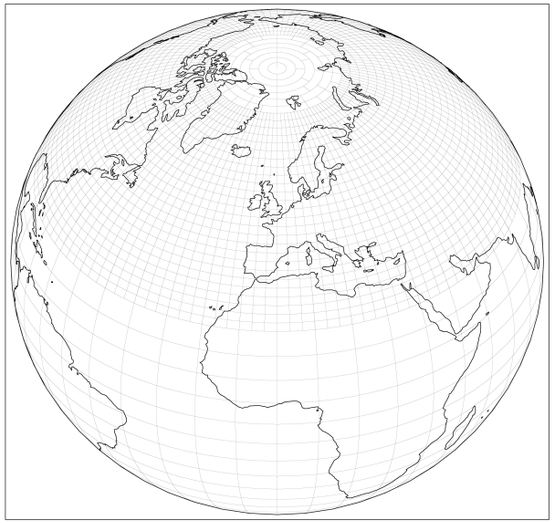
Variables and Equations in an Atmospheric (Physical) Model

- **Variables**:
  - Pressure p
  - Density ρ
  - Temperature T
  - Wind components (u, v, w)
- **Equations**:
  - Momentum equation (3 components)
  - Thermodynamic equation
  - Continuity equation
  - Equation of state (perfect gas)

Fundamental Equations

- ***Momentum equations on a rotating sphere:*** Express the wind acceleration in response to different forces: gravity, gradient force, Coriolis force, dissipation
- ***Thermodynamic equation:*** Expresses the conservation of energy; importance of diabatic heating by absorption and emissions of radiative energy (solar and terrestrial), and of adiabatic processes (e.g., compression of air)
- ***Continuity equation:*** Expresses the conservation of mass

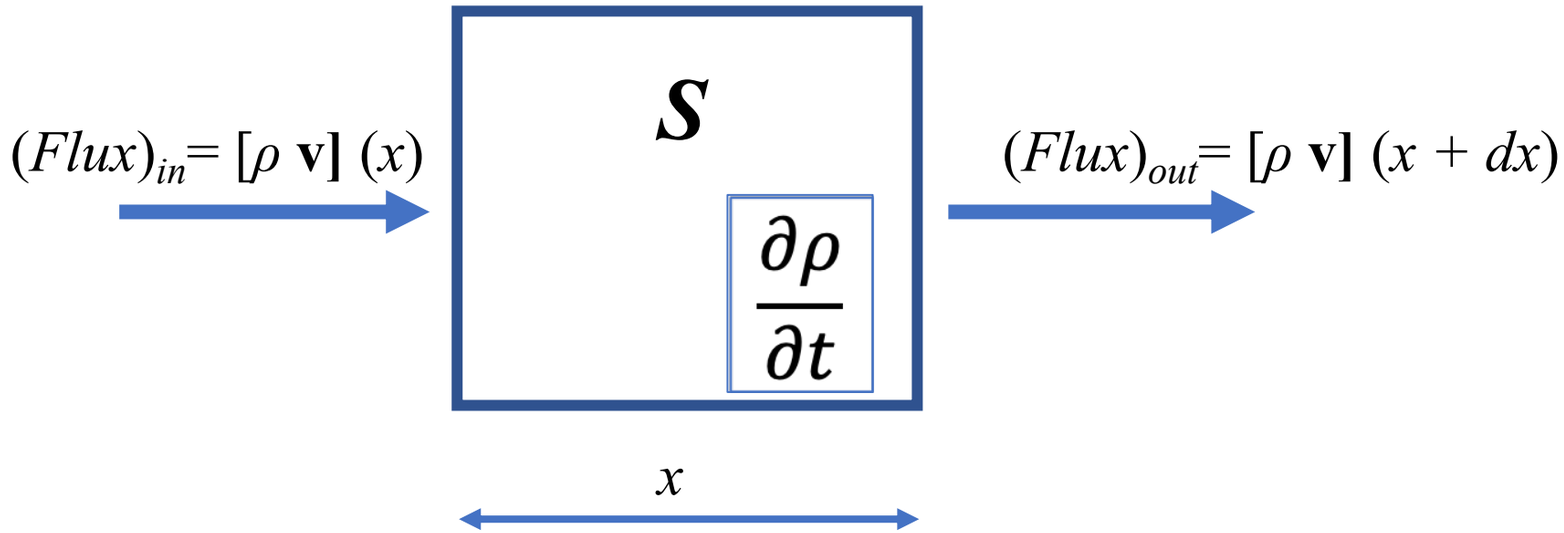
Chemical Composition of the Atmosphere



Concentration of atmospheric trace gas i:

$$\frac{d\rho_i}{dt} = \left(\frac{\partial \rho_i}{\partial t}\right)_{emission} + \left(\frac{\partial \rho_i}{\partial t}\right)_{deposition} + \left(\frac{\partial \rho_i}{\partial t}\right)_{transport} + \left(\frac{\partial \rho_i}{\partial t}\right)_{chemistry}$$

Continuity Equation for a Chemical Species



$$\frac{\partial \rho}{\partial t} = \frac{(Flux)_{in} - (Flux_{out})}{\Delta x} + S = -\frac{\partial (\rho\ \mathbf{v})}{\partial x} + S$$

Continuity Equation for a Chemical Species

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \ \mathbf{v}) = S$$

where

ρ is the mass density of the chemical species

$\mathbf{v}$ is the wind velocity vector

S is the local chemical source of the chemical species

Continuity equation for Chemical Species

Mathematically describes the dynamical and chemical processes that determine the distribution of chemical species

flux form:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}) = S_i$$

Transport

Chemical forcing

advective form:

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = \frac{S_i}{\rho_a}$$

where,

ρ_i is the mass (or number) density of species i

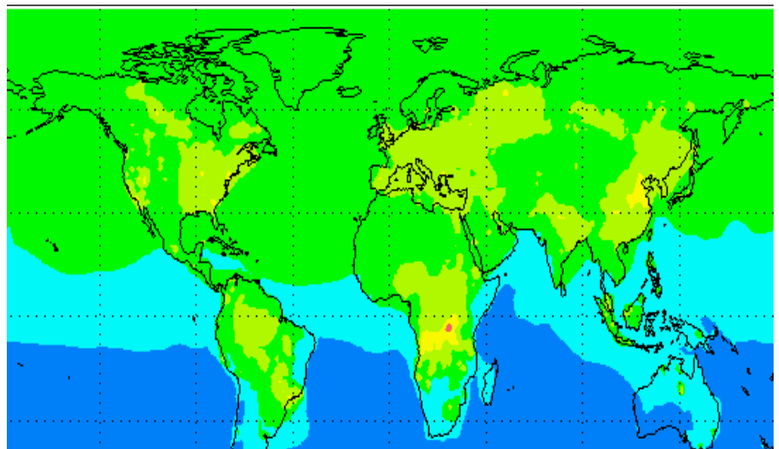
ρ_a is the air mass (or number) density

$f_i = \frac{\rho_i}{\rho_a}$ is the mass (or volume) mixing ratio

S_i is the production and loss rate of species i

$\mathbf{v}$ is the wind velocity vector

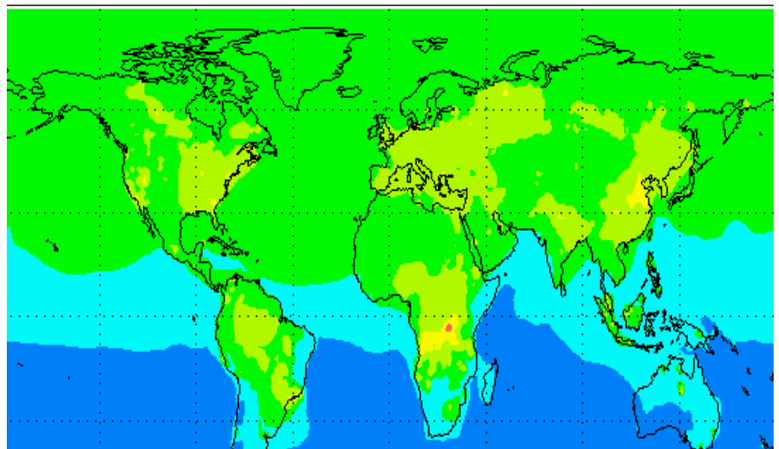
Part 3. Types of Chemical- Transport Models



Types of models

- **Box (compartment) models:**
  understand the principles of feedback cycles
- **1D column models:**
  development of parameterisations
- **1D Lagrangian (trajectory) models:**
  transport studies
- **2D (Eulerian) models:**
  zonal mean state of the atmosphere (often in the stratosphere)
- **3D (Eulerian or Lagrangian) models:**
  detailed description of several processes in time and space

Part 4. Numerical Solutions



Solving the continuity equation for N chemical species

- *N* species leads to *N* coupled non-linear equations which rarely have an analytic solution.
- System is solved with numerical methods at discrete locations (“grid-points”)
- Differentials replaced by finite differences
- Finite resolution (time or space) implies some transport processes are unresolved (e.g. diffusion)
- Chemistry and transport handled as separate operations

Finite Difference Methods

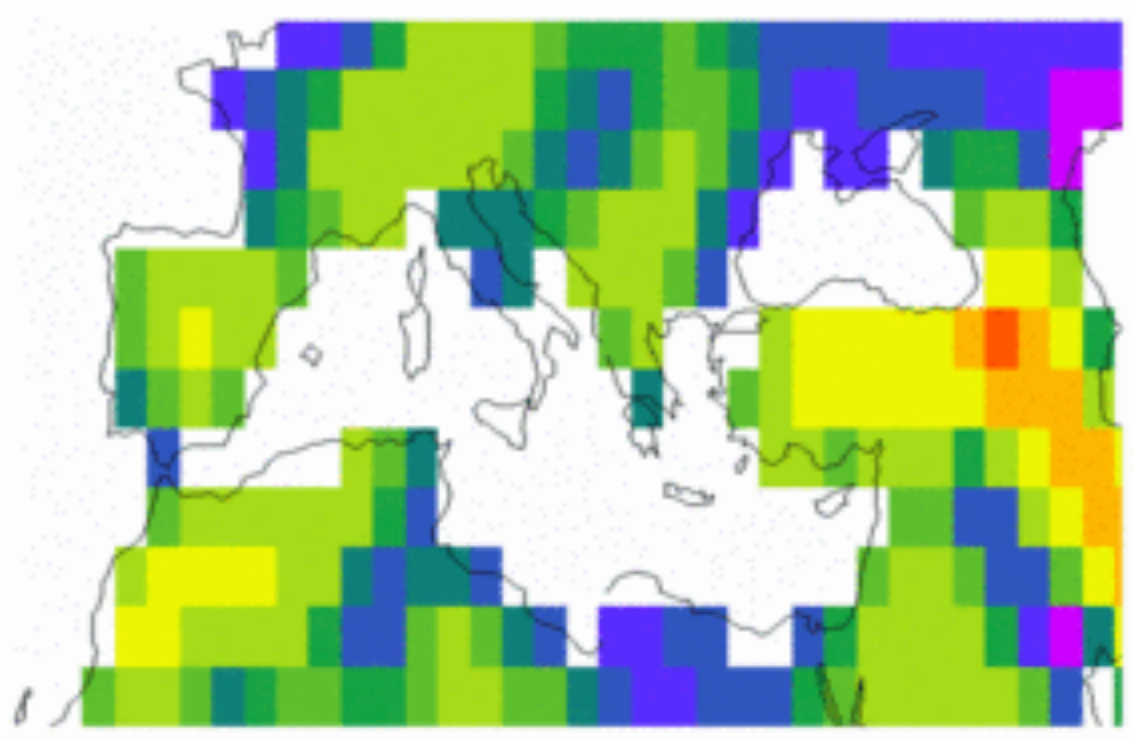
- In these methods, the space (or time) derivatives are replaced by finite difference approximations, and the solutions are produced at specified points in time and space.
- For example, *df/dx* is approximated at location *x by*

$$[f(x + \Delta x) - f(t - \Delta x)]/ 2\,\Delta x$$

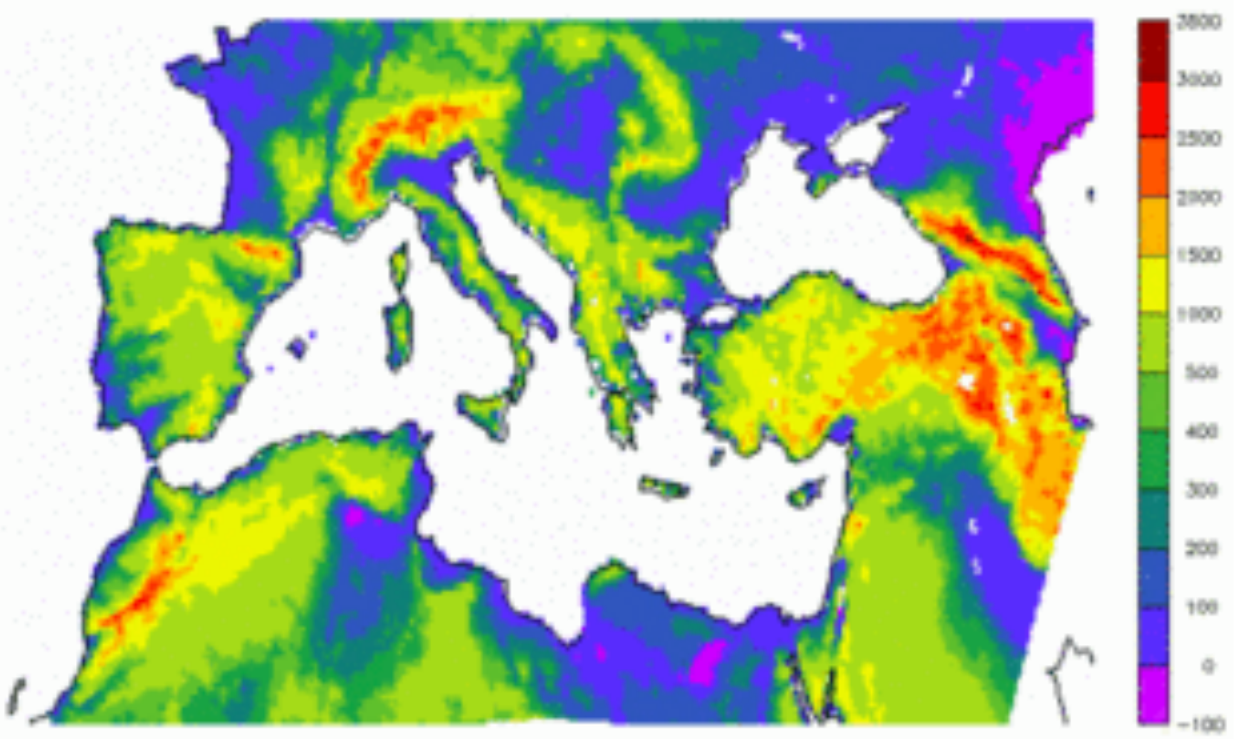
with a truncation error of $O(\Delta x^2)$, if Δx is the grid space

- Different algorithms exist to solve the differential equation
  - $df/dx = F\,[f(x), x]$.
  - **Explicit methods** (*F* is evaluated at time t) require very small grid space Δx to provide stable and accurate solutions;
  - **Implicit methods** (*F* is evaluated at time $x + \Delta x$) are more difficult to solve, but the solution is unconditionally stable.

Model Resolution



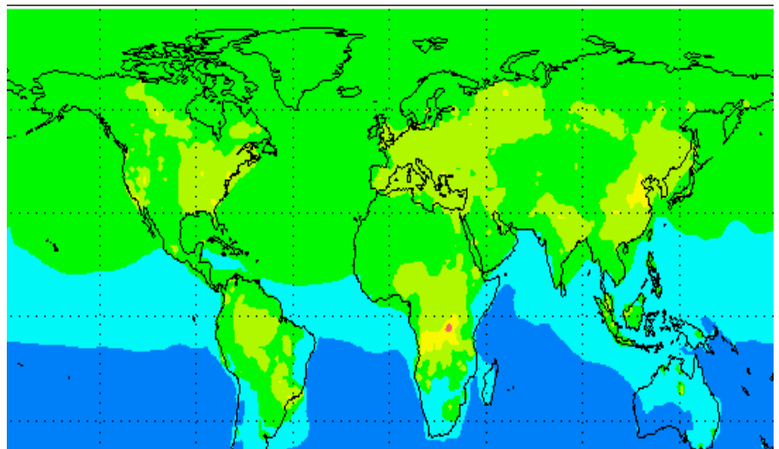
200 km



25 km

Part 3. Numerical Solutions

- 1. Transport
- 2. Chemistry
- 3. Surface Processes



The treatment of Advection

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla}.\left(\rho \vec{v}\right)$$

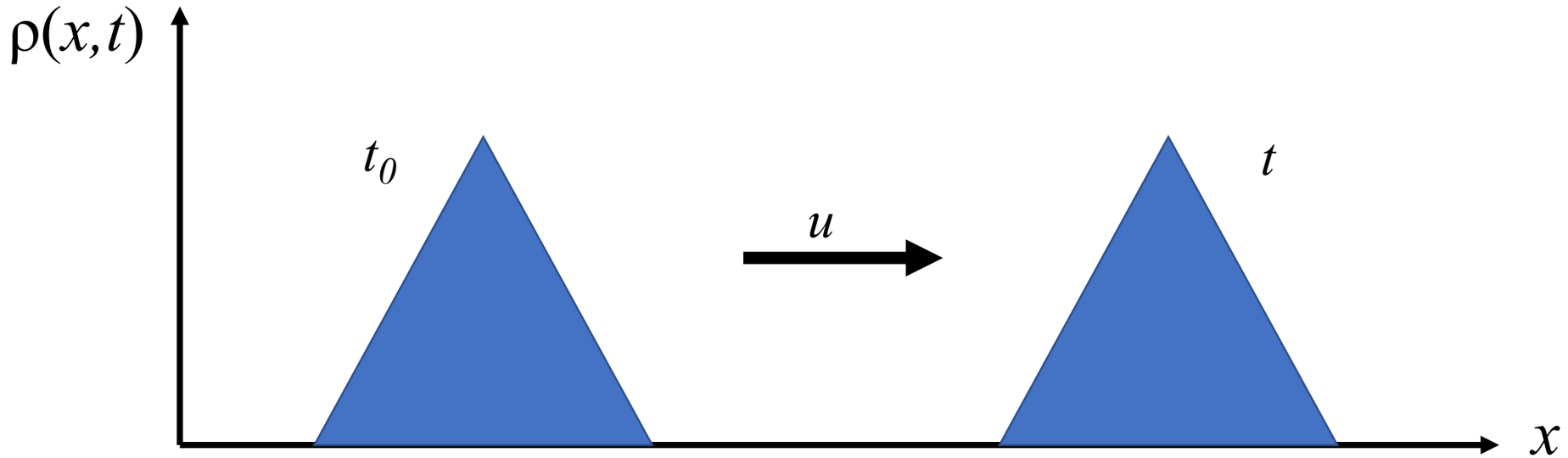
The simple one-dimensional case

The analytic (exact solution) for a constant wind speed u is known!

$$\frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial \rho(x,t)u}{\partial x}$$

The initial function at $t = t_0$ is $\rho_0(x)$

The function at time t is $\rho(x,t) = \rho_0(x\text{-}ut)$



Numerical Approximation of the Advection Equation

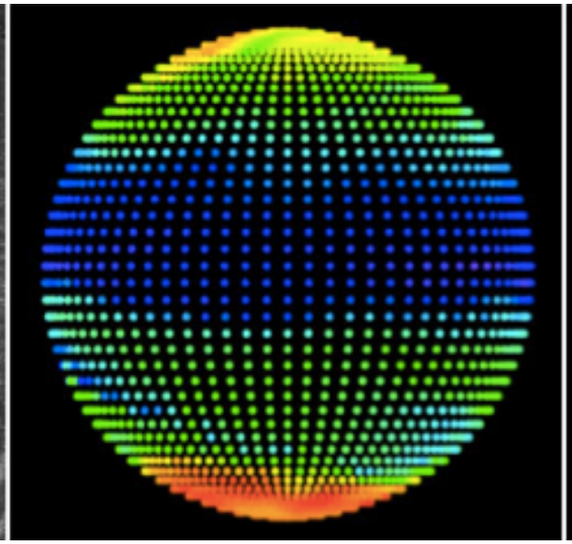
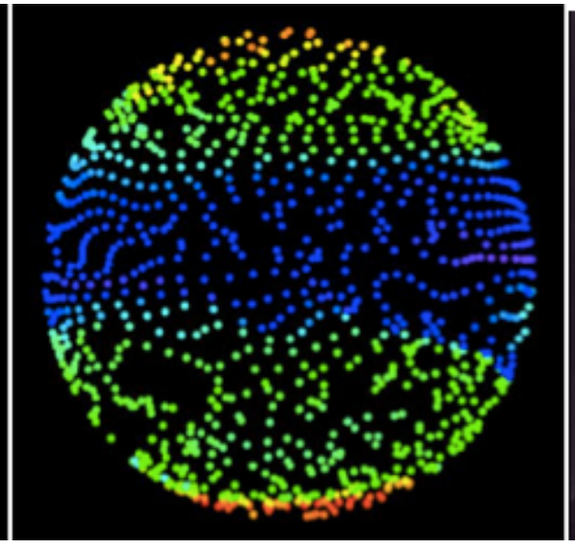
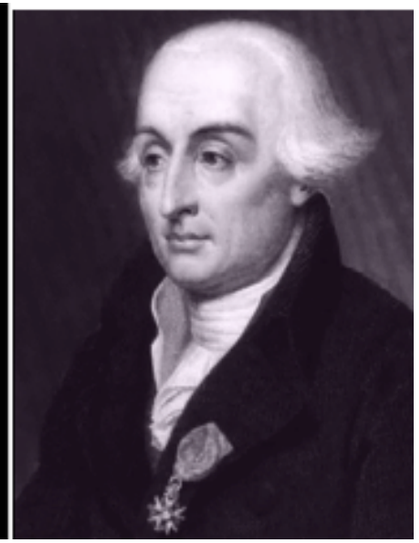
Desired properties of an advection scheme:

- accuracy
- stability
- mass conservation
- monotonicity (shape preservation)
- positive definite fields
- local
- efficient

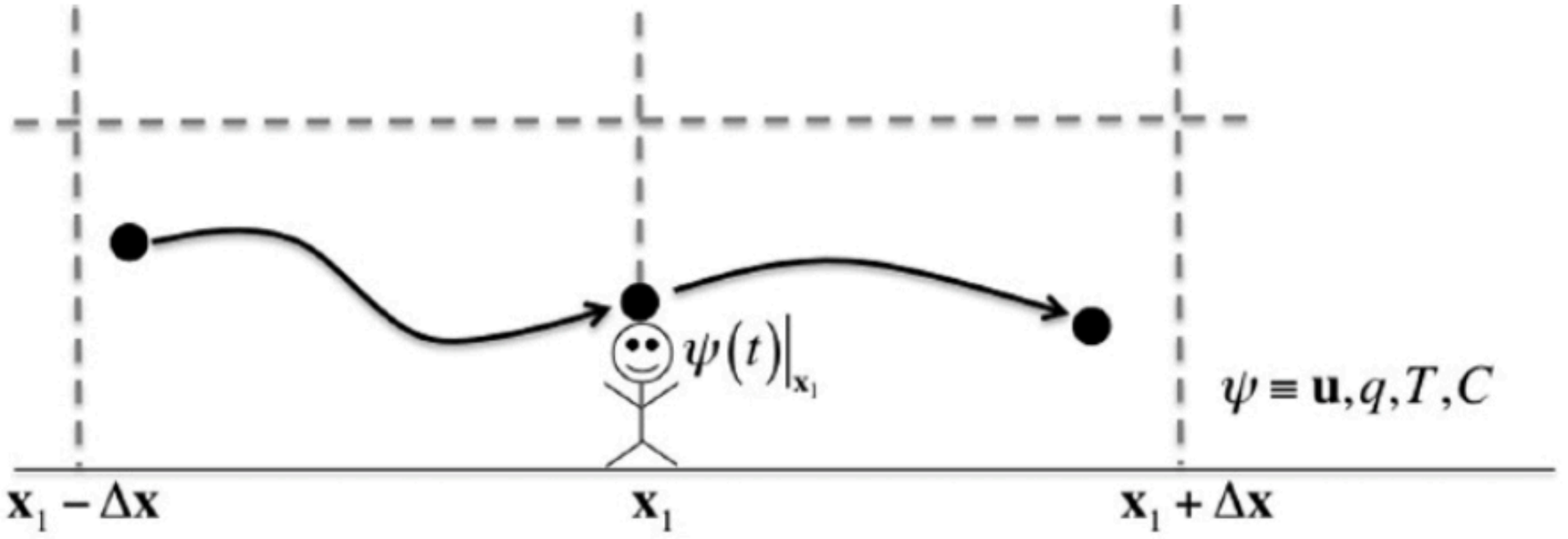
Three groups of algorithms:

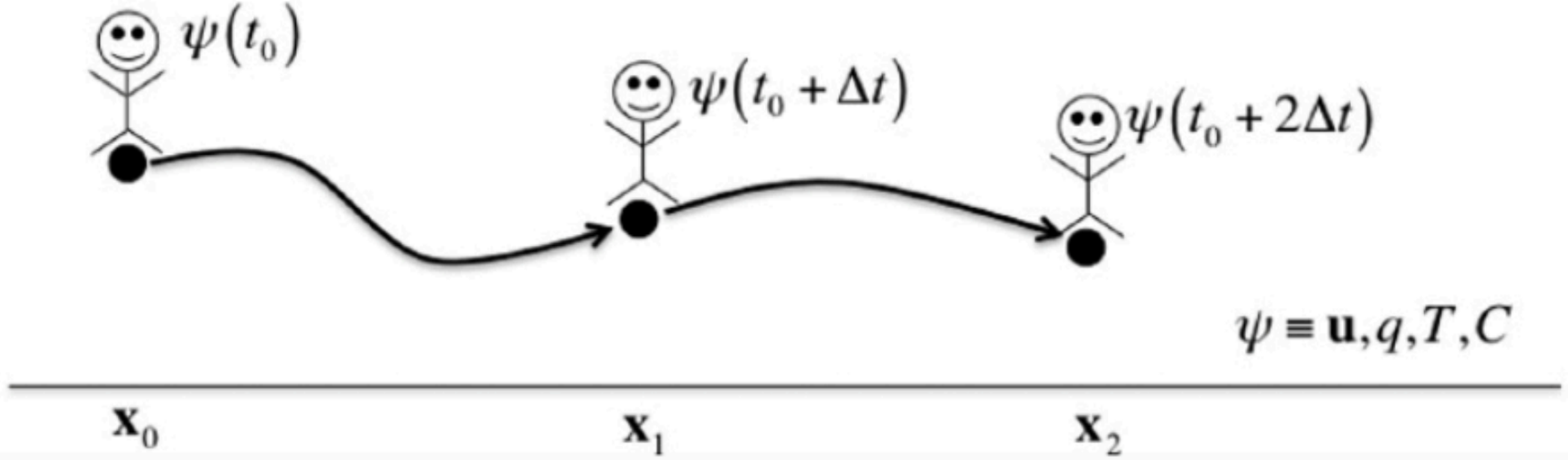
- Eulerian
- Lagrangian
- Semi-Lagrangian

Euler versus Lagrange

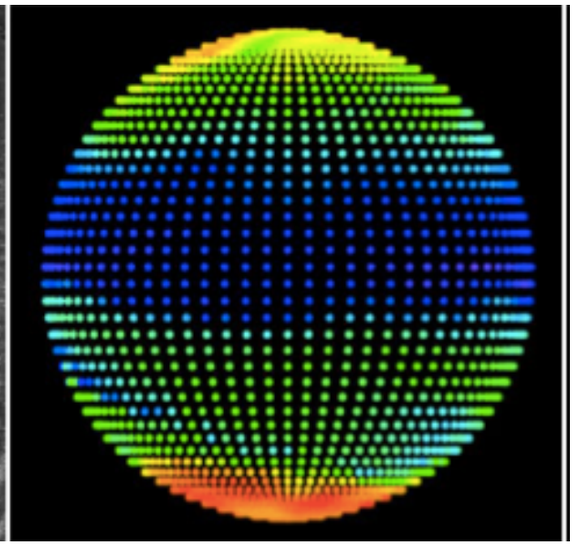





Two different representations of advection





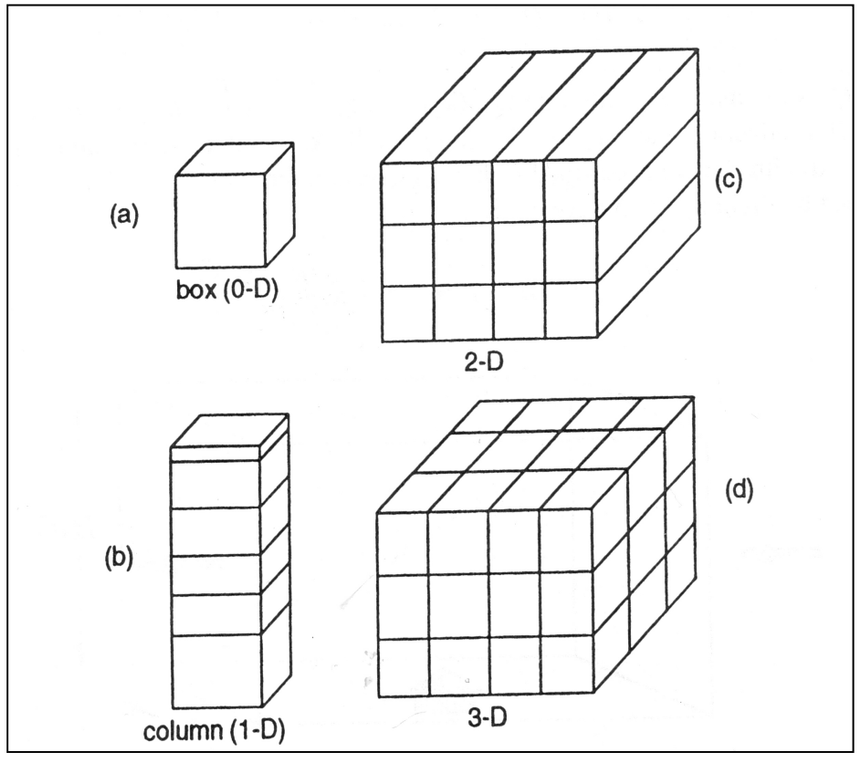
Euler

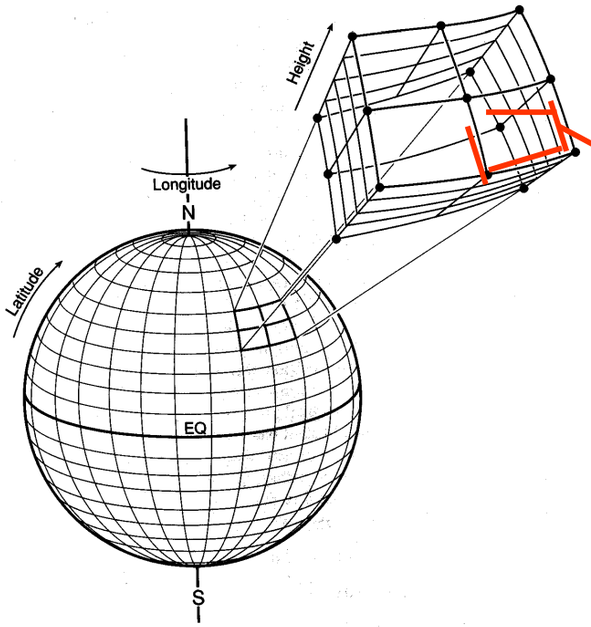


An Eulerian View

Mass Balance on Several Fixed Atmospheric Boxes

Current Models:
Up to ~ 10^6 grid boxes





Mass balance equation is solved for each box of the grid.

→For a global model:
Horizontal Résolution: 50-300 km
Vertical Résolution : ~0.1 - 1 km

Elementary Numerical Methods

Let's assume the one dimensional advection equation with constant flow velocity c: It is a partial differential equation. $\frac{\partial u}{\partial t} + c\frac{\partial u}{\partial x} = 0$

	Forward-in-time	*Centered-in-time*	*Backward-in-time*
Forward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_i^{n+1}}{\Delta x} = 0$
Centered-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_{i-1}^{n+1}}{2\Delta x} = 0$
Backward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^{n+1}-u_{i-1}^{n+1}}{\Delta x} = 0$

Elementary Numerical Methods

Let's assume an partial differential equation. $\frac{\partial u}{\partial t} + c\frac{\partial u}{\partial x} = 0$

	Forward-in-time	*Centered-in-time*	*Backward-in-time*
Forward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_i^{n+1}}{\Delta x} = 0$
Centered-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_{i-1}^{n+1}}{2\Delta x} = 0$
Backward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^{n+1}-u_{i-1}^{n+1}}{\Delta x} = 0$

Forward-in-time-backward-in-space: the upwind scheme

$$u_i^{n+1} = u_i^n - \frac{c\Delta t}{\Delta x}\left(u_i^n - u_{i-1}^n\right)$$

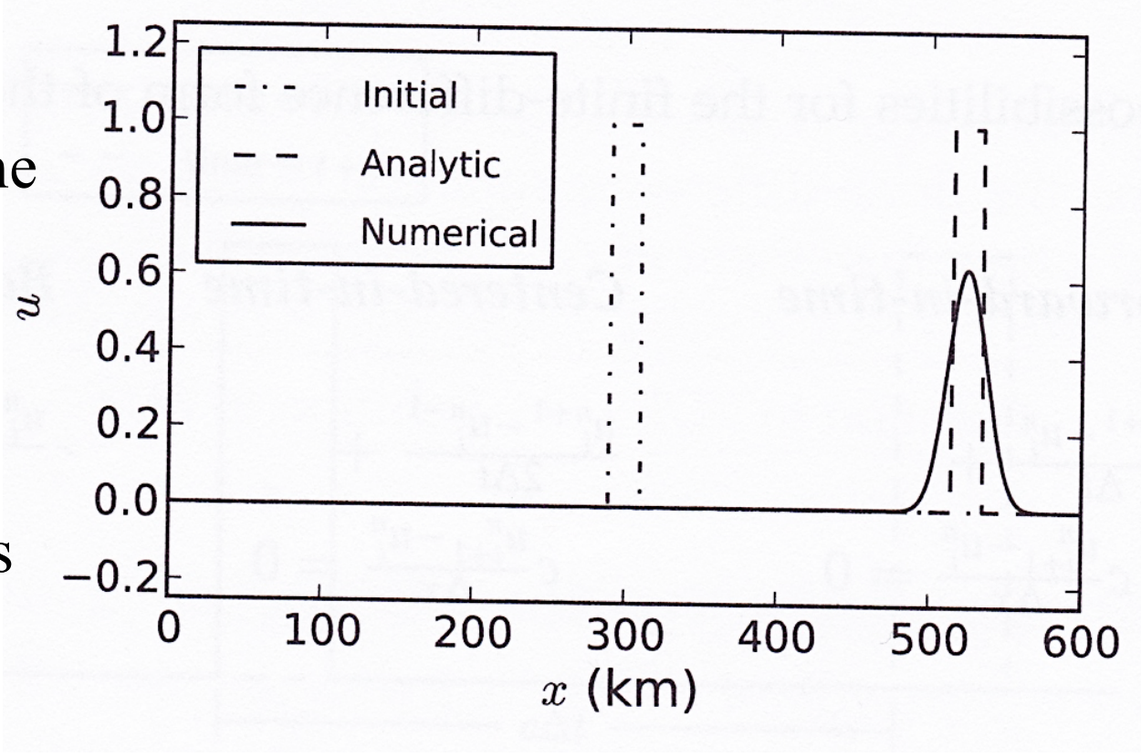
i is the index for space (x), *n* is the index for time (t)

For c > 0, this is the upwind scheme.

At each time step, the values on the right side of the equation are known and the value if *u* at time *n*+1 can be found.

As shown by the graph, the numerical solution is different from the analytic solution. The solution is diffusive, but it is positive.

500 steps;
c = 15 ms^{-1}; Δx = 1 km and Δt = 30



Stability of the methods

Table 4.3: Stability criteria for forward-in-time, forward-in-space and for forward-in-time, backward-in-space schemes.

Forward-in-time, Backward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$c > 0$ *upwind*	stable if $\lvert c\Delta t/\Delta x\rvert \leq 1$
		$c < 0$ *downwind*	always unstable
Forward-in-time, Forward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$c < 0$ *upwind*	stable if $\lvert c\Delta t/\Delta x\rvert \leq 1$
		$c > 0$ *downwind*	always unstable

The Courant-Friedrichs-Lewy stability condition or CFL condition

Elementary Numerical Methods

Let's assume an partial differential equation. $\frac{\partial u}{\partial t} + c\frac{\partial u}{\partial x} = 0$

	Forward-in-time	*Centered-in-time*	*Backward-in-time*
Forward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_i^{n+1}}{\Delta x} = 0$
Centered-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_{i-1}^{n+1}}{2\Delta x} = 0$
Backward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^{n+1}-u_{i-1}^{n+1}}{\Delta x} = 0$

Elementary Numerical Methods

Let's assume an partial differential equation. $\frac{\partial u}{\partial t} + c\frac{\partial u}{\partial x} = 0$

	Forward-in-time	*Centered-in-time*	*Backward-in-time*
Forward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_i^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_i^{n+1}}{\Delta x} = 0$
Centered-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n-u_{i-1}^n}{2\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_{i+1}^{n+1}-u_{i-1}^{n+1}}{2\Delta x} = 0$
Backward-in-space	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^{n-1}}{2\Delta t} + c\frac{u_i^n-u_{i-1}^n}{\Delta x} = 0$	$\frac{u_i^{n+1}-u_i^n}{\Delta t} + c\frac{u_i^{n+1}-u_{i-1}^{n+1}}{\Delta x} = 0$

Center-in-space, center-in-time: The leapfrog method

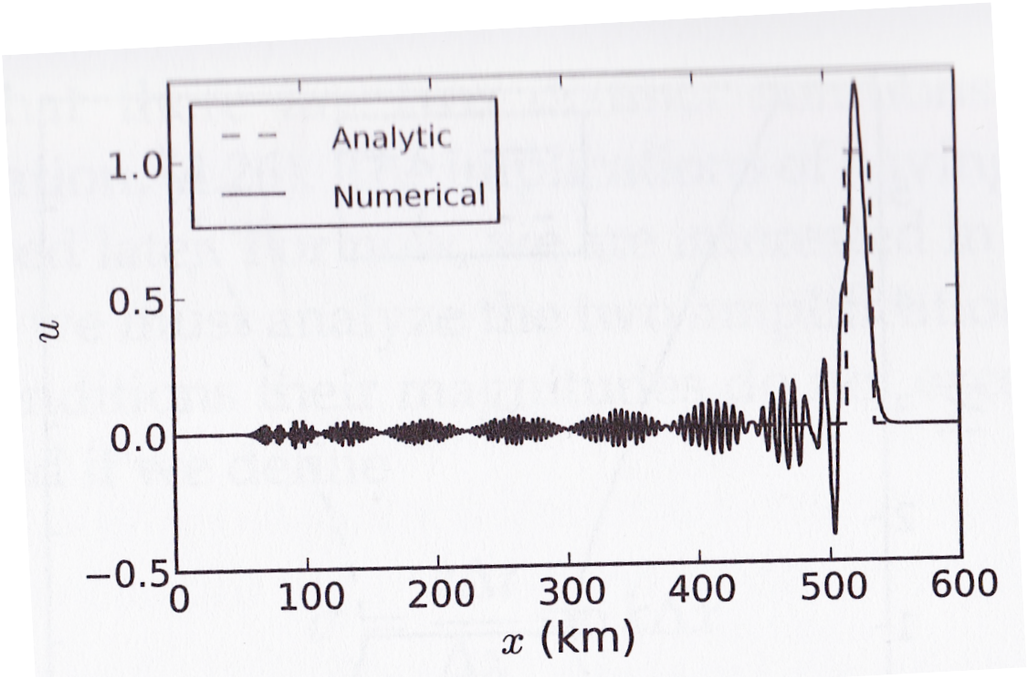
$$\frac{u_i^{n+1} - u_i^{n-1}}{2\Delta t} + c\frac{u_{i+1}^n - u_{i-1}^n}{2\Delta x} = 0,$$

$$u_i^{n+1} = u_i^{n-1} - \frac{c\Delta t}{\Delta x}\left(u_{i+1}^n - u_{i-1}^n\right).$$

Amplification factor = 1

Has a computational mode in addition to a physical mode

Computational mode need to be filtered.



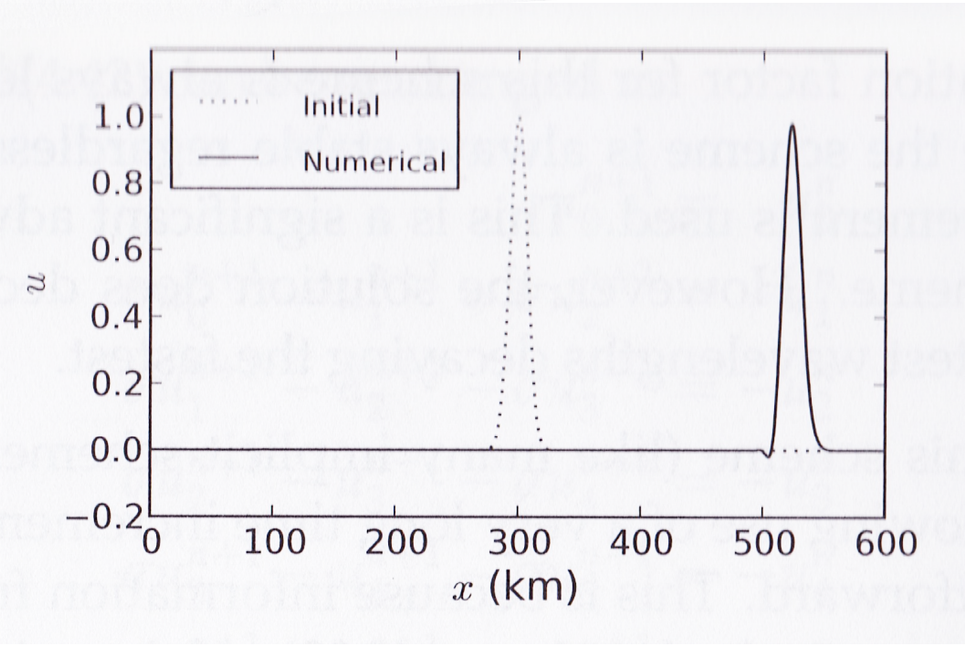


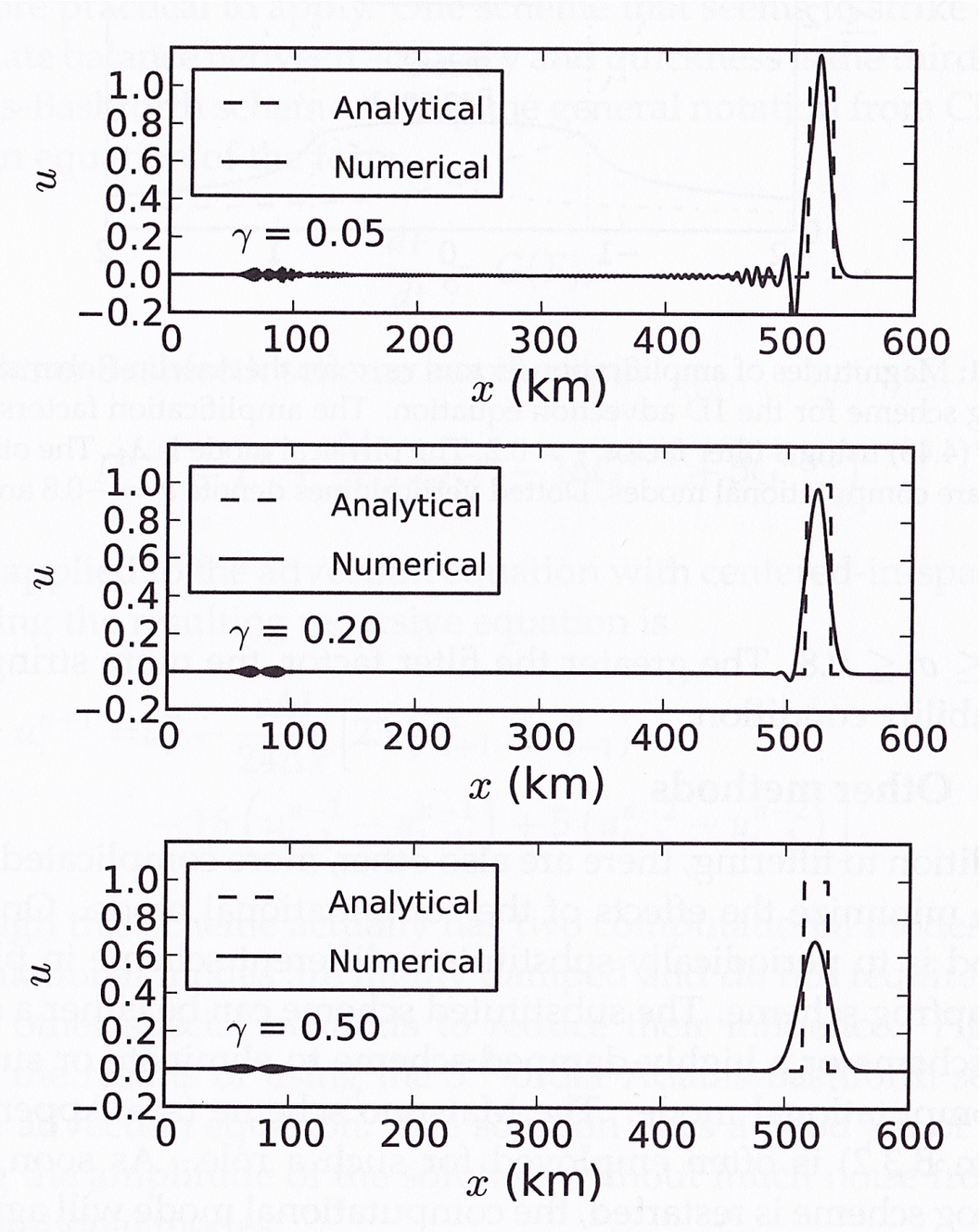
Figure: after 500 steps, c = 15 m s^{-1}, Δx = 1 km and Δt = 30 s

Filtering the Leapfrog solution

$$u_i^{n+1} = u_i^{n-1} - \frac{c\Delta t}{\Delta x}\left(u_{i+1}^n - u_{i-1}^n\right).$$

$$\tilde{u}_i^n = u_i^n + \gamma\left(u_i^{n+1} - 2u_i^n + u_i^{n-1}\right).$$

The Asselin Roberts filter with an adjustable filter factor “gamma”



Solving the Eulerian Advection Equation

$$\frac{\partial C_i}{\partial t} = -u \frac{\partial C_i}{\partial x}$$

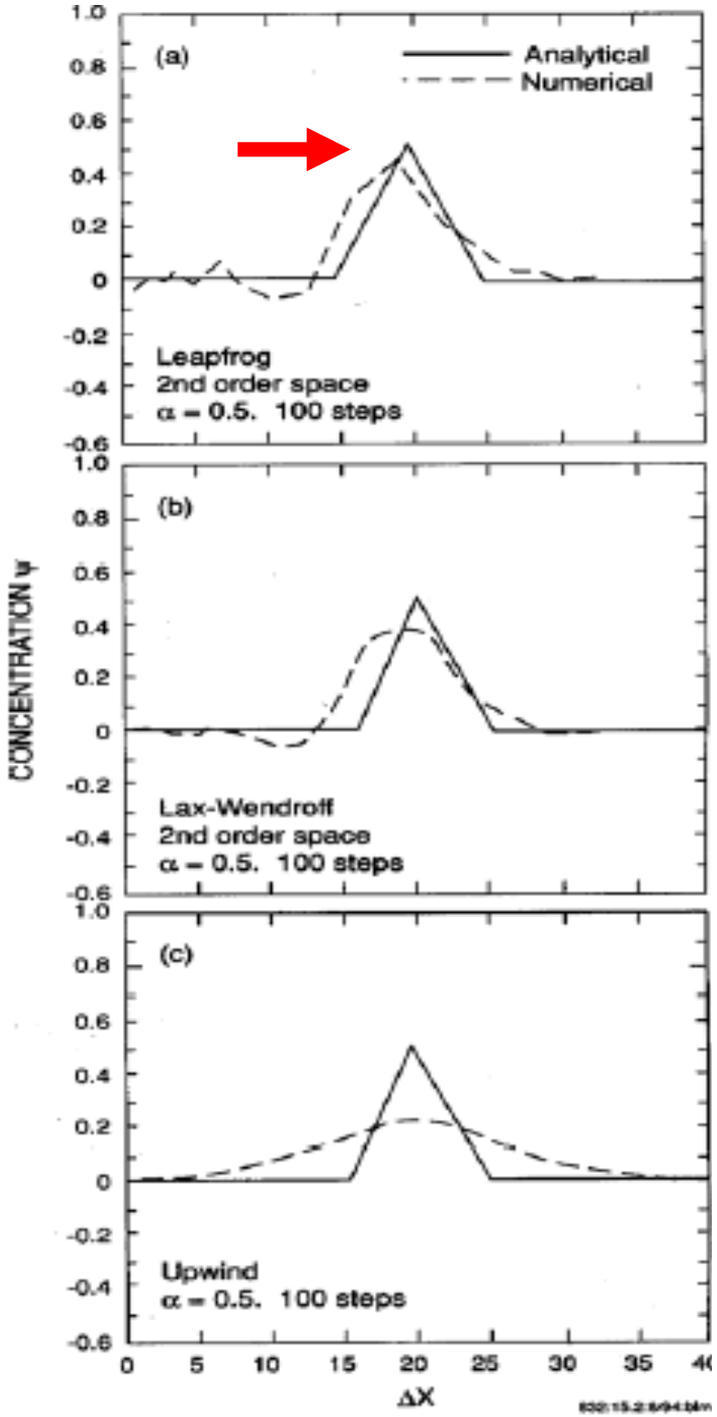
- Equation is *conservative:* need to avoid diffusion or dispersion of features. Also need mass conservation, stability, positivity…

- All schemes involve finite difference approximation of derivatives : order of approximation → accuracy of solution

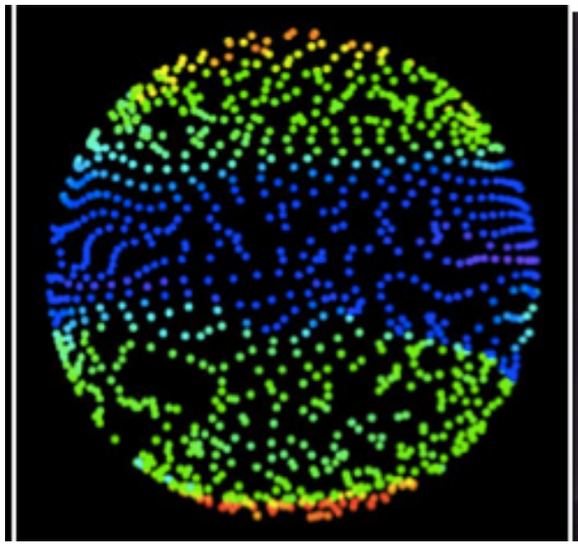
- Classic schemes: leapfrog, Lax-Wendroff, Crank-Nicholson, upwind, moments…

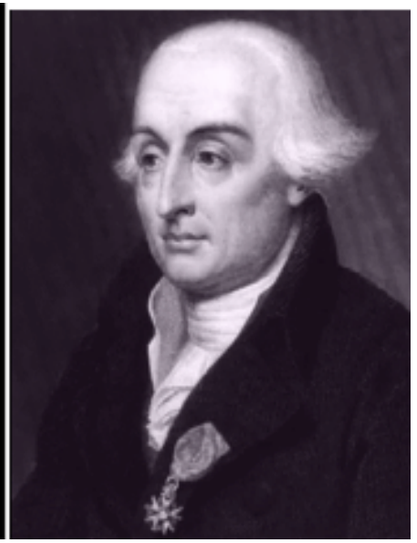
- Stability requires Courant number $u\Delta t/\Delta x < 1$
  … limits size of time step

- Addressing other requirements (e.g., positivity) introduces

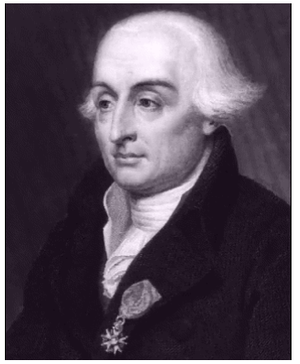


Lagrange



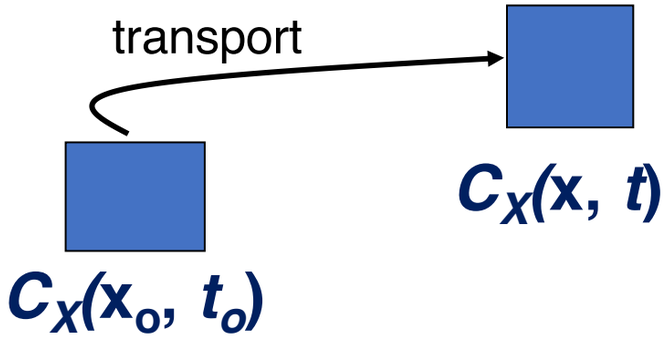


A Lagrangian View



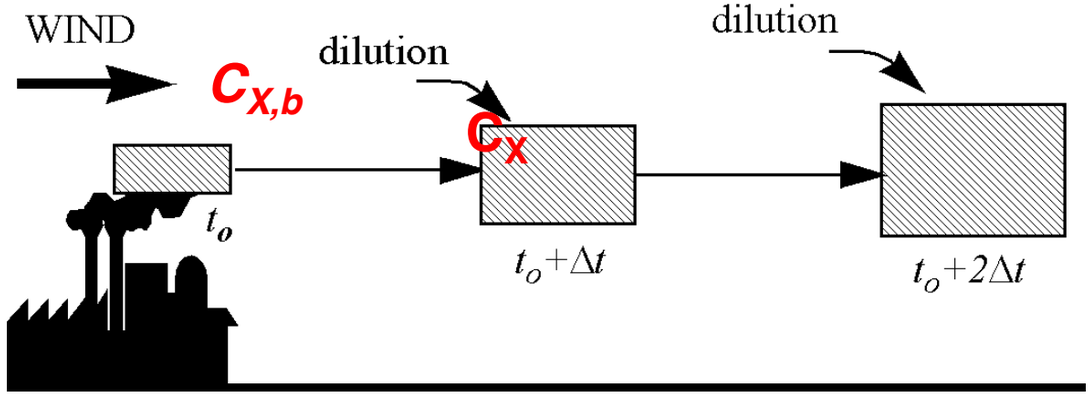
Following a Single Air Parcel

$$d\boldsymbol{X}/dt = \boldsymbol{v}(\boldsymbol{X},t)$$



$$\frac{dC_X}{dt} = E + P - L - D$$

Following an Air Parcel in a Plume

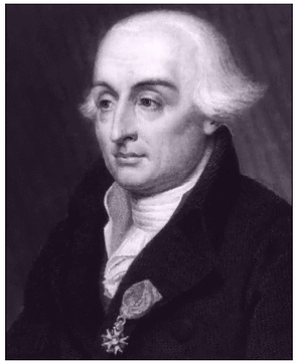


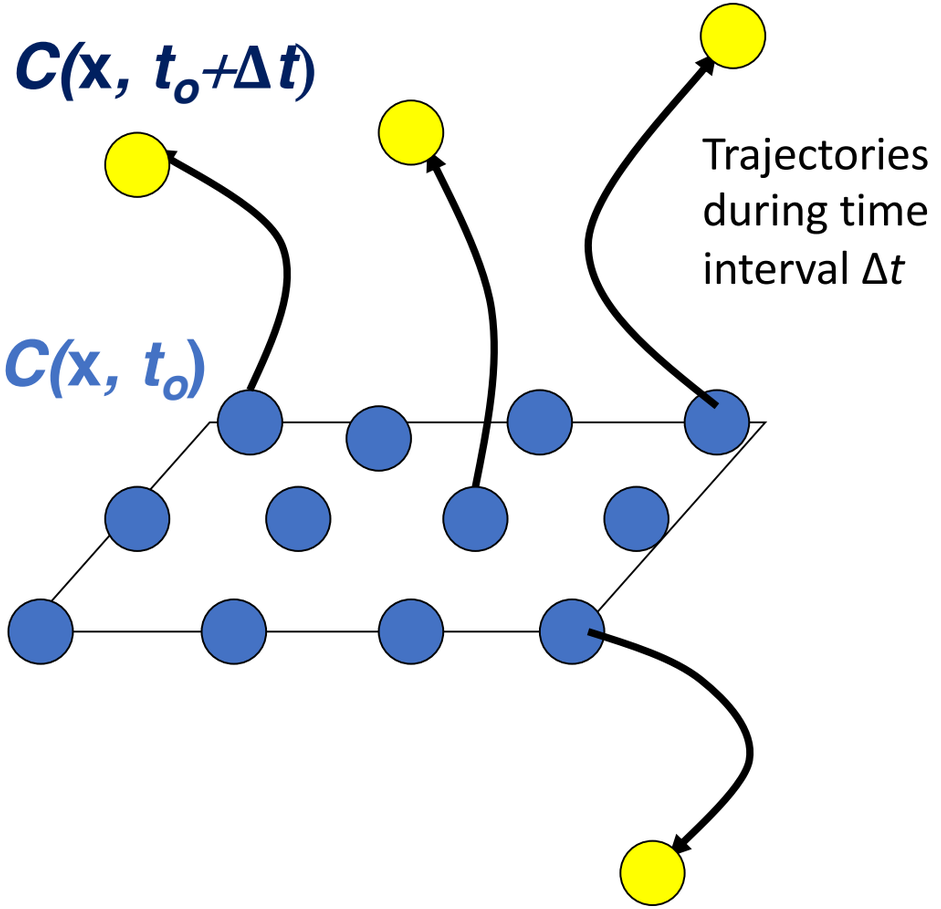
$$\frac{dC_X}{dt} = E + P - L - D - k_{dilution}(C_X - C_{X,b})$$

A Lagrangian View

Following a Large Number of Air Parcels

Concentration field at time *t*, defined by *n* particles





PROS over Eulerian models:

- no Courant number restrictions
- no numerical diffusion/dispersion
- easily track air parcel histories
- invertible with respect to time

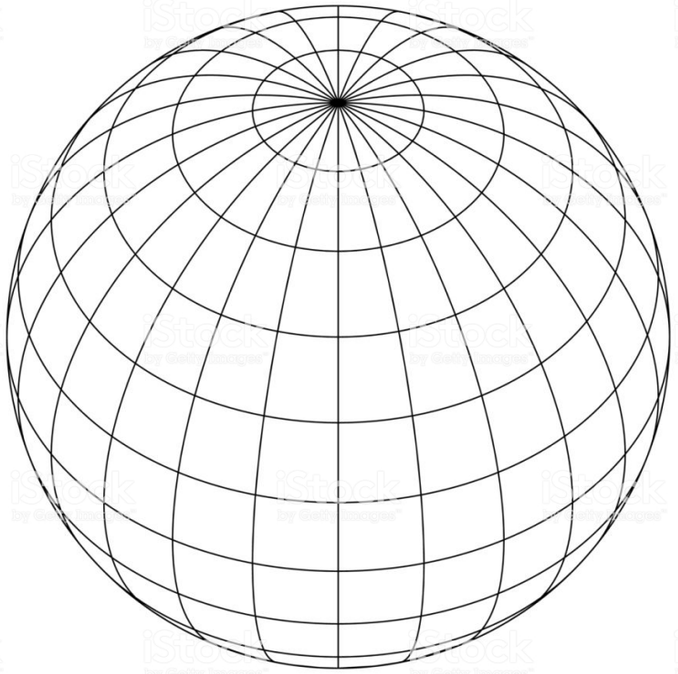
CONS:

- need very large # points for statistics
- inhomogeneous representation of domain
- convection is poorly represented
- nonlinear chemistry is problematic

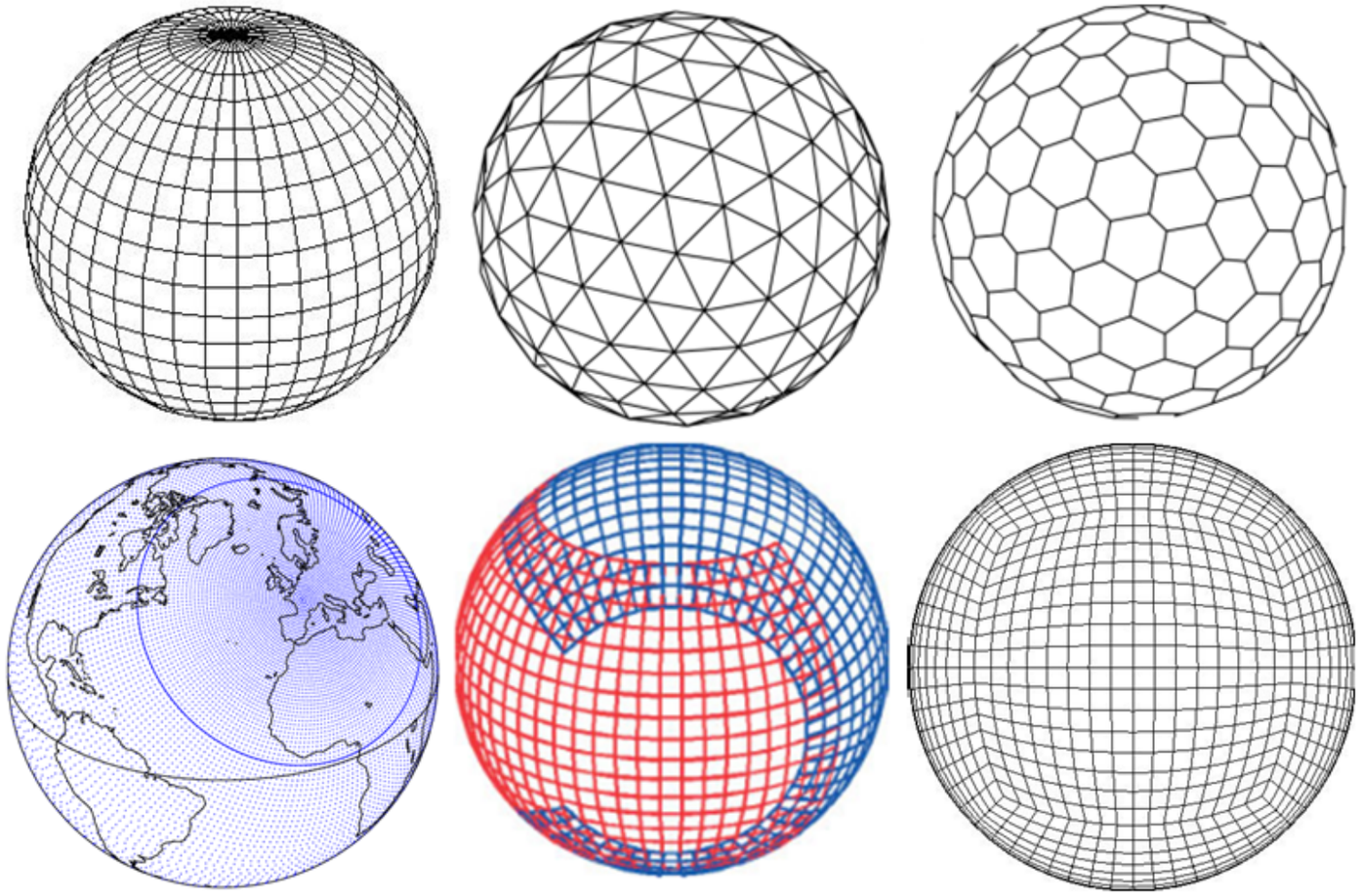
There is no single advection scheme that is universally best.

- ***Eulerian Methods*** are limited by the CFL Condition that constraints the choice of the time.
- ***Low-order*** algorithms such as the upstream method preserve the sign of the solution, but are excessively diffusive.
- ***Higher-order*** algorithms are generally not monotonic and occasionally produce undesired negative values.
-
- ***Lagrangian methods*** are popular for source-oriented and receptor-oriented transport problems in which one is concerned with transport from a point source or transport contributing to concentrations at a receptor point.
- However, they do not provide the regular full-domain solution achievable by Eulerian methods and cannot properly represent nonlinear chemistry or aerosol microphysics.

Grid-point models



Problem at the poles !



Advection

- Desired properties of an advection scheme:
  - accuracy
  - stability
  - mass conservation
  - monotonicity (shape preservation)
  - positive definite fields
  - local
  - efficient

- Reviews of transport algorithms are given by Oran and Boris (1987), Rood (1987), etc.

- Three groups of algorithms:
  - Eulerian

Assume a property (such as the concentration) than is transported in direction *x* with a constant velocity *c*

example : one - dimensional advection equation

$$\frac{\partial \psi}{\partial t} + \frac{\partial F}{\partial x} = 0$$

flux $F = c\,\psi$

solved e.g. by the 'leap - frog' method :

$$\psi_j^{n+1} = \psi_j^{n-1} - \frac{\Delta t}{\Delta x}\left[F_{j+1}^{n} - F_{j-1}^{n}\right]$$

Stable if Courant - Friedricks - Lewy (CFL)

condition is satisfied :

$$\frac{|c|\Delta t}{\Delta x} \leq 1$$

Courant-Friedrichs-Lewy (CFL) condition:

$$\frac{|c|\Delta t}{\Delta x} \leq Const, \; with \; Const \approx 1$$

The time step must be small enough, so that an air parcel does not pass through more than 1 grid box during one time step.

This is a major restriction for many global models beacuse near the pole, the CFL condition is often violated unless very small timesteps are adopted. Eulerian methods are routinely used in regional models.

Solution: Modified grids towards high latitudes or other

Advection I: Eulerian Methods

- Other discretizations are possible:
- The Euler forward (explicit) scheme is unconditionally unstable
- The Upwind method is diffusive
- The Leapfrog method is not monotonic
- Improved methods: Smolarkiewicz, Bott, Prather.
- The CFL condition must be verified to ensure stability.
- Only nonlinear algorithms produce stable solutions, maintain steep gradients, and preserve monotonicity.

Advection I: Eulerian Methods

The Prather Scheme

- In this method, the transported property (tracer mixing ratio) is expressed in each grid box by a quadratic function in the x, y, and z directions (including cross terms). This function is decomposed into orthogonal polynomials over each grid box. Zeroth, first and second order moments are calculated over each box.
- Transport is performed sequentially in the 3 directions x, y, and z.
- The first step is to decompose the moments for each gridbox between the fraction for the gridbox that will be moved by advection into the neighboring box, and the fraction that will remain in the original box.

Advection I: Eulerian Methods

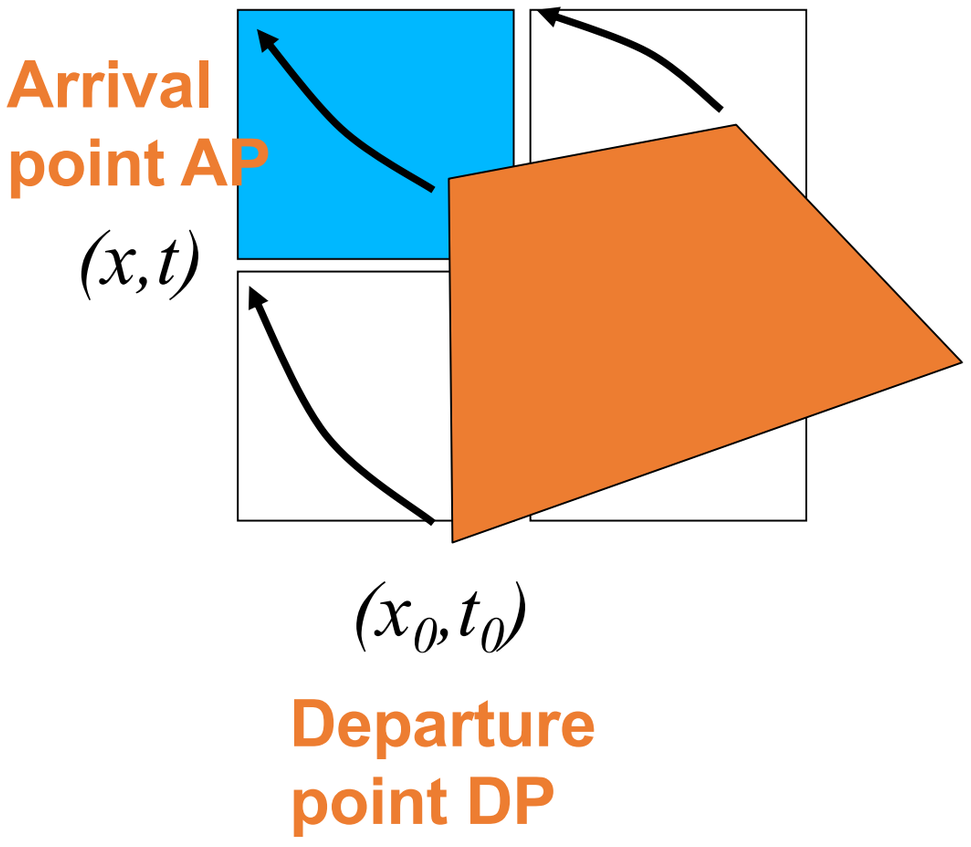
The Prather Scheme

- In the second step, which represents the advection in 1 direction, new moments are calculated in each grid box through the addition of the moments calculated at the previous timestep in the two adjacent sub-grid boxes that contribute to the tracer in a grid box at the new timestep.
- Dividing of the moments in a given grid box in sub-moments, and reforming the moments (by addition of sub-moments) after an advection step, guarantees conservation of moments (i.e., mass) during the advection process.

Advection II: Lagrangian Methods

- In Lagrangian schemes, distinct air parcels, in which tracers are assumed to be homogeneously mixed, are followed as they are displaced by the winds. In the absence of source/sinks processes, the tracer mixing ratio remains constant in the air parcel.
- Lagrangian methods are relatively simple in concept and are not subject to spurious diffusion. Errors can, however, accumulate over the integration. Typically 100,000 parcels are used in a global transport model. Parcels may “bunch up” in certain areas and leave others without parcels to track. This problem is avoided in the Semi-Lagrangian methods where at every new time step, one examines the back trajectory of the parcel that arrives at a given grid point of the model.

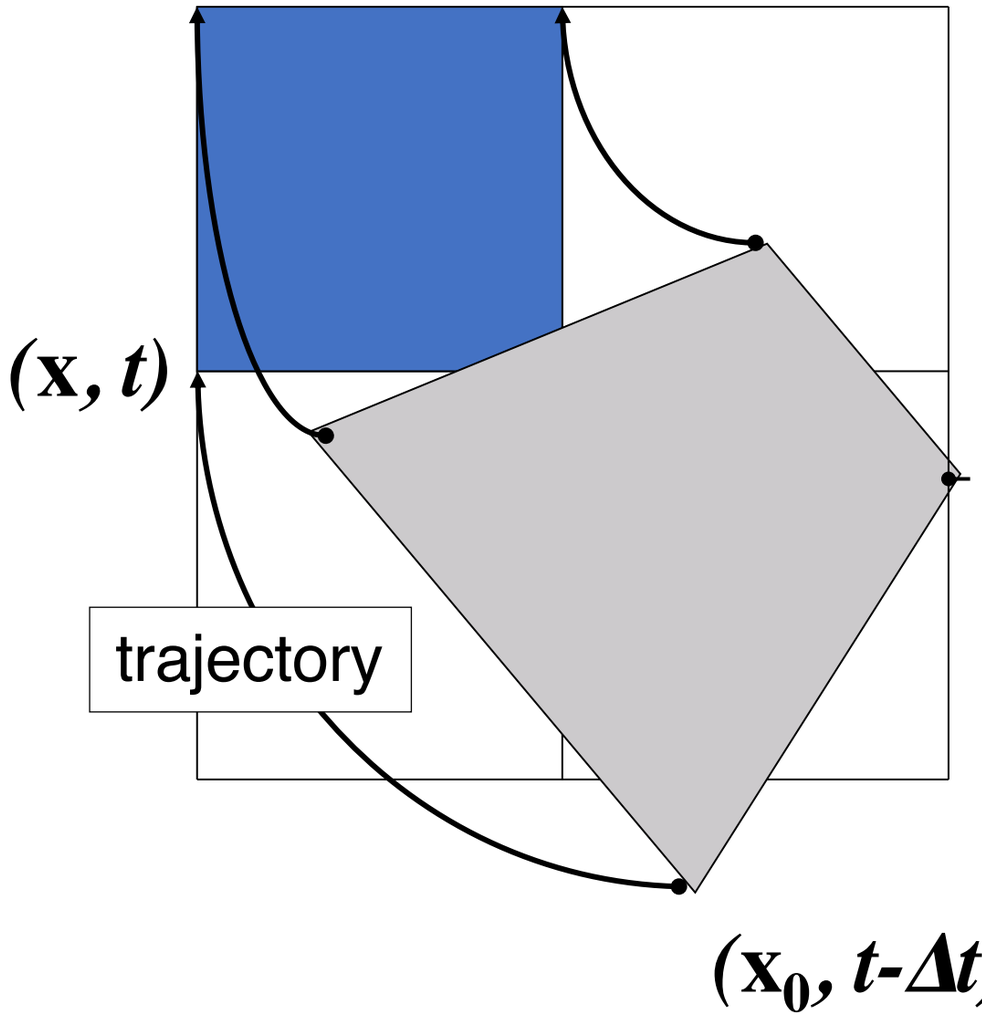
In semi-Lagrangian transport schemes, a backward trajectory is computed for each corner point of a grid cell. The new mixing ratio *f* of species *i* is then computed by interpolation („remapping“) of the concentration field of timestep t_0 onto the model grid at timestep *t*.



Thus $f_{AP}\,(\boldsymbol{x},t) = f_{DP}\,(\boldsymbol{x}_0,\, t_0)$

The location of the upstream departure point is found by solving the equation $d\boldsymbol{x}/dt = \boldsymbol{v}\,(\boldsymbol{x},\, t)$. This equation has to be solved iteratively since **v** varies with along the back

Advection III: Semi-Lagrangian Transport



$$\mathbf{X}_0 = \mathbf{X} + \int_t^{t-\Delta t} \mathbf{v}(\mathbf{X}, t)\, dt$$

Accuracy depends greatly on Interpolation scheme used.

Common in modern GCMs

Advection III: Semi-Lagrangian Methods

- The accuracy of the semi-Lagrangian scheme depends on the accuracy of
  - The determination of the location of the departure point (DP)
  - The determination of the tracer mixing ratio at the DP, and hence on the interpolation scheme that is used. A linear interpolation leads to excessive smoothing. Cubic interpolation is preferred, but is computationally expensive.
- The major advantage of the SLT method is that it is not restricted by the CFL condition, and the timestep is chosen by accuracy considerations. It gives minor phase errors, minimizes computational dispersion, preserves shapes and can handle sharp discontinuities
- The major disadvantage of the SLT scheme is that it does not formally conserve integral invariants such as total mass or energy.

Advection III: Conservative Semi-Lagrangian Methods

- To address this issue, rather than considering variables at specific grid points, one can transport integral quantities or ***average*** values over finite cell volumes (or cell areas in the case of 2-D formulations).
- In finite-volume-based Semi-Lagrangian methods, the value of the advected field at a new time level is just the average value of the departure cell defined by its upstream position at the previous timestep.
- Lin and Rood (1996) have developed a mass conservative finite volume semi-Lagrangian method, in which the boundaries (“ departure walls” rather than “departure points”) of the grid volumes are transported to the next step (“arrival walls”). Mass is conserved in the box during a timestep. The CFL restriction does not apply.

example: one-dimensional diffusion equation

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial x}\left(K \frac{\partial \psi}{\partial x} \right)$$

$K > 0$ is the so-called diffusion coefficient

Fully explicit solution:

$$\frac{\psi_j^{n+1} - \psi_j^n}{\Delta t} = \frac{K}{(\Delta x)^2}\left(\psi_{j-1}^n - 2\psi_j^n + \psi_{j+1}^n \right)$$

only stable if

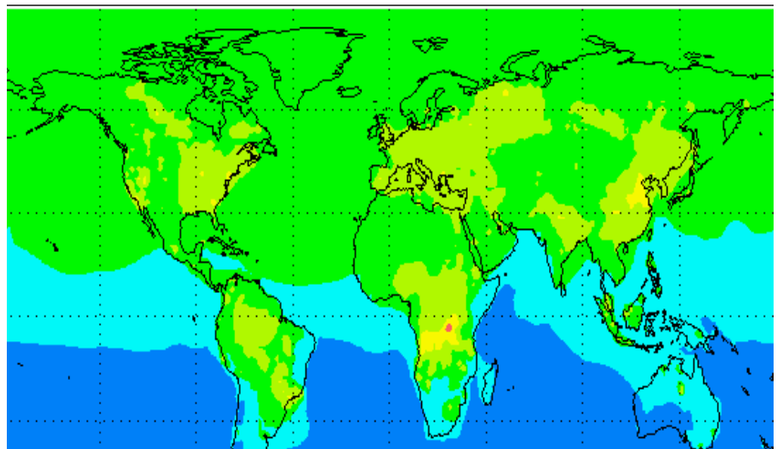
$$\frac{2K\Delta t}{(\Delta x)^2} \leq 1$$

Fully implicit solution:

$$\frac{\psi_j^{n+1} - \psi_j^n}{\Delta t} = \frac{K}{(\Delta x)^2}\left(\psi_{j-1}^{n+1} - 2\psi_j^{n+1} + \psi_{j+1}^{n+1} \right)$$

Part 3. Numerical Solutions

- 1. Transport
- 2. Chemistry
- 3. Surface Processes



Simplest method is fully explicit :

$$\mathbf{f}^{n+1} = \mathbf{f}^{n} + \Delta t \cdot \mathbf{S}(t_n, \mathbf{f}^{n}) / \rho_a$$

Euler Forward

$\mathbf{f}^{n+1}$ expressed in terms of known quanities

Requires very small time-steps.

Fully implicit is stable for any Δt :

$$\mathbf{f}^{n+1} = \mathbf{f}^{n} + \Delta t \cdot \mathbf{S}(t_{n+1}, \mathbf{f}^{n+1}) / \rho_a$$

Euler backward

However, $\mathbf{S}$ contains non-linear terms, and accuracy is comprimised for large Δt.

Iterative techniques are often used to improve the accuracy of implicit methods.

Prominent is the Newton-Raphson iteration which requires that

Chemical forcing (S)
(i.e. production and loss)

Das Bild kann nicht angezeigt werden.

First-order forcing
Photolysis, airglow, …

$$\frac{\mathbf{S}(\mathbf{f},\mathbf{x},t)}{\rho_a} = \mathbf{e}(\mathbf{x},t) - \mathbf{A}(\mathbf{x},t)\cdot\mathbf{f} + \mathbf{B}(\mathbf{f},\mathbf{x},t)\cdot\mathbf{f}$$

External forcing
Independent of **f**

Non-linear forcing
Bi-molecular and
tri-molecular reactions

Chemistry: Solving df/dt = S/ρ

- Shimazaki writes the source term

$$\frac{\mathbf{S}(\mathbf{f},\mathbf{x},t)}{\rho_a} = \mathbf{e}(\mathbf{x},t) - \mathbf{B}(\mathbf{f},\mathbf{x},t)\cdot\mathbf{f}$$

and

$$\mathbf{f}_{(m+1)}^{n+1} = [\mathbf{f}^{n} + \mathbf{e}(\mathbf{f}_{(m)}^{n+1},\mathbf{x},t^{n+1})\Delta t]/[1+\mathbf{B}(\mathbf{f}_{(m)}^{n+1},\mathbf{x},t^{n+1})\Delta t]$$

Iterations (m) are performed for nonlinear cases.

- Hesstvedt proposes a semi-analytic solution

$$f_i^{n+1} = (f_i)_{ss} + [f_i^{n} - (f_i)_{ss}]\exp(-B_i(f_i^{n}, t^{n+1})\Delta t$$

where

$$(f_i)_{ss} = e_i(x,t) / B_i(f_i^{n+1}, x, t)$$

Chemistry: Solving df/dt = S/ρ

- A multi-step method very appropriate for “stiff” systems has been developed by Gear (1971).
- This algorithm is composed of the so-called backward difference formulas up to order six.
- The method is extremely robust and stable but does require solving nonlinear algebraic systems (like Euler backward algorithm).
- Time step and order of the method are continuously adapted to meet user-specified solution error tolerances.
- Codes require much computer memory and tine; not practical for multi-dimensional models.

Quasi steady state approximation

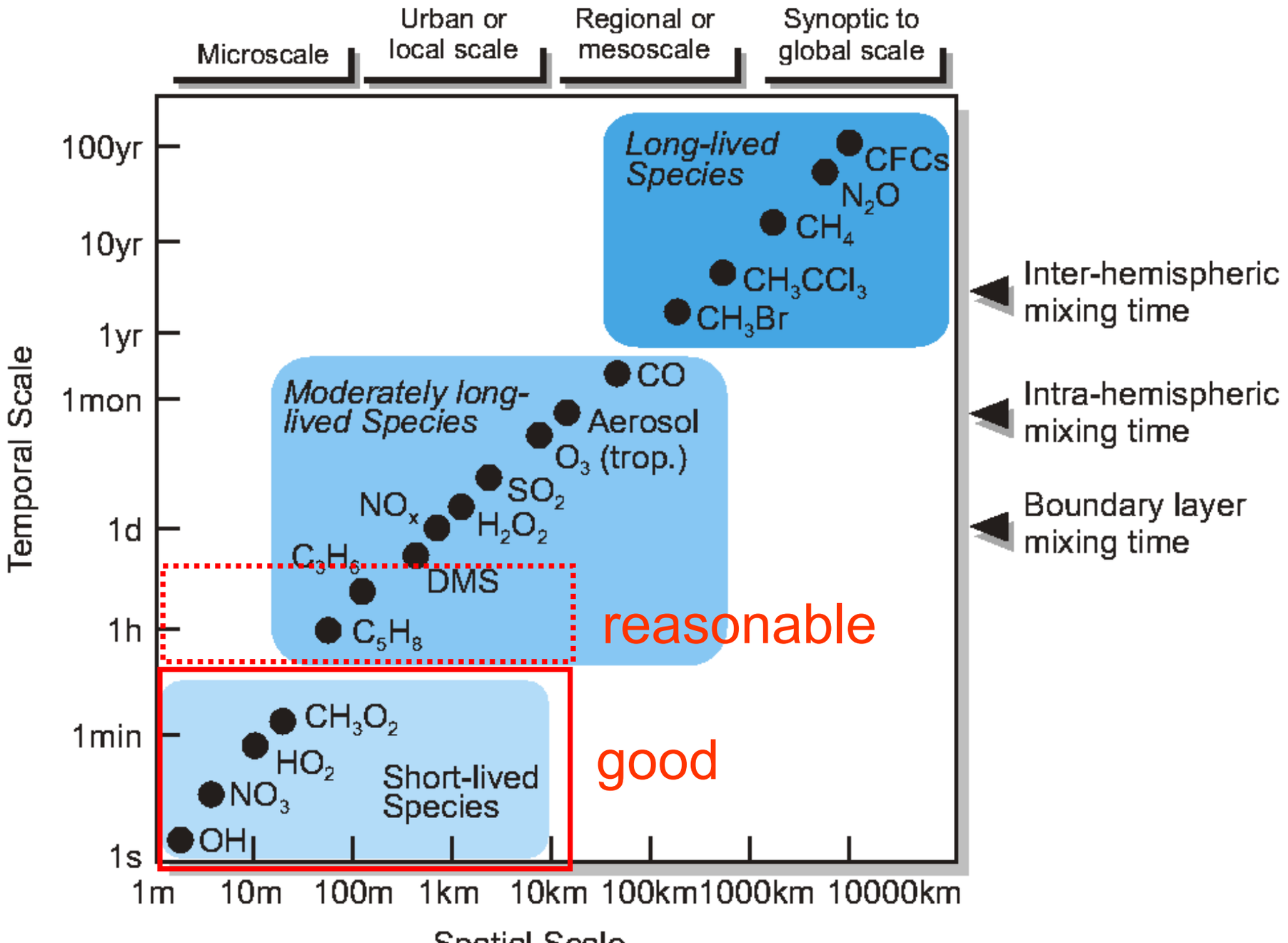
If the loss of a chemical species is much faster than its production (and fast compared to the length of a day), it is generally a reasonable assumption to assume that it is in „dynamic steady state“, i.e. dX/dt = 0.

Example:

$$\frac{d\mathrm{O}\left(^1D\right)}{dt} = j_{O^1D} \cdot \mathrm{O}_3 - k_1 \cdot \mathrm{O}\left(^1D\right) \cdot \mathrm{M} - k_2 \cdot \mathrm{O}\left(^1D\right) \cdot \mathrm{H_2O}$$

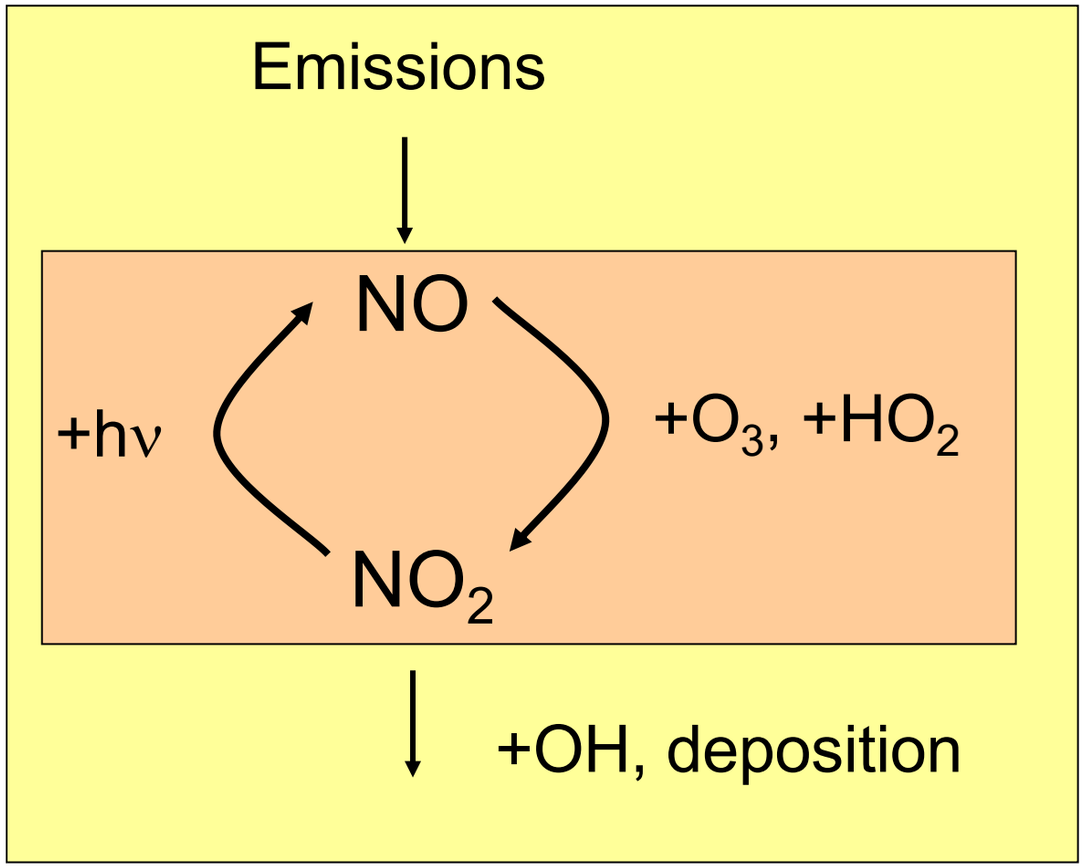
$$\frac{d\mathrm{O}\left(^1D\right)}{dt} = 0 \quad \text{thus} \quad \mathrm{O}\left(^1D\right) = \frac{j_{O^1D} \cdot \mathrm{O}_3}{k_1 M + k_2 \mathrm{H_2O}}$$

Validi


Microscale
Urban or local scale
Regional or mesoscale
Synoptic to global scale
Temporal Scale
100yr
10yr
1yr
1mon
1d
1h
1min
1s
Long-lived Species
CFCs
N_2O
CH_4
CH_3CCl_3
CH_3Br
Moderately long-lived Species
CO
Aerosol
O_3 (trop.)
SO_2
NO_x
H_2O_2
C_3H_6
DMS
C_5H_8
Short-lived Species
CH_3O_2
HO_2
NO_3
OH
reasonable
good
Inter-hemispheric mixing time
Intra-hemispheric mixing time
Boundary layer mixing time
1m
10m
100m
1km
10km
100km
1000km
10000km

Chemical Families

A „trick“ to make the QSSA approach work for long-lived species as well is the definition of chemical „families“: Species are grouped together so that the fast reactions don‘t change the group concentration.



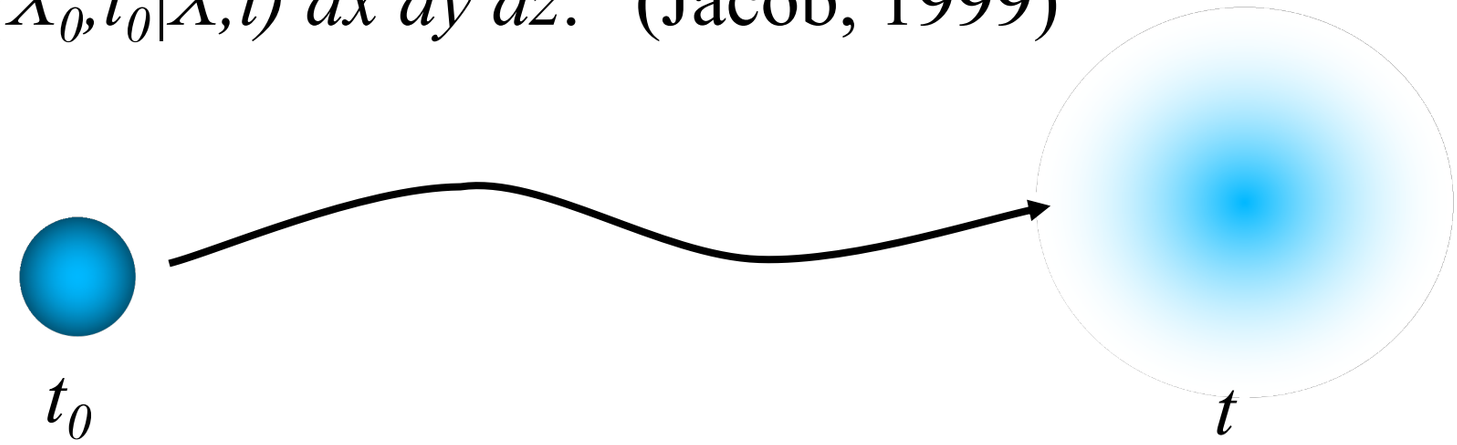
Example:

$NO_x = NO + NO_2$

$$\frac{d\mathrm{NO}}{dt} = \mathrm{Emissions} + j_{NO_2} \cdot \mathrm{NO_2} - \mathrm{NO}\left(k_1 \cdot \mathrm{O_3} + k_2 \cdot \mathrm{HO_3}\right)$$

$$\frac{d\mathrm{NO_2}}{dt} = \mathrm{NO} \cdot \left(k_1 \cdot \mathrm{O_3} + k_2 \cdot \mathrm{HO_3}\right) - j_{NO_2} \cdot \mathrm{NO_2} - k_3 \cdot \mathrm{NO_2} \cdot \mathrm{OH} - \mathrm{deposition}$$

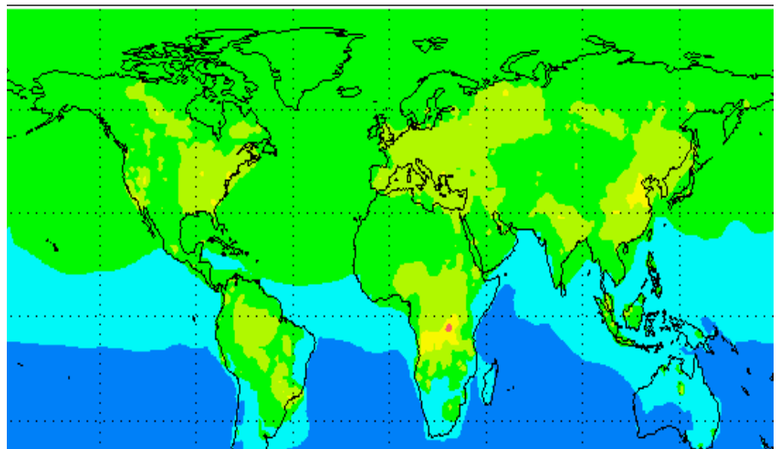
Lagrangian (or trajectory) models are in fact 3-dimensional in that they take account of the horizontal and vertical transport of an air parcel. „We define a transition probability density $Q(X_0,t_0|X,t)$, such that the probability that the fluid element will have moved to within volume (dx,dy,dz) centered at location X at time t is $Q(X_0,t_0|X,t)\ dx\ dy\ dz$.“ (Jacob, 1999)

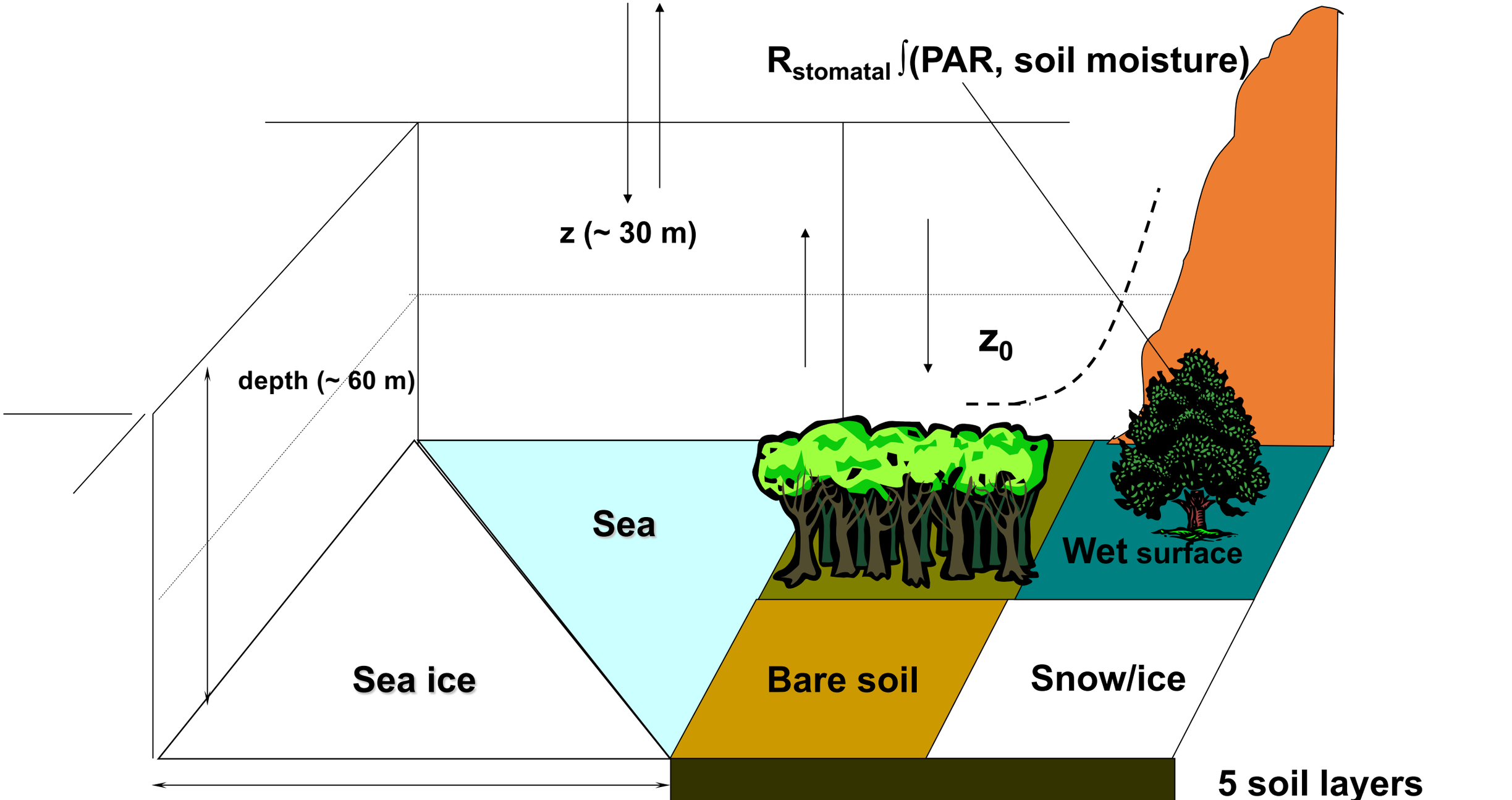


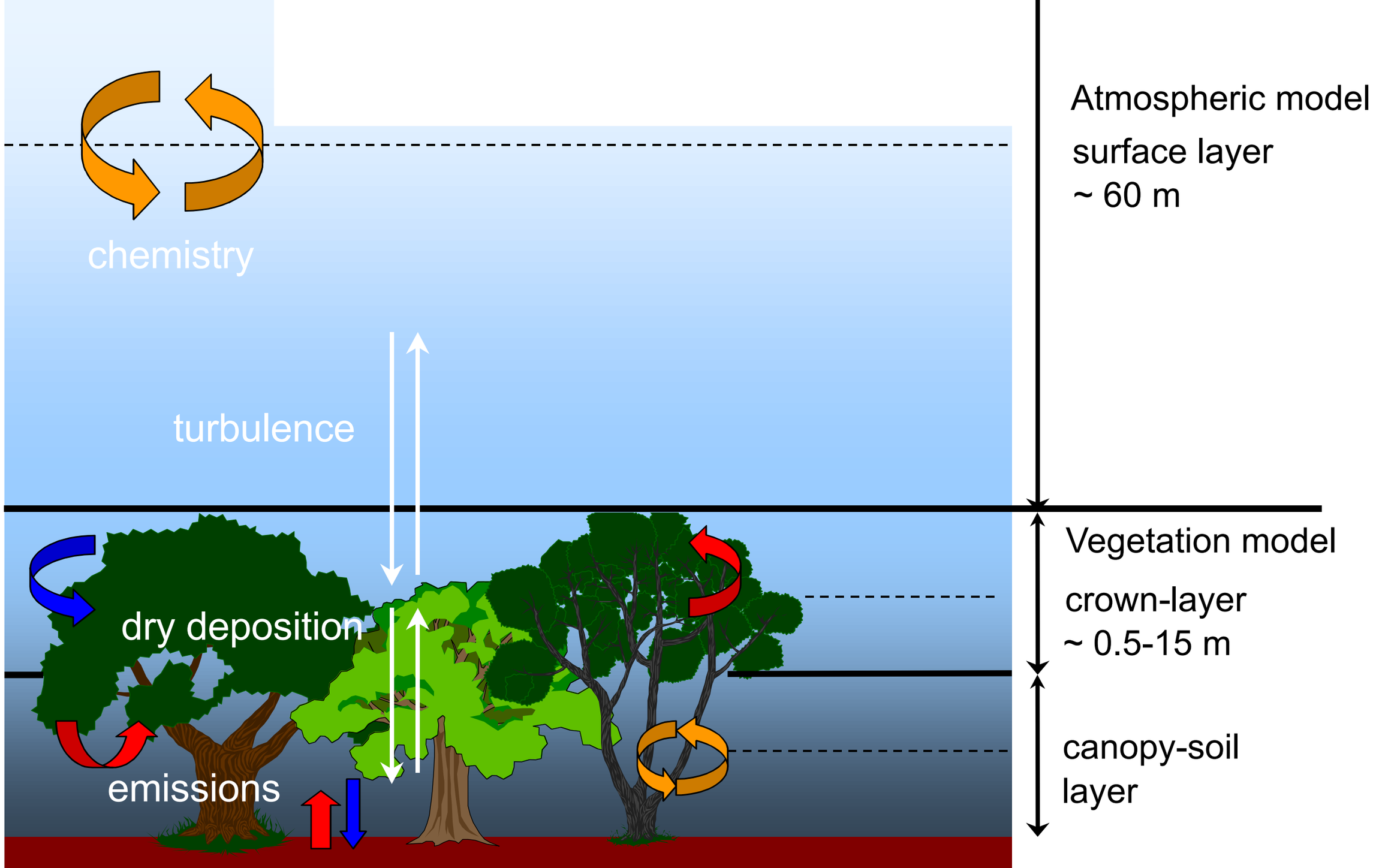
While this approach implicitely accounts for small-scale processes like diffusion or convection, it has disadvantages, because it neglects mixing of air parcels, and the quantity Q is not directly observable. One way of using the lagrangian technique efficiently is the particle model, where Q is approximated by a large number of point-

Part 3. Numerical Solutions

- 1. Transport
- 2. Chemistry
- 3. Surface Processes




$R_{stomatal} \int$(PAR, soil moisture)
z (~ 30 m)
z_0
depth (~ 60 m)
Sea
Wet surface
Sea ice
Bare soil
Snow/ice
5 soil layers


chemistry
turbulence
dry deposition
emissions
Atmospheric model
surface layer
~ 60 m
Vegetation model
crown-layer
~ 0.5-15 m
canopy-soil
layer

Emissions (1)

In current models, emissions are typically specified as monthly mean mass fluxes. These are read from file and interpolated to time *t*.

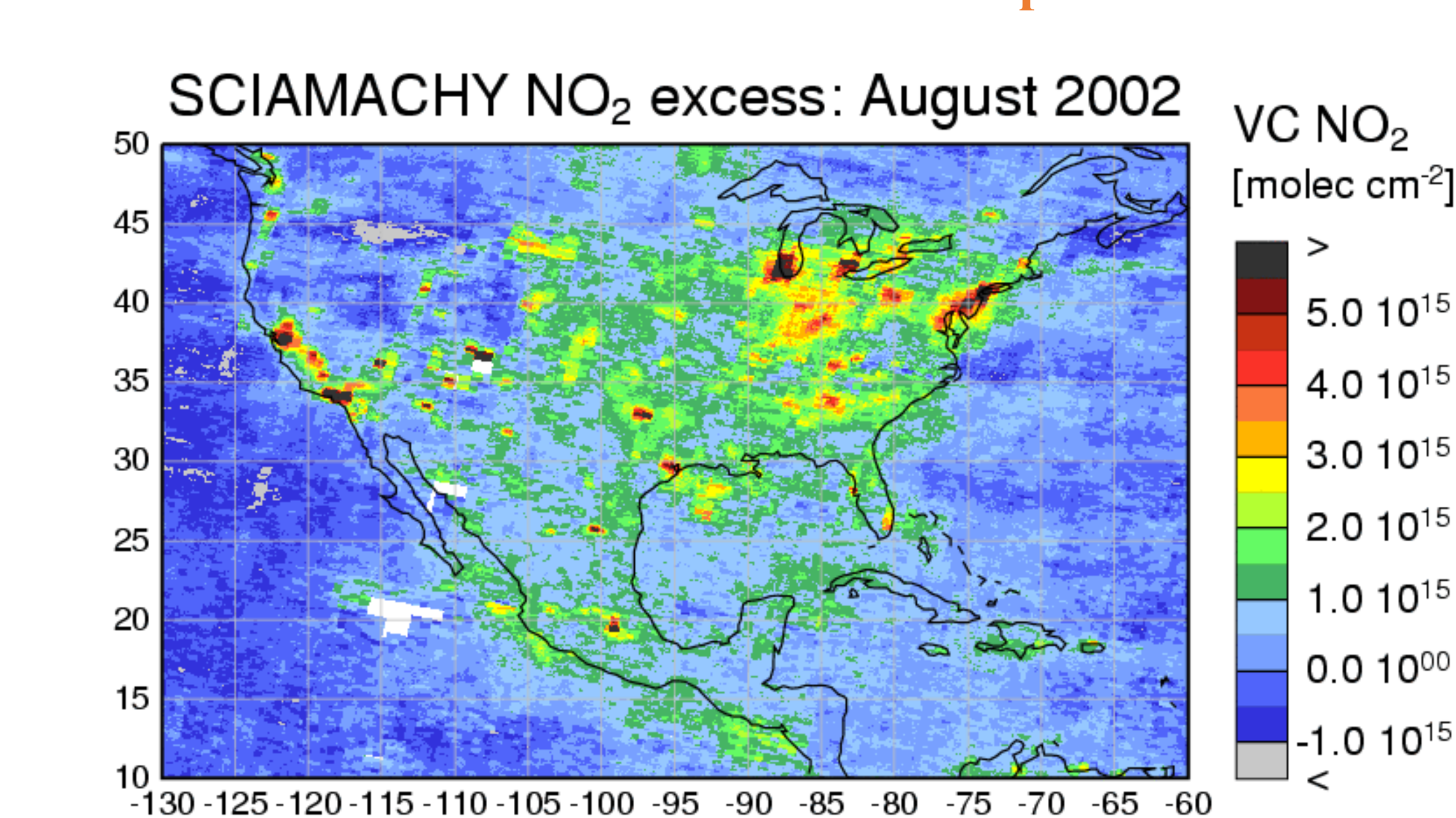
The compilation of emissions inventories is a labour-intensive task, and these inventories still constitute one of the major uncertainties in modeling. Today, first attempts have been made to estimate emissions based on satellite and in-situ observations and using „inverse“ models.

Emissions (2)

Typical categories of „bottom-up“ emissions inventories include:

- fossil fuel combustion
- biofuel combustion
- vegetation fires
- biogenic emissions (plants and soils)
- volcanic emissions
- oceanic emissions
- agricultural emissions (incl. fertilisation)

etc.


SCIAMACHY NO2 excess: August 2002
VC NO2
[molec cm-2]
>
5.0 10^15
4.0 10^15
3.0 10^15
2.0 10^15
1.0 10^15
0.0 10^00
-1.0 10^15
<
50
45
40
35
30
25
20
15
10
-130 -125 -120 -115 -110 -105 -100 -95 -90 -85 -80 -75 -70 -65 -60

(Dry) Deposition

Transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation

Controlling factors: atmospheric turbulence, chemical properties of species, and nature of the surface

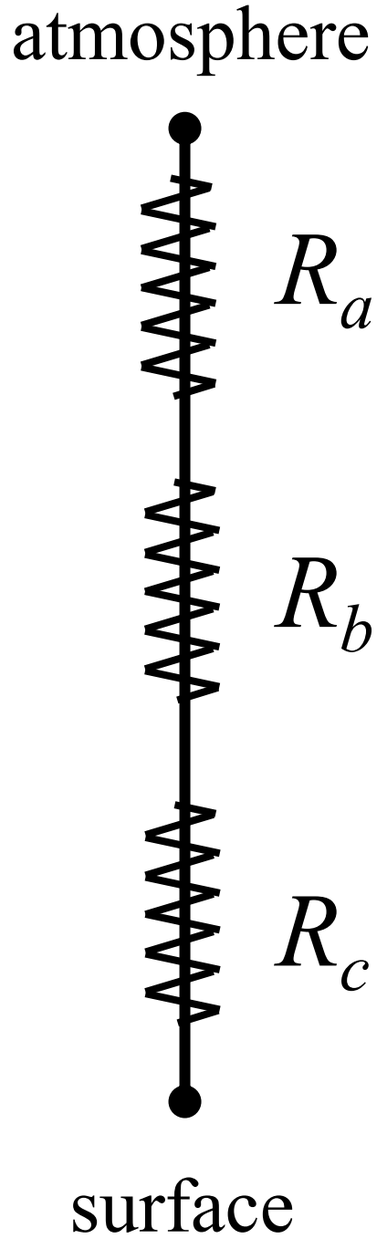
Deposition flux: $$F = -v_d C$$

v_d: deposition velocity
C: concentration of species at reference height (~10 m)

Resistance analog

$$v_d = \frac{1}{R_a + R_b + R_c}$$

R_a = aerodynamic resistance.
R_b = quasi laminar boundary layer resistance
R_c = canopy resistance



$$R_a + R_b + R_c$$

R_a

Resistance of:

dynamic sublayer

interfacial sublayer

vegetation sublayer

R_b

Resistance of:

laminary sub-layer

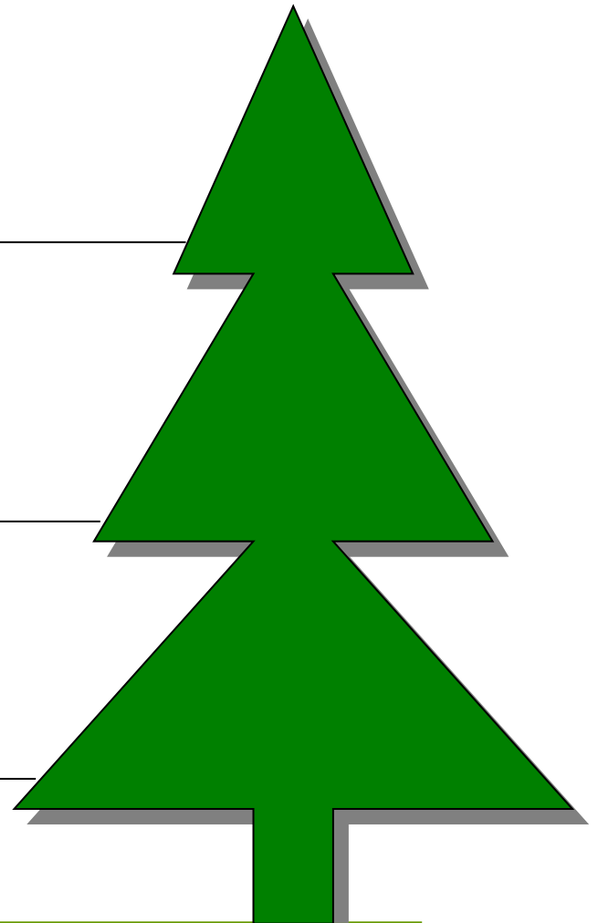
R_c

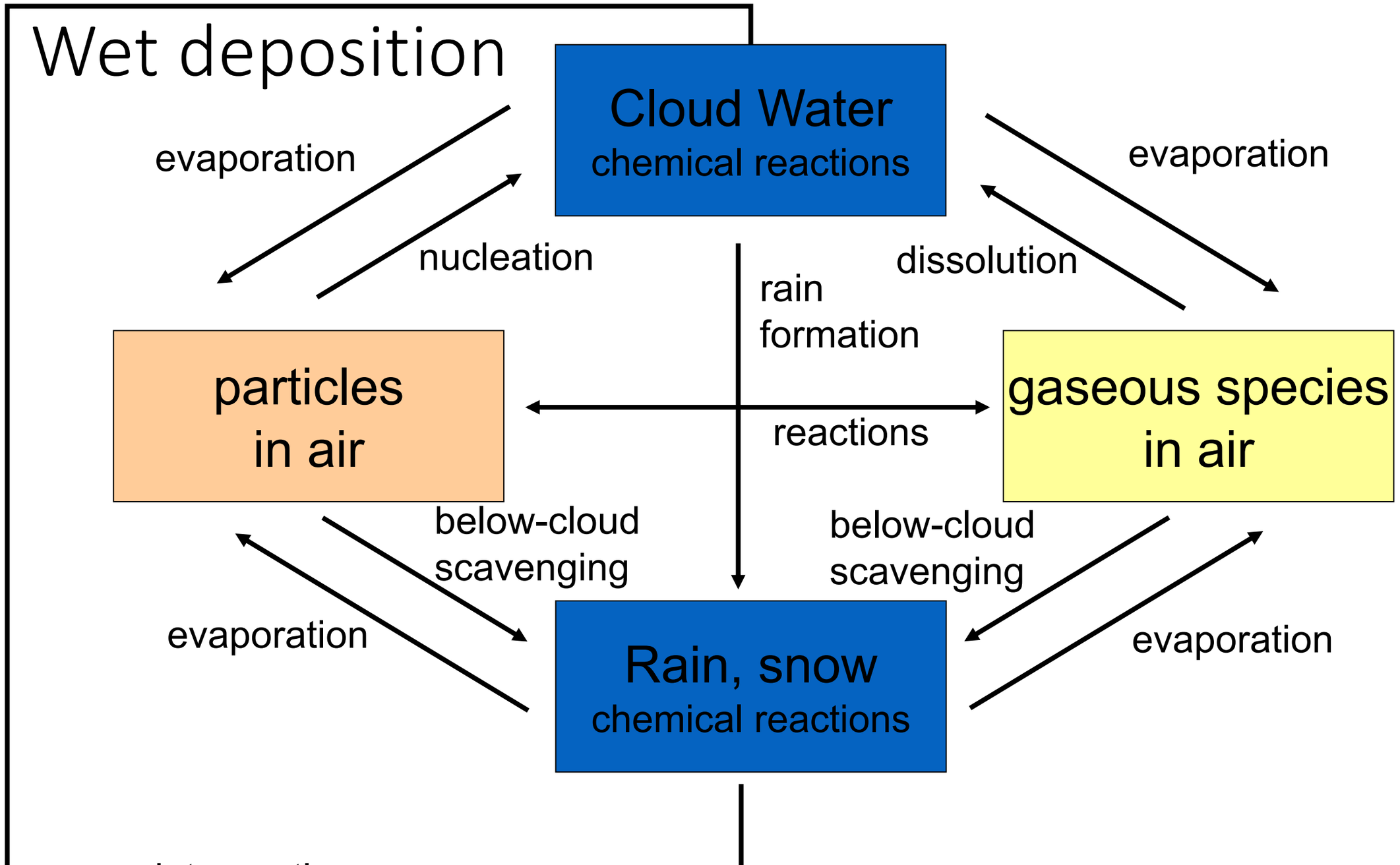
Resistance of:

wet surface

stomata

dry surface




Wet deposition
Cloud Water
chemical reactions
evaporation
nucleation
evaporation
dissolution
rain
formation
particles
in air
gaseous species
in air
reactions
below-cloud
scavenging
below-cloud
scavenging
evaporation
evaporation
Rain, snow
chemical reactions

The End