Introduction to Atmospheric Chemistry: A long-term Perspective

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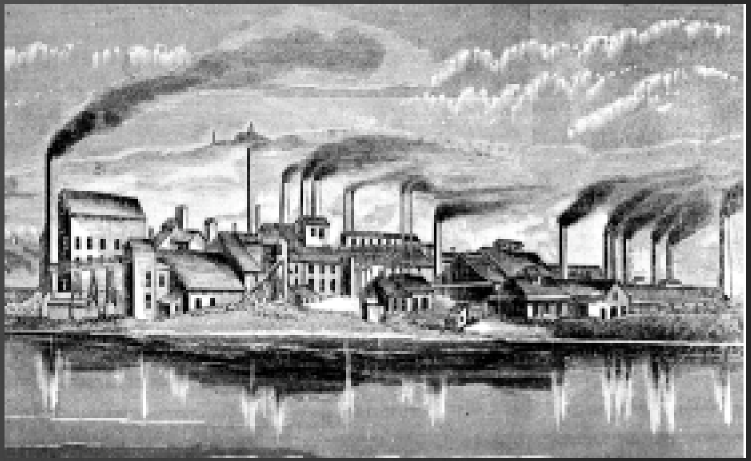
Outline

- Historical Milestones
- Approaches (Observations, Modeling, Data Assimilation)
- Some Key Definitions
- Today's Scientific Challenges
- References
- Thanks to Pierre Coheur, Cathy Clerbaux, Claire Granier, Daniel Jacob and Trissevgeni Stravakou for their input.

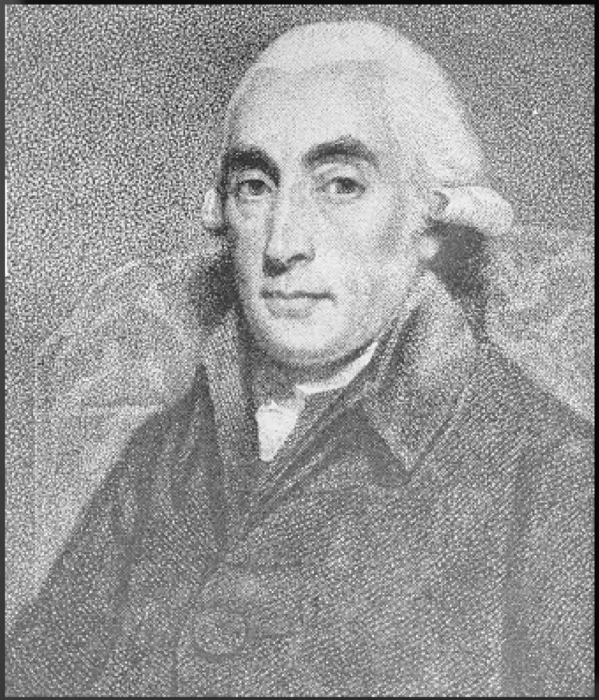
Historical Milestones



Fire-Air and Foul-air

- **Leonardo da Vinci** (1452-1519) in Italy and **John Mayow** (1641-1679) in Great Britain discovered that air is composed of "***fire-air***" that supports combustion and life, and "***foul-air***" that does not.
- *Carbon dioxide* is discovered around 1750 by **Joseph Black** (1728-1799).
- *Nitrogen* is identified several years later by **Daniel Rutherford** (1749-1819).

Joseph Black



Oxygen


Priestley

"Fire-Air" was isolated in 1773 by Swedish chemist **Carl Wilhelm Scheele** (1742-1786), in 1774 by British scientist **Joseph Priestley** (1733-1804). It was called oxygen by French chemist **Antoine-Laurent Lavoisier** (1743-1794).


FIG. 50.—C. W. SCHEELE, 1742-1786
(From a posthumous portrait by Falander.)

Lavoisier: The Father of Modern Chemistry.

	Noms nouveaux.	Noms anciens correſpondans.
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofete. Baſe de la mofete.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobolt	Cobolt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtene.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'Epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

Lavoisier's List of the Elements (1789).

At the height of the French Revolution, he was accused by Jean-Paul Marat of selling adulterated tobacco and of other crimes, and was eventually guillotined a year after Marat's death.


John William Strutt

Noble Gases

- **John William Strutt** known as **Lord Rayleigh** (1842-1919) and **Sir William Ramsay** (1852-1919) identified ***argon*** and other noble gases in the atmosphere. This discovery gave Ramsey the Nobel Prize for Chemistry in 1904.


William Ramsay

The Discovery of Ozone

- In 1840, **Christian Fredrich Schönbein** (1799-1868) detects the same peculiar odor in the oxygen liberated during the electrolysis of acidulated water.
- Schönbein names this property "**ozone**" after the Greek word όζειν (ozein, to smell).

Air Pollution: An Old Problem (1)

- Throughout Antiquity, air pollution in the form of smoke was identified as the cause of the blackening of the temples in Rome.
- Philosopher and Astronomer Moses Maimonides (1135-1204 from Cordova in the Almoravid Empire –today Spain) notes that air is often "turbid, thick, misty and foggy".
- In the 1300's, King Edward I prohibits the use of coal near the Royal Palace in London
- In 1661, John Evelyn in his book entitled *Fumifugium*, describes a "horrid smoake" that pollutes rain and the air.

Air Pollution: An Old Problem (2)

- The word "*smog*" is introduced by British physician Harold Des Voeux (smoke + fog)
- French scientists M. Ducros introduces the term "*acid rain*" (pluie acide) in 1845
- The impact of air pollution on rainfall acidity is considered by Angus Smith in his book "*Air and Rain*" in 1872.
- Major air pollution incidents are occurring in industrial areas during f the 20th century: Meuse Valley in Belgium (1929), Donora, PA (1948) Seveso, Italy (1976), Bhopal, India (1984, causing the death of more than 2000 people).

Historical Perspective

a. Local Air Pollution

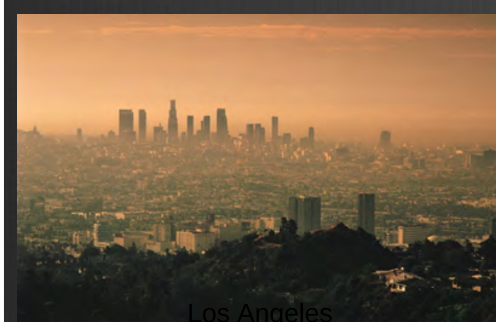
1900-1970: Local Pollution

2000

London, 1952

London Smog

1873	Londres	1000 morts (?)	*smog* soufré
1909	Glasgow	1000 morts	*smog* soufré
1930	Vallée de la Meuse (Belgique)	60 morts	*smog* soufré
1948	Donora (États-Unis)	20 morts	*smog* soufré
1952	Londres : *Great Smog*	4000 morts	*smog* soufré
1962	Londres	750 morts (?)	*smog* soufré
1966	New York (24-30 novembre)	168 morts	*smog* soufré
1984	Bhopal (Inde)	2000 morts	accident chimique
1986	Tchernobyl (URSS)	?	accident nucléaire



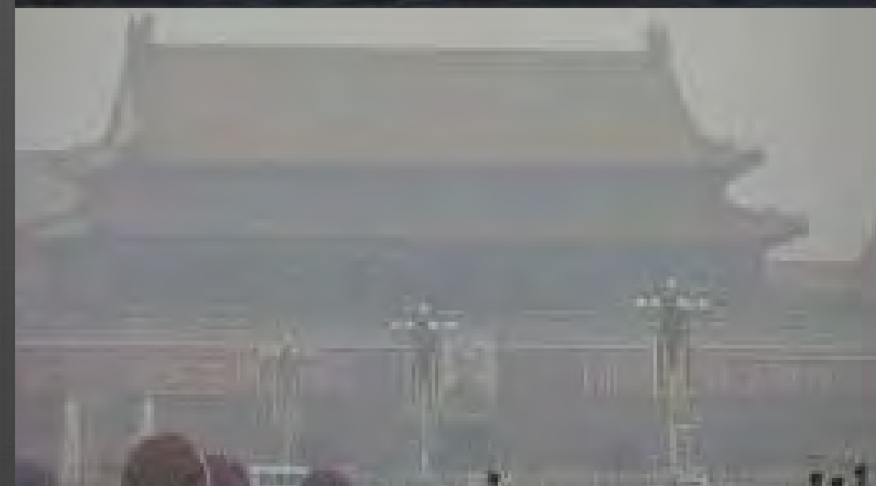
Los Angeles

Photochemical Smog
(Los Angeles)

From
Pierre
Coheur

Smog in London



Air Pollution: An Old Problem (3)

- Accute summertime air pollution episodes are observed in large urban areas like Los Angeles, Mexico City and Tokyo.
- Biochemist Arie Jan Haagen-Smit suggests in 1950 that the formation of near-surface ozone is produced by the action of sunlight on a mixture of reactive hydrocarbons and nitrogen oxides released by refineries and automobiles

Historical Perspective

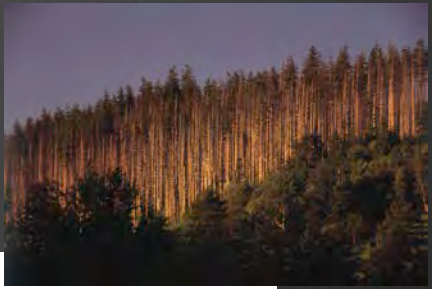
b. Acid Rain

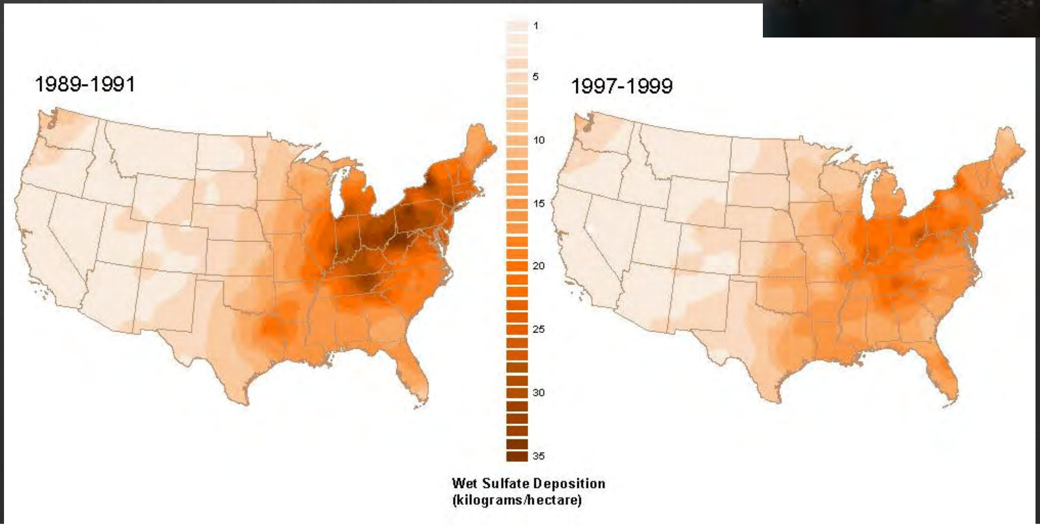
1900

1970: Acid Rain and transboundary Pollution

2000

"Air quality in any European country is measurably affected by emissions from other European countries… [and] if countries find it desirable to reduce substantially the total deposition of sulphur within their borders, individual national control programmes can achieve only limited success" (OCDE, 1977)





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Historical Perspective

c. Intercontinetal Transport of Air Pollutants

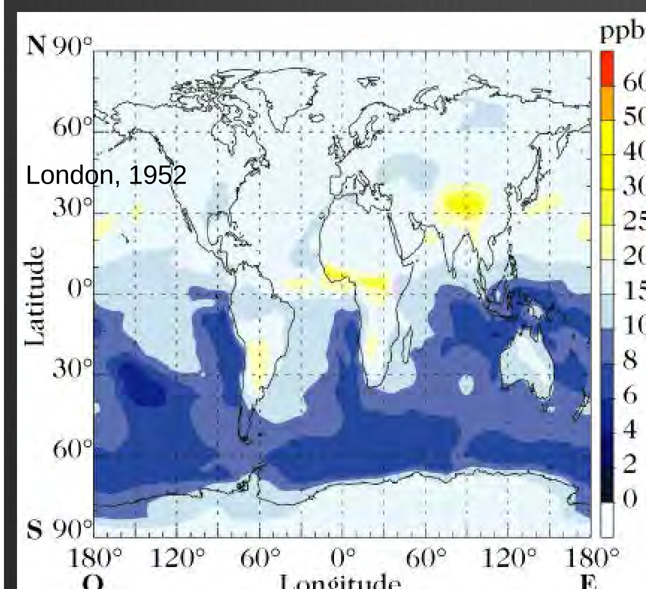
1900-1970: Local Pollutions

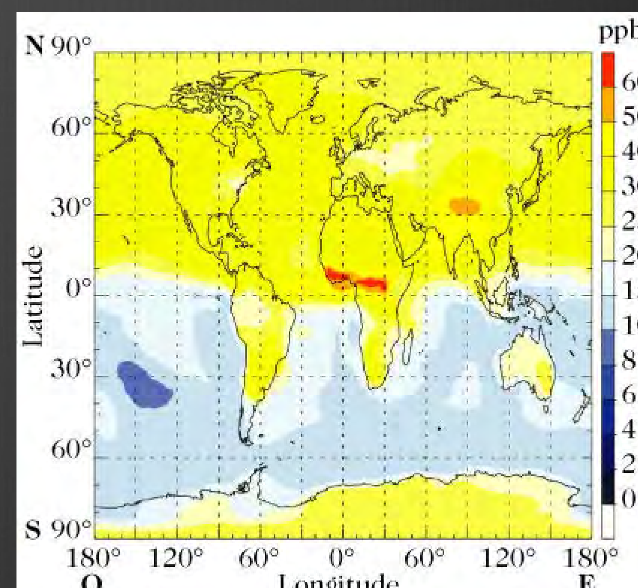
1990: Transboundary Pollution (regional → global))

Pre-industrial Period

Present

Surface $[O_3]$





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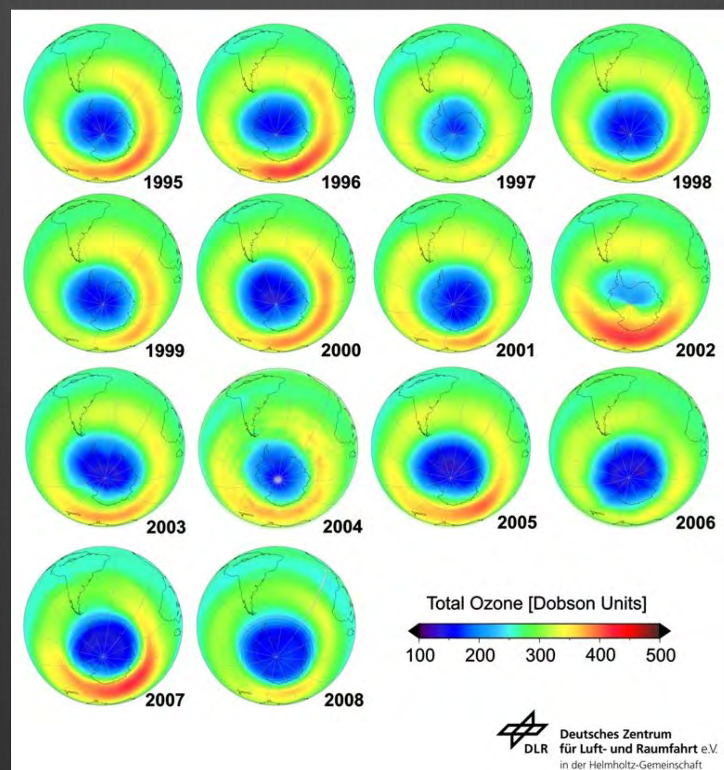
Historical Perspective

d. Ozone Depletion

1900 — 1985: ozone hole — 2000



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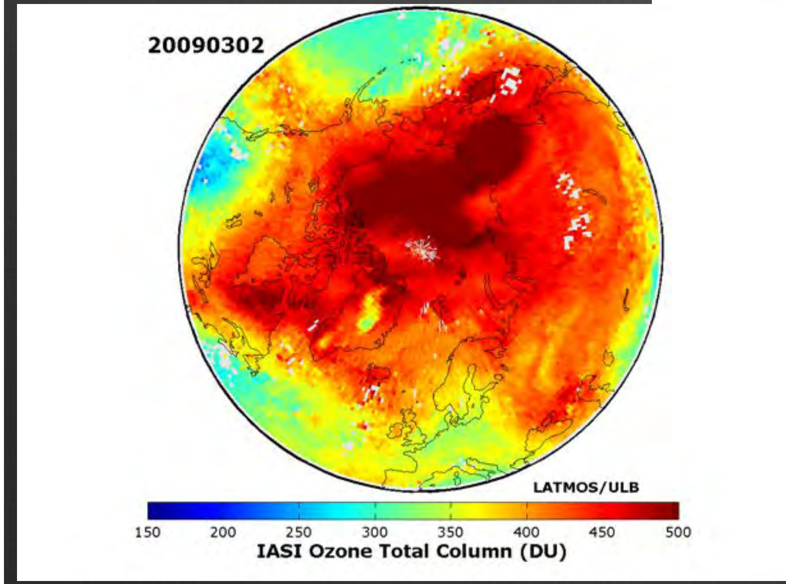
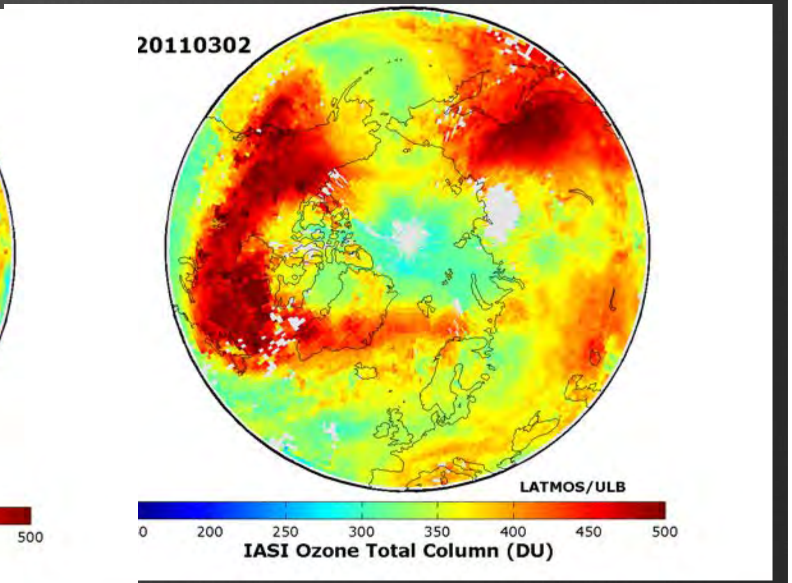
Historical Perspective

d. Ozone depletion

1900 — 1985: Ozone hole — 2000

Ozone Destruction in the Arctic in 2009 and 2011





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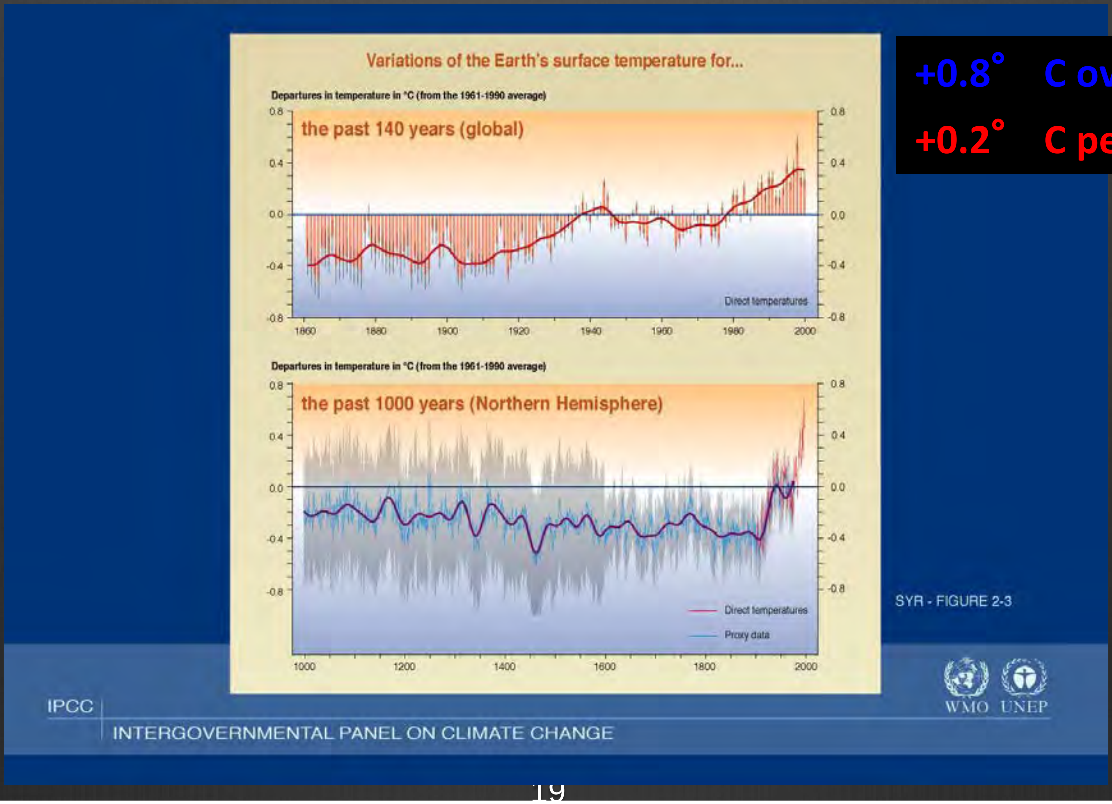
Shortcut to IASIO3.mp4.lnk

Historical Perspective

e. Climate Change

1900

2000



+0.8° C over the last century

+0.2° C per 10 years since 1975

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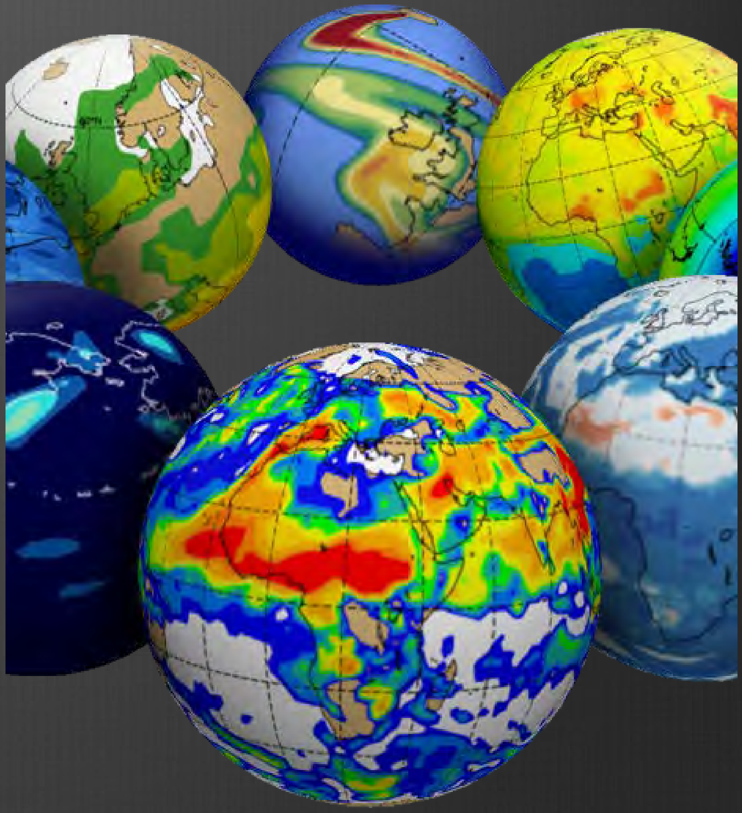
The Approaches

Observations
Modeling
Data Assimilation

The Approaches

Observations



Large number and diversity of trace species pose a great challenge with regard to a thorough understanding of the complex chemical and physical processes and interactions involved.

Measurement - Techniques for Atmospheric Trace Gases

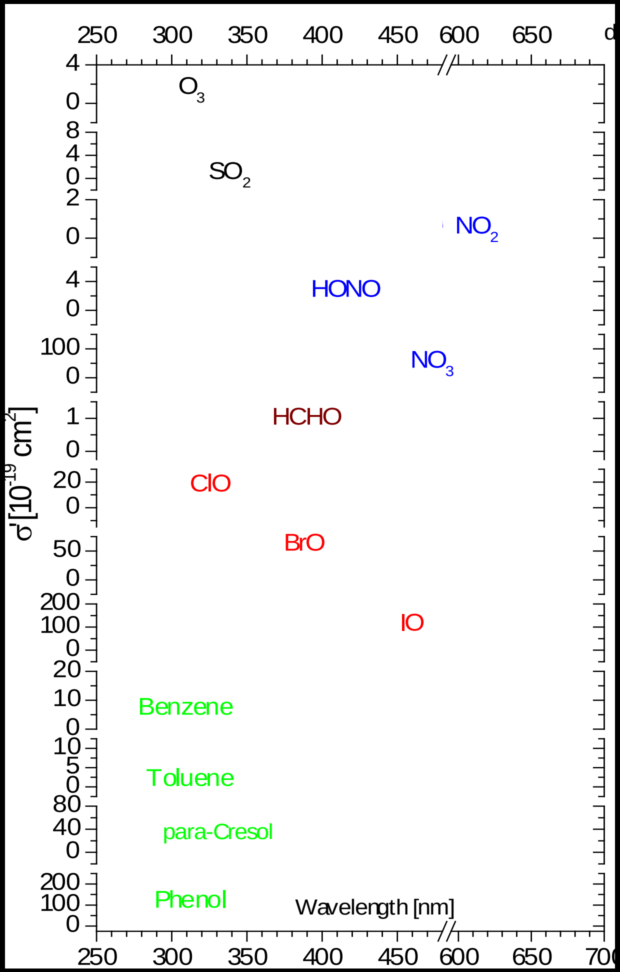
Require-ments

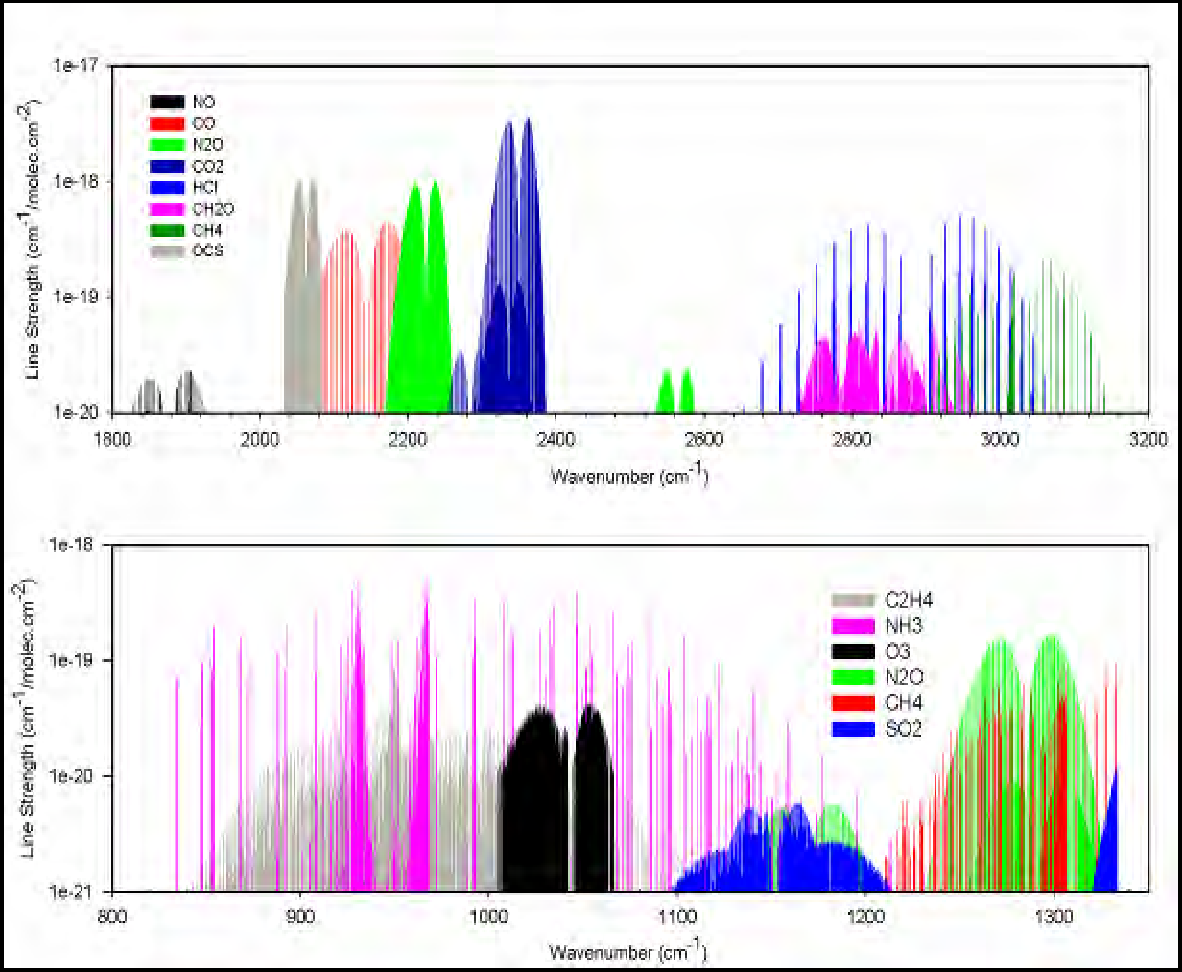
- **Sensitivity:** Even at mixing ratios of $\approx 10^{-13}$, (0.1 ppt, about 2×10^6 molec./cm^3) some species (like OH, IO) significantly influence atmospheric chemistry.
- **Specificity:** The result of the measurement of a particular species must not be influenced by any other trace species present in the air.
- **Spatial coverage:** In-situ vs. remote sensing
- **Time resolution**
- **Calibration** should be easy (inherent?), stable, ...
- Simple design and use of the instruments, unattended operation, portability …

Appli-cations

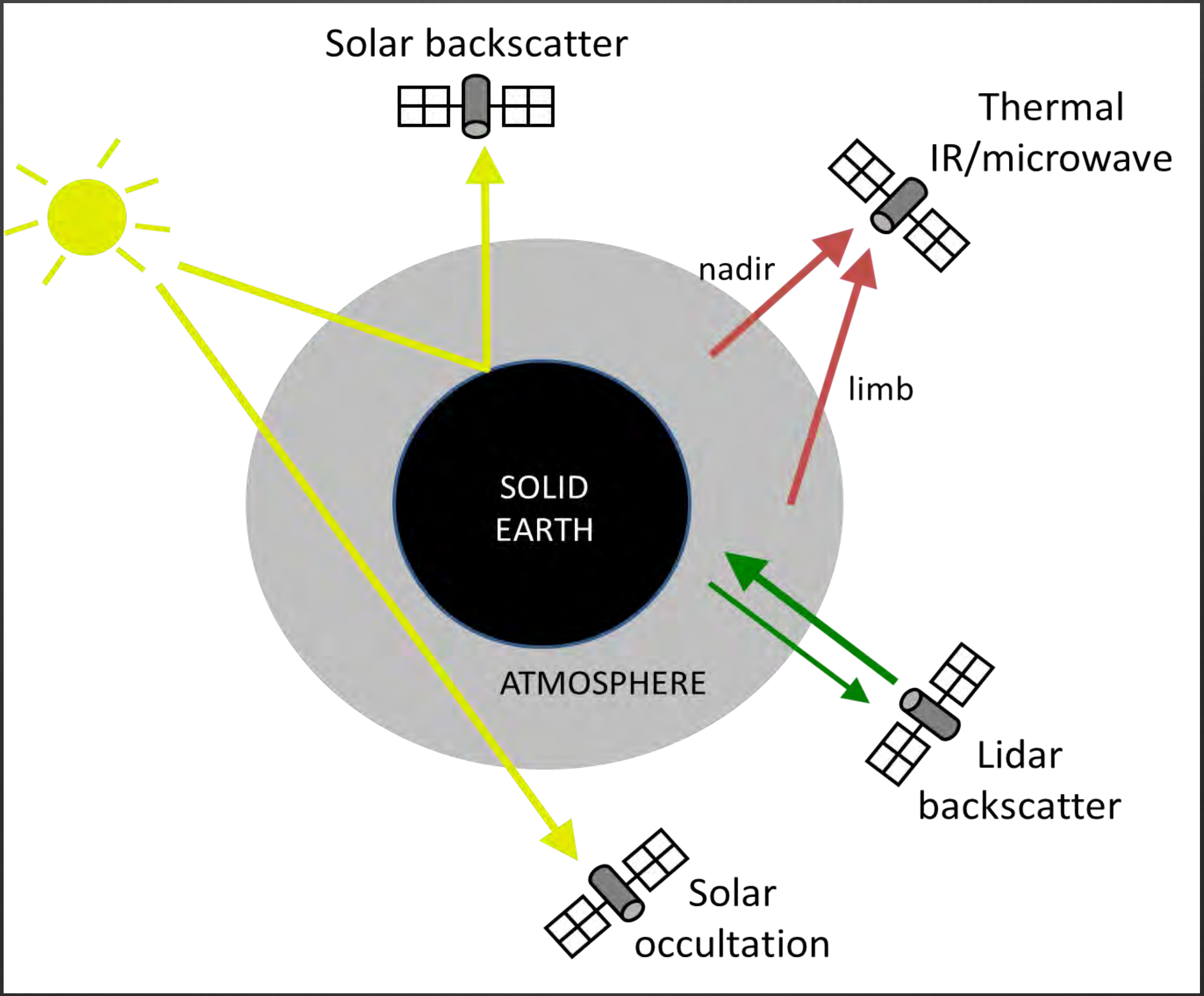
- **Long Term Observations – Global Change**
  - Stratospheric ozone trend
  - Change of Stratospheric chemistry (NDACC)
  - Stratospheric (chlorine) source-gases in the troposphere
  - Tropospheric ozone trend (GAW)
  - Greenhouse gase
- **Regional Episodic Events**
  - Pollution monitoring
  - Urban plume evolution
  - Continental plumes
  - Antarctic Ozone Hole
  - Polar boundary-layer ozone loss events
- **Fast in-situ (Photo)chemistry - Process studies**
  - Free radical (OH/HO_2) photochemistry

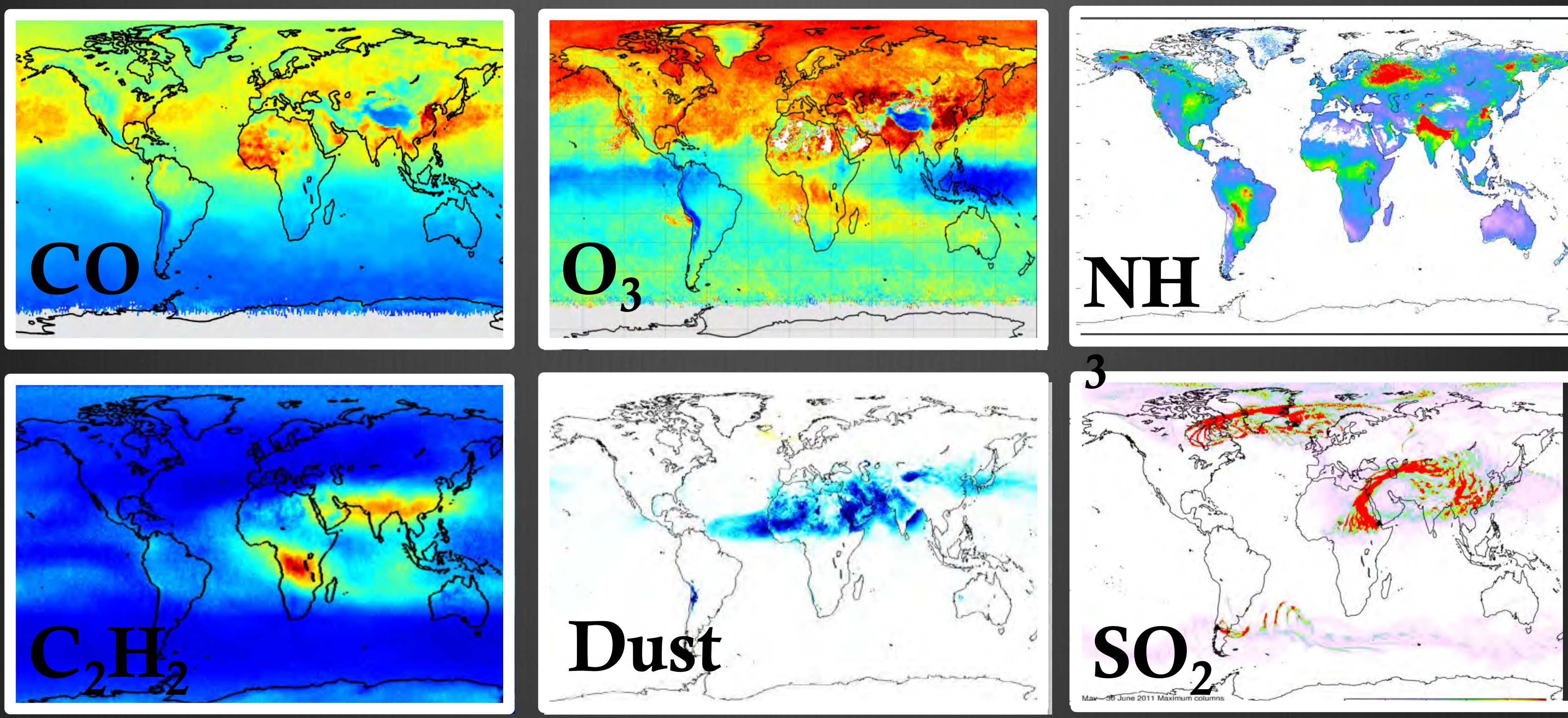
Absorption of trace gases in UV-IR





Different views from Space



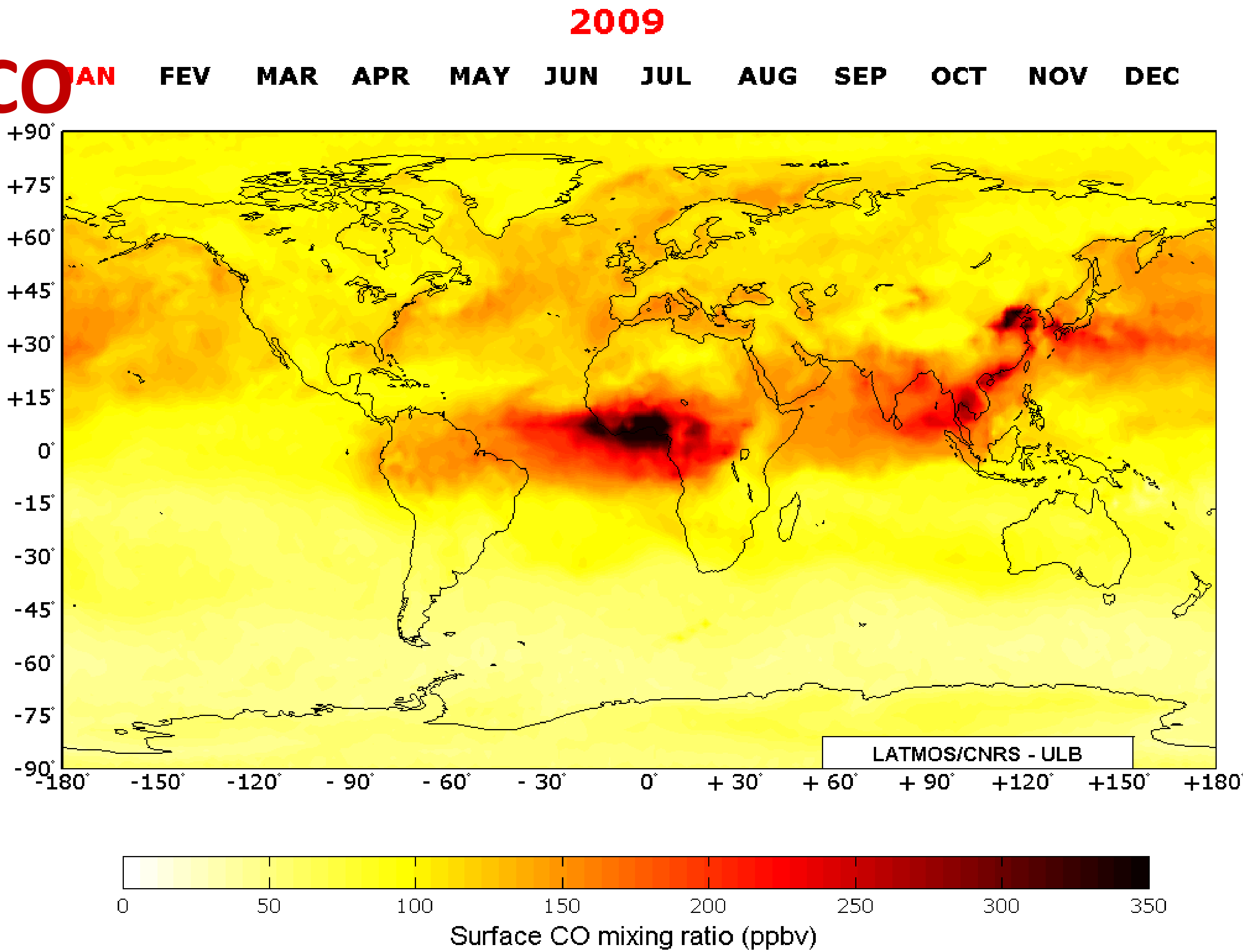


→ We can now monitor a large number of chemical species on the global scale

LATMOS ULB

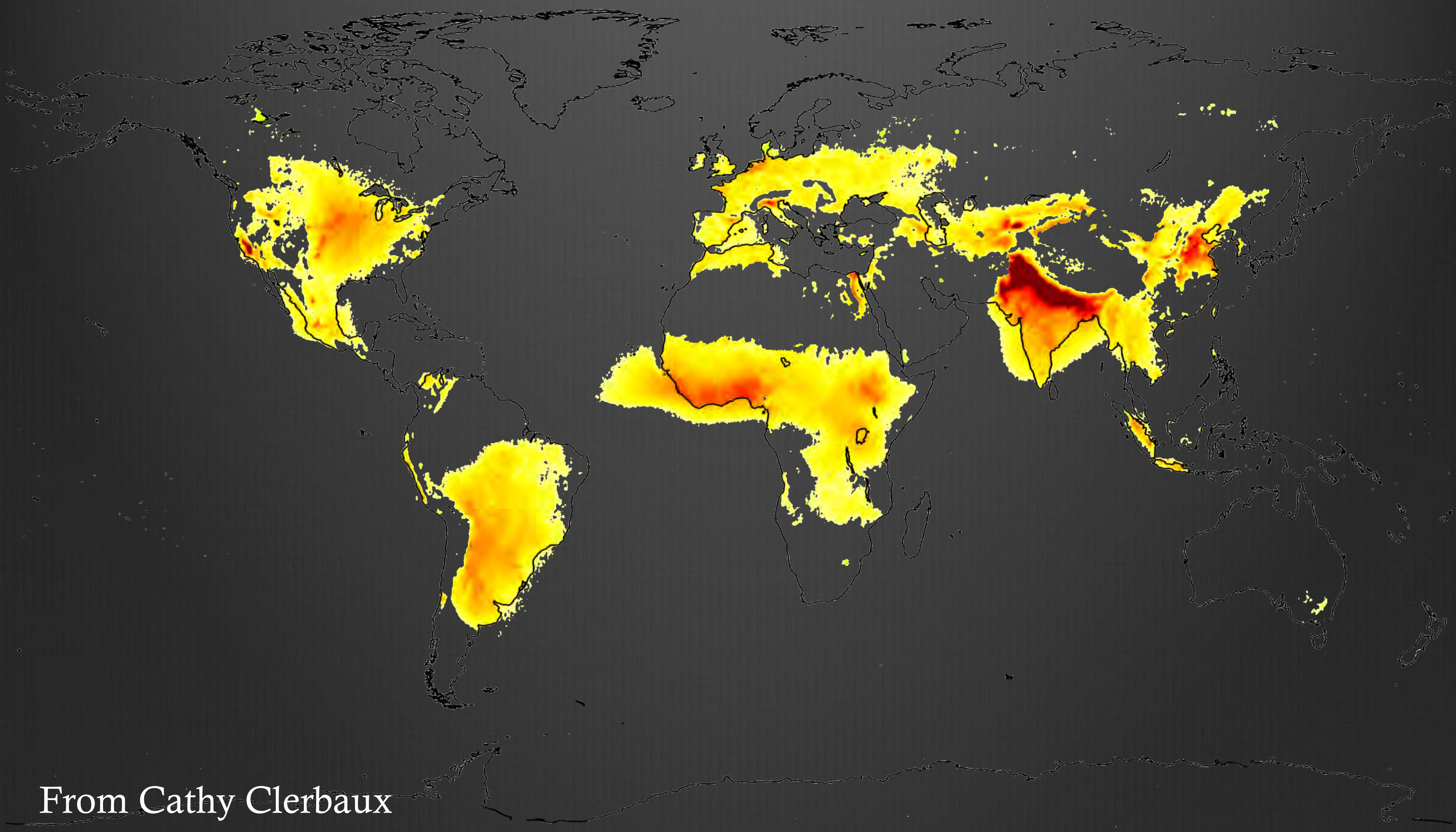
From Cathy Clerbaux

CO



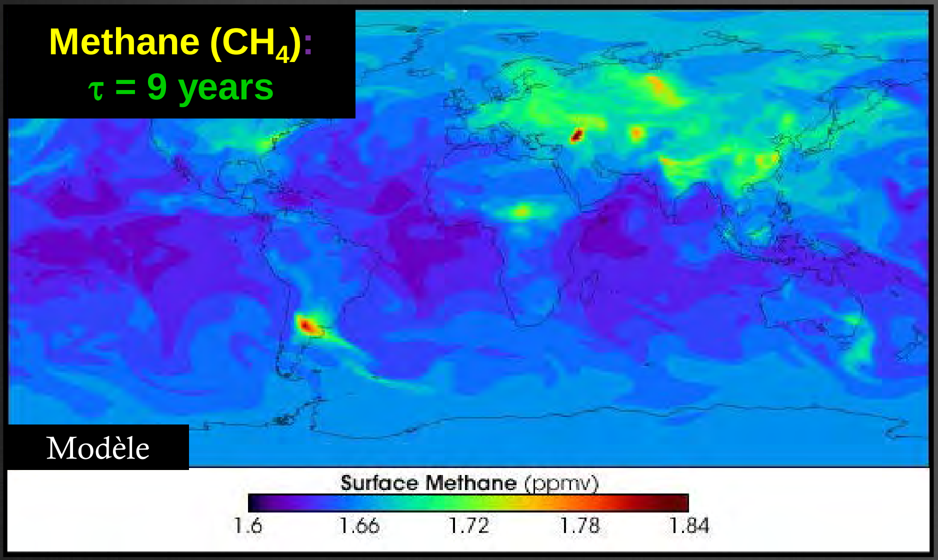
Courtesy M. George, LATMOS

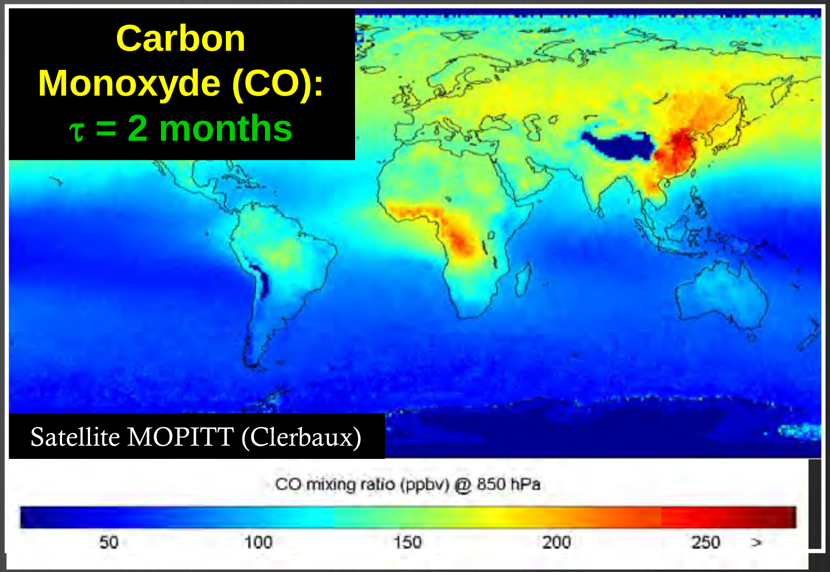
IASI ammonia (NH_3)
7 years (2008-2014)

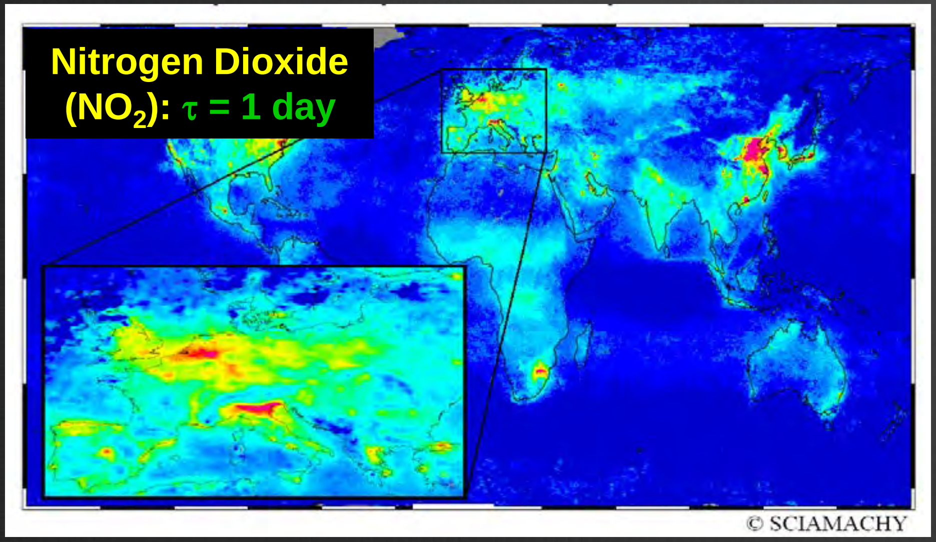


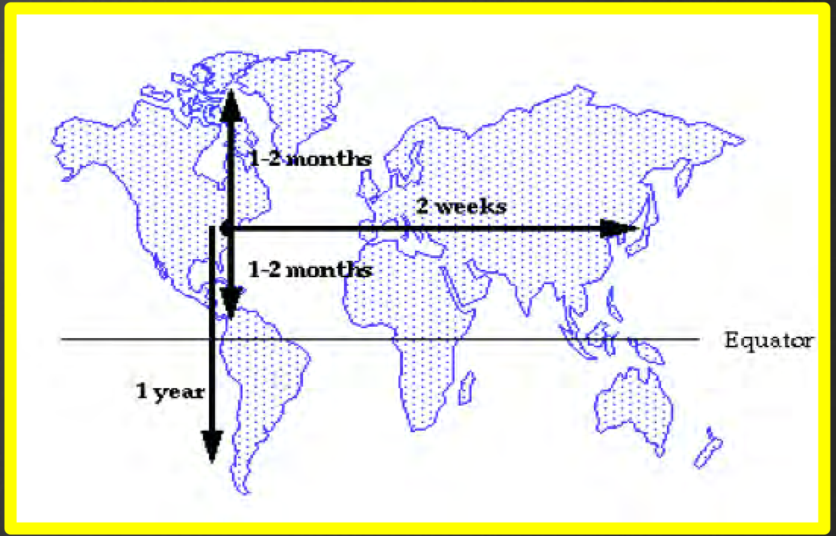
From Cathy Clerbaux

Horizontal Distributions

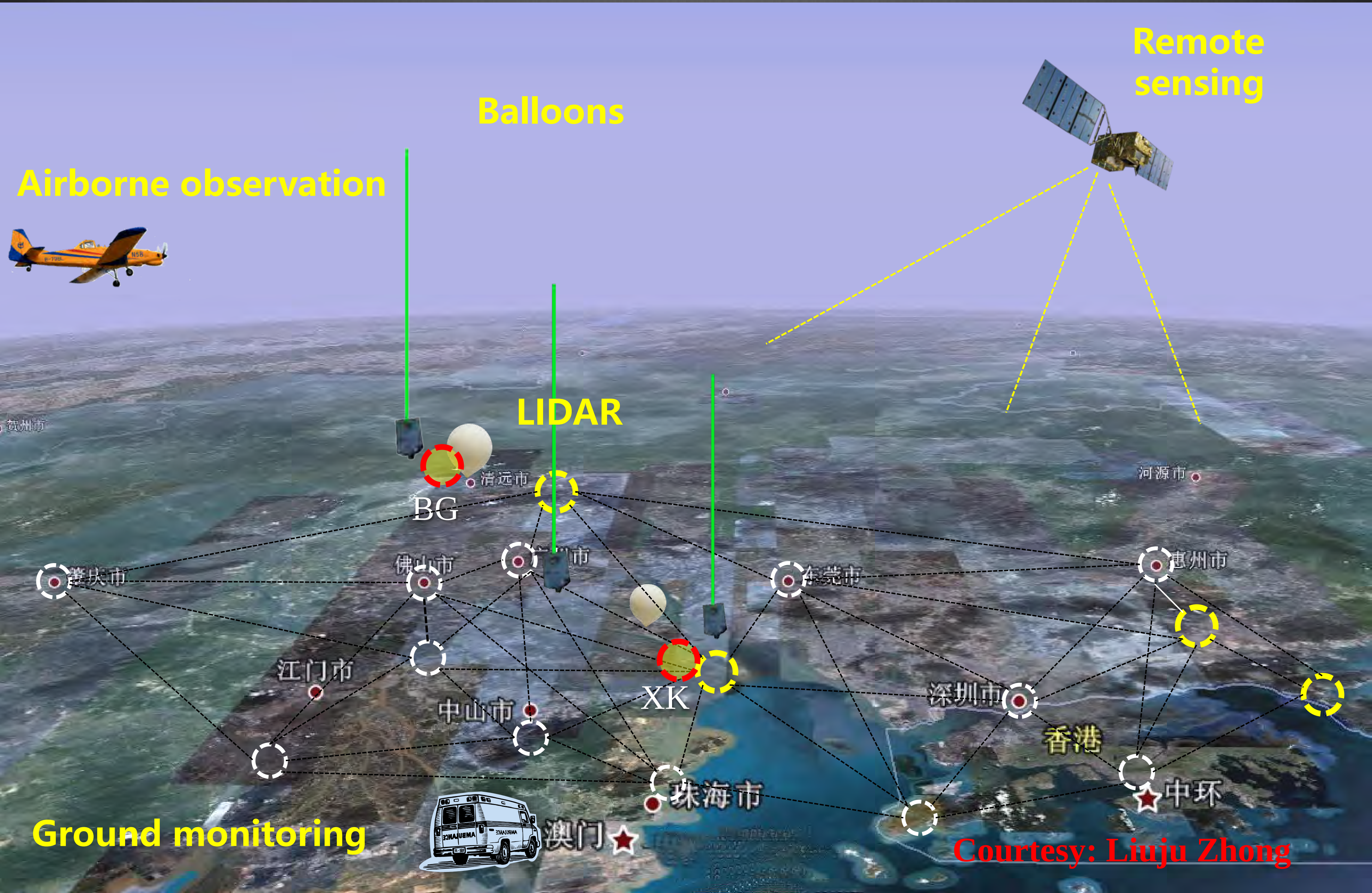




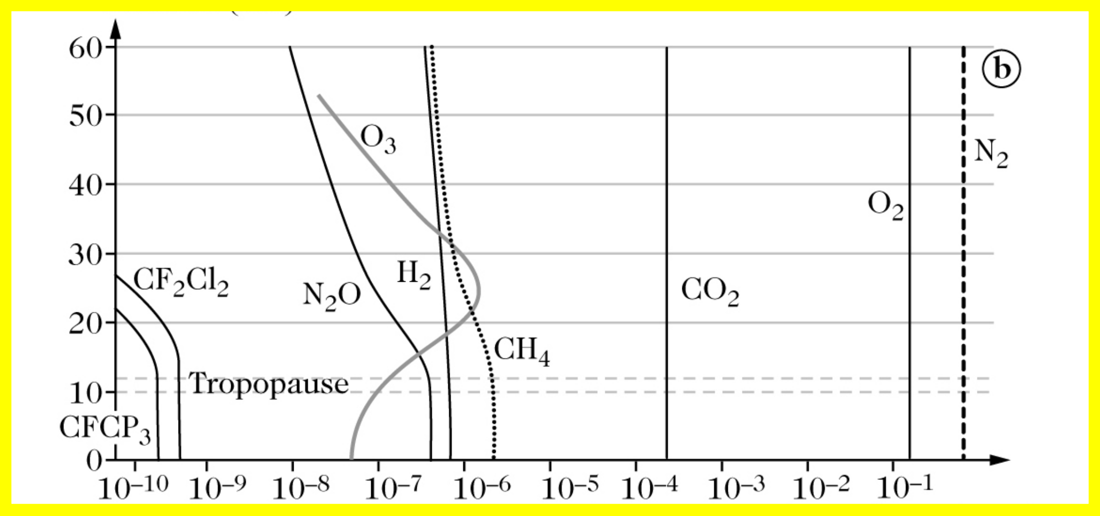


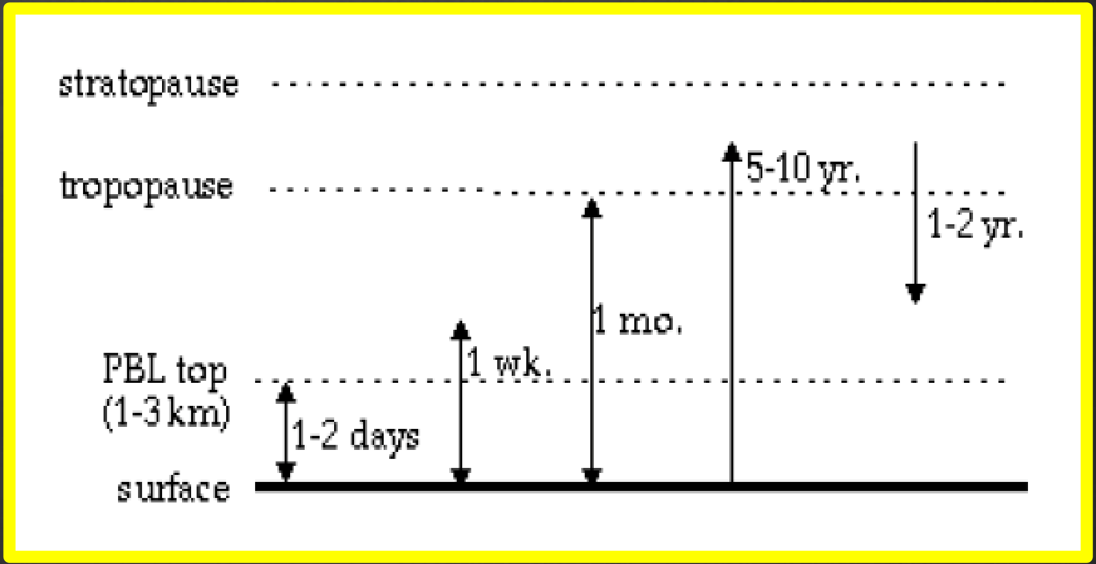


Three-dimensional observation system



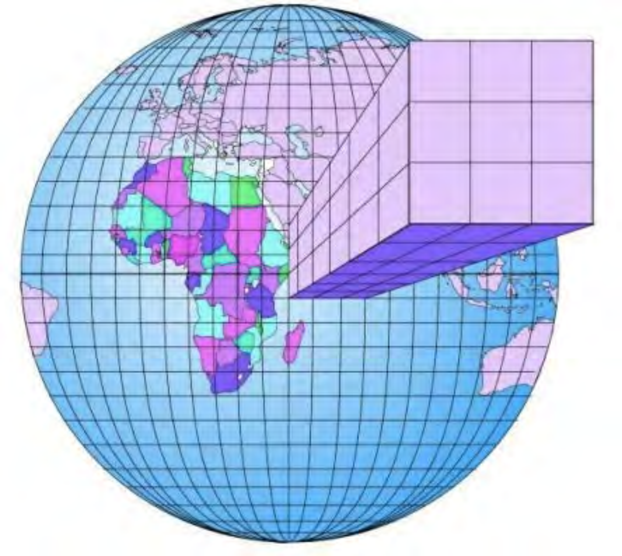
Vertical Distributions and Exchanges





The Approaches

Modeling



What is a Model?

A model is:

- **an idealized representation or abstraction of an object** with the purpose **to demonstrate the most relevant or selected aspects** of the object or **to make the object accessible to studies**
- **a formalized structure** used to account for an **ensemble of phenomena** between which certain **relations** exist.
- Some kind of **prototype, image, analog or substitute** of a **real system.**
- An object that is conceptually **isolated**, technically **manipulated** and socially **communicated.**

What is a Model?

- **Purpose of models**: To obtain a theoretically or practically manageable system by reducing its complexity and removing details that are not relevant for specific consideration.

- **Citation** by Alexander von Humbolt (The Cosmos): "By suppressing details that distract, and by considering only large masses, one rationalizes what cannot be understood through our senses".

Different Types of Models

- **Conceptual Models** help to assess the consequences of some hypotheses. These models are usually very simple and focused on some issue, but trigger interest and sometimes new research. There is no attempt to reproduce perfectly the real world. Examples: The Daisy model of Lovelock (the Earth acts as a thermostat).

- **Detailed Models** try to reproduce as closely as possible the real world. Their success depends on the level of fidelity in representing real situations. Examples: Numerical Weather Forecast Models.

Theory and Model

- A scientific model is an abstract representation of the essential aspect of an object or an ensemble of objects, usually expressed as figures, diagrams, symbols that are useful to scientific understanding.
- A theory is a conceptual system described in a language that accounts for an ensemble of phenomena (and attempts to explain them).
- Models as complements of theories. Models to be used when theories are too complex to handle. Models as preliminary theories.

What is a Model?

- Simulation modeling represents a way to create **virtual copies** of the Earth in cyberspace. These virtual copies (often supported by computing devices) can be submitted to **all kinds of forcings** and experiments without jeopardizing the true specimen.

- For example, it is possible to explore the domains in the **Earth system "phase space"** that are reachable without creating catastrophic and irreversible damage to mankind.

Variables and Equations

- Variables: Pressure p
  - Density $\boxed{\rho}$
  - Temperature T
  - Wind components (u, v, w)
  - Concentration of (many) interacting chemical species
- Equations:
  - Momentum equation (3 components)
  - Thermodynamic equation
  - Continuity equation for air
  - Equation of state (perfect gas)
  - Continuity equations for chemical species

Fundamental Equations

- ***Momentum equations on a rotating sphere:*** Express the wind acceleration in response to different forces: gravity, gradient force, Coriolis force
- ***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 for air :*** Expresses the conservation of mass
- *Continuity equation for chemical species*: expresses the change in concentration resulting from transport, chemical reactions, microphysical processes, emission, surface deposition

Chemical Transport Models

The atmospheric evolution of a species X is given by the *continuity equation*

$$\frac{\partial[X]}{\partial t} = E_X - \nabla \bullet (\mathbf{U}[X]) + P_X - L_X - D_X$$

local change in concentration with time

emission

transport (flux divergence; U is wind vector)

chemical production and loss (depends on concentrations of other species)

deposition

This equation cannot be solved exactly ⇨ need to construct *model* (simplified representation of complex system)

Chemical Transport Models

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Improve model, characterize its error

Define problem of interest

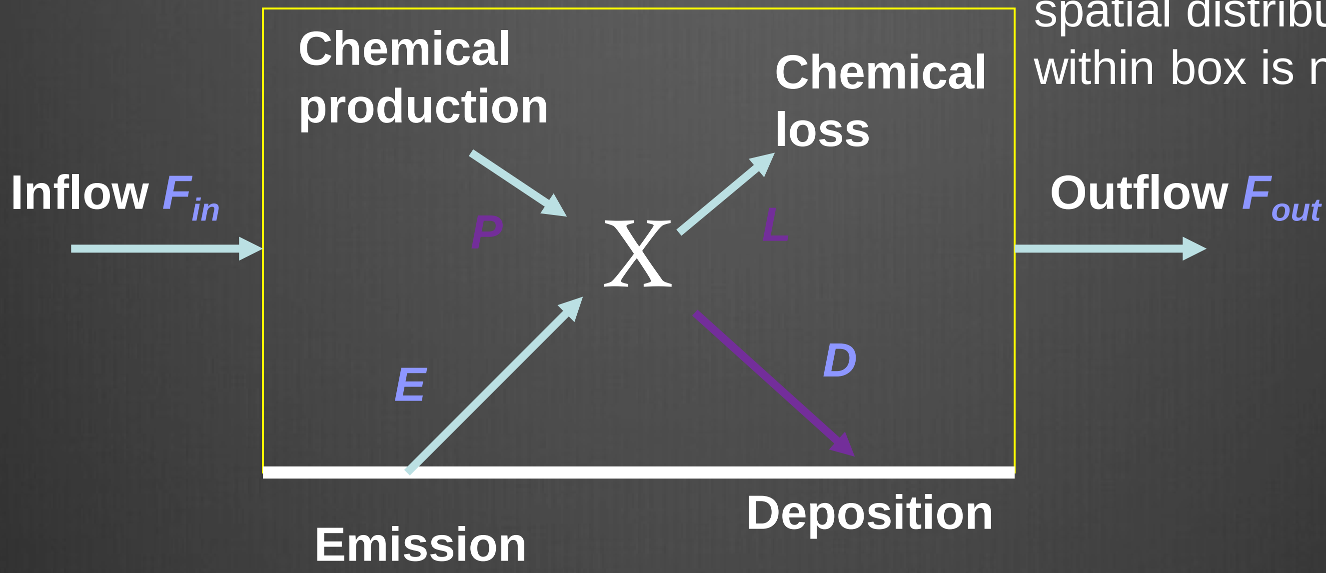
Design model; make assumptions needed to simplify equations and make them solvable

Design observational system to test model

Evaluate model with observations

Apply model: make hypotheses, predictions

One Box Model



Atmospheric "box"; spatial distribution of X within box is not resolved

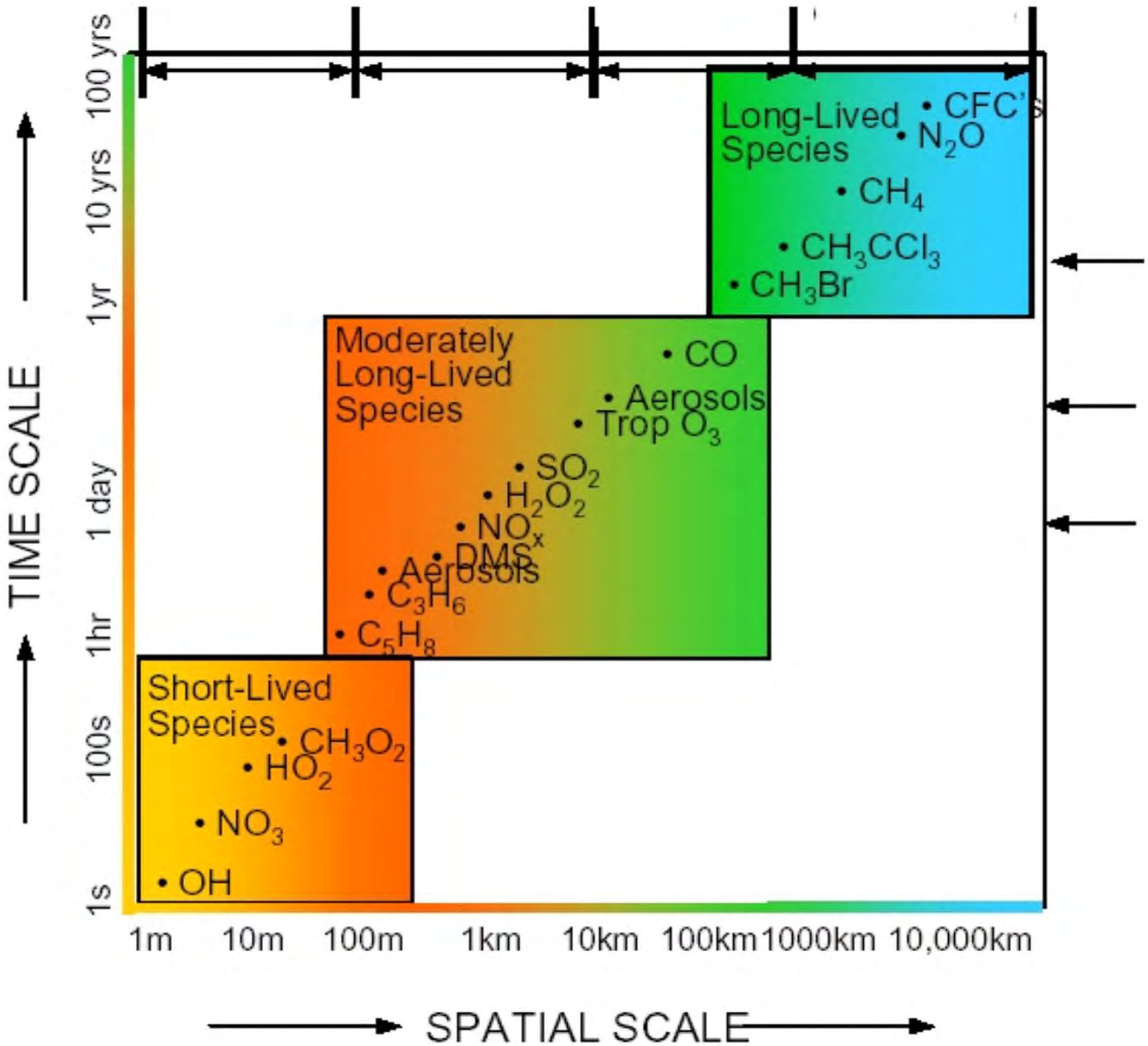
Mass balance equation: $$\frac{dm}{dt} = \sum \text{sources} - \sum \text{sinks} = F_{in} + E + P - F_{out} - L - D$$

Atmospheric lifetime: $$\tau = \frac{m}{F_{out} + L + D}$$

Fraction lost by export: $$f = \frac{F_{out}}{F_{out} + L + D}$$

Lifetimes add in parallel: $$\frac{1}{\tau} = \frac{F_{out}}{m} + \frac{L}{m} + \frac{D}{m} = \frac{1}{\tau_{export}} + \frac{1}{\tau_{chem}} + \frac{1}{\tau_{dep}}$$

Loss rate constants add in series: $$k = \frac{1}{\tau} = k_{export} + k_{chem} + k_{dep}$$



TIME SCALE
100 yrs
10 yrs
1yr
1 day
1hr
100s
1s
Long-Lived Species
CFC's
N_2O
CH_4
CH_3CCl_3
CH_3Br
Moderately Long-Lived Species
CO
Aerosols
Trop O_3
SO_2
H_2O_2
NO_x
DMS
Aerosols
C_3H_6
C_5H_8
Short-Lived Species
CH_3O_2
HO_2
NO_3
OH
1m
10m
100m
1km
10km
100km
1000km
10,000km
SPATIAL SCALE

Atmospheric Reactions

Photolysis

Unimolecular

$$X \xrightarrow{h\nu} Y + Z$$

$$v = J_\lambda [X]$$

$$J_\lambda = \int_\lambda q_\lambda(X)\sigma_\lambda(X) I_\lambda d\lambda$$

Quqntum Yield

Absorption cross section (cm^2 $molecules^{-1}$)

Actinic Flux cm^{-2} s^{-1}

Thermal Reactions

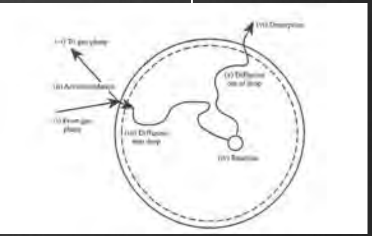
Bimolecular

$$A + B \xrightarrow{k_r} C + D$$

Termolecular

$$A + B \xrightarrow[M]{k_r} AB$$

Heterogenous Reactions



$$v = \frac{1}{4}\gamma \bar{\upsilon}_A A_p n_A$$

« uptake coefficient »
= reaction probability

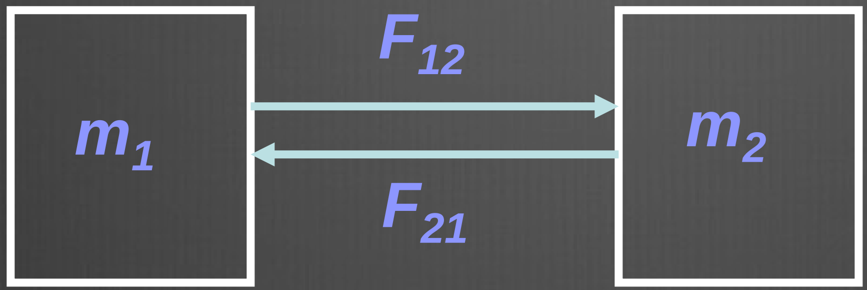
Thermal velocity of A

Surface of collision per volume of air (cm^2 cm^{-3})

Density

Two-Box Model

defines spatial gradient between two domains



Mass balance equations:

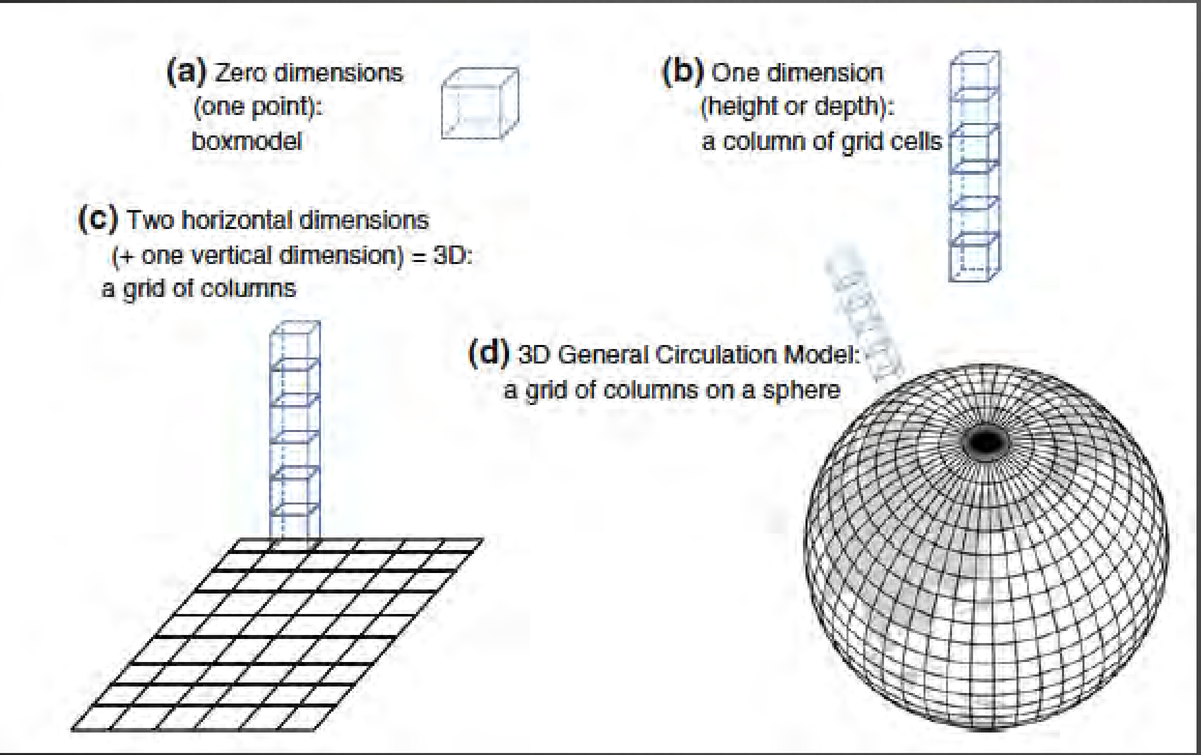
$$\frac{dm_1}{dt} = E_1 + P_1 - L_1 - D_1 - F_{12} + F_{21}$$

(similar equation for dm_2/dt)

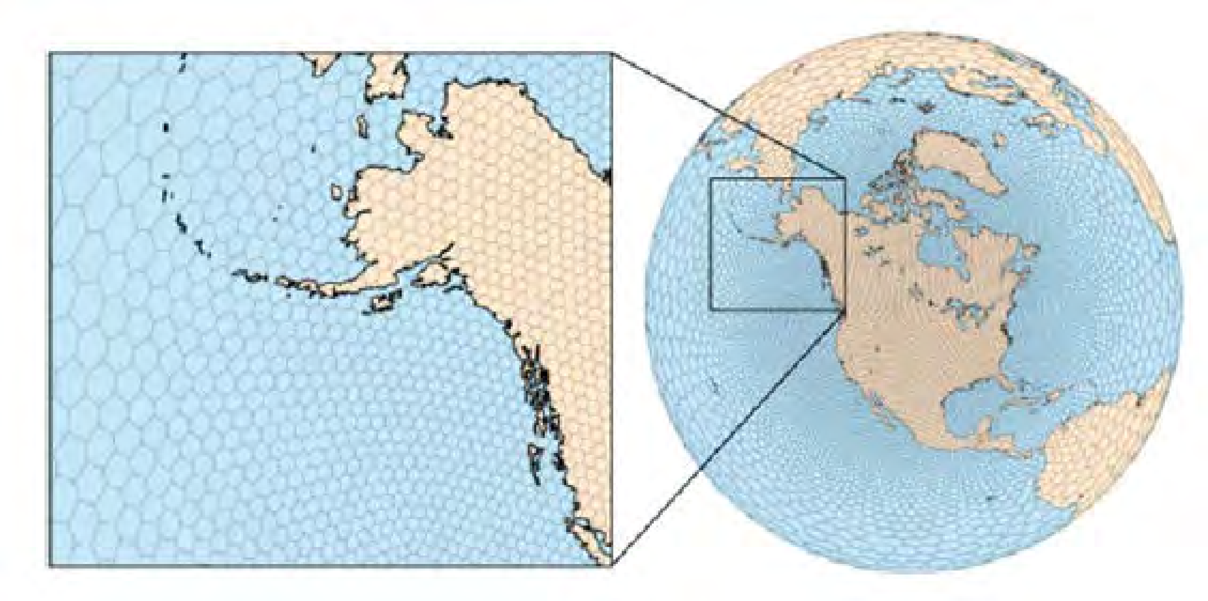
If mass exchange between boxes is first-order:

$$\frac{dm_1}{dt} = E_1 + P_1 - L_1 - D_1 - k_{12}m_1 + k_{21}m_2$$

⇨ system of two coupled ODEs (or algebraic equations if system is assumed to be at steady state)



Multi-box Model

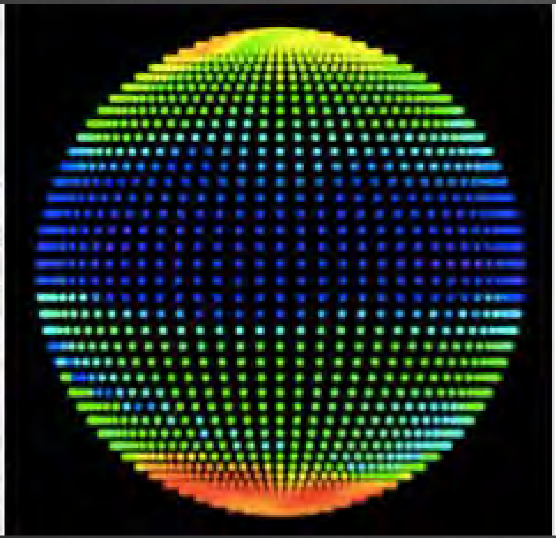
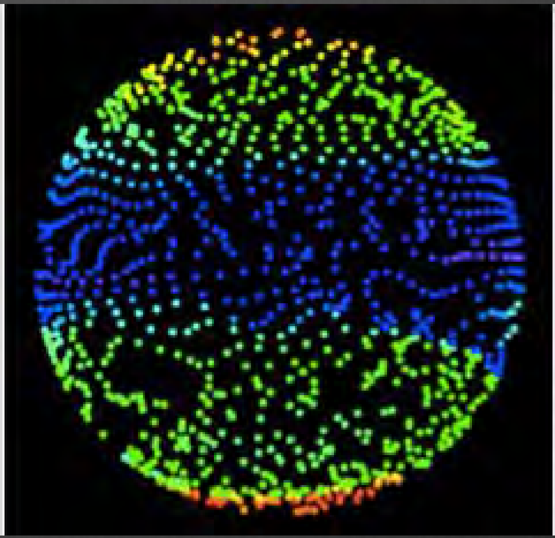


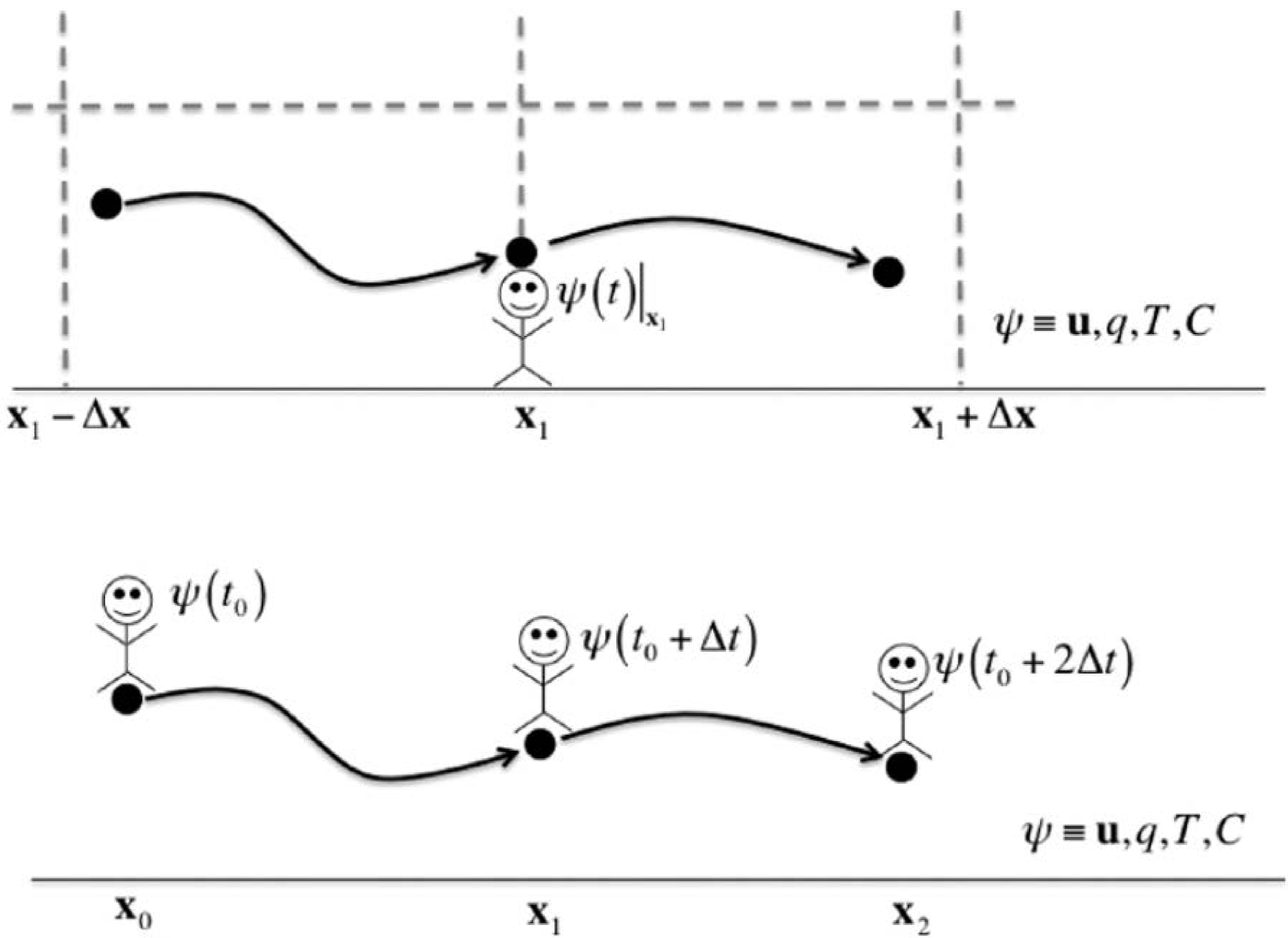
Advection

- 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

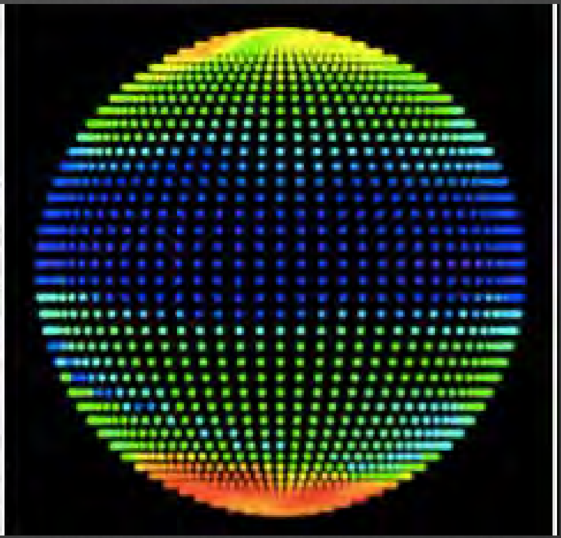
Euler versus Lagrange

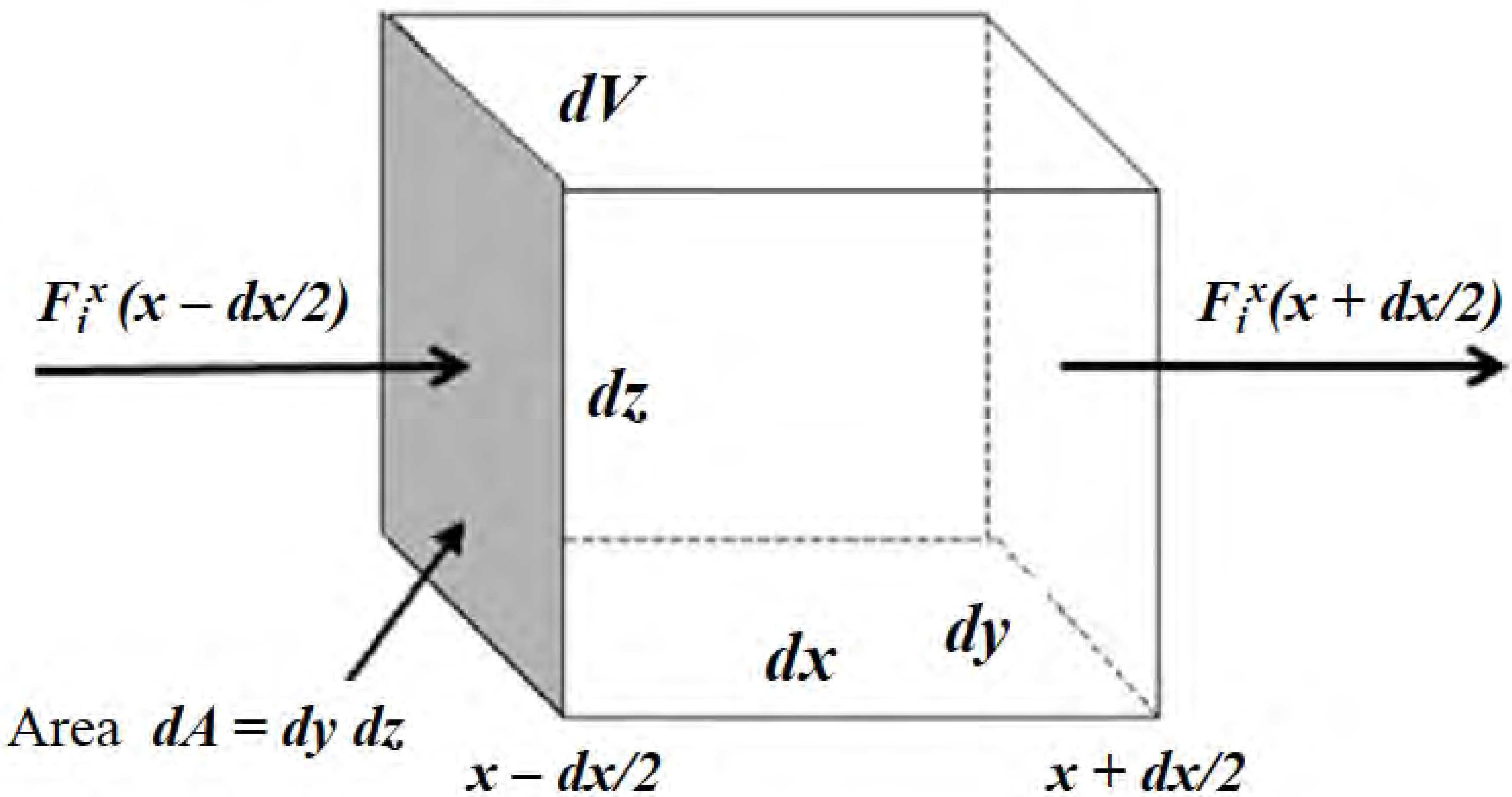




$\psi(t)|_{\mathbf{x}_1}$
$\psi \equiv \mathbf{u}, q, T, C$
$\mathbf{x}_1 - \Delta\mathbf{x}$
$\mathbf{x}_1$
$\mathbf{x}_1 + \Delta\mathbf{x}$
$\psi(t_0)$
$\psi(t_0 + \Delta t)$
$\psi(t_0 + 2\Delta t)$
$\psi \equiv \mathbf{u}, q, T, C$
$\mathbf{x}_0$
$\mathbf{x}_1$
$\mathbf{x}_2$

Euler





$$\left[\frac{\partial \rho_i}{\partial t}\right]_{adv} = \frac{\left[F_i^x\left(x - dx/2\right) - F_i^x\left(x + dx/2\right)\right]\,dydz}{dxdydz} = -\frac{\partial F_i^x}{\partial x} = -\frac{\partial\left(\rho_i u\right)}{\partial x}$$

Continuity Equation

Eulerian form of the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\ \mathbf{v}) = 0$$

where

ρ is the mass density of air

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

Continuity equation for Chemical Species

The continuity equation describes the dynamical and chemical processes that determine the distribution of chemical species

flux form:

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

advective form:

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

where,

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

ρ_a is the air mass (or number) density

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

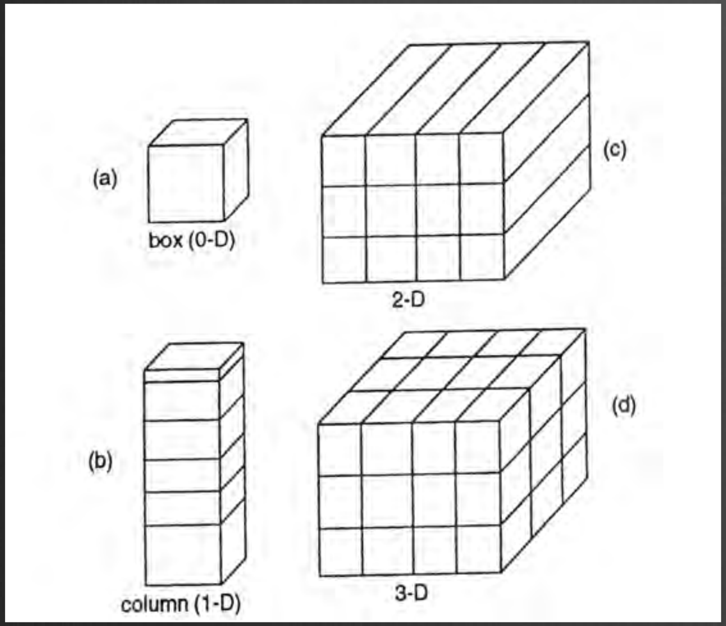
S_i is the production and loss rate of species i

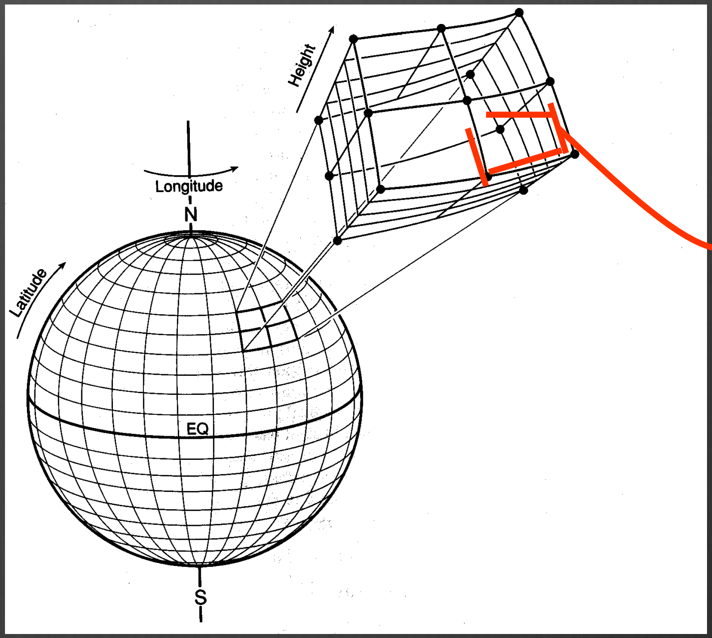
$\mathbf{v}$ is the wind velocity vector

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

Numerical Approaches to Solve the Continuity Equation

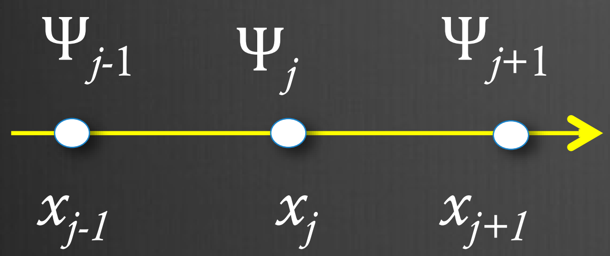
- ***Finite Difference Method:*** The derivatives are approximated by finite differences. Each unknown function is described by its values at a set of discrete *gridpoints.* The partial differential equation is replaced by a system of algebraic equations, which can be solved by standard methods.

- ***Finite Volume Method:*** The functions are represented by their value averaged over specified intervals called *grid cells* or *gridboxes*.

- ***Spectral and finite element methods***: The functions are expanded by a linear combination of orthogonal basis functions, and the coefficients appearing in these expansions become the unknowns.

Advection: Eulerian Methods

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



$$\frac{\partial \psi}{\partial x} \simeq \frac{\Psi_j - \Psi_{j-1}}{\Delta x}$$

$$\frac{\partial \psi}{\partial x} \simeq \frac{\Psi_{j+1} - \Psi_{j-1}}{2\Delta x}$$

*E*xample: one-dimensional advection equation:

Let's assume that ψ represents the density of a chemical species (velocity c is assumed constant)

$$\frac{\partial \psi}{\partial t} + c\frac{\partial(\psi)}{\partial x} = 0$$

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

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

Stable if Courant-Friedricks-Lewy (CFL) condition is satisfied:

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

Advection: Eulerian Methods

Courant-Friedrichs-Lewy (CFL) condition:

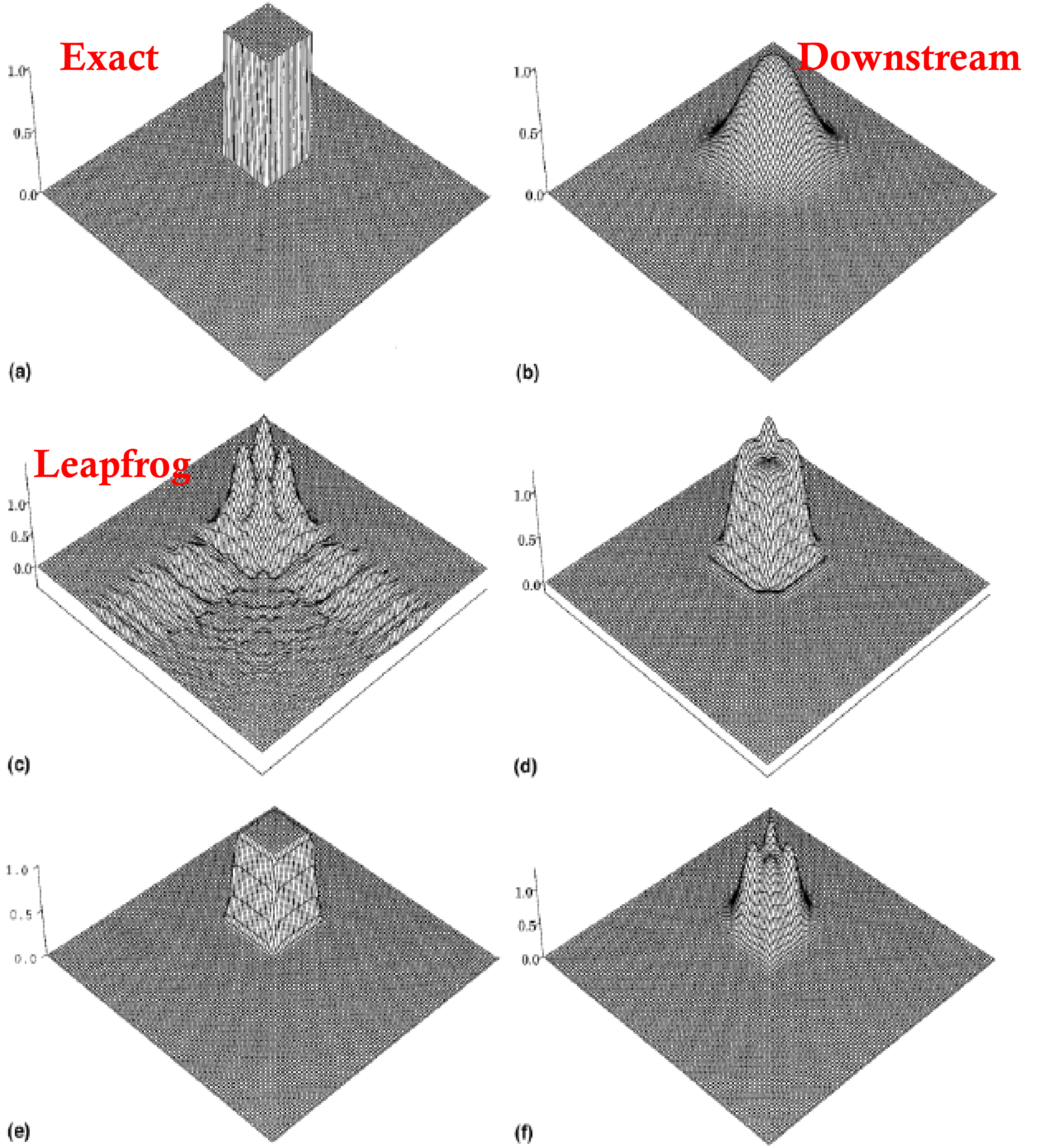
$$\frac{|c|\,\Delta t}{\Delta x} \leq 1$$

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.

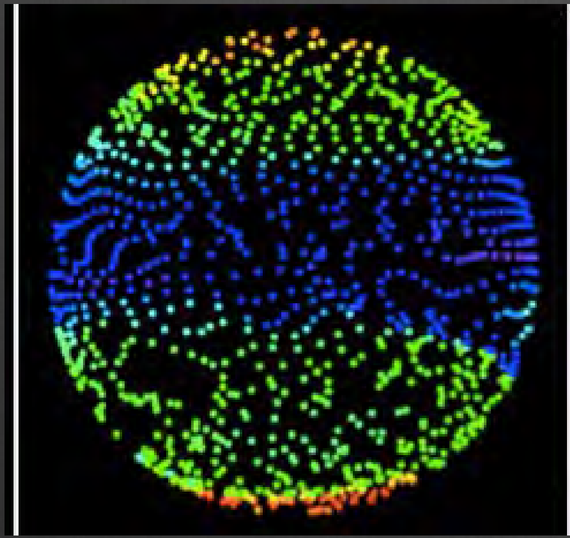
This is a major restriction for many global models beacuse near the pole, the CFL condition is often violated unless very small timesteps are adopted. Eulerian methods are routinely used in regional models.

Solution: Modified grids towards high latitudes or other algorithms

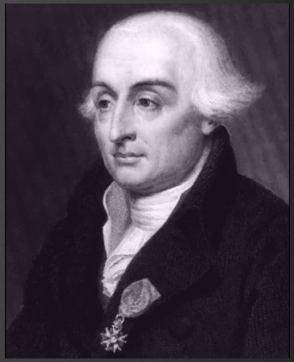
Numerical simulations of the rotation of a square function by different Eulerian algorithms.



Lagrange

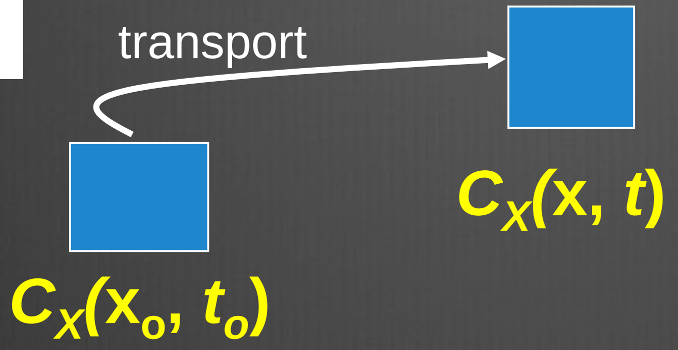


A Lagrangian View



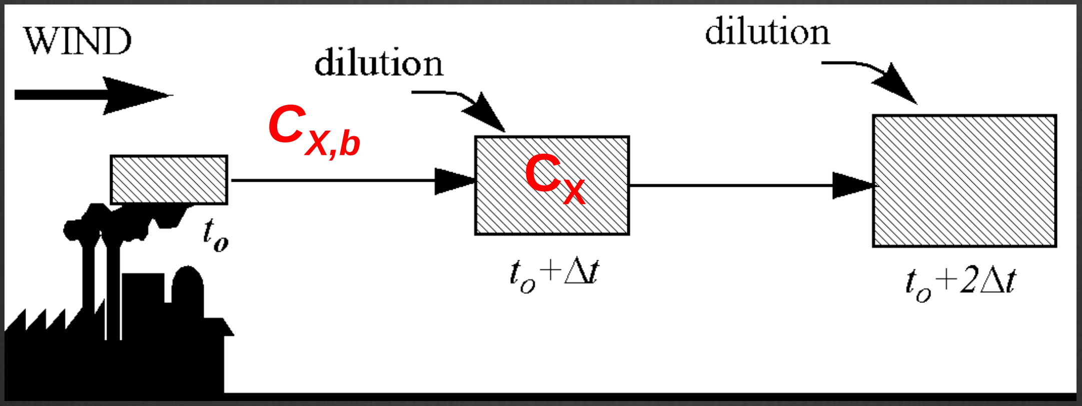
Following a Single Air Parcel

$$dX/dt = v(X,t)$$

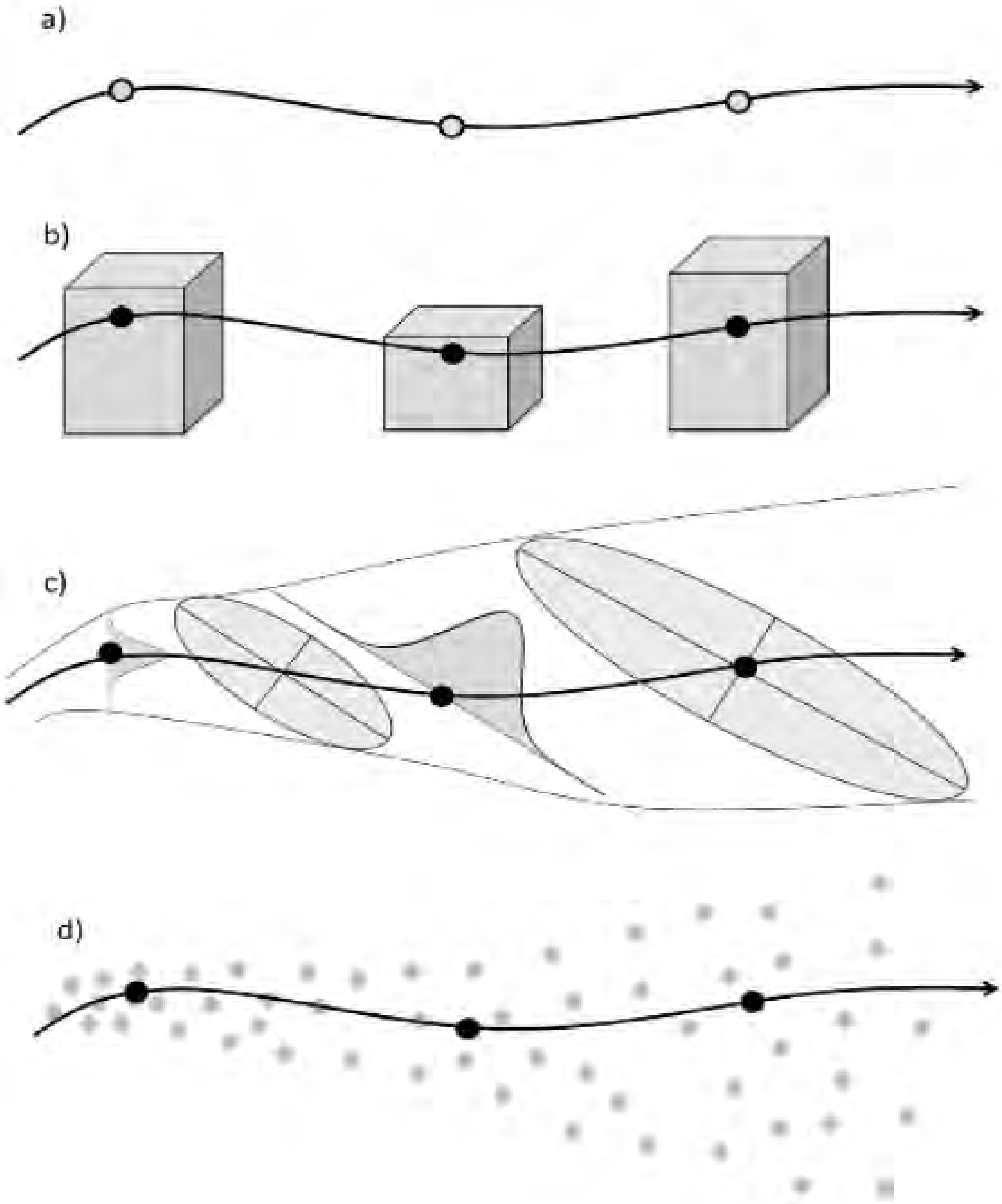


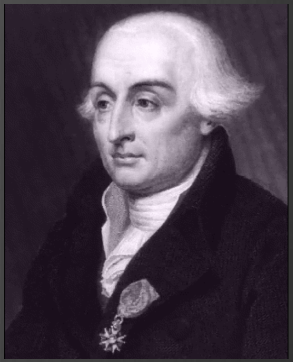
$$\frac{dC_X}{dt} = E + P - L - D$$

Following an Air Parcel in a Plume



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



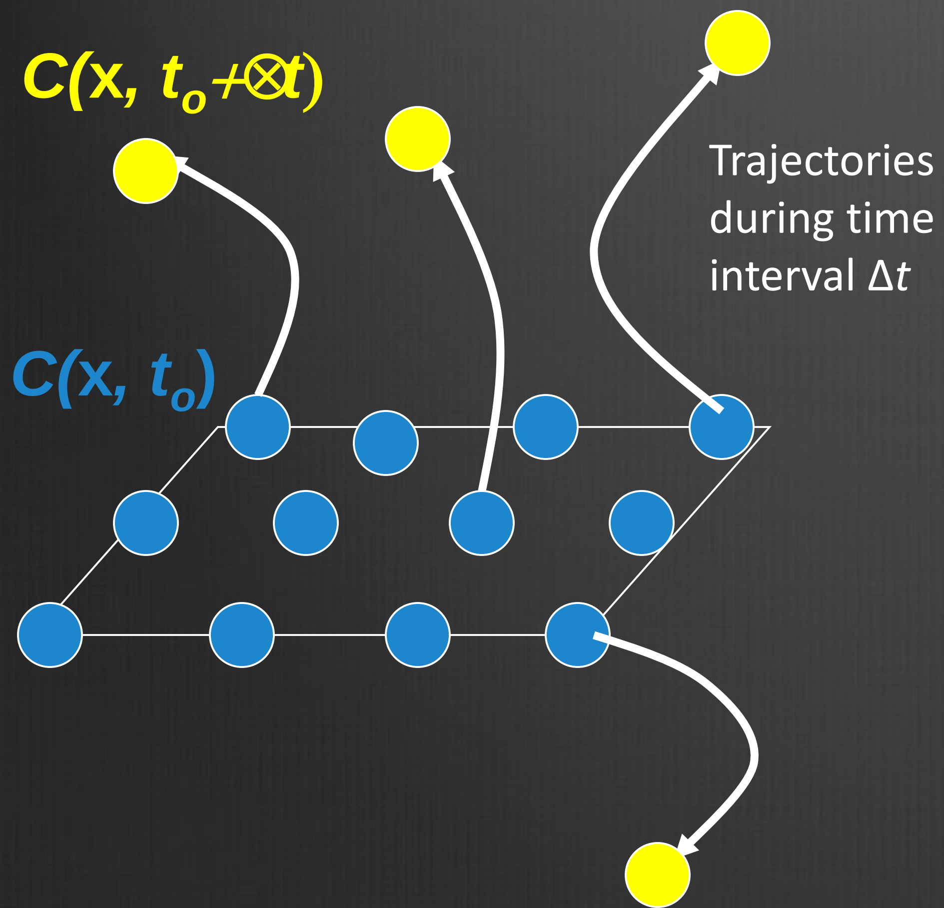


Differentes approaches for treating Lagrangian transport

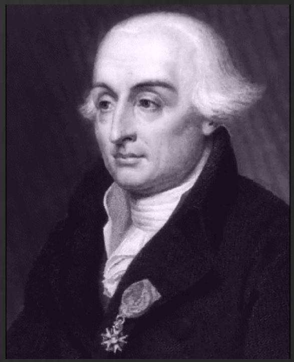
A Lagrangian View

Following a Large Number of Air Parcels

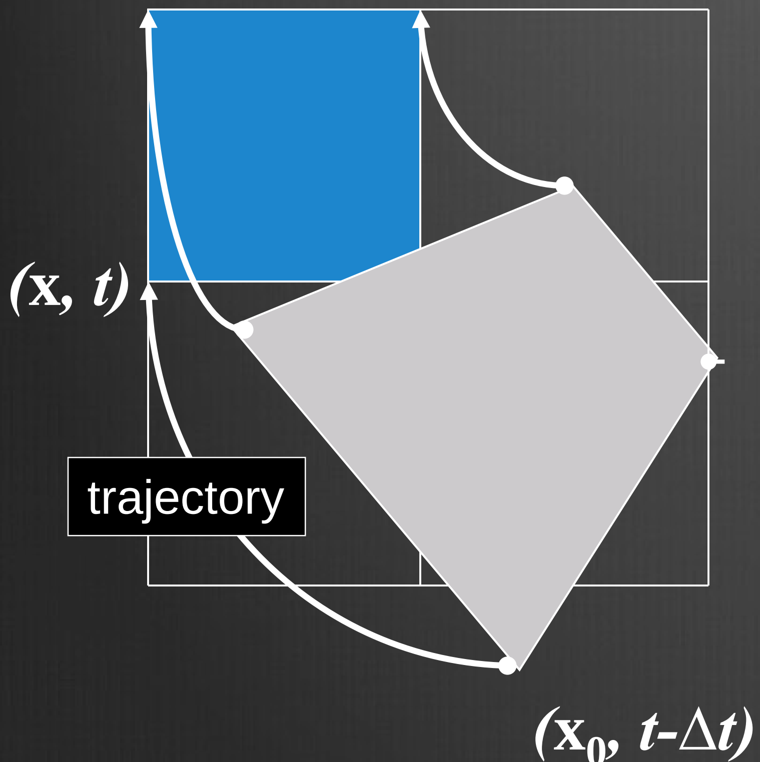
Concentration field at time *t*, defined by *n* particles



Numerical stable method
No numerical diffusion
No mixing
Spatial coverage uneven



Advection: 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

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.

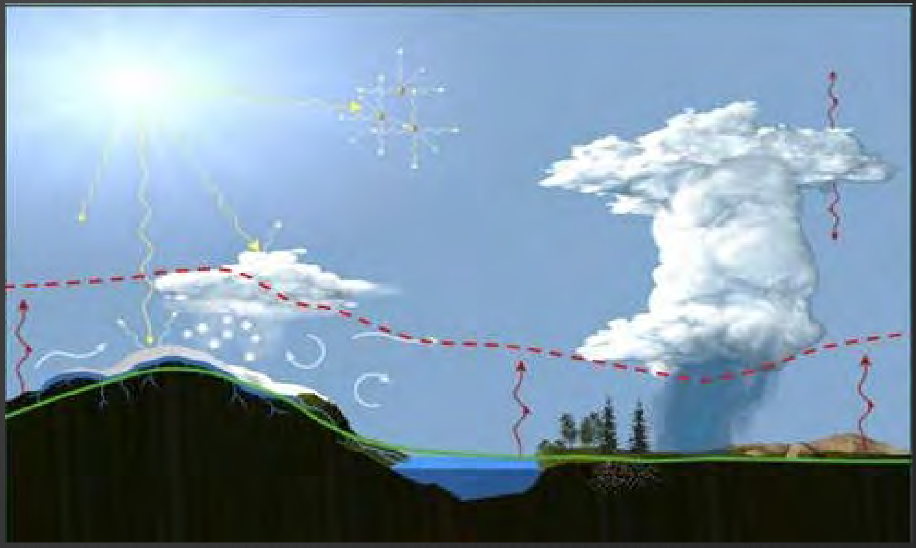
- ***Low-order*** algorithms such as the upstream method preserve the sign of the solution, but are excessively diffusive. ***Higher-order*** algorithms are generally not monotonic and occasionally produce undesired negative values.

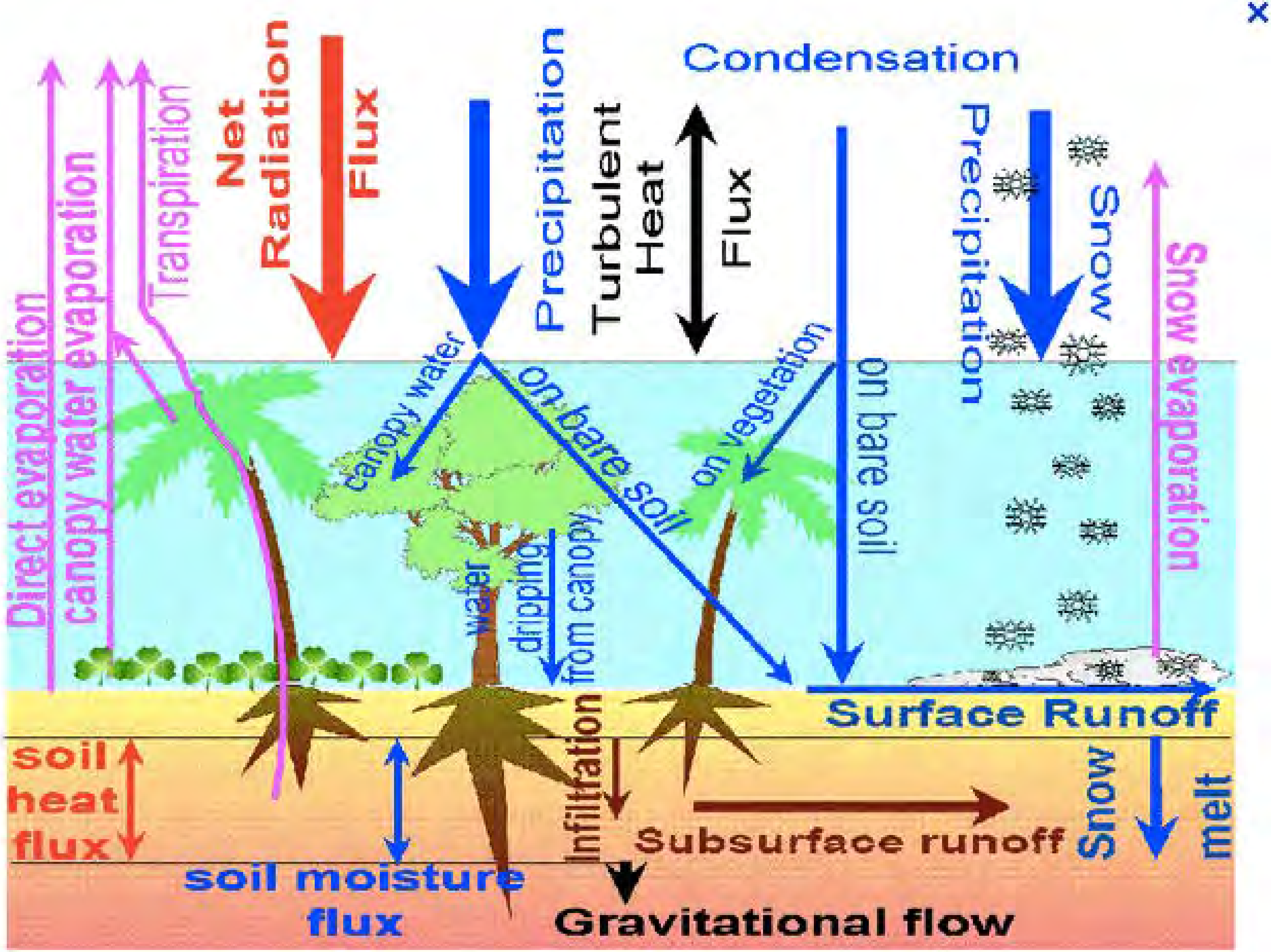
- Modern schemes are often upstream-based Eulerian finite-volume methods that are mass conservative, positive definite, and possess good phase-error characteristics. step.

- ***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.

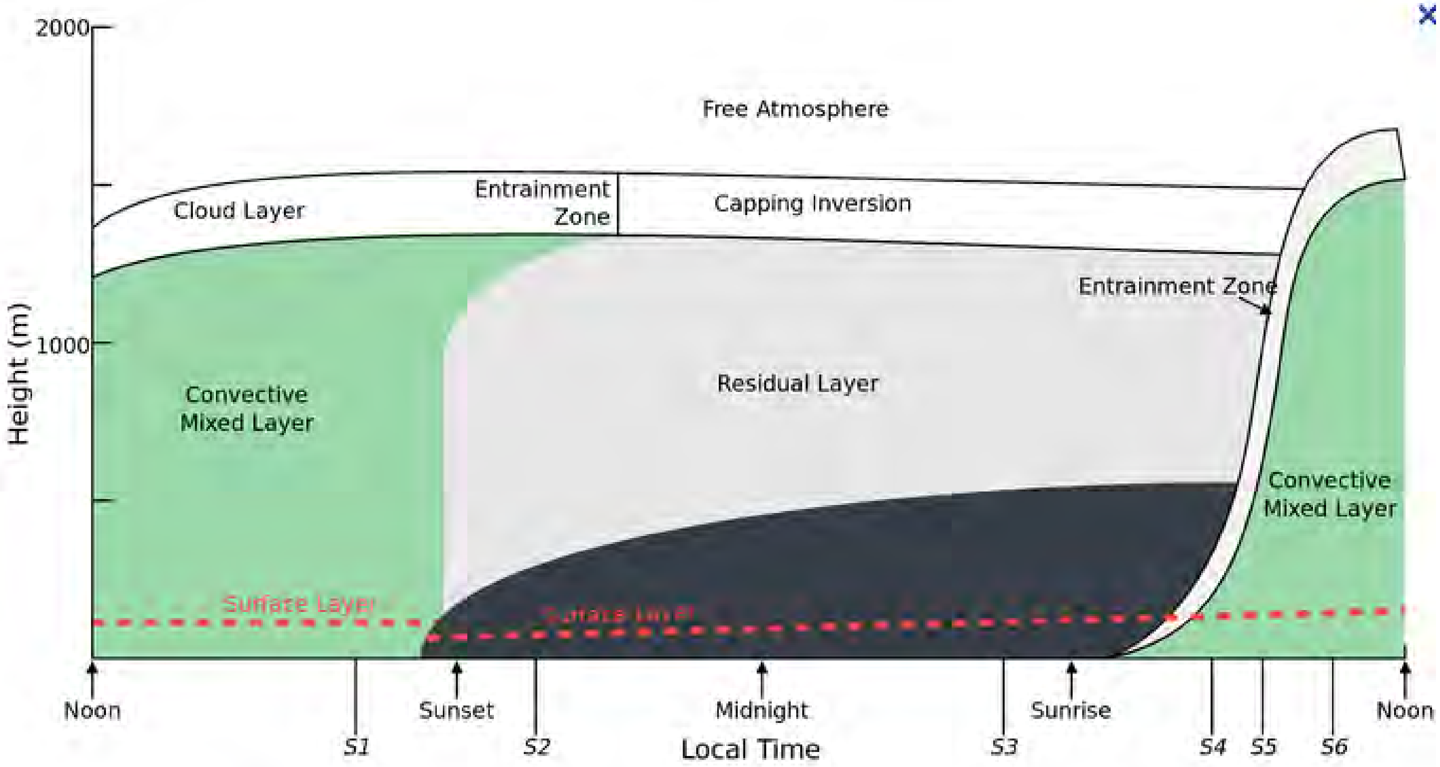
- ***Semi-Lagrangian methods*** are very popular in global CTMs because their numerical stability is not as severely constrained by choice of time step as in the case of Eulerian schemes.

Sub-Grid (unresolved) Transport

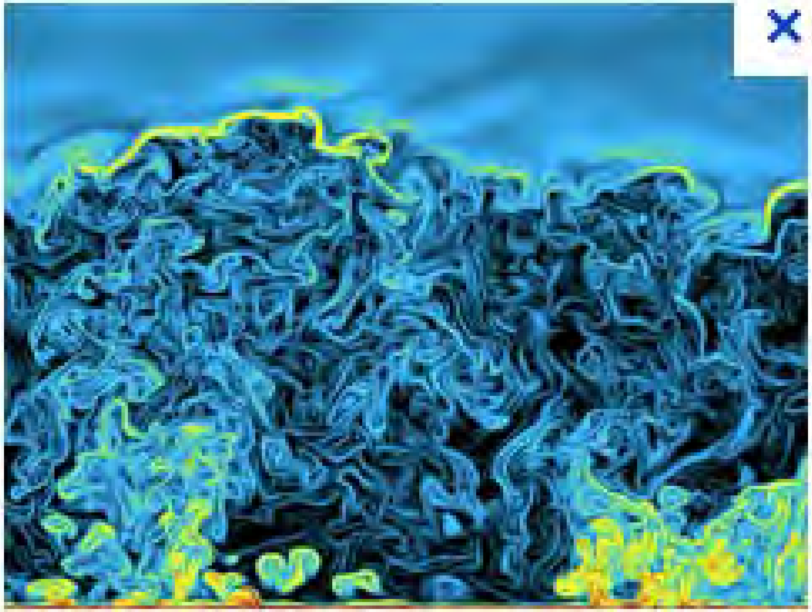


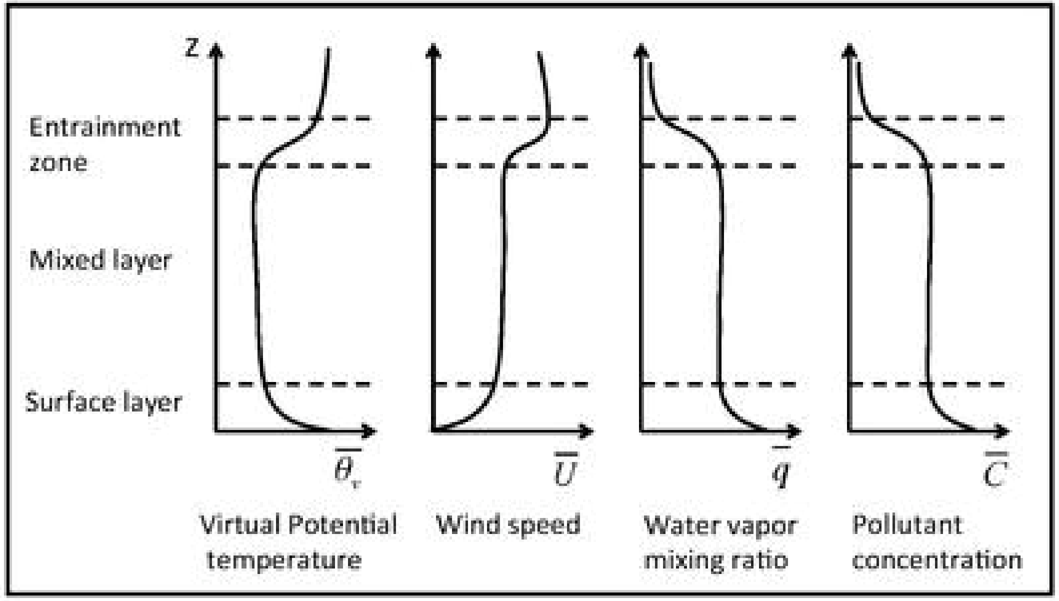


x
Condensation
Direct evaporation
Canopy water evaporation
Transpiration
Net Radiation Flux
Precipitation
Turbulent Heat Flux
Snow Precipitation
Snow evaporation
canopy water
on bare soil
on vegetation
on bare soil
water dripping from canopy
Surface Runoff
soil heat flux
soil moisture flux
Infiltration
Subsurface runoff
Snow melt
Gravitational flow



Planetary Boundary layer





Representation of Turbulence

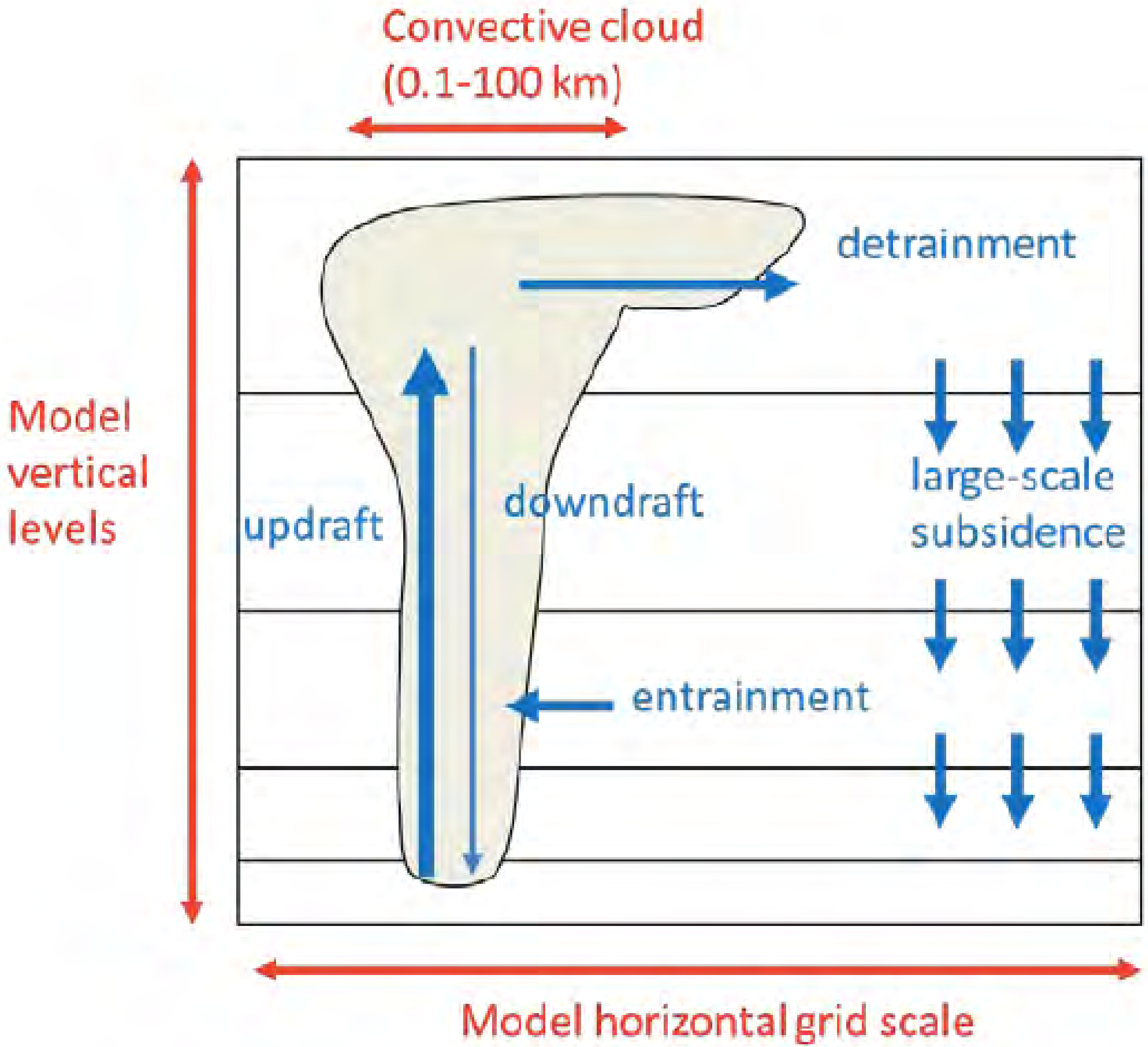
- ***Direct Numerical Simulation (DNS)***: Resolves the entire range of turbulent scales. Extremely expensive and intractable for flows with complex configurations.

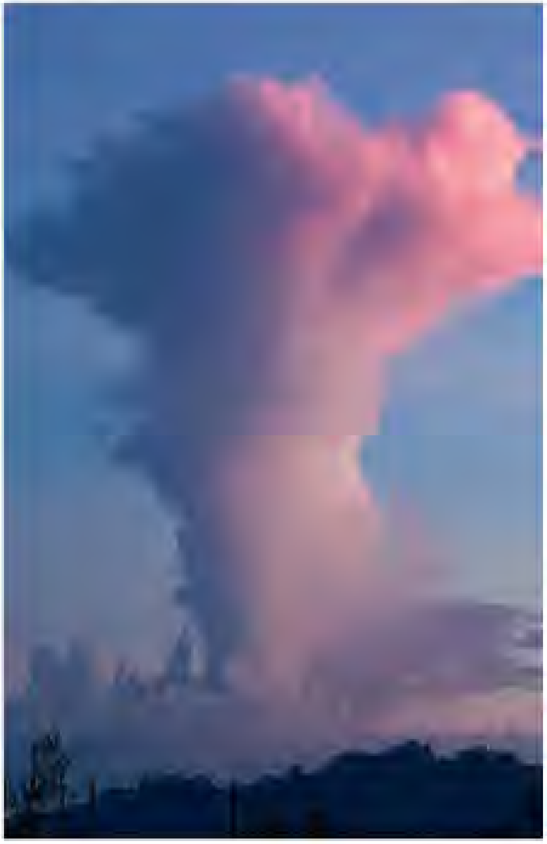
- ***Large Eddy Simulations (LES)***.Only the largest scales of the turbulence are resolved. Samllest scales are filtered out and their effects are modeled by using subgrid paramterizations.

- ***Reynolds Averaging***: The physical quantities are decomposed into a mean (resolved) value and a departure from the mean (eddy component). The correlation terms between eddy variables can be calculated from additional equations, but with the introduction of higher-order terms. The problem requires closure assumptions.

- ***PDF methods***: The approach is similar to the kinetic theory of gases. The flow is represented by a large number of particles whose velocity is expressed by a probability density function. One solves the transport equation of the PDF.

Convective Transport

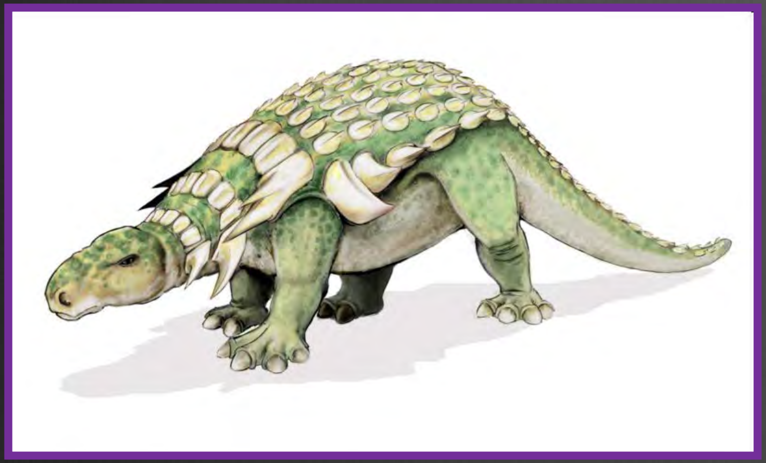


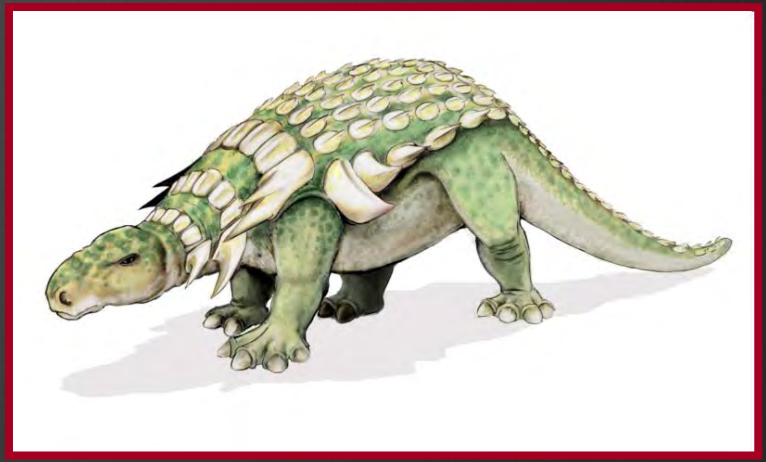


The Approaches

Assimilation

Forward problem

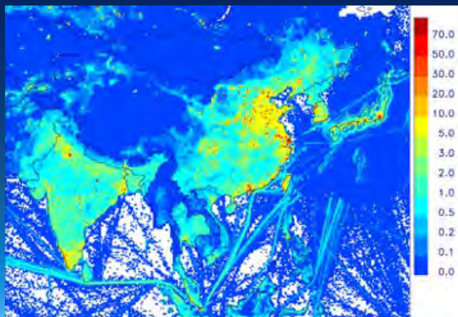




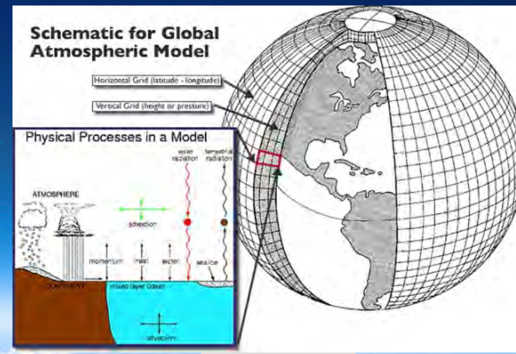
Inverse problem

From Cathy Clerbaux.

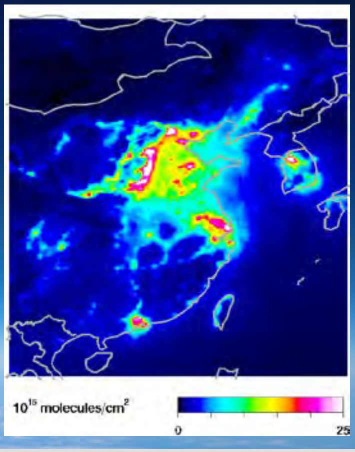
the FLUX INVERSION IS…



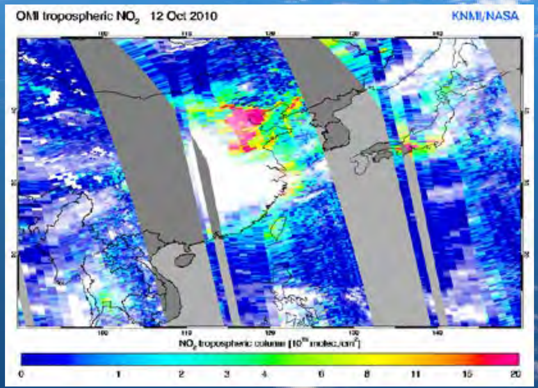
A priori emissions



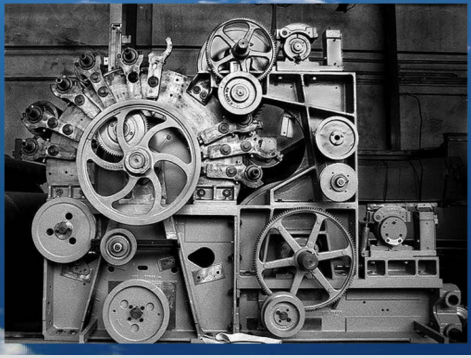
CTM



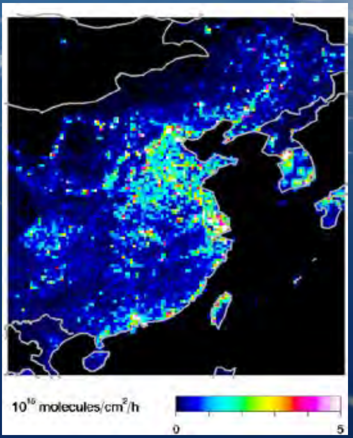
Concentrations



Satellite observations

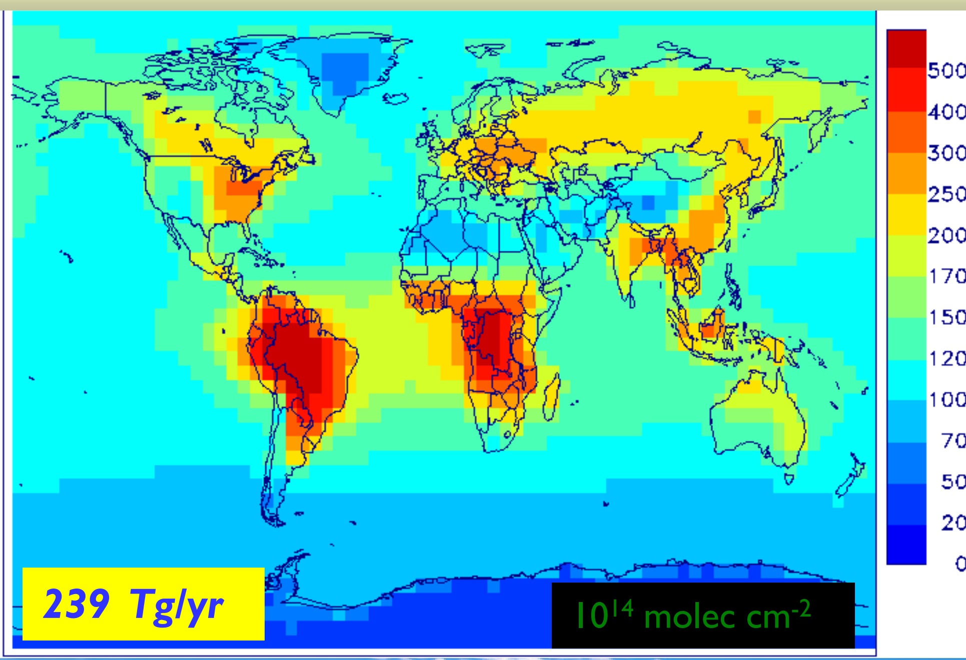


Inversion algorithm

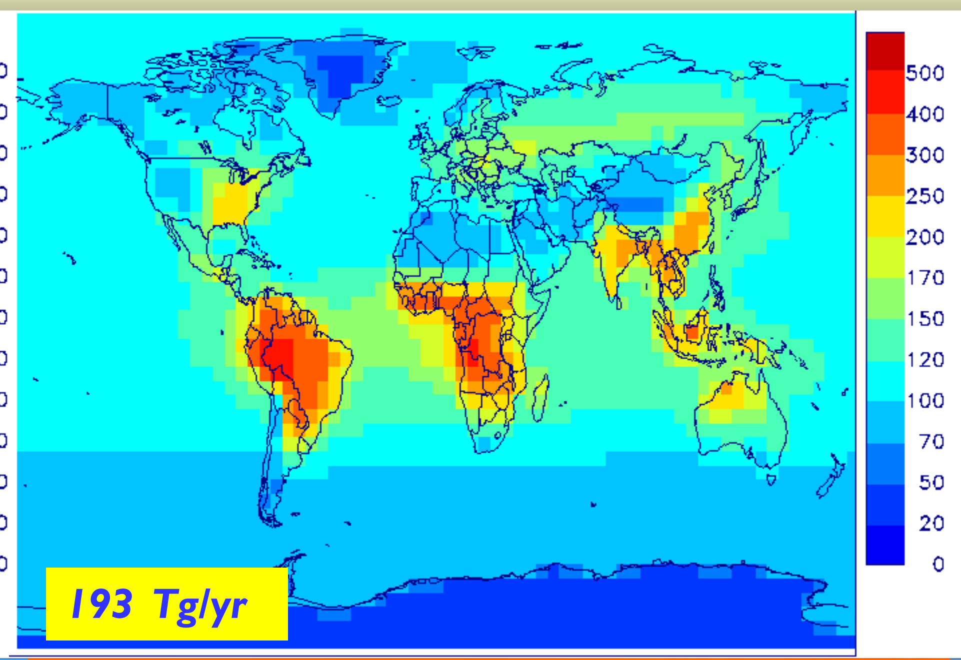


Updated Emissions

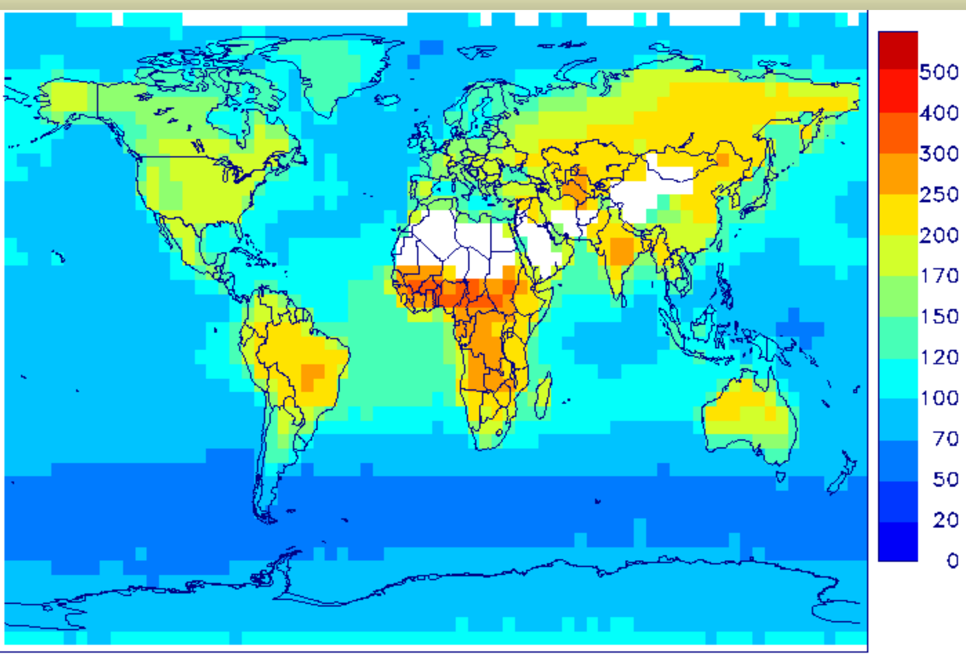
IMAGES CH_3OH column – *Jacob et al*



IMAGES CH_3OH column – *MEGANv2.1*

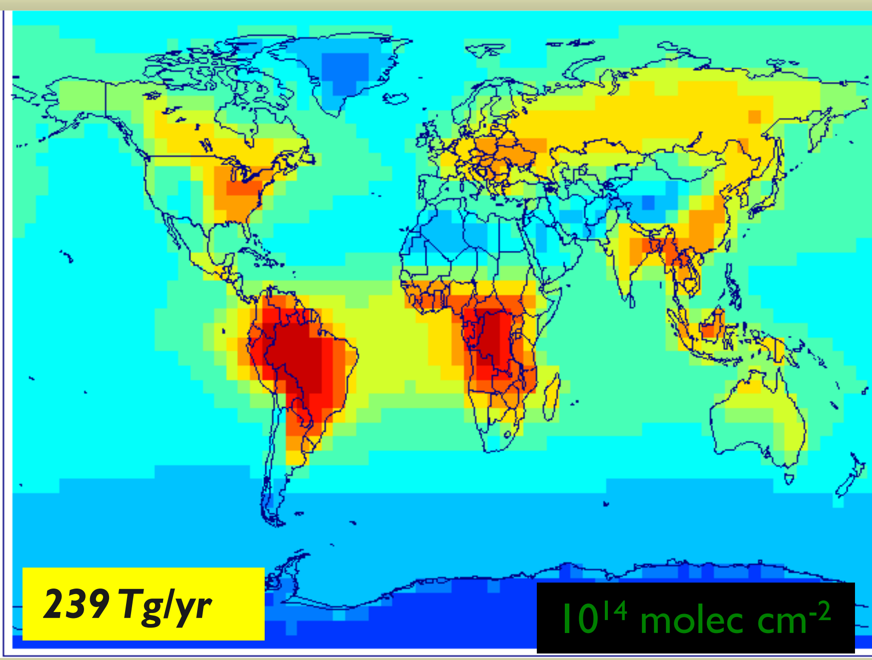


IASI CH_3OH column - 2009

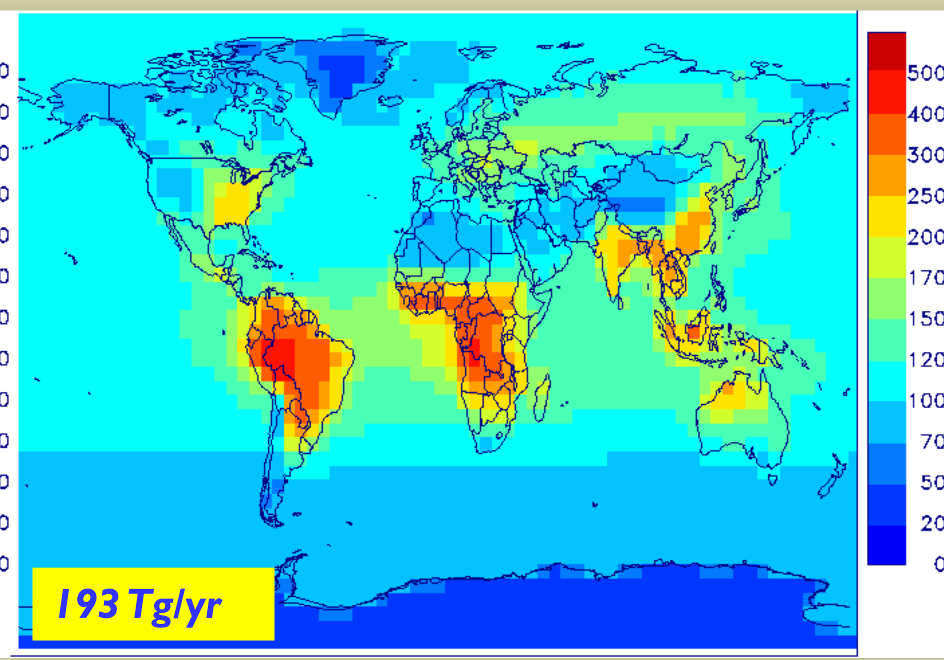


- Higher columns over majority of continents
- Largest overestimation in Amazonia (x 2-3), Africa & Indonesia (x1.5-2), moderate in Europe, US
- Model closer to IASI when MEGANv2.1 is used, *BUT* persistent overestimation in Tropics

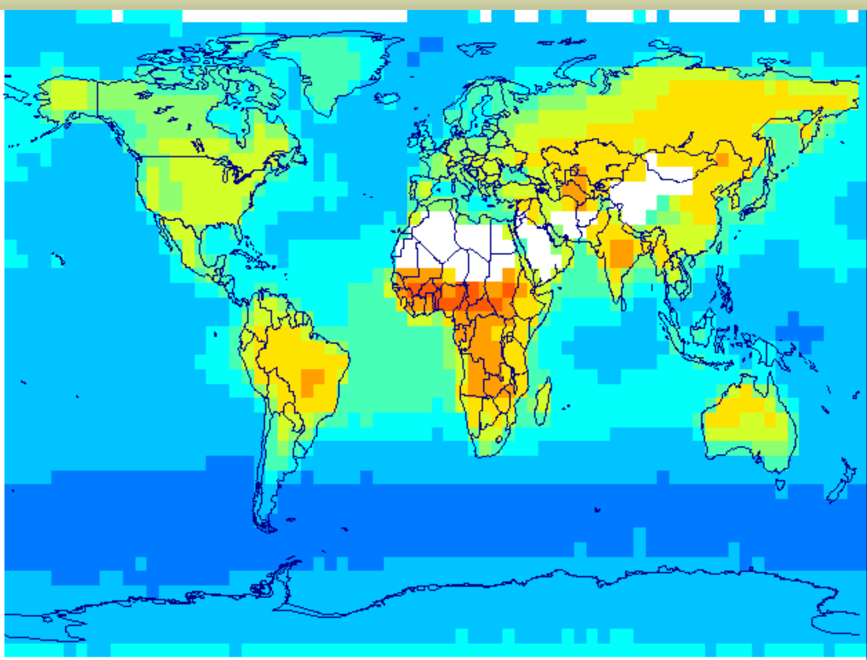
IMAGES CH_3OH column – *Jacob et al.*



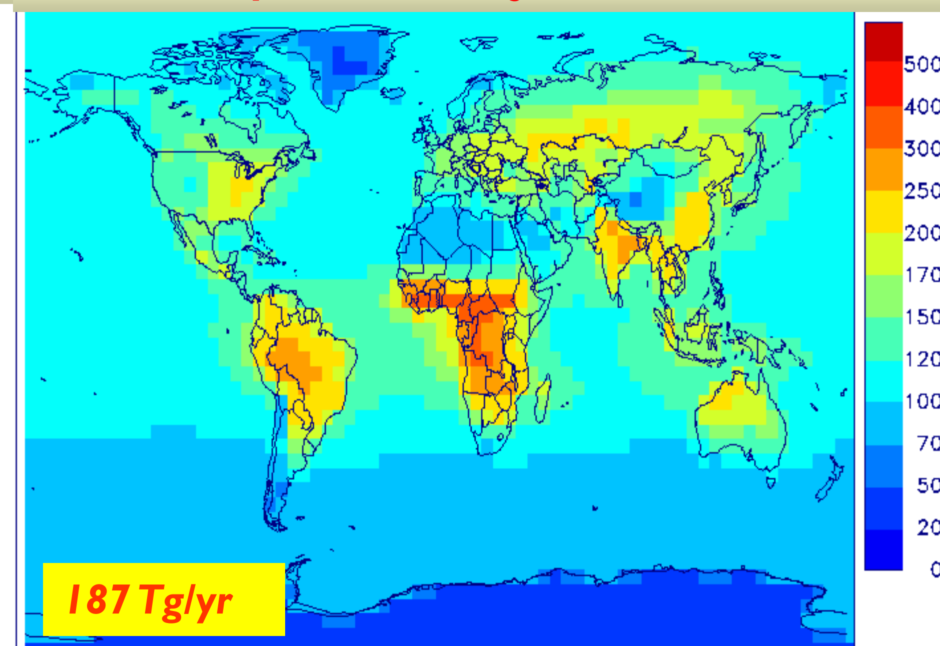
IMAGES CH_3OH column – *MEGANv2.1*



2009 IASI CH_3OH column



Optimized CH_3OH column



Some Key Definitions

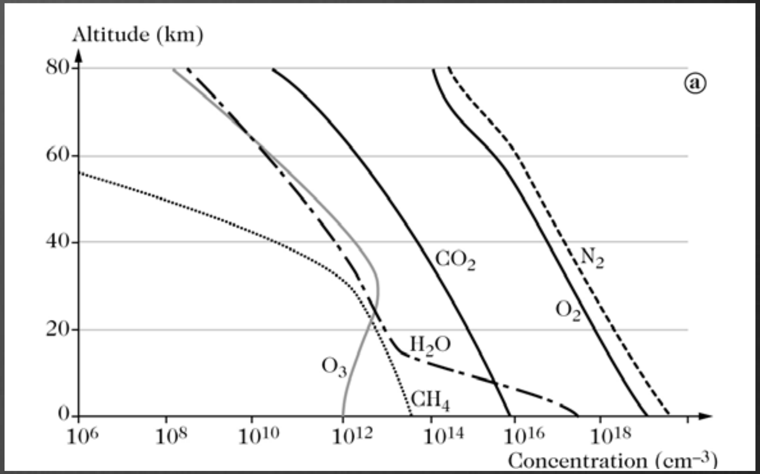
Concentration and Mixing Ratio

Molecular Concentration

Number Density

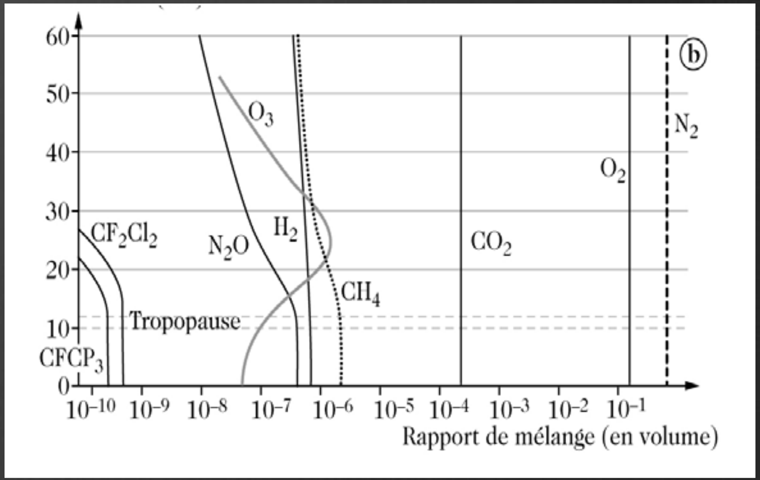
n_X,: number of molecules of gas X per unit volume of air

$$n_X = C_X n_a$$



Volume Mixing ratio:

C_X, is the number of moles of gas X in a volume V per mole of air in the same volume.



Parts per millions in volume = ppmv = ppm = 10^{-6} mole/mole of air

Parts per billions in volume = ppbv = ppb = 10^{-9} mole/mole of air

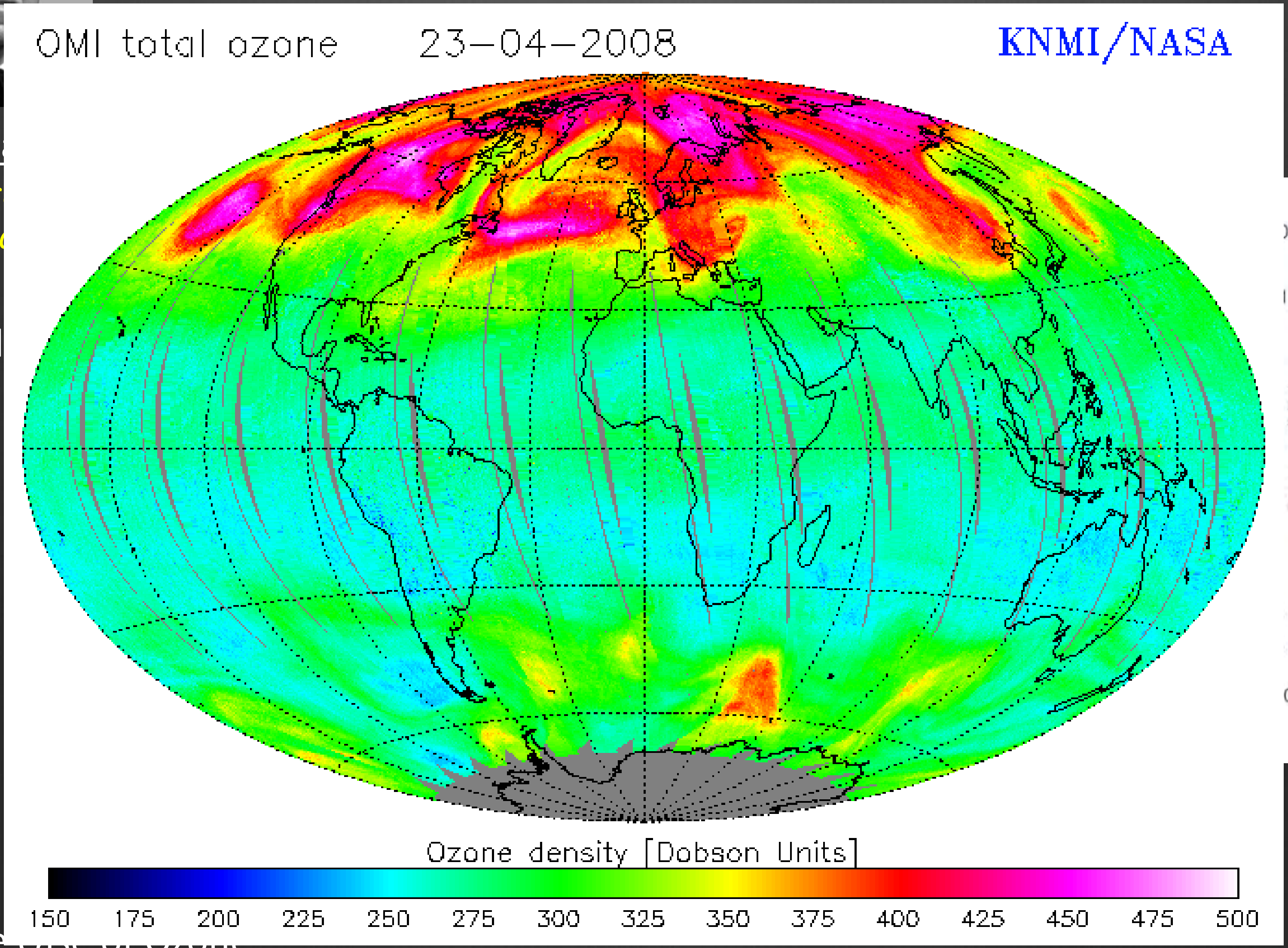
Parts per trillions in volume = pptv = ppt = 10^{-12} mole/mole of air

Vertical Column

Total a

Molec
integr

Total



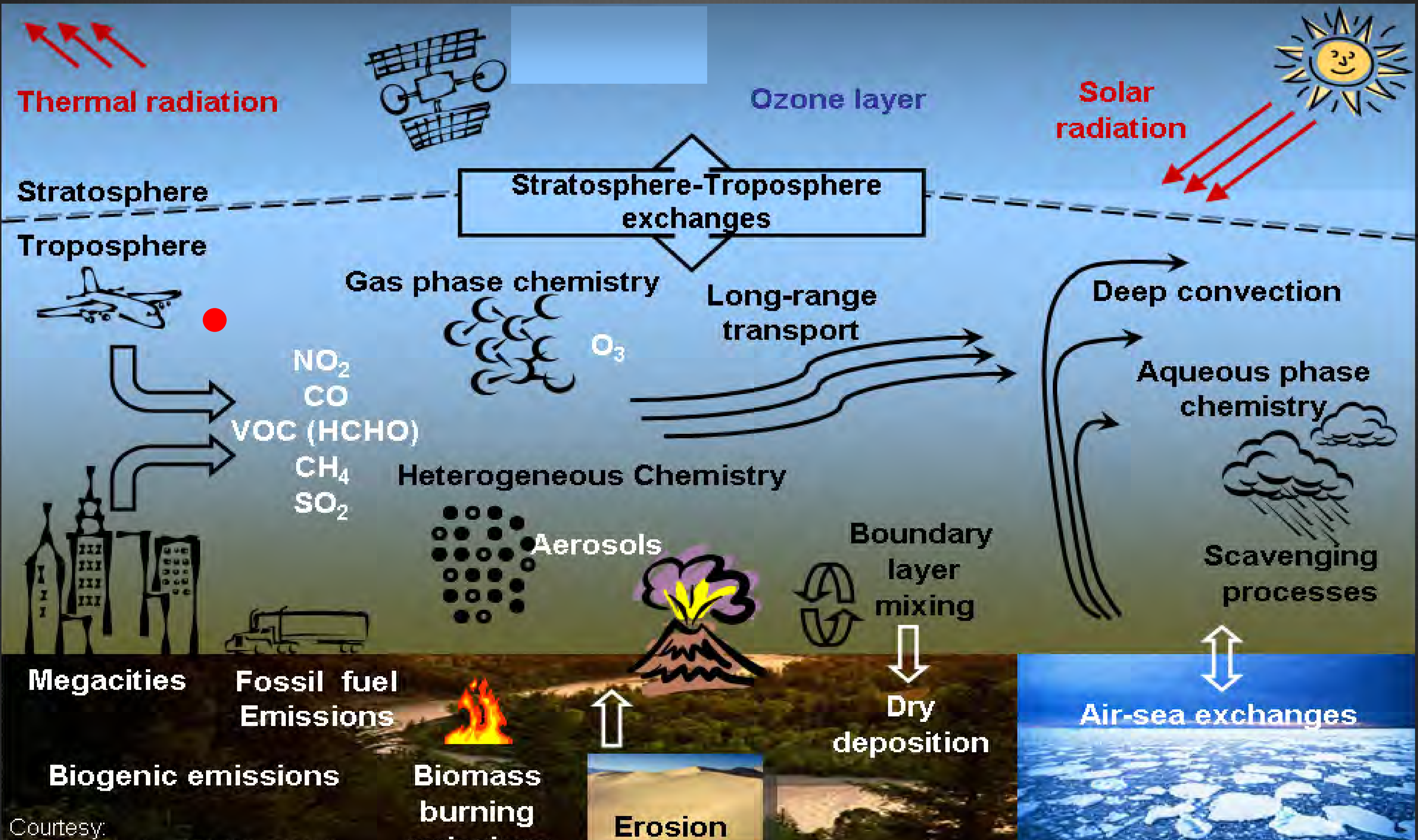
Partial

In the case of Ozone,
often expressed in Dobson Units (DU)

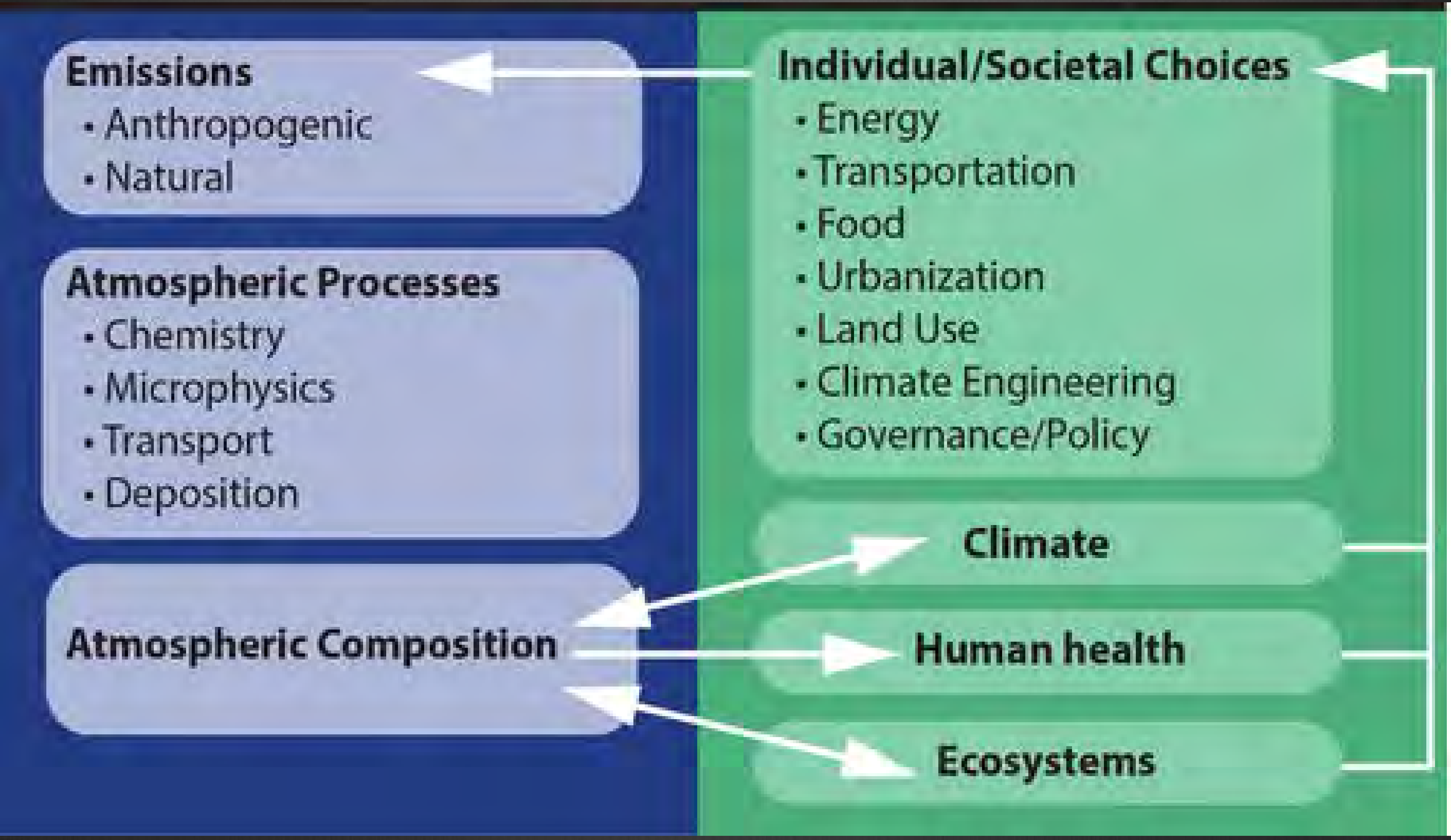
$1\ \text{DU} = 2.69 \times 10^{16}$ molécules cm^{-2}

Today’s Scientific Challenges

Developing a Predictive Understanding of the Complex Atmospheric System and its Interactions with the Whole Earth System



Atmospheric Chemistry in the Context of Society's Development (IGAC)



Grand Challenges

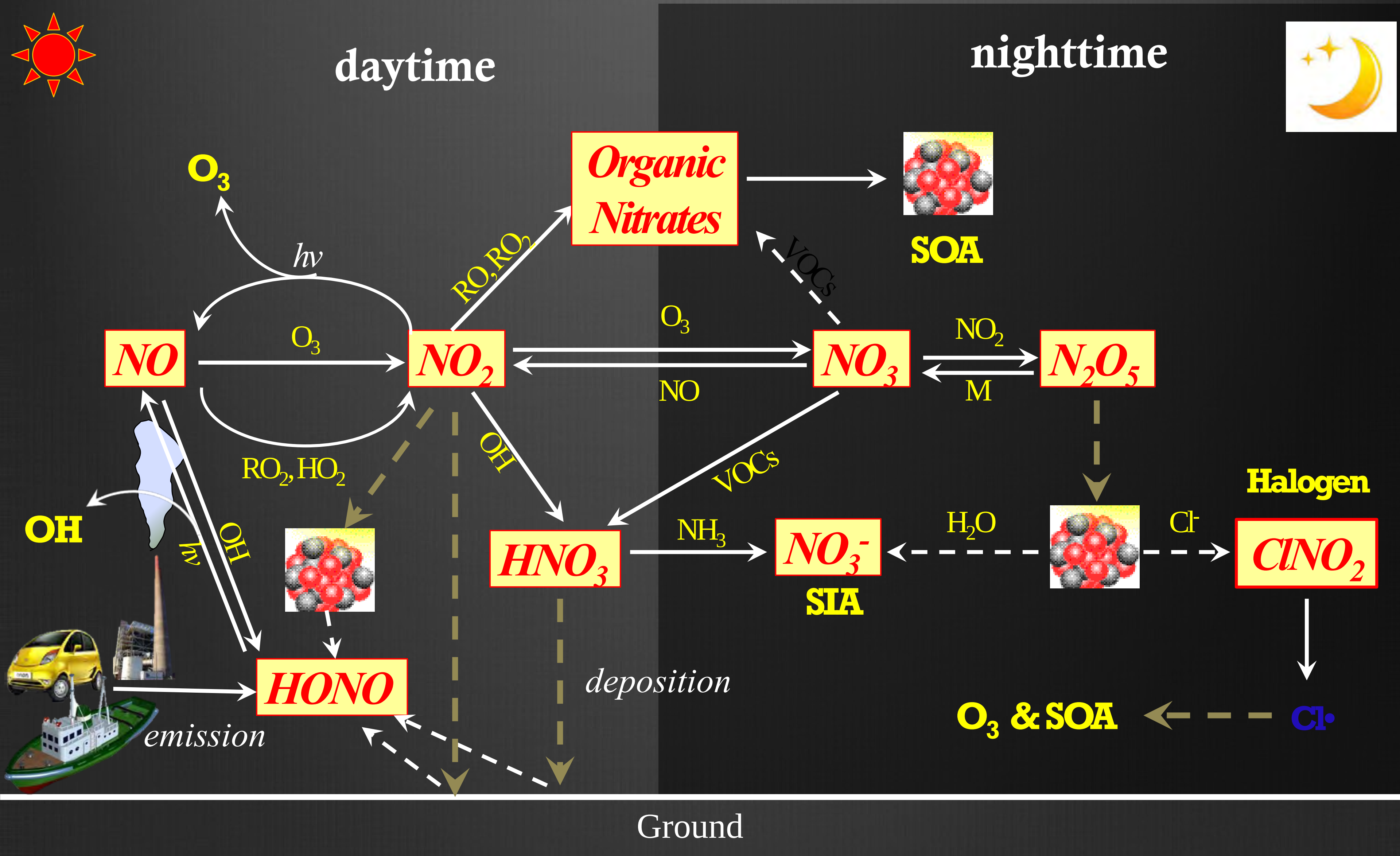
- Emissions Inventories including natural emissions (biogenic, fires, etc.) Interactions with surface ecosystems, natural emissions and surface deposition. Land-use changes and urbanization.

- Interaction between meteorology and chemistry/aerosols, specifically tropical dynamics and convective systems and precipitation. Global and regional transport of pollutants. Sub-grid exchanges, specifically in the PBL.

- Chemical transformations, specifically of organic compounds, formation of ozone and hydroxyl radicals. Role of heterogeneous reactions (e.g., HONO) for the formation and fate of oxidants. Role of halogens. Nighttime chemistry.

- Formation of secondary organic and non-organic aerosols. Assessment of direct and indirect climate effects of aerosols, and their implications for tropospheric gas-phase chemistry

Nitrogen Oxides and Radicals



Grand Challenges

- Systematic Analysis of observations (surface stations, satellites, campaigns, etc.) and Assimilation of observations, specifically of space observations.
- Development and dissemination of relevant information in regions with vulnerability of population (human health, agricultural productivity and other impacts).
- Assessment of direct and indirect effects of aerosols and their implications for tropospheric chemistry
- Interactions between atmospheric composition, biogeochemical cycles and water cycle. Impacts of aerosol and gas deposition on ecosystems and glaciers.

References


Atmospheric Chemistry and Global Change
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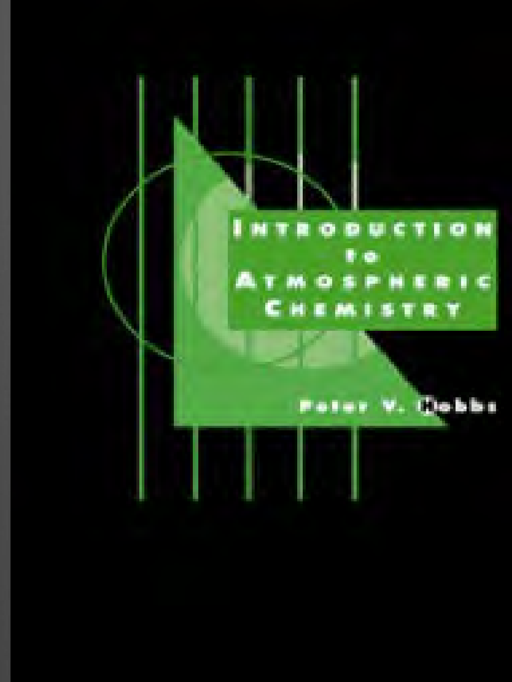
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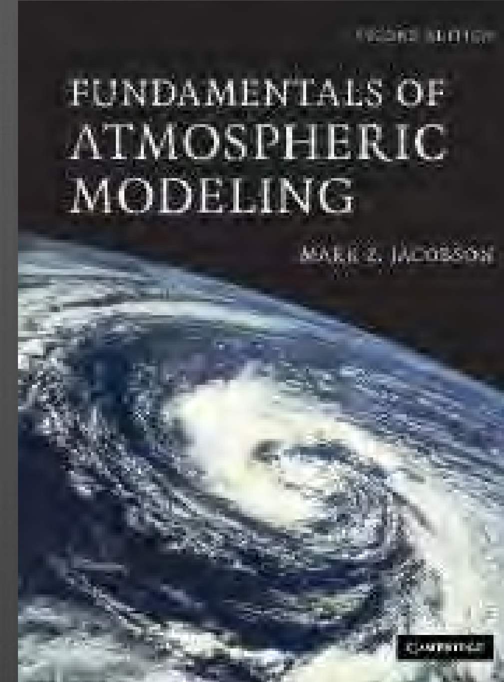
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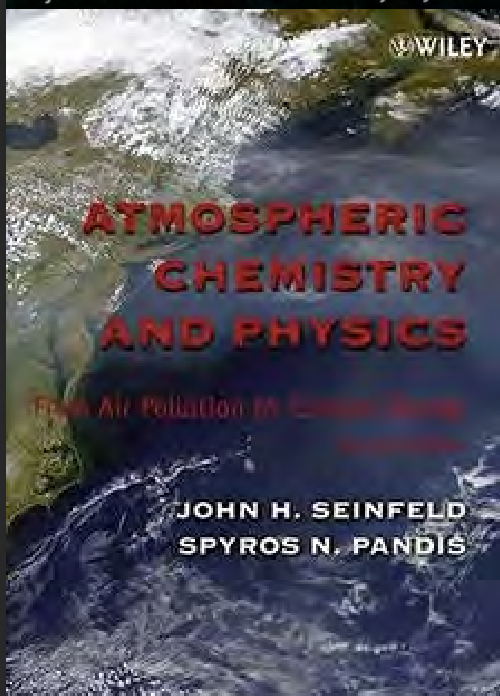
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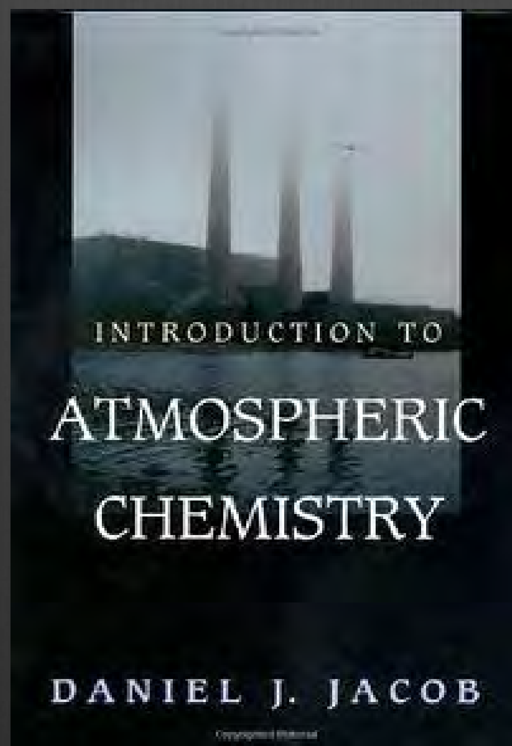
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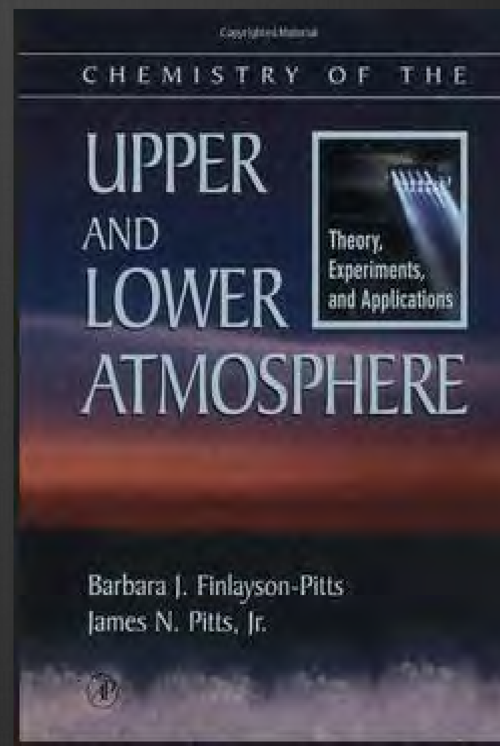
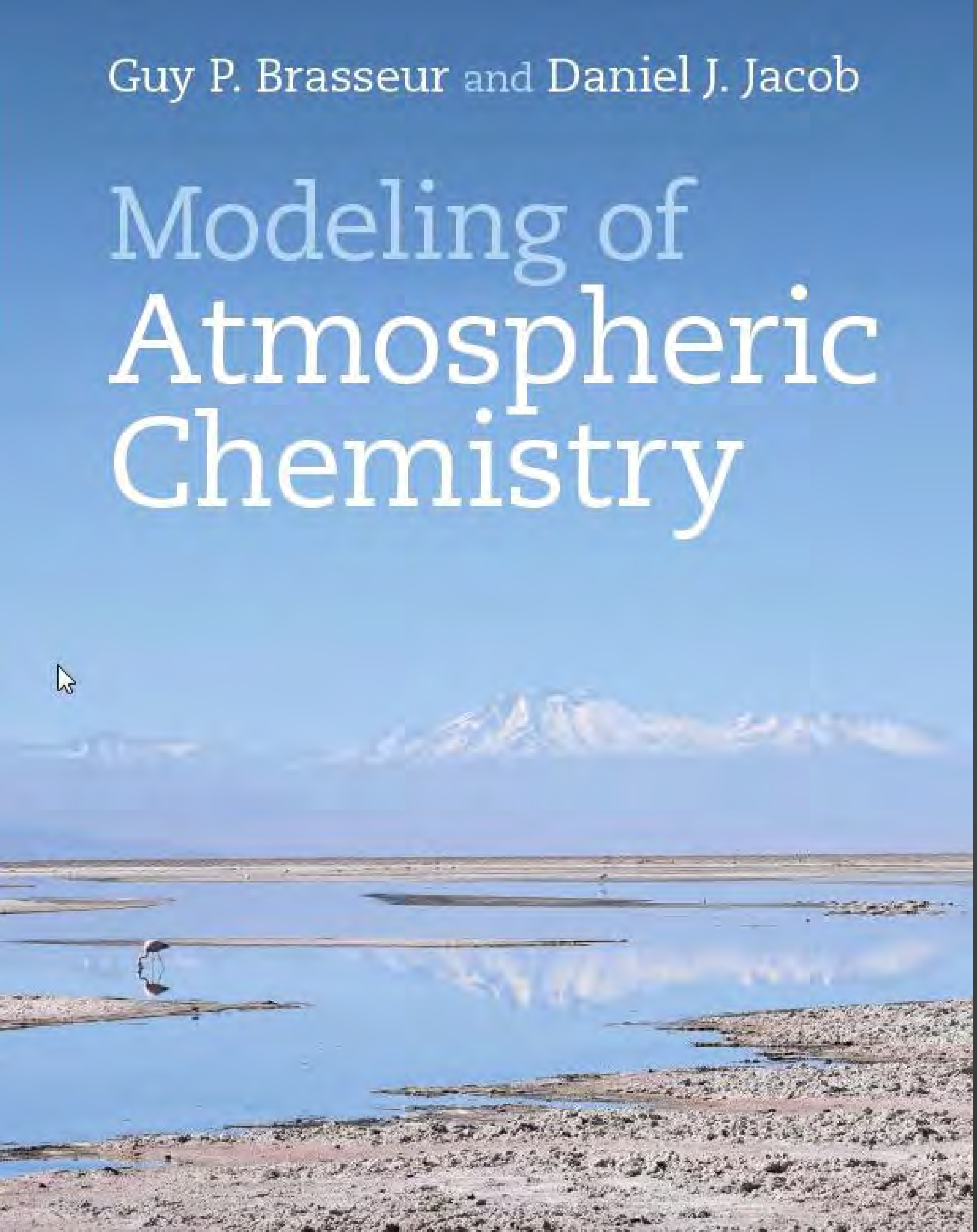
CHEMISTRY
DANIEL J. JACOB


CHEMISTRY OF THE
UPPER
AND
LOWER
ATMOSPHERE
Theory,
Experiments,
and Applications
Barbara J. Finlayson-Pitts
James N. Pitts, Jr.



The book will be published at the end of 2016. The text can be found on the site of Daniel Jacob at Harvard with a password “ctm”