清華大學
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大气化学模式简介

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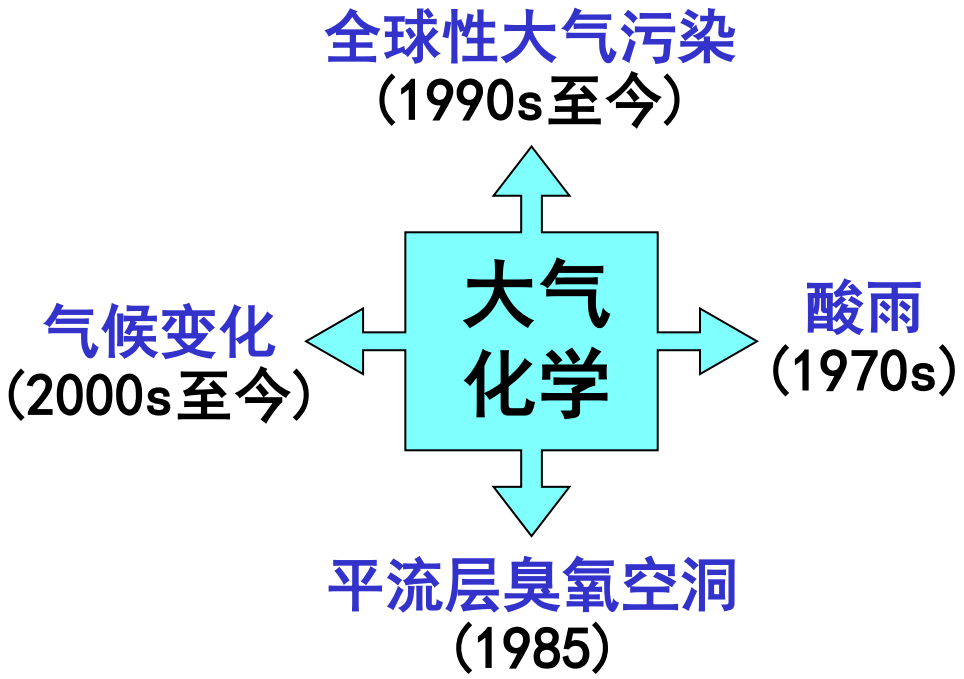
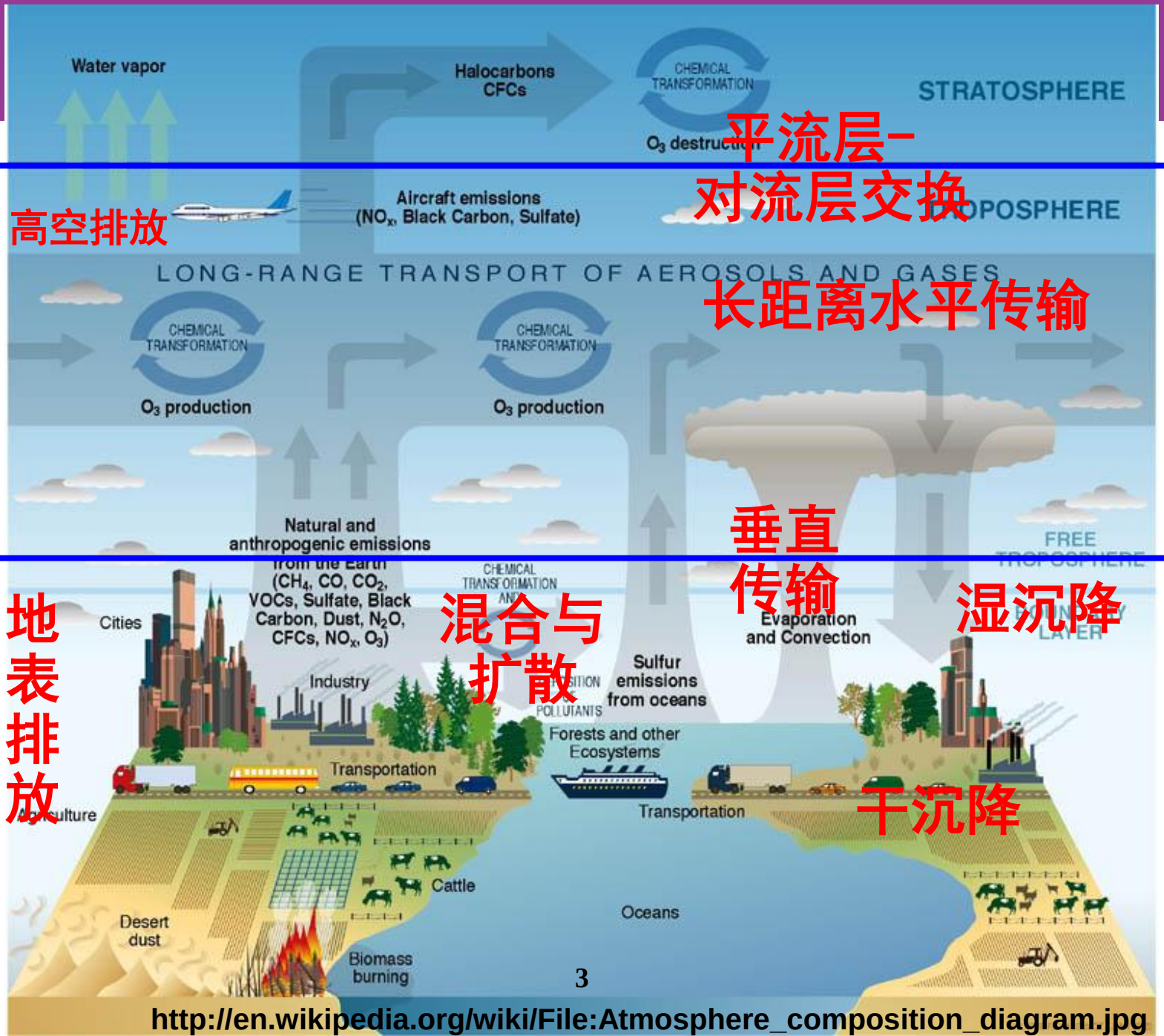
CENTER FOR EARTH SYSTEM SCIENCE
清华大学地球系统科学研究中心

大气化学

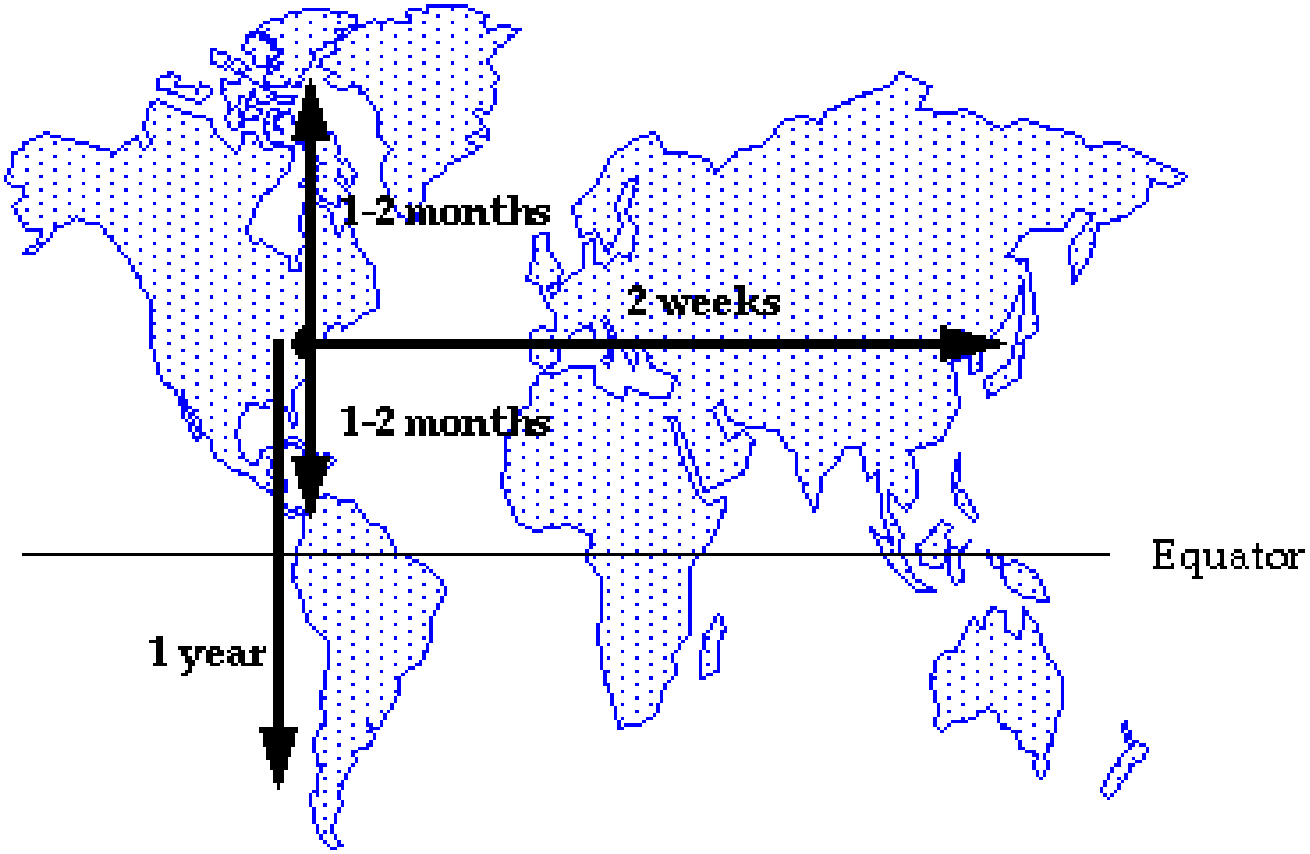
- 大气中化学物质（CO_2、O_3、气溶胶、沙尘等）的**来源、化学反应、演化、传输、沉降**
- 大气化学与**空气污染和公共健康**密切相关





http://en.wikipedia.org/wiki/File:Atmosphere_composition_diagram.jpg

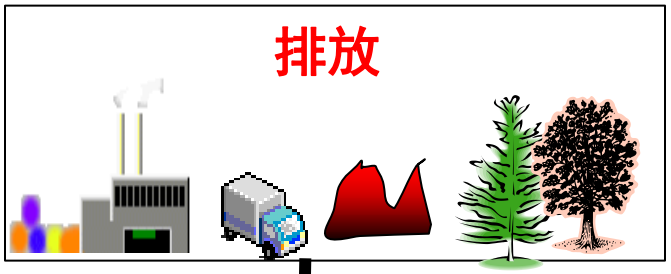
全球尺度的大气化学传输



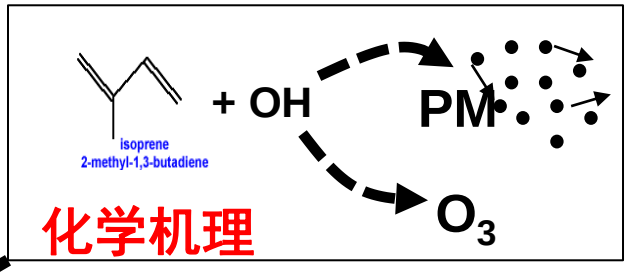
空气在平流层中各方向上进行水平传输大约需要的时间[***Introduction to atmospheric chemistry, Daniel Jacob, 1999***]

Model as the central analytical tool to address key challenges in understanding the science

排放



气象场



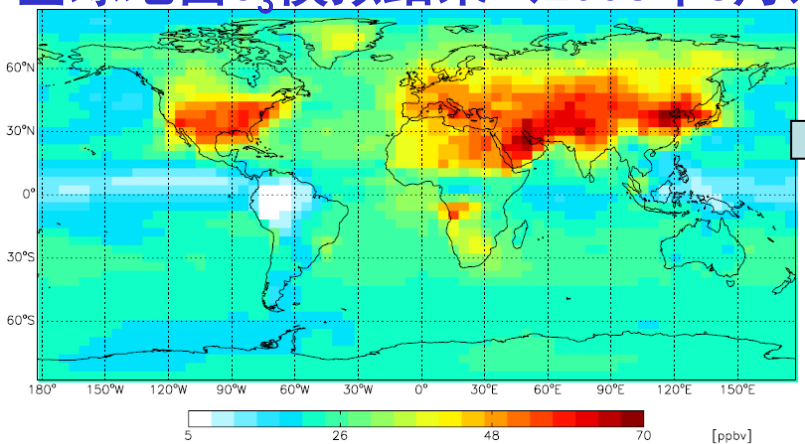
化学机理

Chemical Transport Models

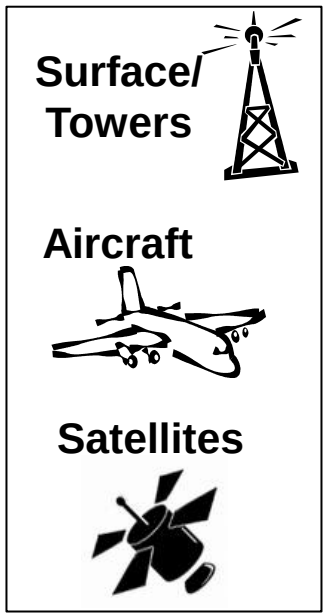
参数化方案

Past → Present → Future?

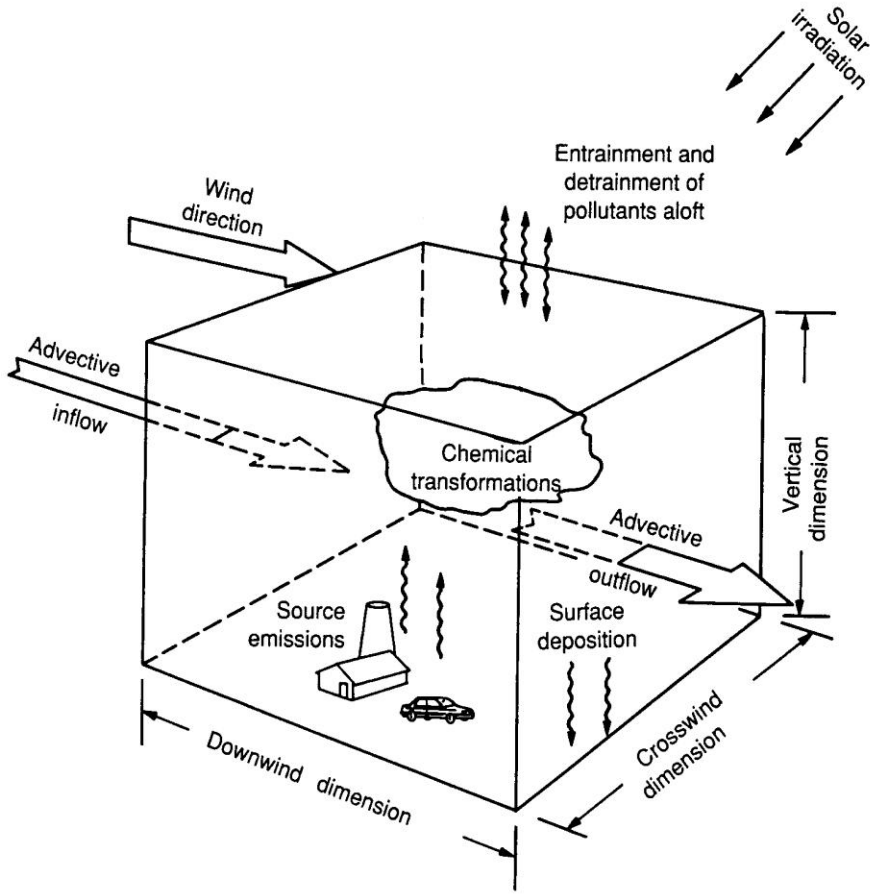
全球地面0_3模拟结果（2006年6月）



观测数据



最简单的一维箱式模型(box model)



输入值包括：

- **气象场**
- **排放**
- **化学参数**
- **动力学参数**

浓度变化 = 排放源 (emission)＋化学源(chemical production)－化学汇(chemical loss)－地表吸附(deposition)＋所有边界的净通量(net fluxes through the boundaries)

化学物质的质量连续性方程

Mass balance (or "continuity") equation for [X](x,*t*)

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

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

[ ] is our general notation for concentration, with three different measures:

1. **Mixing ratio (or mole fraction)**
2. **Number density, mass concentration**
3. **Partial pressure**

梯度算子

Gradient operator in Cartesian-altitude coordinates

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}$$

Dot product of gradient operator with velocity vector

Divergence term

$$\nabla \bullet \mathbf{v} = \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right) \bullet \left(\mathbf{i}u + \mathbf{j}v + \mathbf{k}w\right) = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}$$

$$\mathbf{i} \bullet \mathbf{i} = 1 \qquad \mathbf{j} \bullet \mathbf{j} = 1 \qquad \mathbf{k} \bullet \mathbf{k} = 1$$

$$\mathbf{i} \bullet \mathbf{j} = 0 \qquad \mathbf{i} \bullet \mathbf{k} = 0 \qquad \mathbf{j} \bullet \mathbf{k} = 0$$

平流传输方程的数值解

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

数值解的要求：

- Accuracy（准确）
- Stability （稳定）
- Mass conservation （质量守恒）
- Positivity（正向）

数值解的稳定性条件

Introduce Courant number for stability:

$$\varepsilon = u\Delta x / \Delta t$$

Classic schemes of the advective form

- Taylor expansion in space

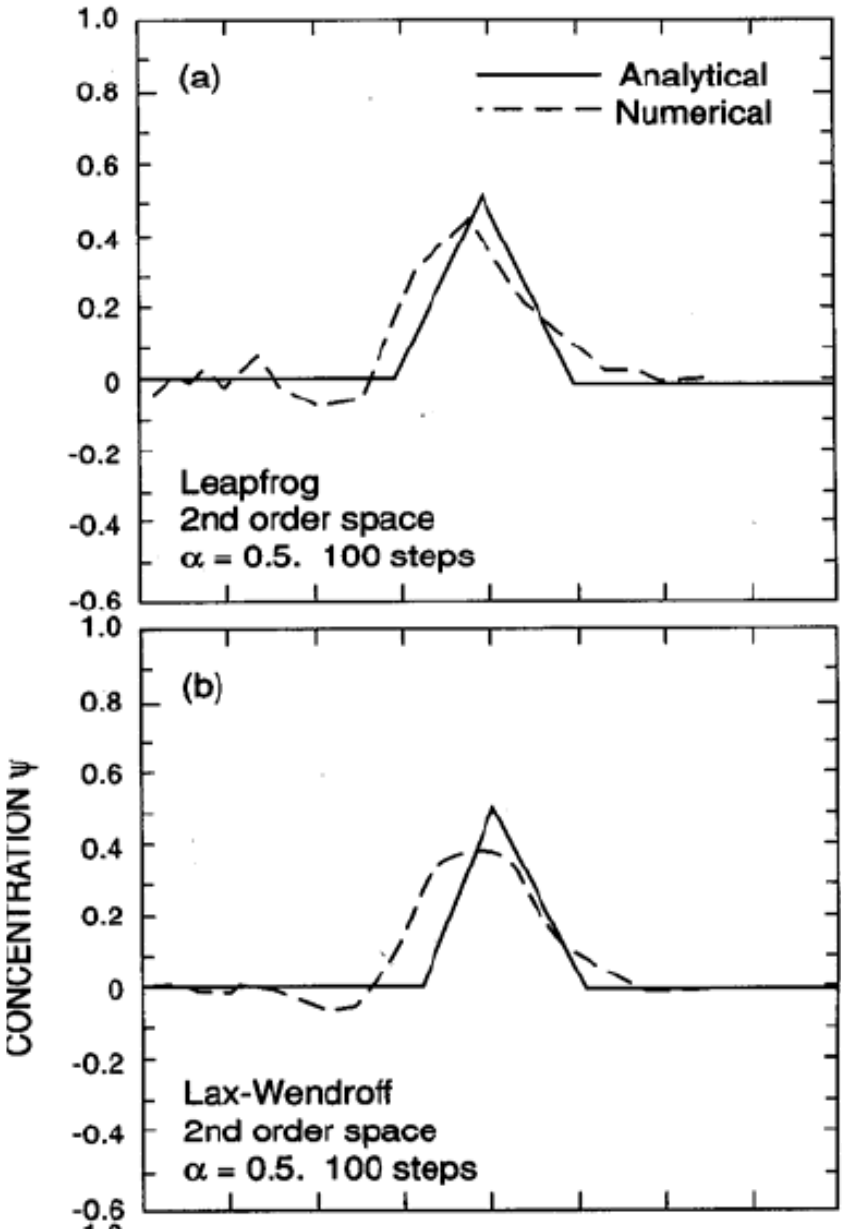
$$C_{i\pm1,t} = C_{i,t} \pm \Delta x \frac{\partial C_{i,t}}{\partial x} + \frac{\Delta x^2}{2}\frac{\partial^2 C_{i,t}}{\partial x^2} \pm \frac{\Delta x^3}{6}\frac{\partial^3 C_{i,t}}{\partial x^3} + \ldots$$

$$\frac{\partial C}{\partial x} = \frac{C_{i+1,t} - C_{i,t}}{\Delta x} + \mathrm{O}(\Delta x) \quad \text{(forward)}$$

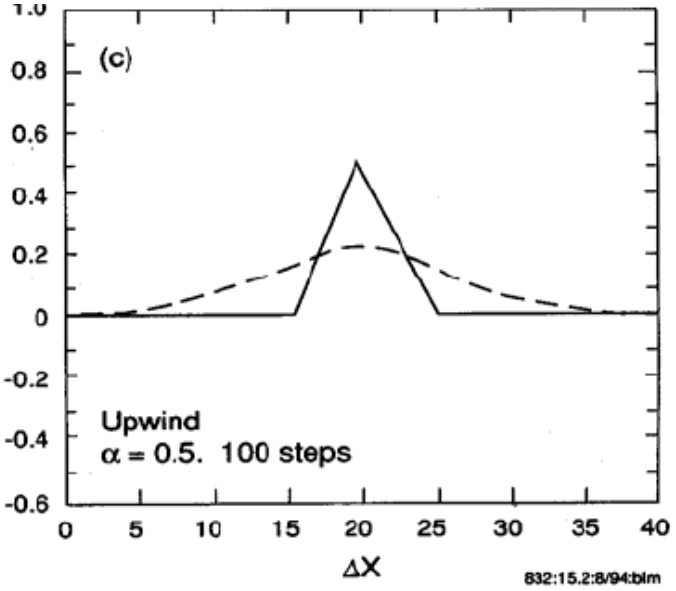
$$\frac{\partial C}{\partial x} = \frac{C_{i,t} - C_{i-1}}{\Delta x} + \mathrm{O}(\Delta x) \quad \text{(backward)}$$

$$\frac{\partial C}{\partial x} = \frac{C_{i+1,t} - C_{i-1}}{2\Delta x} + \mathrm{O}(\Delta x^2) \quad \text{(centered)}$$

Classic schemes of the advective form



- Forward Euler scheme
- Leapfrog scheme
- Lax-Wendroff scheme
- Upstream scheme
- Semi-Lagrangian scheme



Rood, 1987

对流层中关键氧化剂的发现过程

- *"The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen…Methane and CO are chemically quite inert in the troposphere"* [Cadle and Allen, Atmospheric Photochemistry, *Science*, 1970]
- Lifetime of CO estimated at 2.7 years (removal by soil) leads to concern about global CO pollution from increasing car emissions [Robbins and Robbins, Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants, *SRI report*, 1967]

FIRST BREAKTHROUGH:

- Measurements of cosmogenic ^{14}CO place a constraint of ~ 0.1 yr on the tropospheric lifetime of CO [Weinstock, *Science*, 1969]

SECOND BREAKTHROUGH:

- Tropospheric OH ~$1x10^6$ cm^{-3} predicted from $O(^1D)+H_2O$, results in tropospheric lifetimes of ~0.1 yr for CO and ~2 yr for CH_4 [Levy, *Science*, 1971, *J. Geophys. Res.* 1973]

THIRD BREAKTHROUGH:

- Methylchloroform observations provide indirect evidence for OH at levels of 2-$5x10^5$ cm^{-3} [Singh, *Geophys. Res. Lett. 1977*]

…but direct measurements of tropospheric OH had to wait until the 1990s

OZONE PRODUCTION IN TROPOSPHERE

Photochemical oxidation of CO and volatile organic compounds (VOCs) catalyzed by hydrogen oxide radicals (HO_x) in the presence of nitrogen oxide radicals (NO_x)

HO_x = H + OH + HO_2 + RO + RO_2
NO_x = NO + NO_2

Oxidation of CO:

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

Oxidation of VOC:

$$RH + OH \rightarrow R + H_2O$$
$$R + O_2 + M \rightarrow RO_2 + M$$
$$RO_2 + NO \rightarrow RO + NO_2$$
$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$
$$RO + O_2 \rightarrow R'CHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$

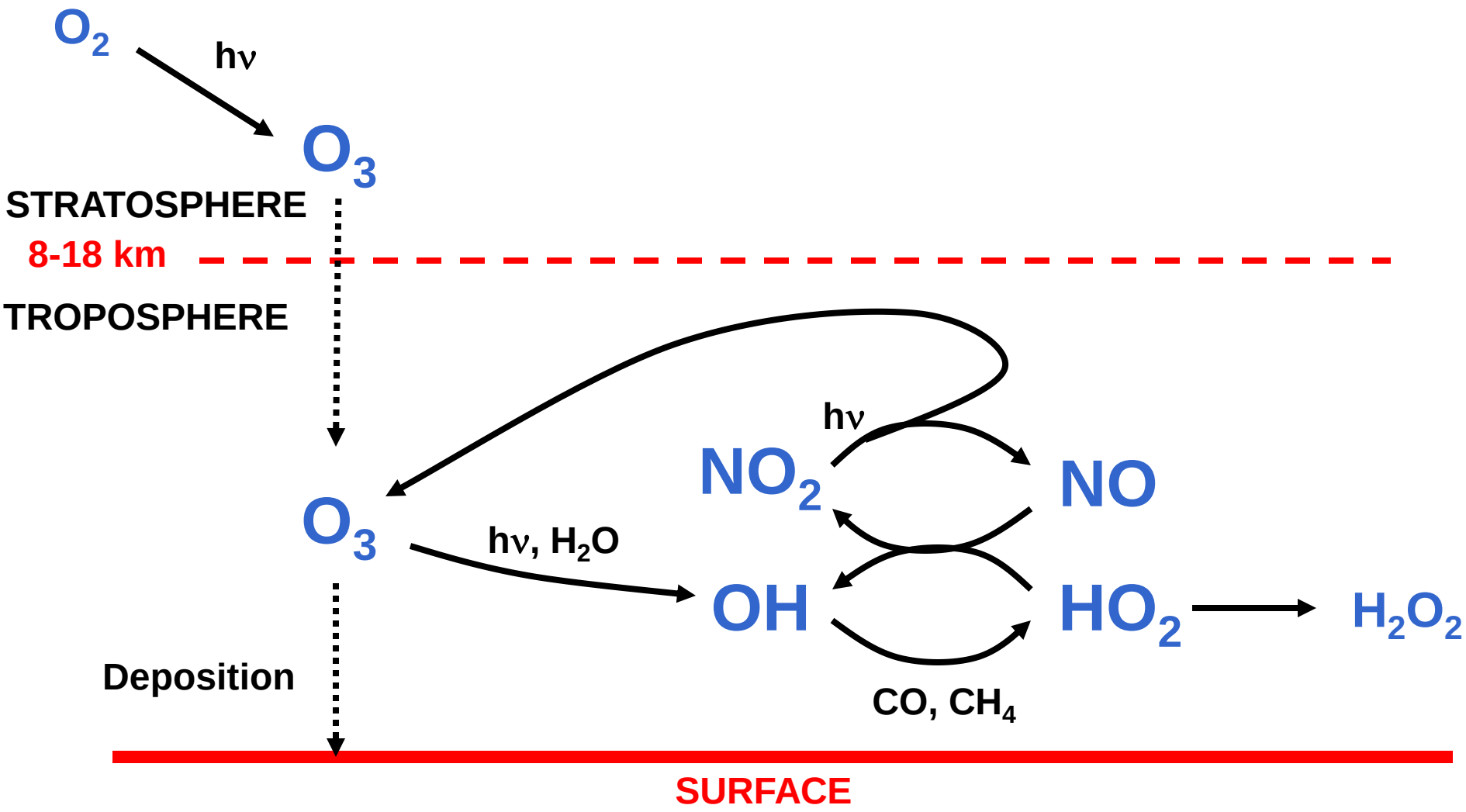
Net: $RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$

OH can also add to double bonds of unsaturated VOCs

RO can also decompose or isomerize; range of carbonyl products

Carbonyl products can react with OH to produce additional ozone, or photolyze to generate more HO_x radicals (branching reaction)

RADICAL CYCLE CONTROLLING TROPOSPHERIC OH AND OZONE CONCENTRATIONS



大气化学传输模式中的化学过程模拟

$$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2$$

$$Rate_1 = k_1[NO][O_3]$$

$$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M$$

$$Rate_2 = k_2[O][O_2][M]$$

$$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\cdot$$

$$Rate_3 = J[NO_2]$$

$$\dot{N}O_2 + O \longrightarrow \dot{N}O + O_2$$

$$Rate_4 = k_3[NO_2][O]$$

ODEs For Set of Reactions

$$\frac{d[NO]}{dt} = P_c - L_c = \text{Rate}_3 + \text{Rate}_4 - \text{Rate}_1 = J[NO_2] + k_3[NO_2][O] - k_1[NO][O_3]$$

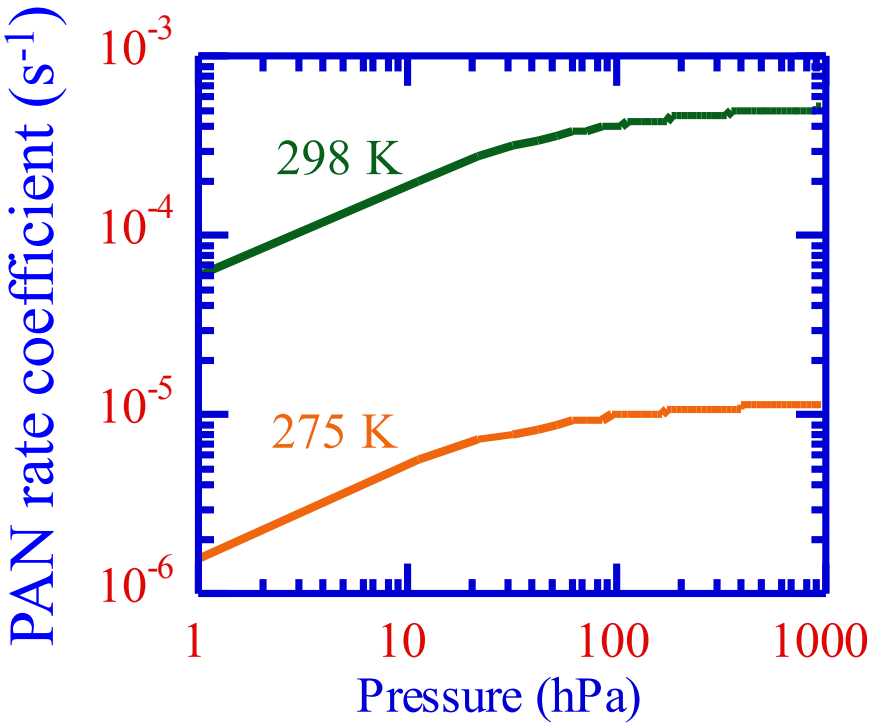
$$\frac{d[NO_2]}{dt} = P_c - L_c = \text{Rate}_1 - \text{Rate}_3 - \text{Rate}_4 = k_1[NO][O_3] - J[NO_2] - k_3[NO_2][O]$$

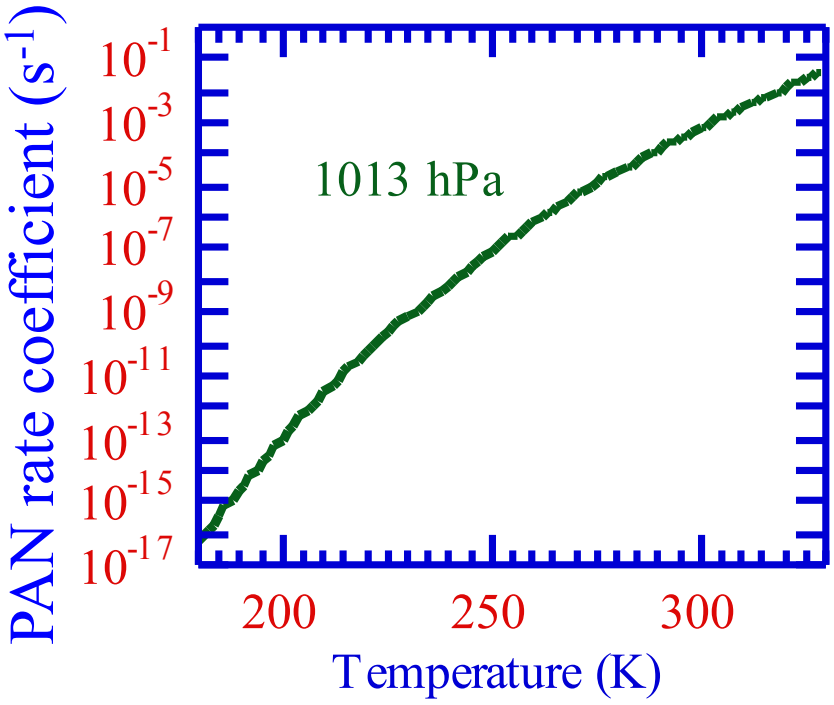
$$\frac{d[O]}{dt} = P_c - L_c = \text{Rate}_3 - \text{Rate}_2 - \text{Rate}_4 = J[NO_2] - k_2[O][O_2][M] - k_3[NO_2][O]$$

$$\frac{d[O_3]}{dt} = P_c - L_c = \text{Rate}_2 - \text{Rate}_1 = k_2[O][O_2][M] - k_1[NO][O_3]$$

化学反应常数

PAN rate coefficient as a function of pressure and temperature, respectively





Jacobson, 2000; Fig. 10.2

Chemistry Operator

- In each model grid, for a single species

$$\frac{dn}{dt} = P - L$$

- For *p* chemically interacting species, *p* coupled ODEs (p typically on the order of 100)

$$\frac{dn_i}{dt} = P_i(\mathbf{n}) - L_i(\mathbf{n})$$

- Stiff equation system (刚性方程）

Stiff System of Equations

Example:

$CH_4 + OH \rightarrow CH_3 + H_2O$

k = 6.2×10^{-15} cm^3 $molec^{-1}$ s^{-1} at 298K

$[OH\cdot]$ = 5.0×10^5 molec. cm^{-3}

---> $\tau_{CH_4} = \dfrac{1}{k[OH\cdot]}$ = 10.2 years

$O(^1D) + N_2 \rightarrow O + N_2$

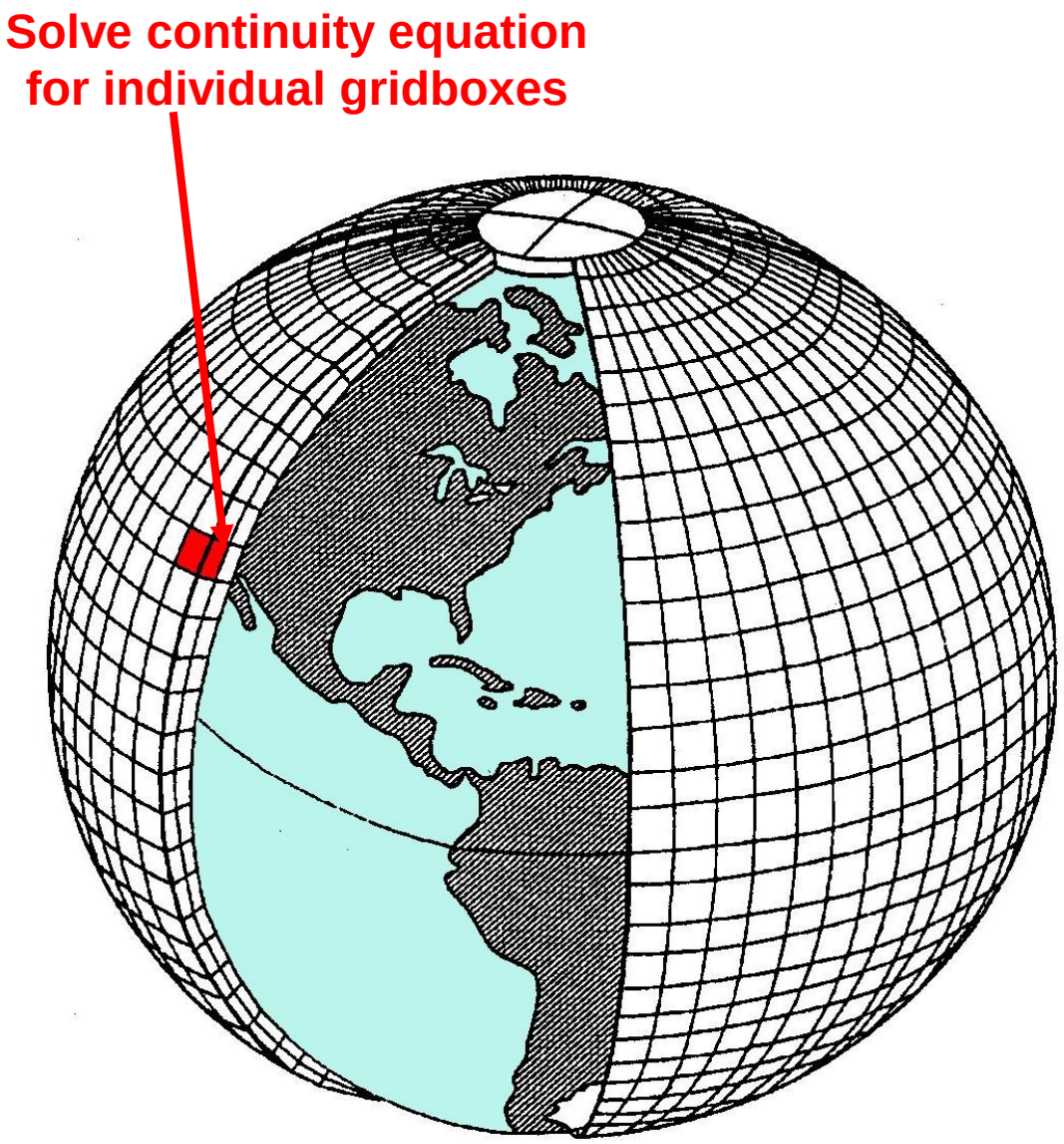
k = 2.6×10^{-11} cm^3 $molec^{-1}$ s^{-1} at 298K

$[N_2]$ = 1.9×10^{19} molec. cm^{-3}

---> $\tau_{O(^1D)} = \dfrac{1}{k[N_2]}$ = 2×10^{-9} seconds

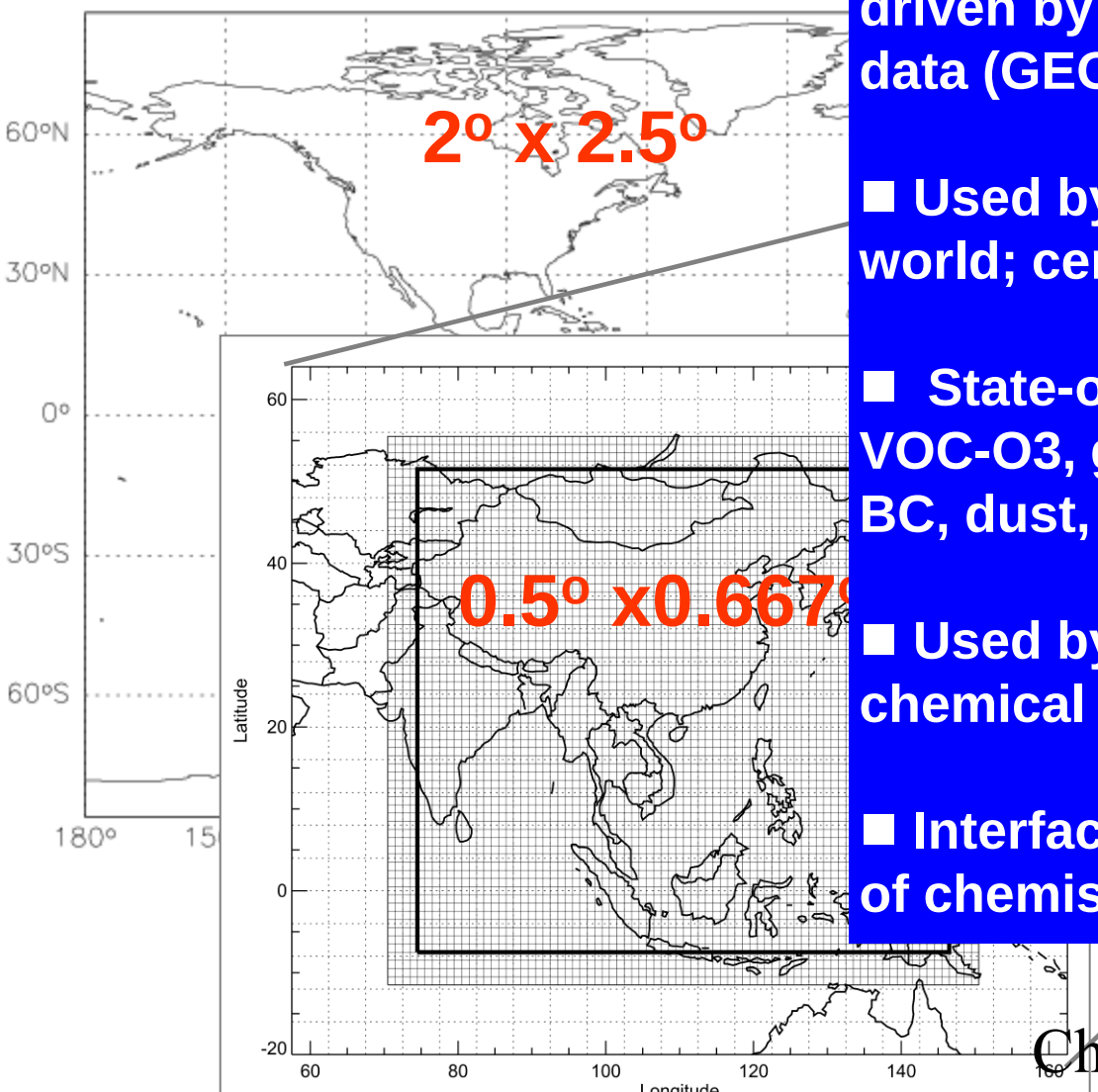
---> stiff set of equations

全球大气化学传输模式



- Models can presently afford ~ 10^6 gridboxes
- In global models, this implies a horizontal resolution of 100-500 km in horizontal and ~ 1 km in vertical
- Drawbacks: “numerical diffusion”, computational expense

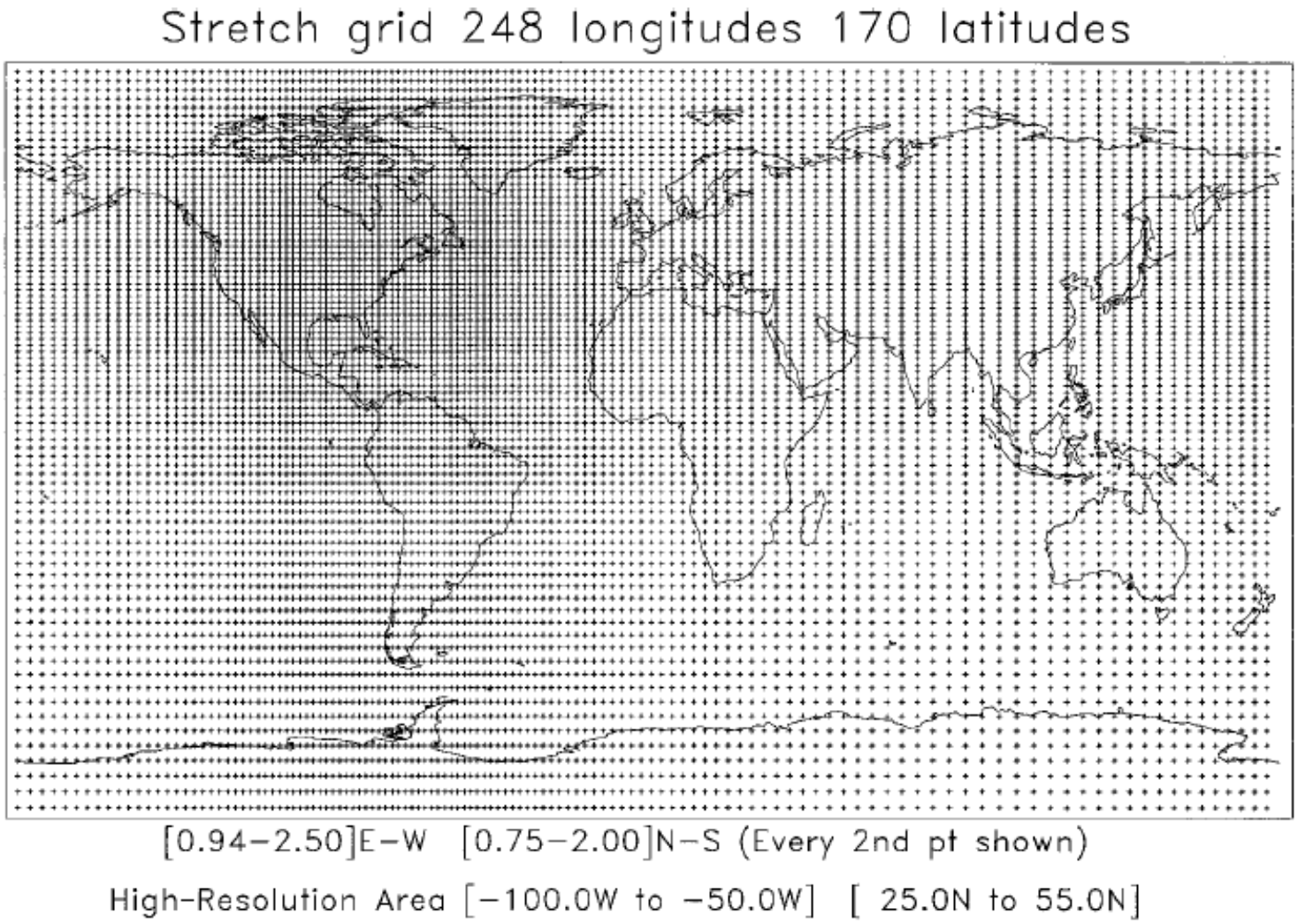
Nested-grid GEOS-Chem chemical transport model developed at CESS



- Chemical transport model (CTM) driven by assimilated meteorological data (GEOS from NASA DAO)
- Used by 30 groups around the world; centrally managed at Harvard
- State-of-the-art chemistry: NOx-VOC-O3, gas-aerosol coupling, SOA, BC, dust, Hg, CH4, CO_2, SF6, etc
- Used by NASA to drive global chemical data assimilation
- Interfaced with GISS GCM for study of chemistry-climate interactions

Wang et al., JGR, 2004;
Chen, Wang, et al., ACP, 2009

Stretched Grid chemical transport model



Allen et al., JGR, 2000

大气化学传输模式可研究的科学问题

- 大气污染物的长距离传输
- “自上而下”的污染物清单校验与反演
- 重要化学物种的源汇分析（budget analysis)
- 污染现象的解释
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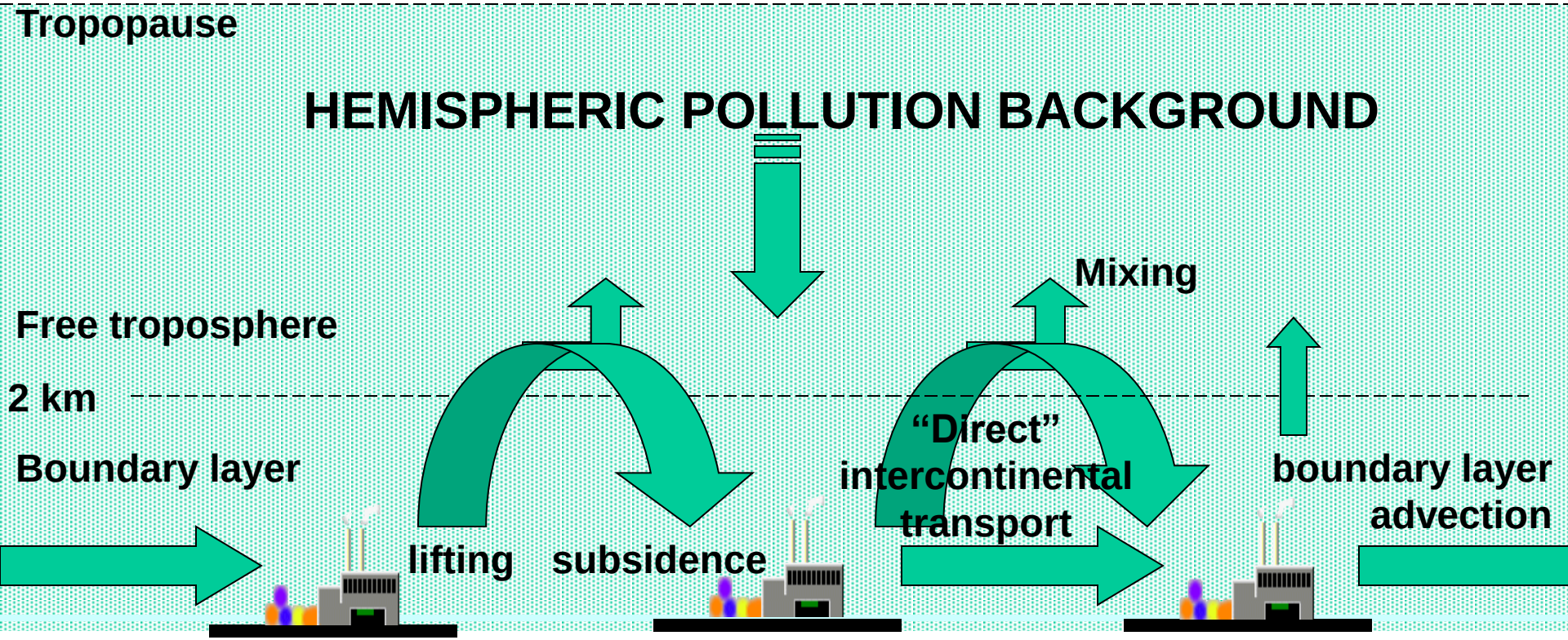
- ……

TWO MODES OF INTERCONTINENTAL INFLUENCE

- **Direct intercontinental transport**: fast (~1 week) transport from source to receptor continent; either by boundary layer advection or by lifting to lower free troposphere followed by subsidence

- **Hemispheric pollution**: pollution mixes in free troposphere, affecting free tropospheric background, in turn affecting surface concentrations by subsidence



HTAP, 2011

Source contributions to intercontinental transport

- **Source attribution (S/A):** **contribution of a particular source to the absolute concentrations at a given location**
- **Source-receptor relationship (S/R):** **the relative extent to which concentrations at a specific location change when a particular source is perturbed in an arbitrary manner**
- **The two approaches give similar results for inert tracers, but different results for reactive species such as ozone**

Model methods to quantify intercontinental transport

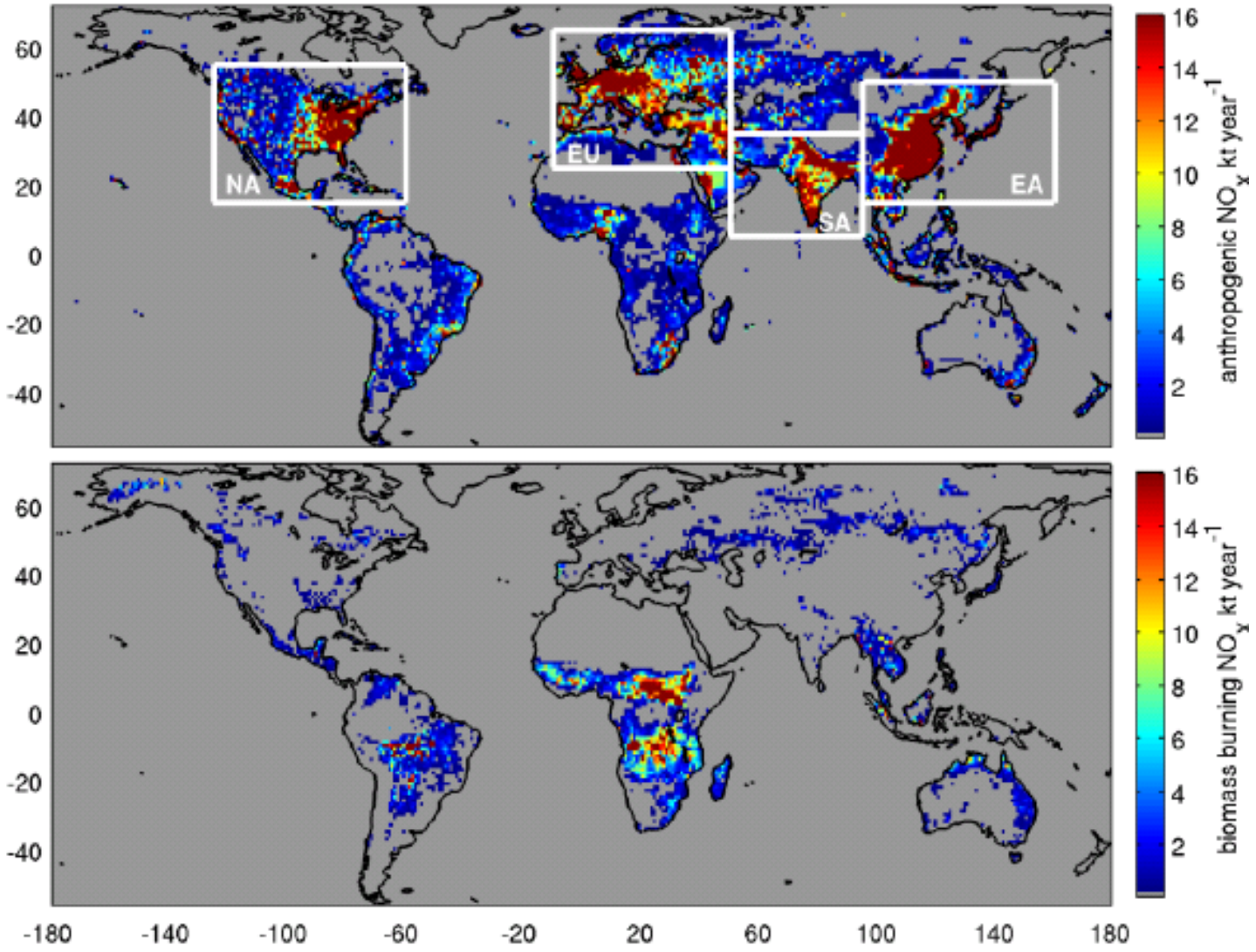
- **Emission sensitivity approach: standard 'control' run and 'perturbation' run.**
- **Tagged tracer method: each tracer tagged by its source region and representing the contribution of that source region**
- **Tagged ozone method: simple; domain-based rather than source-based; not reflecting the contribution of precursor emissions from a given source region**
- **Typically, the sum of the fractional contribution of all tagged tracers does not equal unity (depending on the advection algorithm of the model)**

Coordinated Model Studies: HTAP as an example

Model Study	Brief Description	No. of Participants
SR: Source-receptor studies	Sensitivity study with 20% changes to anthropogenic emissions over four major source regions in 2001 to quantify source-receptor relationships	32
TP: Tracer process studies	Repeat of SR with specified emissions and standardized tracers to explore differences in model transport and mixing processes	25
ES: Event Simulations	Explore model ability to reproduce specific intercontinental transport events observed during the ICARTT campaign in 2004	7
FE: Future emissions studies	Repeat of SR under different scenarios for future emissions in 2030 (RCP8.5) and 2050 (RCP2.6) conditions	4
FC: Future climate studies	Repeat of SR under different climate conditions corresponding to present-day and 2100 SRES-A2 climates	3

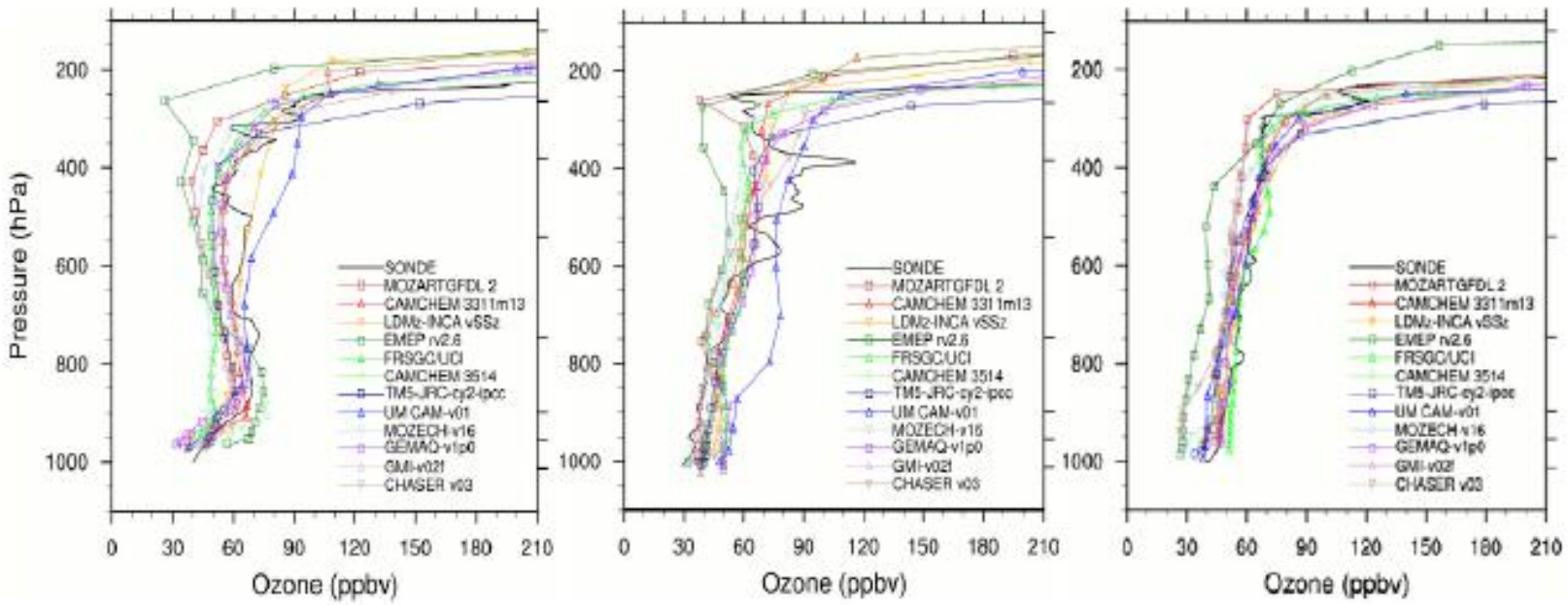
HTAP, 2011

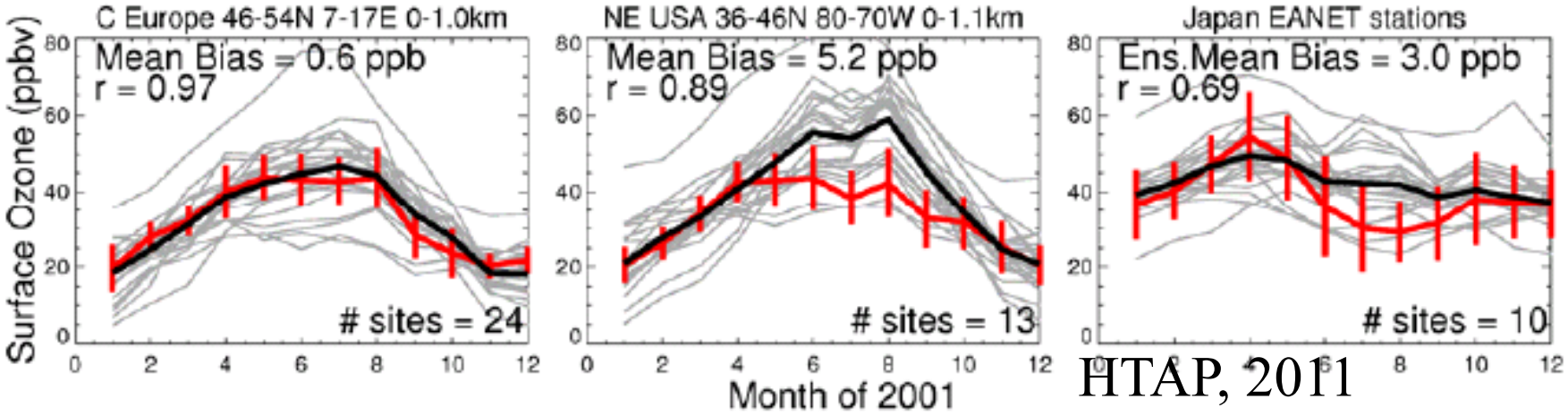
HTAP regions



Model's ability in simulating ozone: mean concentrations

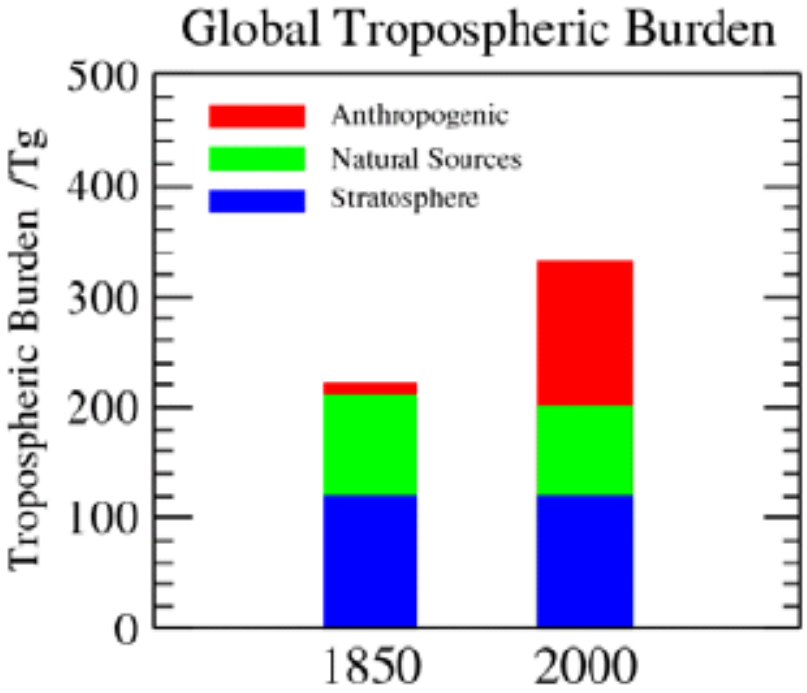
Goose Bay, Canada **Uccle, Belgium** **Yakutsk, Siberia**

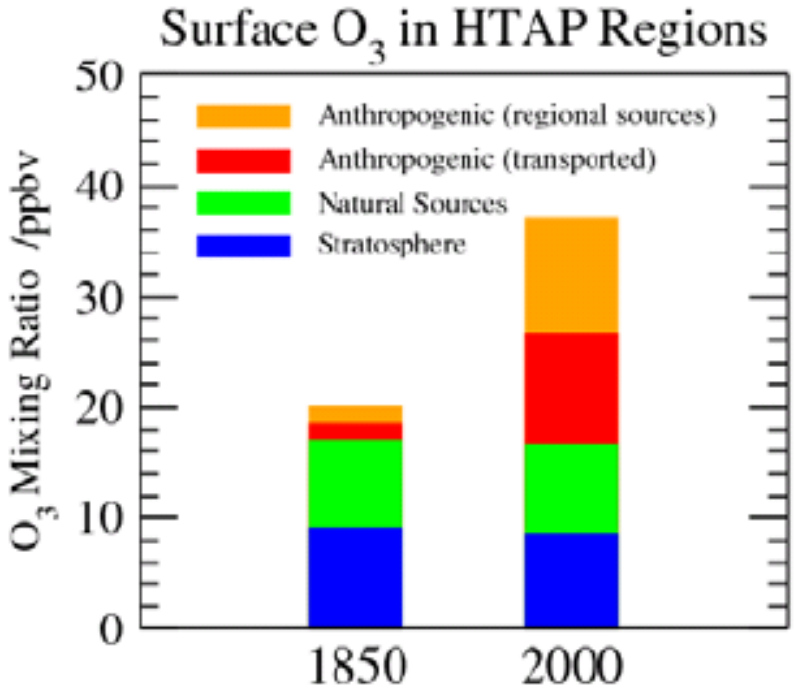




HTAP, 2011

Source Attribution



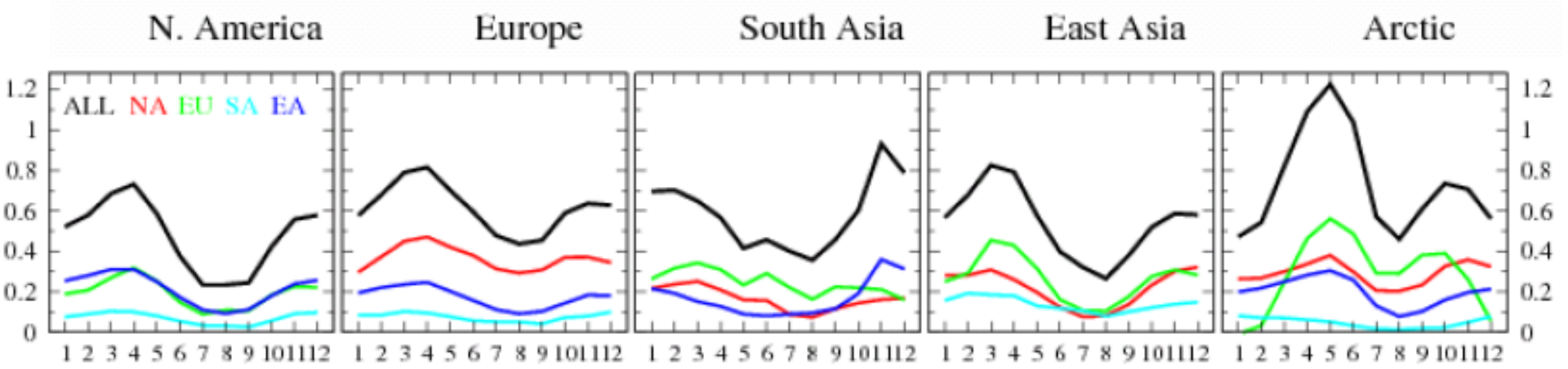


S/R: 20% emission perturbation

	Receptor Region			
Source Region	NA	EU	EA	SA
Annual mean decrease				
NA	1.04(1.03)±0.23	**0.37(0.37)±0.10**	**0.22(0.24)±0.05**	**0.17(0.19)±0.04**
EU	**0.19(0.18)±0.06**	0.82(0.68)±0.29	**0.24(0.24)±0.08**	**0.24(0.25)±0.05**
EA	**0.22(0.23)±0.06**	**0.17(0.17)±0.05**	0.91(0.86)±0.23	**0.17(0.17)±0.05**
SA	0.07(0.07)±0.03	0.07(0.07)±0.03	**0.14(0.13)±0.03**	1.26(1.18)±0.26
Relative annual intercontinental response				
	0.32	0.43	0.40	0.32

HTAP, 2011

Seasonal response



HTAP, 2011

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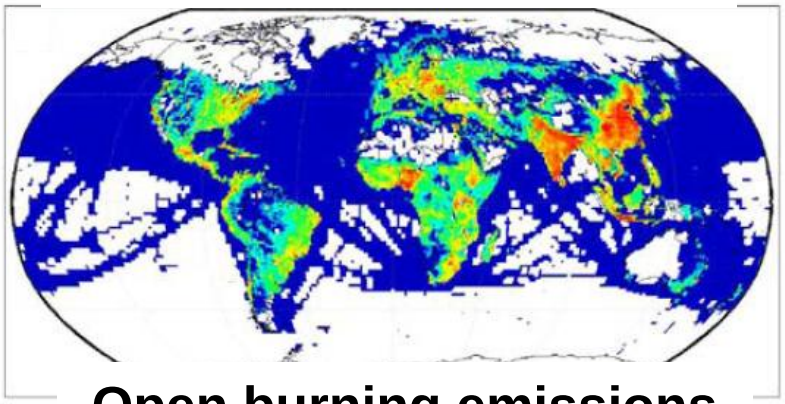
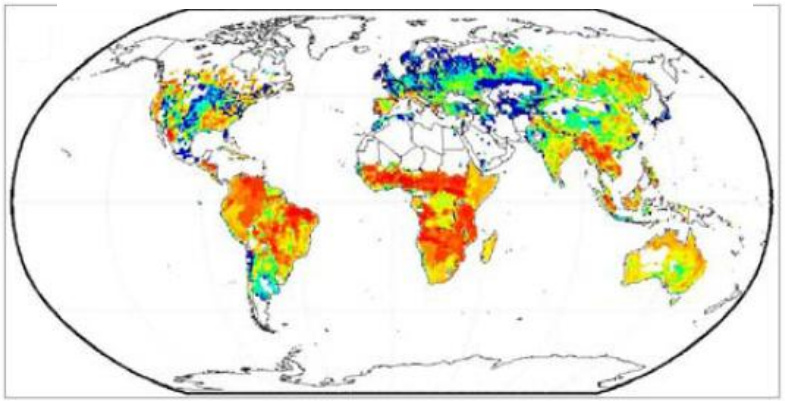
$PM_{2.5}$ component, Black Carbon —— warming agent

Emission and deposition are key processes for BC

Anthropogenic emissions



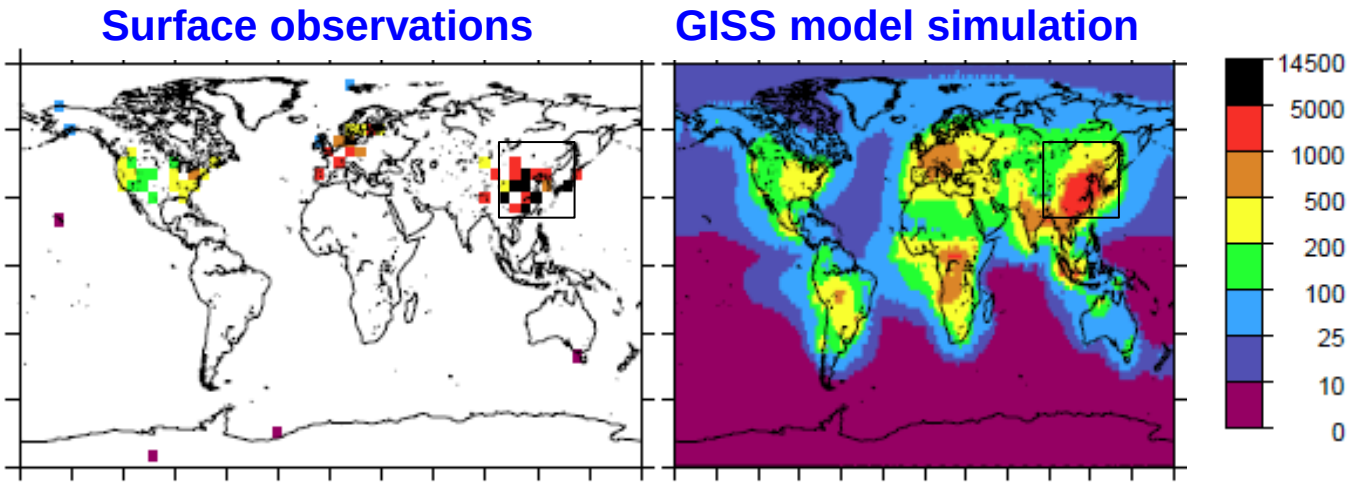
Open burning emissions



Bond et al., 2004

- **China contributes 25% of global BC emissions**
  - **1.3 Tg in 1995,1.1–1.5 Tg in 2000, 1.8 Tg in 2006**
- **All BC inventories have high uncertainty over China**
  - **Bottom-up emission inventories reported uncertainties ranging from 187% to 484% in China** *(Street et al., 2003; Zhang et al., 2009; Lei et al., 2011)*

Surface observations can constrain BC emissions, but results depend on obs/model



Koch et al., ACP, 2009

	Site location	Temporal resolution	Model resolution	Conclusion on emissions
Koch et al., ACP, 2009	16 rural/urban	Annual mean	4×5°	Underestimated by 50%
Kondo et al., JGR, 2011	1 coastal outside China	hourly mean	81×81 km	Accuracy within 30%
Fu et al., ACP, 2012	10 rural	Monthly mean	0.5×0.667°	Underestimated at least by 60%
Wang et al., ACP, 2011	18 rural/selected urban	Annual mean	2×2.5°	Chinese emissions need to be doubled

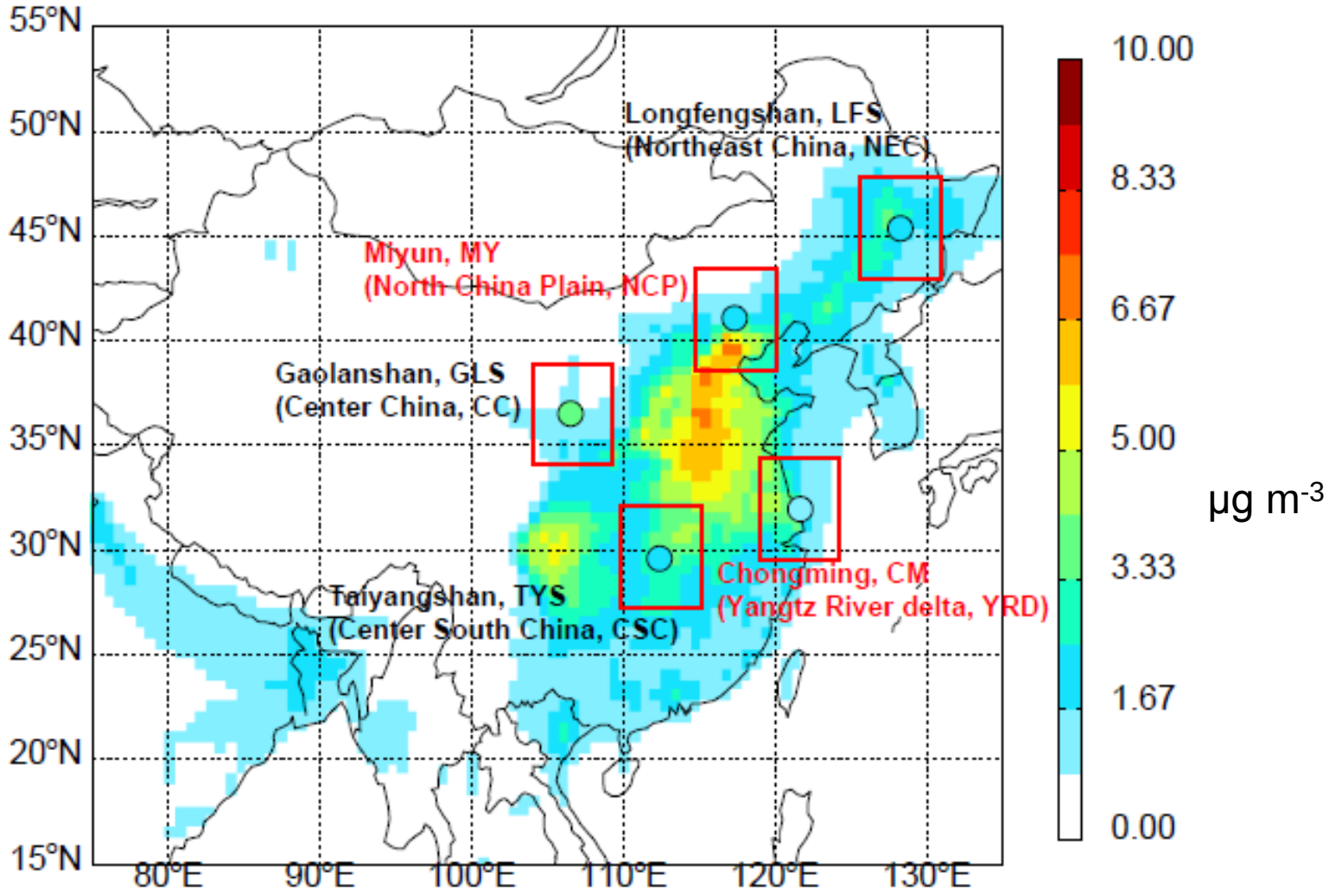
Can we reconcile the different conclusions? Need careful analysis of model and observation

- **Emission data are not the only source of model/observation differences**
  - ✓ **Representativeness of observations**
  - ✓ **Grid resolution**
  - ✓ **Removal processes (wet deposition)**
  - ✓ **Chemistry**
  - ✓ **Transport**

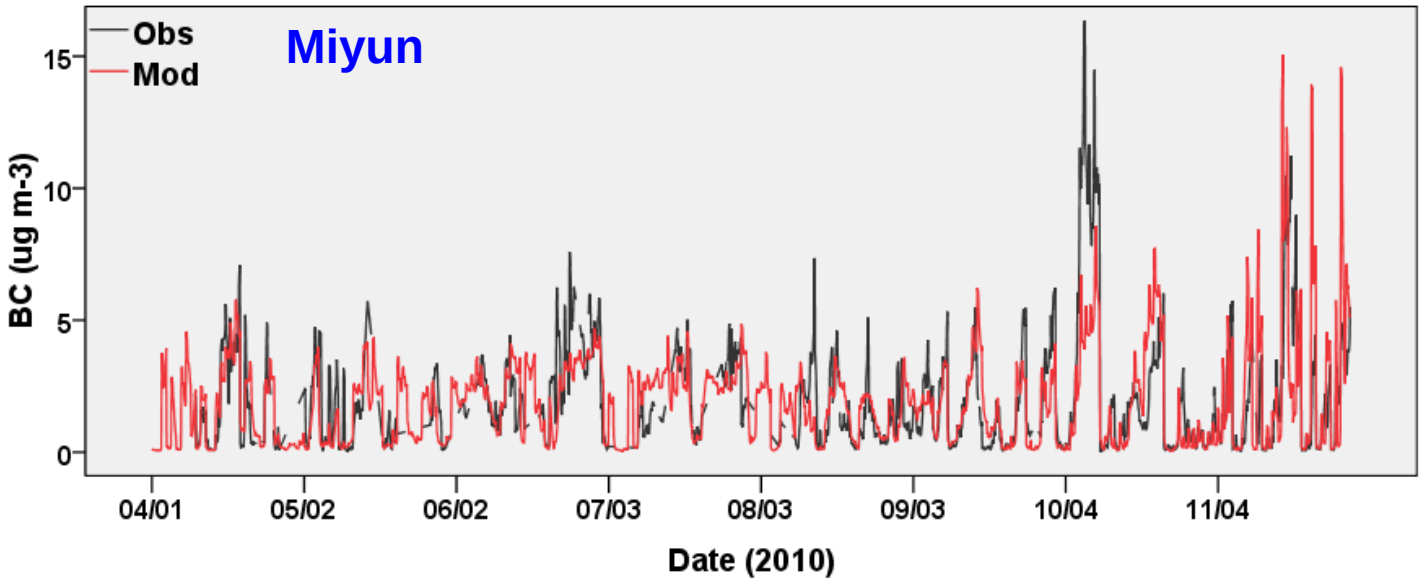
Hourly and monthly BC observations at five rural sites in China

Simulated annual-mean surface BC and previous rural observations

(Wang YX et al., 2011; *Han et al., 2004; Zhou et al., 2006; Cao et al., 2008*)



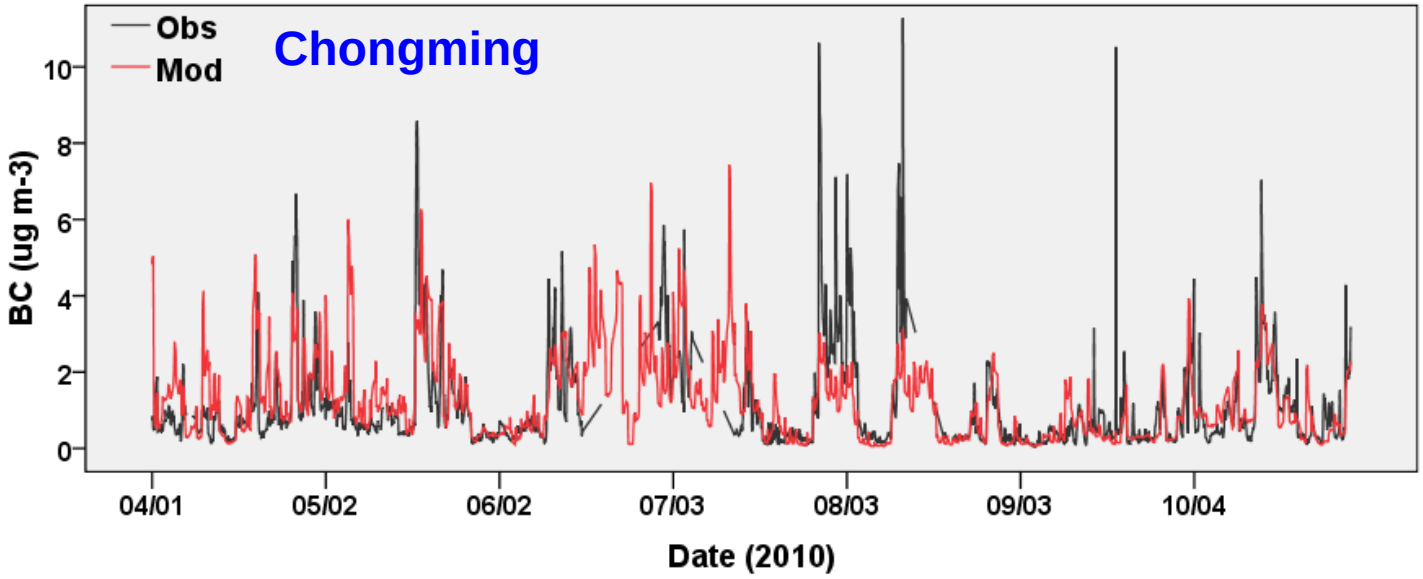
Model results compared with Tsinghua's continuous BC observations



Obs: 2.05 μg m^{-3}

Mod: 1.88 μg m^{-3}

R^2 = 0.37



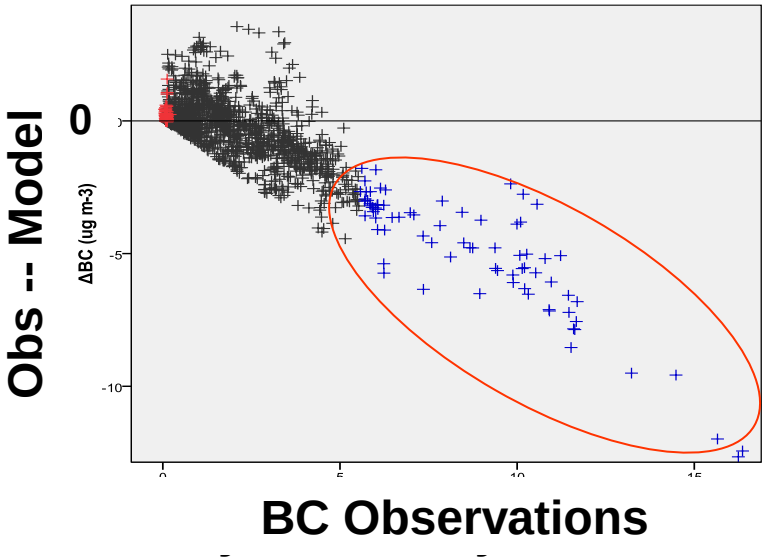
Obs: 1.09 μg m^{-3}

Mod: 1.11 μg m^{-3}

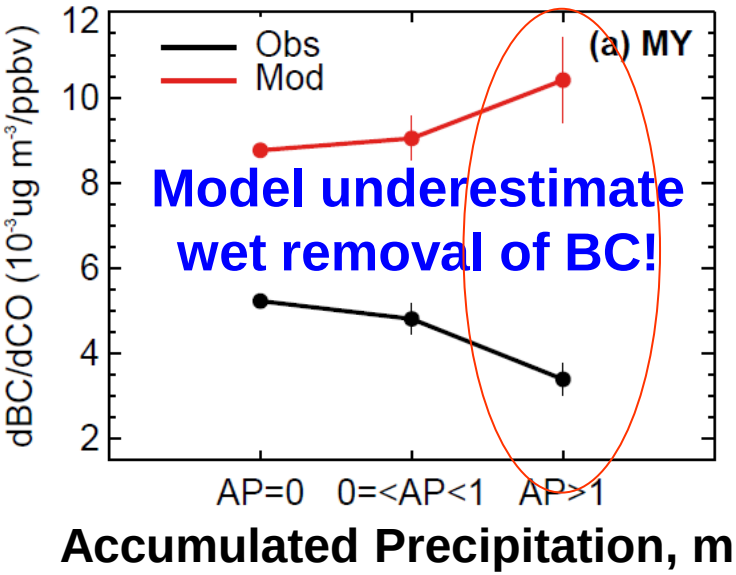
R^2 = 0.36

Careful data selection to minimize model error and observation's representation error

Model bias due to resolution



BC/CO vs precipitation



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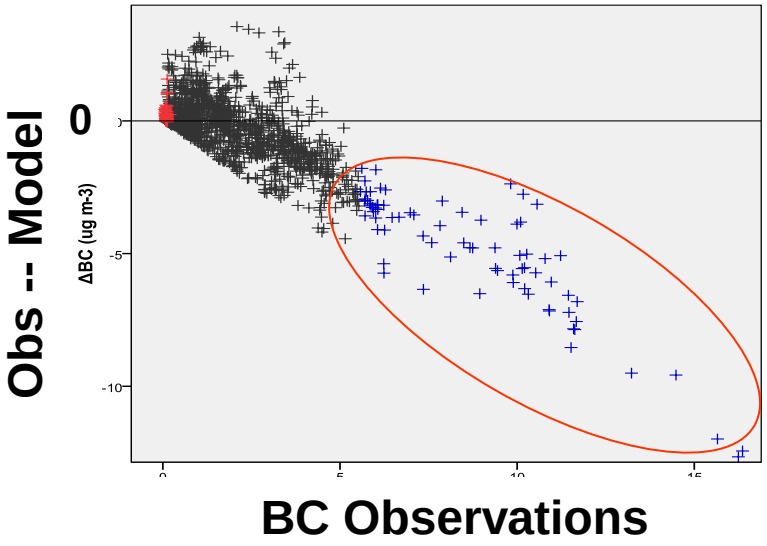

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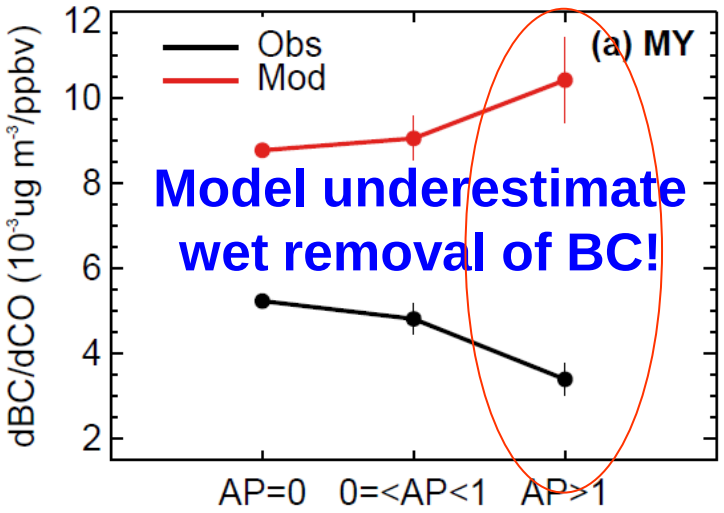

Data selection method	Estimated emission bias at Miyun	Estimated emission bias at Chongming
Monthly-mean data	-9%	+42%
Hourly data (no screening)	-11%	-22%
Exclude high points (<5%)	-18%	-13%
Exclude large precipitation events	-16%	-21%

大气化学传输模式可研究的科学问题

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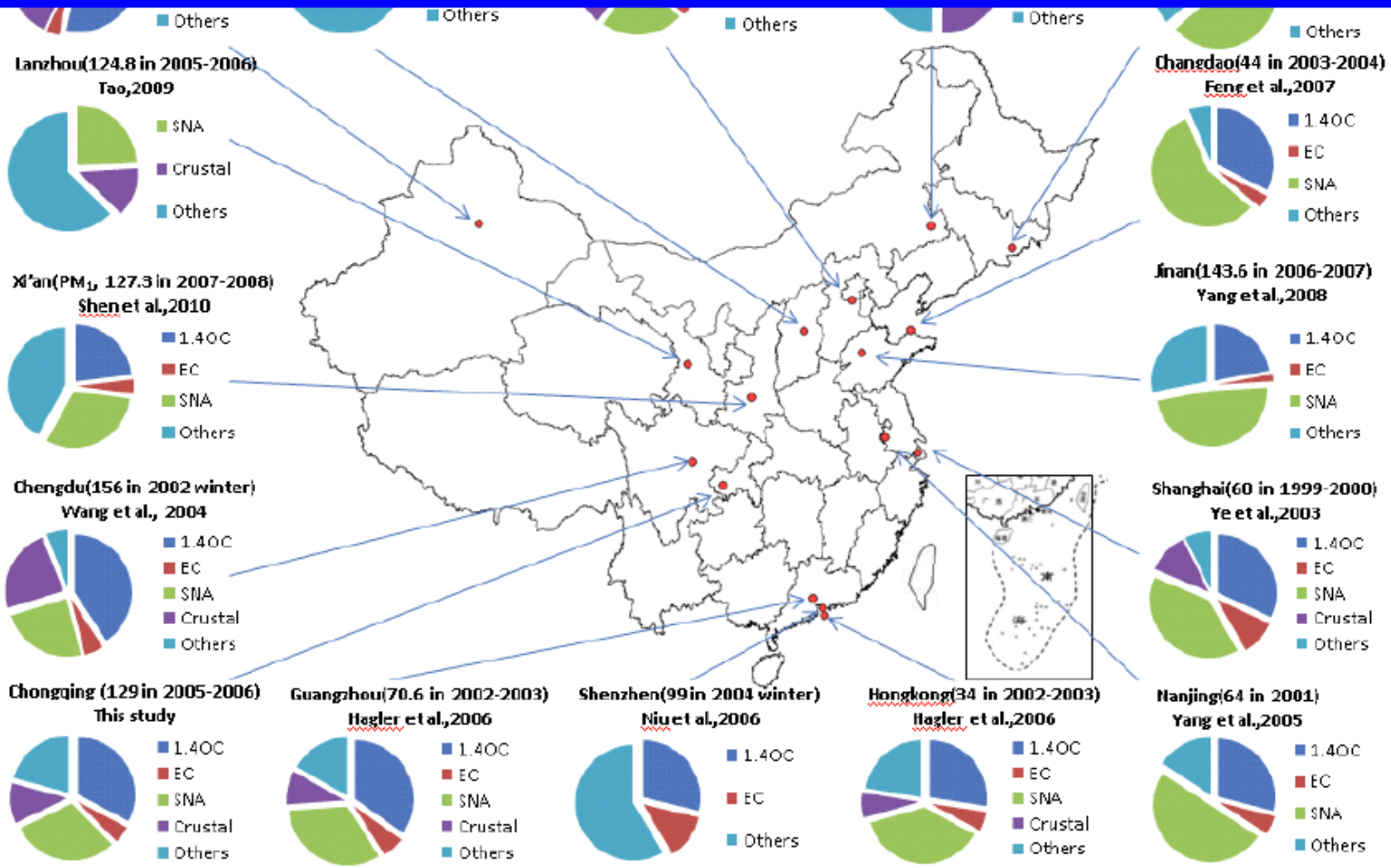
- ……

Is China currently on the right path to mitigate air pollution?

- China's long-term efforts to curb SO_2 emissions – proved success during the 11th FYP (2005-2010)
- Emission control target in the 12th FYP (2011-2015):
  - Continuation of SO_2 emission control: a 8% reduction
  - NOx control target for the first time: a 10% reduction

Sulfate-nitrate-ammonia (SNA) aerosols are important components in $PM_{2.5}$

Secondary inorganic aerosols (sulfate, nitrate, ammonium) account for 30% ~ 60% of $PM_{2.5}$ mass in China!



Yang F. et al., ACP, 2011

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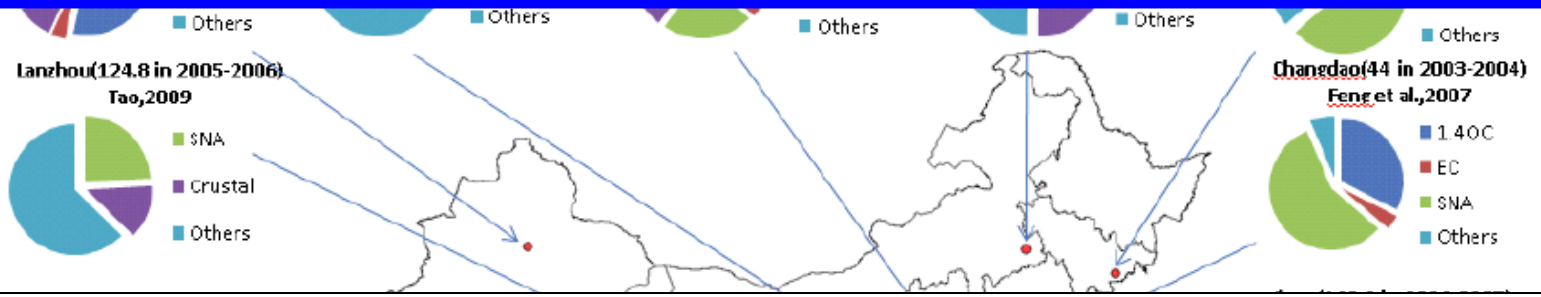
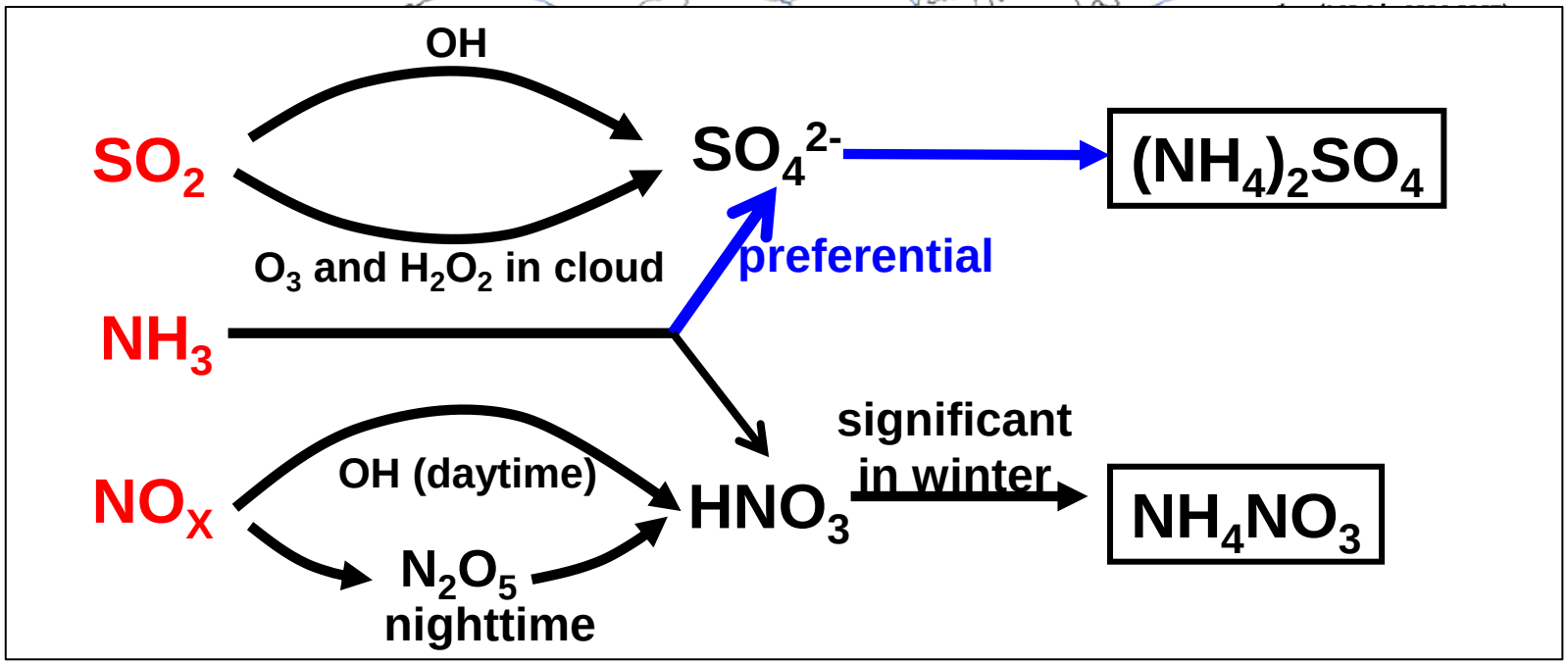
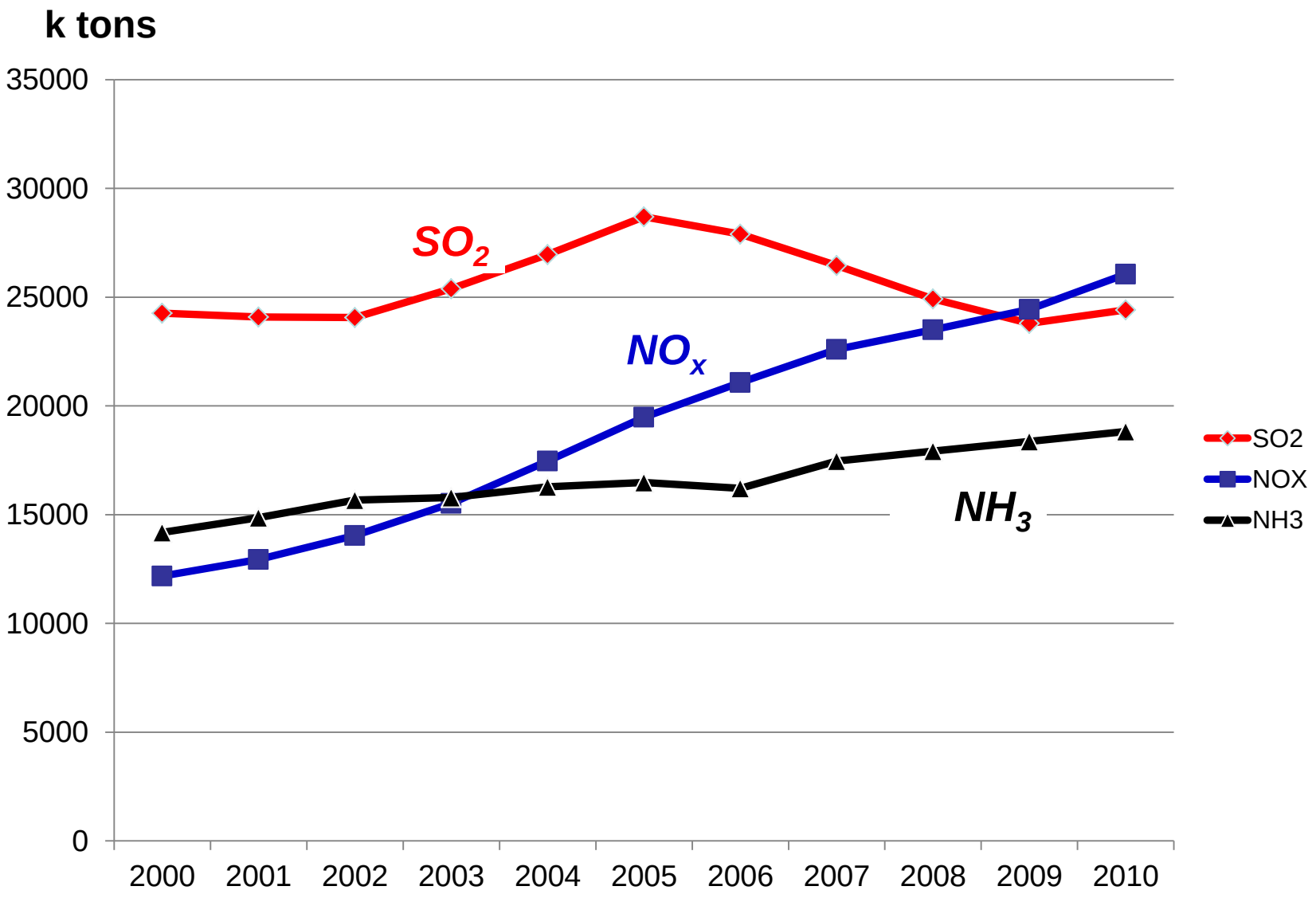
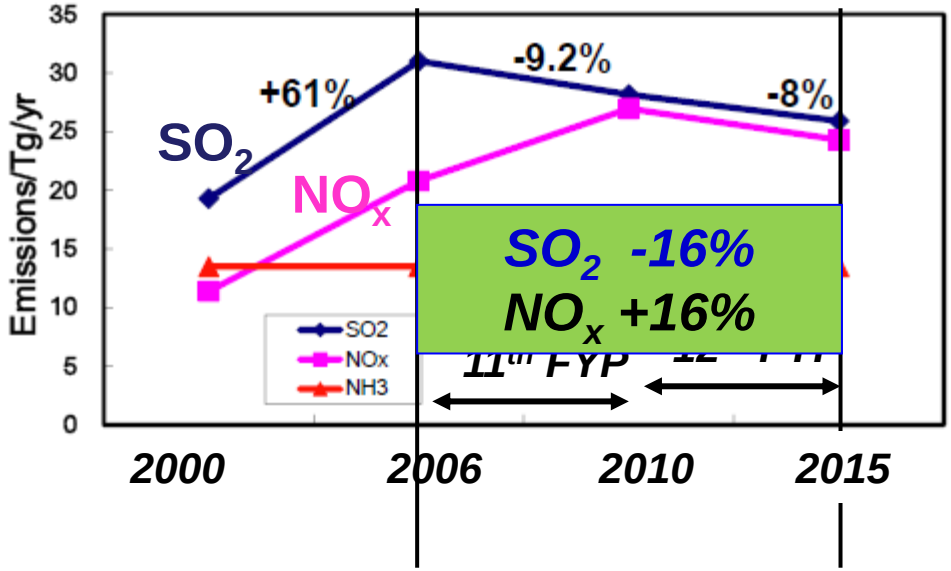




Chinese Emissions of SO_2, NO_x, NH_3

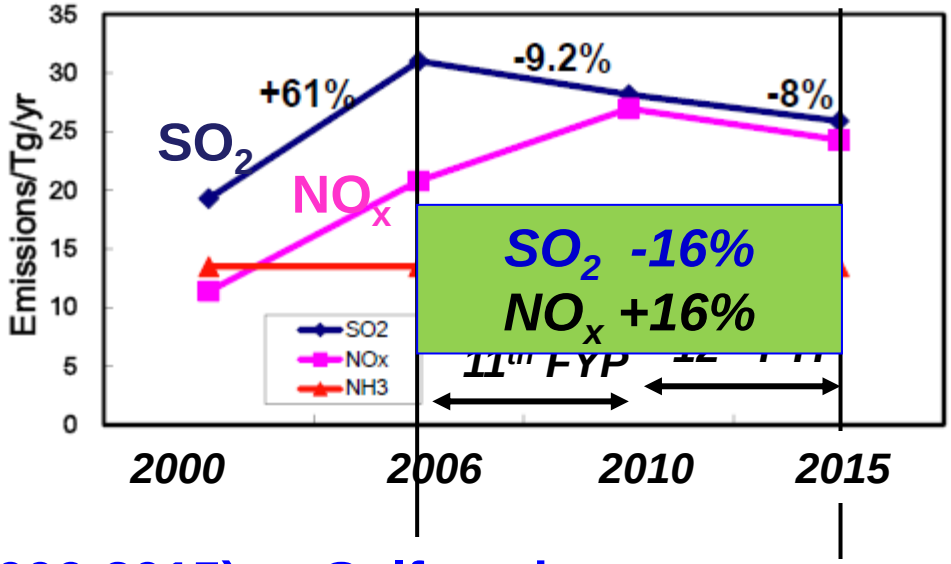


Will sulfate-nitrate-ammonia aerosols decrease in 2015?



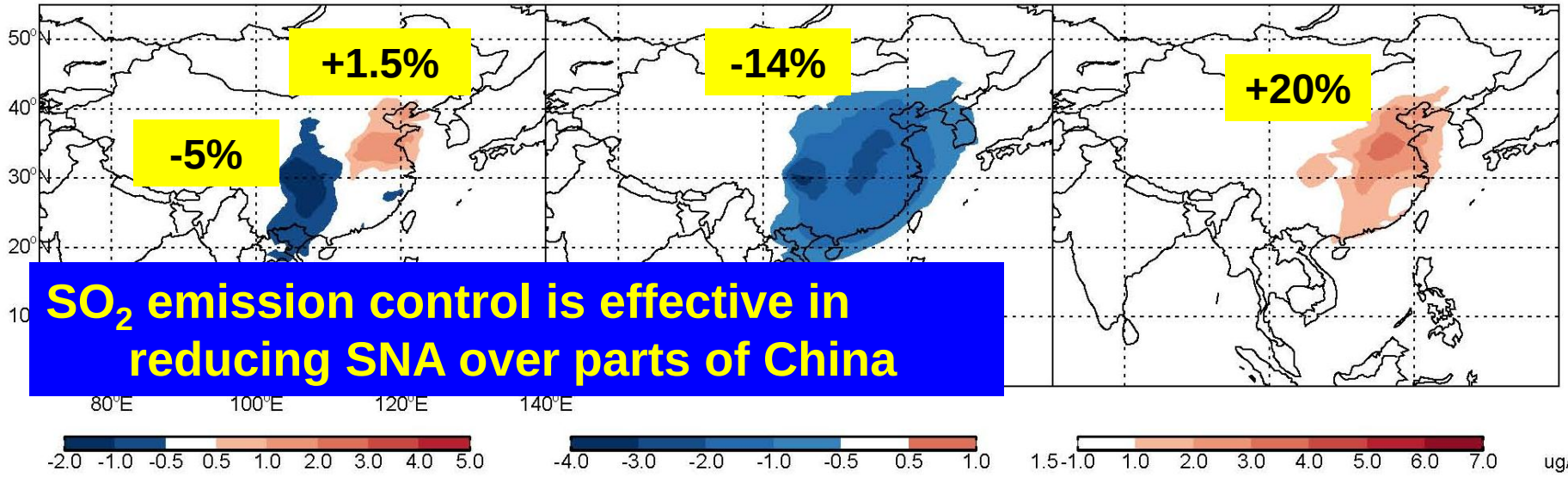
Lu et al., 2011;
Ohara et al., 2010;
Zhang et al., 2009

Will sulfate-nitrate-ammonia aerosols decrease in 2015?



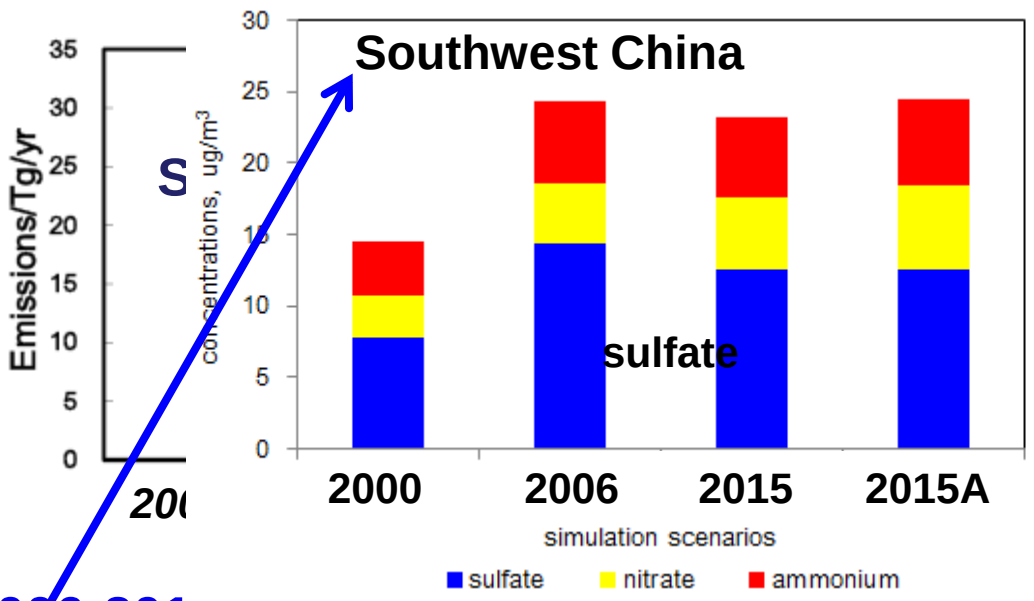
Lu et al., 2011;
Ohara et al., 2010;
Zhang et al., 2009

SNA change (2006-2015) **Sulfate decrease** **Nitrate increase**



SO_2 emission control is effective in reducing SNA over parts of China

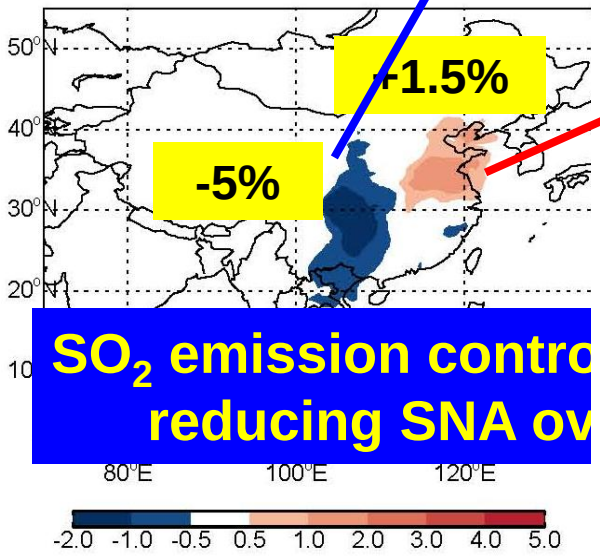
Will sulfate-nitrate-ammonia aerosols decrease in 2015?



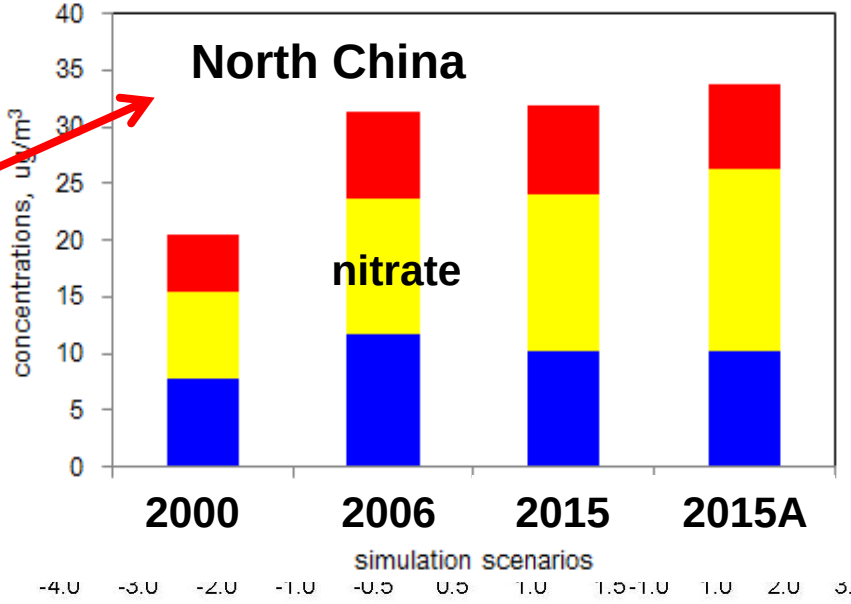
Lu et al., 2011; Ohara et al., 2010; Zhang et al., 2009

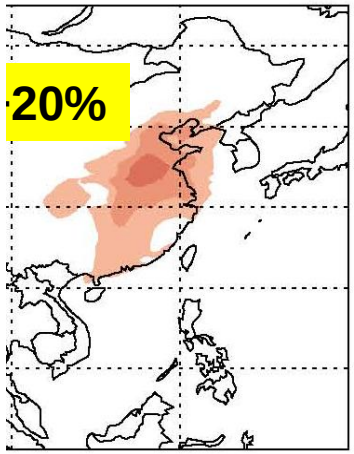
SNA change (2006-201

e increase



SO_2 emission contro reducing SNA ov





Sensitivity of SNA aerosols in 2015 to NH_3 emissions

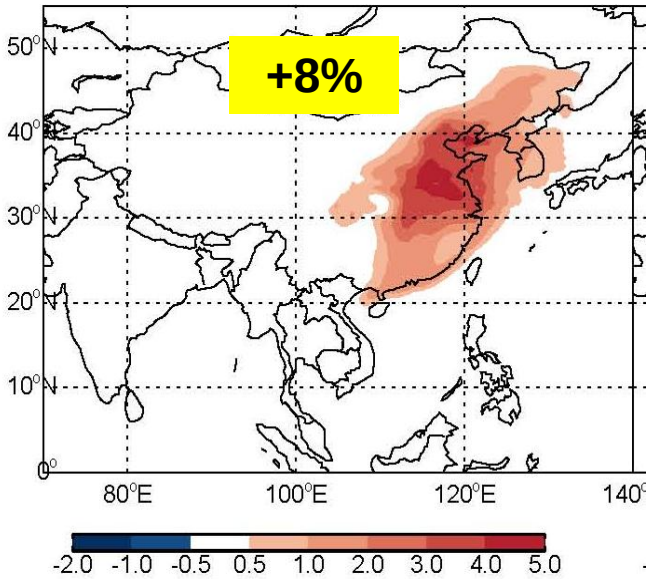
What if NH_3 emissions increase in 2015? A likely scenario.

2006 → *2015*

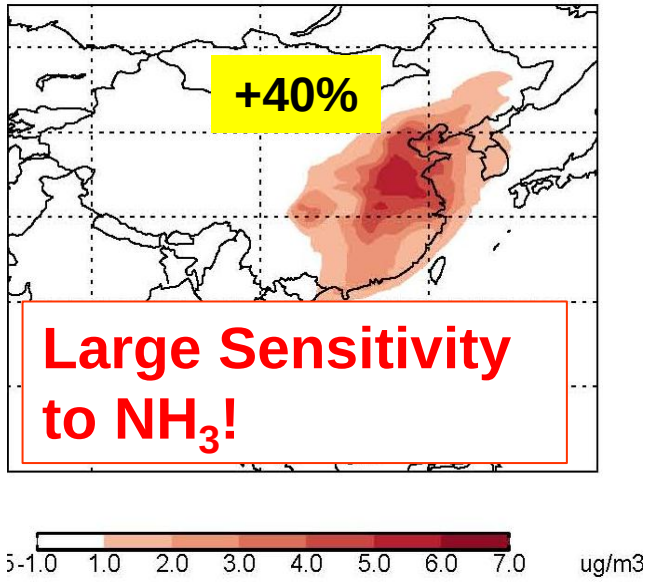
SO_2 -16%
NO_x +16%
NH_3 +16%

Adding +16% NH_3

SNA increase (2006-2015)



More nitrate increase



Policy Implications: If not controlling NH_3 emissions in the future, the benefit of SO_2 reduction on SNA will be completely offset over all of China due to the significant increase of nitrate.

Wang YX, Zhang QQ, et al., ACP, under review

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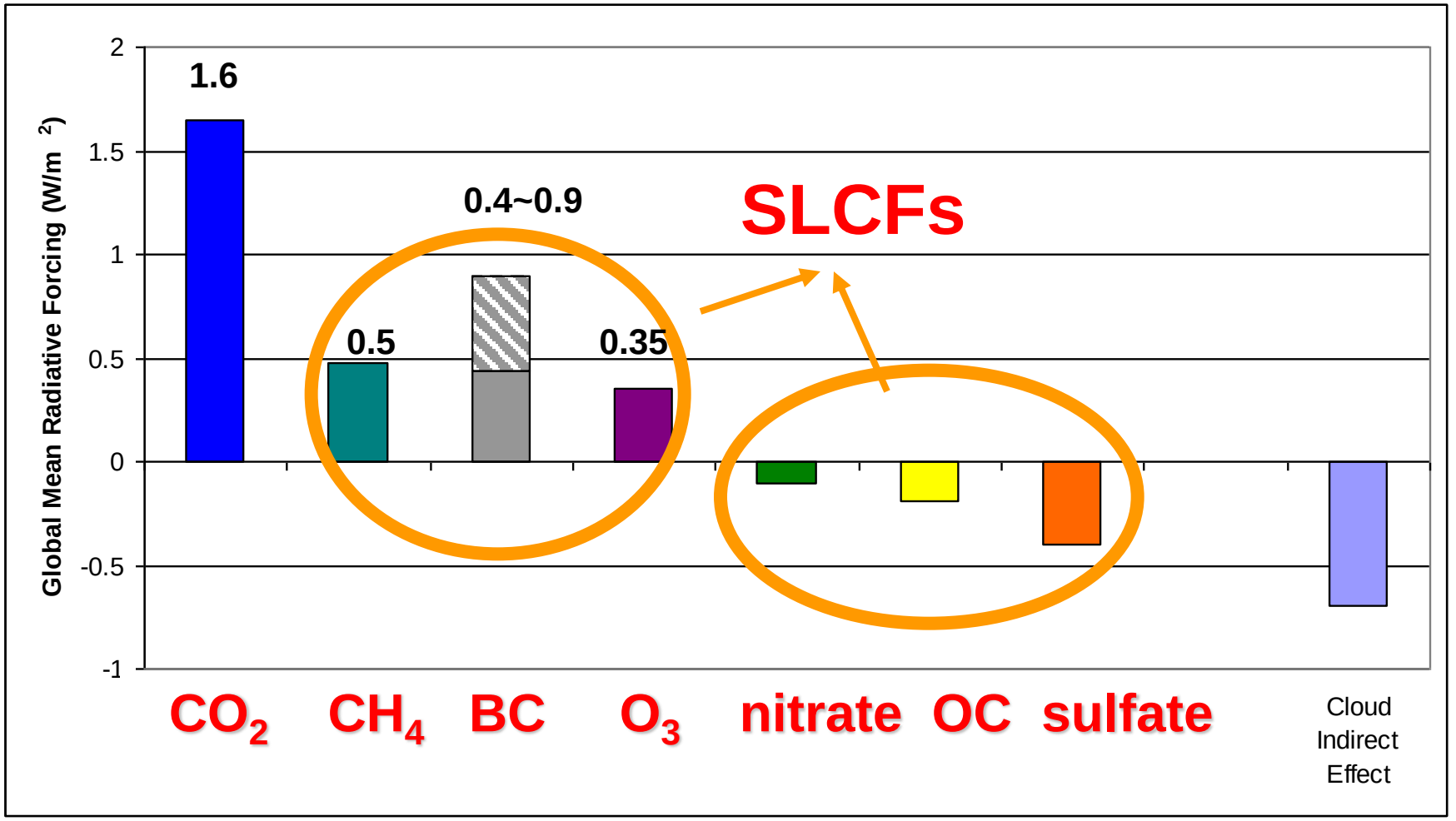
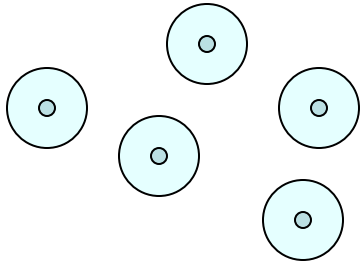
Pollutants as Short-Lived Climate Forcers

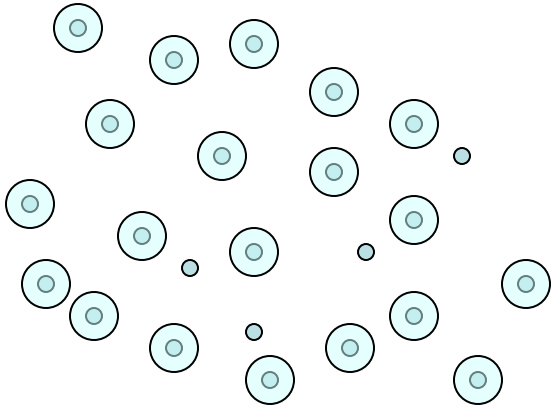


(Adapted from IPCC Synthesis Report, 2007; as well as Ramanathan and Carmichael, 2008)

AEROSOL "INDIRECT EFFECT" FROM CLOUD CHANGES

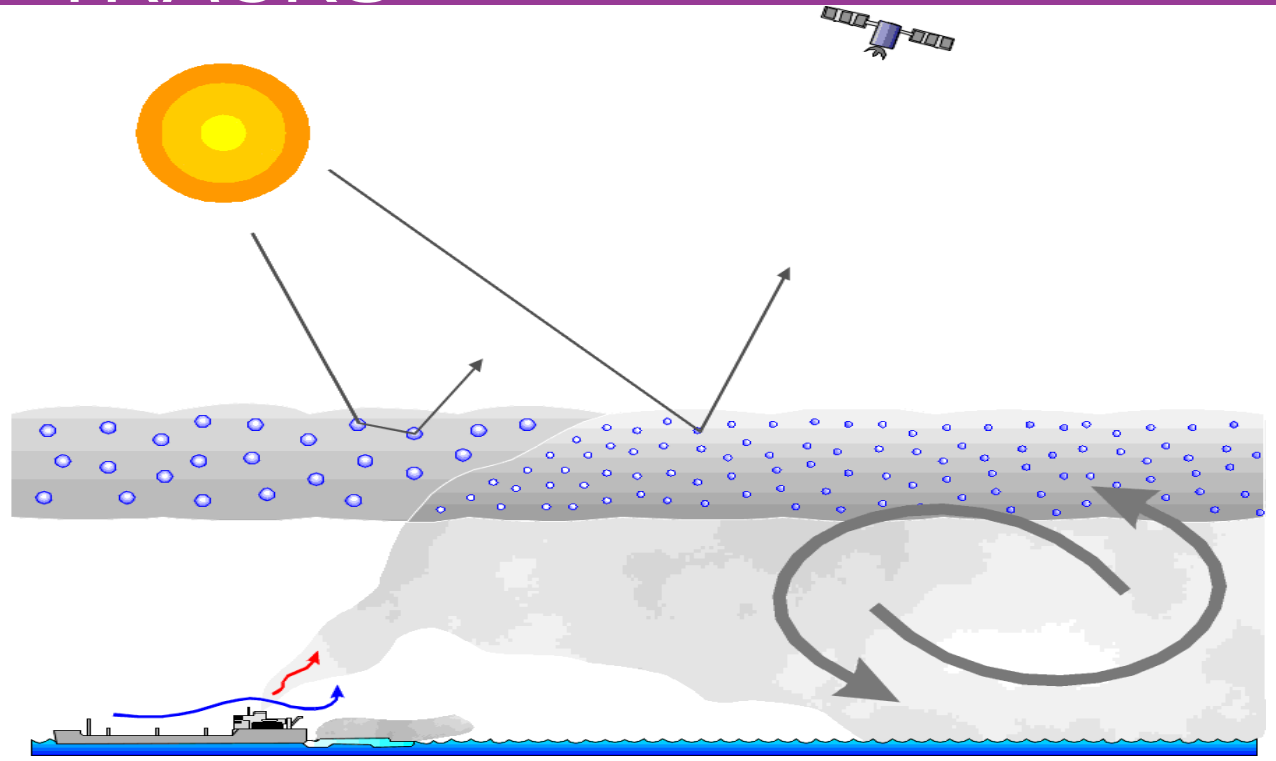


clean cloud (few particles):
large cloud droplets
- **low albedo**
- **efficient precipitation**



polluted cloud (many particles):
small cloud droplets
- **high albedo**
- **suppressed precipitation**

EVIDENCE OF INDIRECT EFFECT: SHIP TRACKS



from D. Rosenfeld

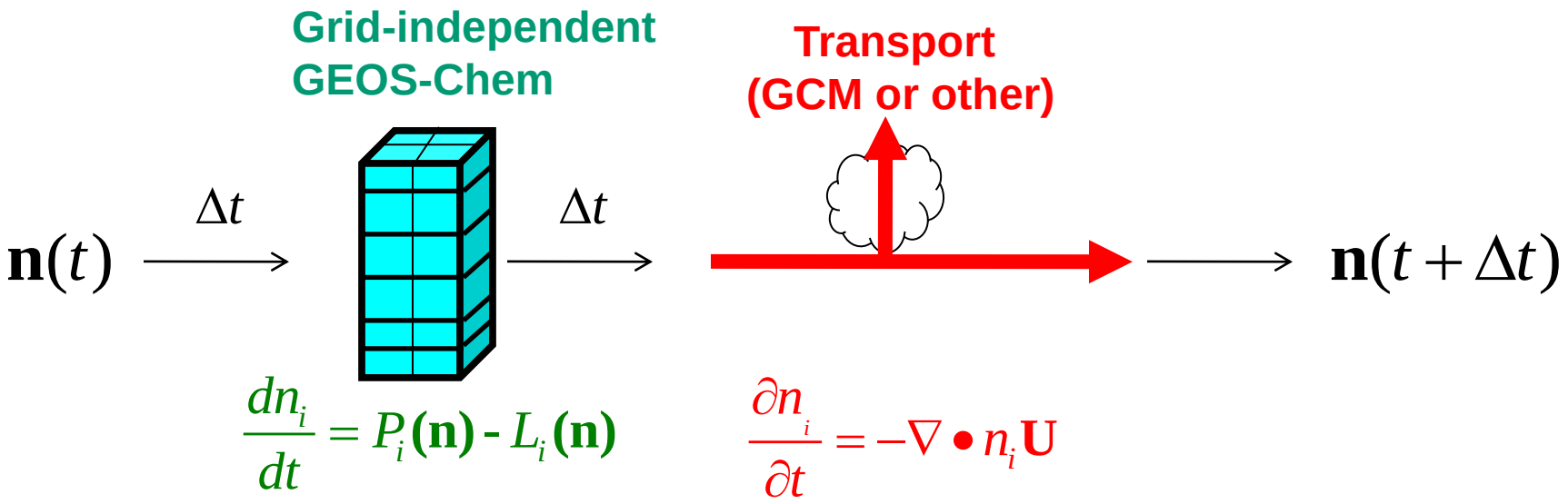
- Particles emitted by ships increase concentration of cloud condensation nuclei (CCN)
- Increased CCN increase concentration of cloud droplets and reduce their avg. size
- Increased concentration and smaller particles reduce production of drizzle
- Liquid water content increases because loss of drizzle particles is suppressed
- Clouds are *optically thicker* and brighter along ship track

Table 1. Overview of the different aerosol indirect effects.[3]

Effect	Cloud Type	Description	Sign of the Radiative Forcing
First indirect aerosol effect (cloud albedo or Twomey effect)	All clouds	For the same cloud water or ice content more but smaller cloud particles reflect more solar radiation	Negative
Second indirect aerosol effect (cloud lifetime or Albrecht effect)	Warm clouds	Smaller cloud droplets decrease the precipitation efficiency thereby prolonging cloud lifetime	Negative
Semi-direct effect	Warm clouds	Absorption of solar radiation by soot leads to an evaporation of cloud droplets	Positive
Glaciation indirect effect	Mixed-phase clouds	An increase in ice nuclei increases the precipitation efficiency	Positive
Thermodynamic effect	Mixed-phase clouds	Smaller cloud droplets inhibit freezing causing supercooled droplets to extend to colder temperatures	Unknown
Surface energy budget effect	All clouds	The aerosol induced increase in cloud optical thickness decreases the amount of solar radiation reaching the surface, changing the surface energy budget	Negative

IPCC, 2001

Development of grid-independent GEOS-Chem model



- **Grid-independent model computes chemical updates on any grid to pass on to a GCM**
- **Allows flexible coupling to different dynamical cores for data assimilation, climate modeling**
- **Presently developed for coupling with NASA GEOS data assimilation system using ESMF interface**
- **Facilitates massively parallel implementation through MPI**
- **Has been developed as part of the standard GEOS-Chem model; will eventually replace standard model in a way transparent to users**

Courtesy of D. Jacob

Thank you!