CHAPTER 5

TROPOSPHERIC CHEMISTRY
&
AIR POLLUTION

Basic Concepts of Chemistry

- Source, sink, production, loss, destruction
- Loading, burden, content, concentration, mixing ratio
- Residence time (burden/loss rate)
- Lifetime (e-folding time???)
- 1 Tg = 10^{12} grams; 1 Pg = 10^{15} grams = 1 Gt
- 1 mole = 6.022 x 10^{23} molecules/atoms

Key Species in the Troposphere

- $O_x = O_3 + O$
- $NO_x = NO + NO_2$
- $NO_y = NO_x + NO_z = NO + NO_2 + NO_3 + 2\ N_2O_5 + HONO + HNO_3 + PAN + PPN + PMN + \ldots$
- CO, CH_4, VOC
- $HO_x = OH + HO_2$
- RO, RO_2
- CFCs, HCFCs, N_2O
- NH_3, NH_4, SO_2, SO_4, OC, BC, sea salts, dust

Basic Concepts of Chemistry

- Photolysis: A + hv --> B + C

  d[A]/dt = - j * [A]

  = - actinic flux * cross_section * yield * [A]

  光化通量

- Reaction: A + B --> C + D

  d[A]/dt = - k * [A] * [B]

  lifetime of A: 1 / (k * [B])

- Equilibrium: A + B <--> C + D

  d[A]/dt = - k * [A] * [B] + k_1 * [C] * [D] = 0

More About the Rate Constant

Bimolecular reactions: Arrhenius form (E is the activation energy)

$$k(T) = A \bullet \exp\left(-\frac{E/R}{T}\right)$$

Termolecular reactions:

$$k_f([M],T) = \left(\frac{k_o(T)[M]}{1+\frac{k_o(T)[M]}{k_\infty(T)}}\right) 0.6^{\left\{1+\left[\log_{10}\left(\frac{k_o(T)[M]}{k_\infty(T)}\right)\right]^2\right\}^{-1}}$$

$$k_o(T) = k_o^{300}\left(\frac{T}{300}\right)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_\infty(T) = k_\infty^{300}\left(\frac{T}{300}\right)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Basic Chemistry

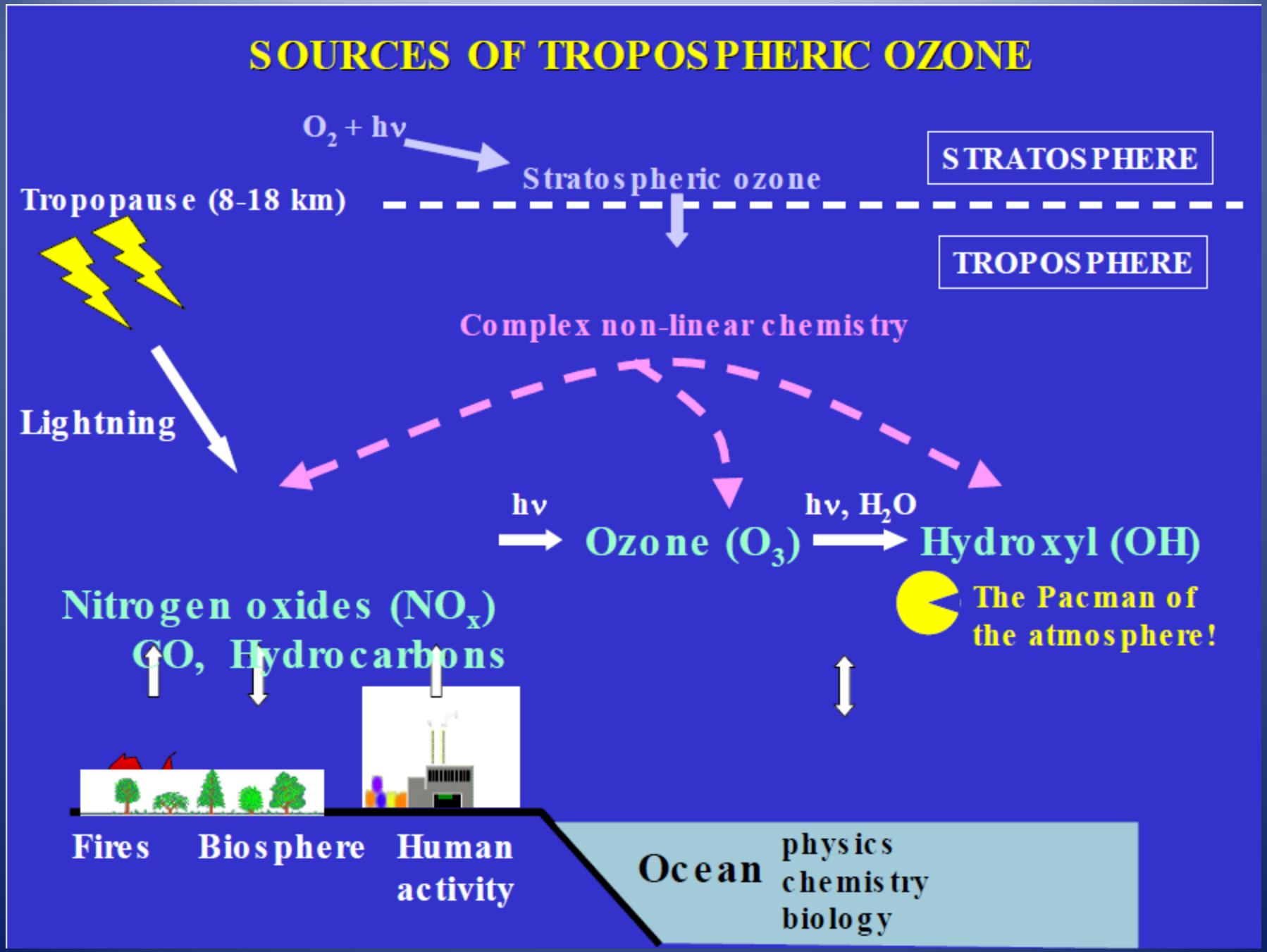
- $NO + O_3 \rightarrow NO_2$ (R1)
- $NO_2 + hv \rightarrow NO + O$ (R2)
- $O + O_2 + M \rightarrow O_3 + M$ (R3)
- Thus, $[NO] / [NO_2] = j_{NO2} / (k * [O_3])$
- Here, O atom is in pseudo steady state
- Without perturbation, this is a null cycle

*** This is one of the most important relations regulating the concentrations of NO, NO_2 and O_3 in the troposphere.

Basic Chemistry

- $OH + CO \rightarrow HO_2 + CO_2$ (R1)
- $OH + VOC \rightarrow RO_2 \rightarrow \ldots \rightarrow HO_2$ (R2)
- $HO_2 + NO \rightarrow NO_2 + OH$ (R3)
- Thus, $[OH] / [HO_2] = k_3 * [NO] / (k_1 * [CO] + k_2 * [VOC])$

*** This is one of the most important relations regulating the concentrations of OH and HO_2 in the troposphere.


SOURCES OF TROPOSPHERIC OZONE
$O_2 + h\nu$
Stratospheric ozone
STRATOSPHERE
Tropopause (8-18 km)
TROPOSPHERE
Complex non-linear chemistry
Lightning
$h\nu$
Ozone (O_3)
$h\nu$, H_2O
Hydroxyl (OH)
The Pacman of the atmosphere!
Nitrogen oxides (NO_x)
CO, Hydrocarbons
Fires
Biosphere
Human activity
Ocean
physics
chemistry
biology

Photochemistry for Tropospheric Ozone

Production

Initiation

$CO + OH (+ O_2) \rightarrow CO_2 + HO_2$

$RH + OH (+ O_2) \rightarrow RO_2 + H_2O$

VOC

Propagation

$NO + RO_2 (+ O_2) \rightarrow Carbonyl + NO_2 + HO_2$

$NO + HO_2 \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O(^3p)$ $(\lambda < 420\ nm)$

$O(^3p) + O_2 + M \rightarrow O_3 + M$

Termination

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$

$OH + NO_2 + M \rightarrow HNO_3 + M$

Destruction

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $(\lambda < 330\ nm)$

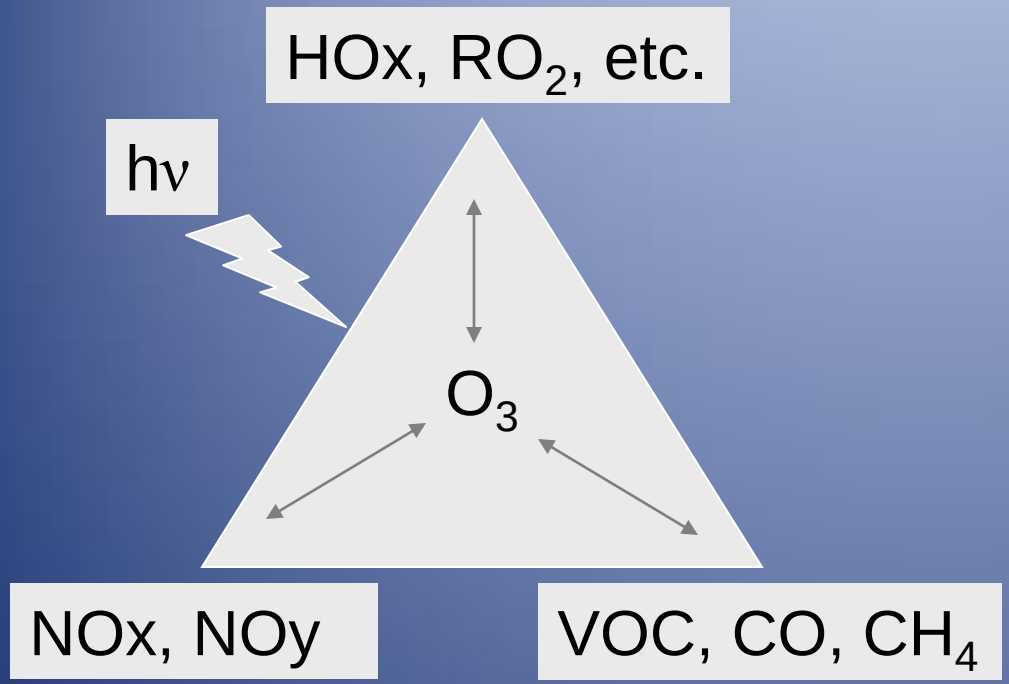
$O(^1D) + H_2O \rightarrow 2OH$

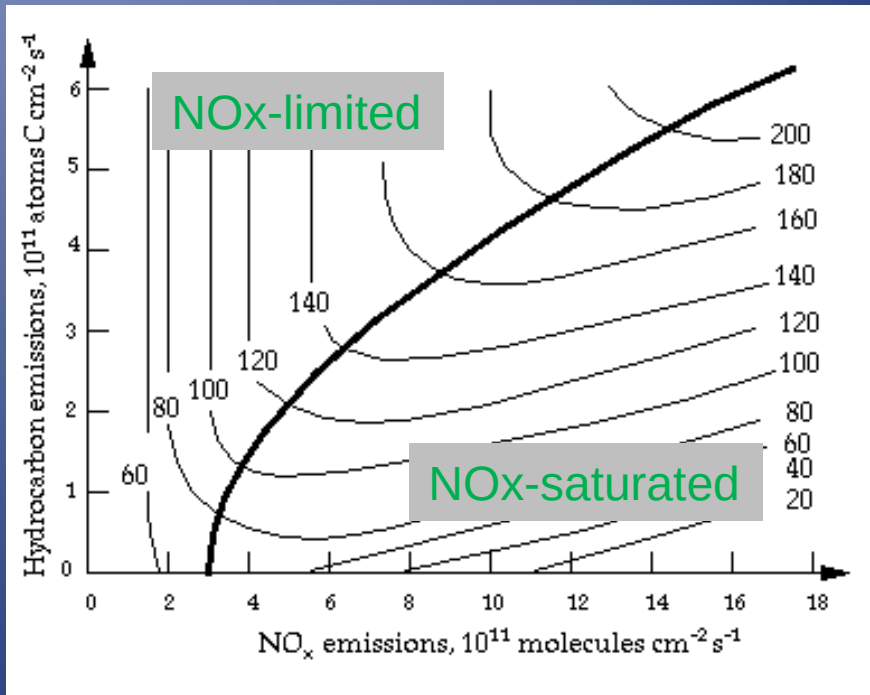
$OH + O_3 \rightarrow O_2 + HO_2$

$HO_2 + O_3 \rightarrow 2O_2 + OH$

$NO + O_3 \rightarrow O_2 + NO_2$

Ozone Formation: Sensitivity to NOx and VOC





More Chemistry

Gaseous chemistry (important if weak hv):

- $NO_3 + VOC \rightarrow HNO_3 + carbonyl$
- $NO + O_3 \rightarrow NO_2 + O_2$
- $NO_2 + O_3 \rightarrow NO_3 + O_2$
- $NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M$
- $NO_3 + VOC \rightarrow \ldots$

} Ozone titration

Heterogeneous chemistry:

- $N_2O_5 + H_2O(s) \rightarrow 2\ HNO_3$
- $NO_2 + H_2O(s) \rightarrow HONO$ (important source of OH!!!)
- $HO_2 + H_2O(s) \rightarrow 0.5\ H_2O_2$ (important in China!!!)

Other nitrogen species

- Peroxyacyl nitrates (PANs) 硝酸过氧酰、过氧酰基硝酸酯
  - most important being peroxyacetyl nitrate
    - $CH_3C(O)OONO_2$ 过氧乙酰硝酸酯
  - formed from oxidation of acetaldehyde 乙醛

$$CH_3CHO + OH\cdot\ (+ O_2) \equiv CH_3C(O)O_2 + H_2O$$

$$CH_3C(O)O_2 + NO_2 + M \rightleftharpoons CH_3C(O)O_2NO_2 + M$$

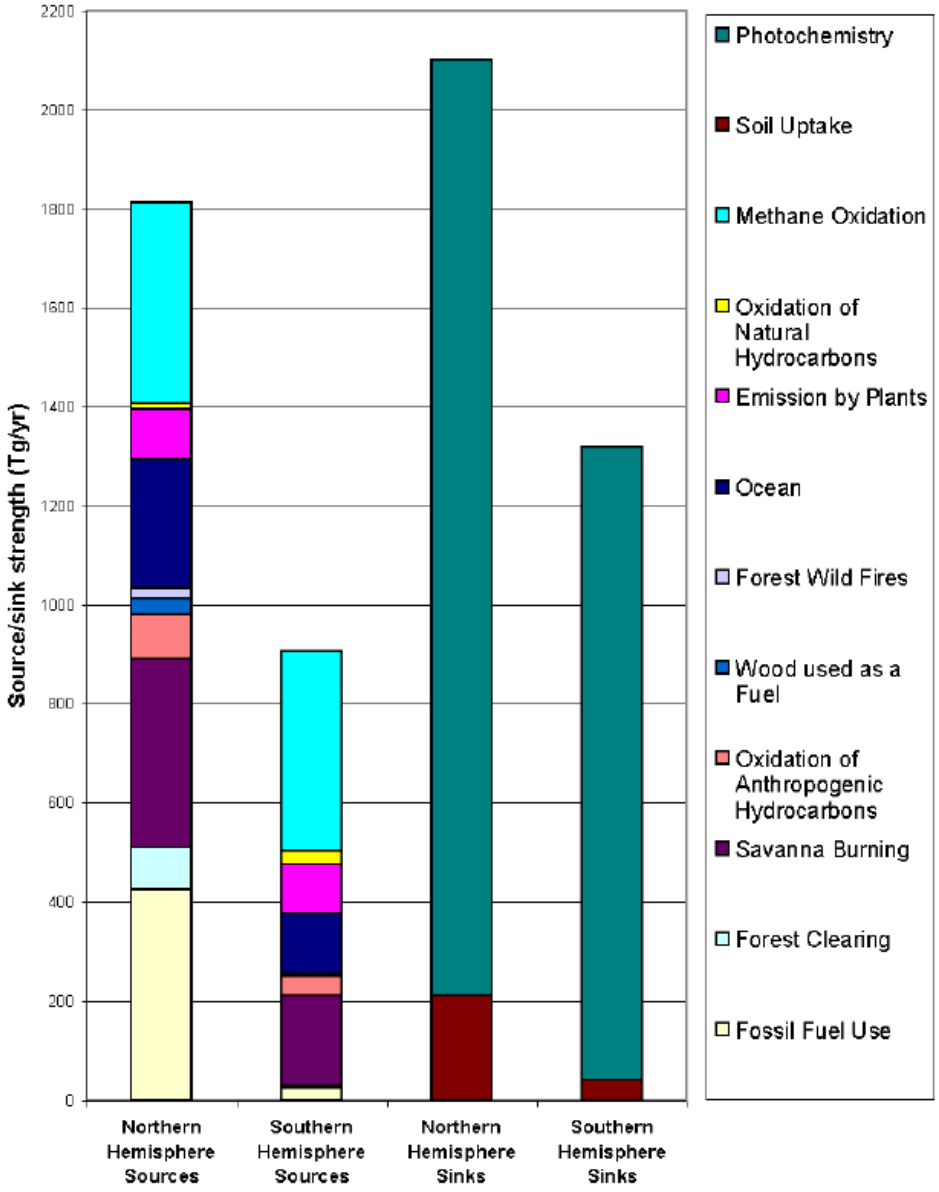
  - decomposition is strongly temperature dependent
    - from 30 minutes at 298K near the surface to several months under upper tropospheric conditions
    - NO_x exported from boundary layer to remote troposphere in the form of PAN
  - observations show PAN is dominant NOy compound in northern hemisphere spring troposphere
    - insoluble

NOx Emissions by Source

NOx Budget

Table 4.8: Estimates of the global tropospheric NO_x budget (in TgN/yr) from different sources compared with the values adopted for this report.

Reference:	TAR	Ehhalt (1999)	Holland *et al.* (1999)	Penner *et al.* (1999)	Lee *et al.* (1997)
Base year	**2000**	**~1985**	**~1985**	**1992**	
Fossil fuel	33.0	21.0	20 - 24	21.0	22.0
Aircraft	0.7	0.45	0.23 -0.6	0.5	0.85
Biomass burning	7.1	7.5	3 - 13	5 - 12	7.9
Soils	5.6	5.5	4 - 21	4 - 6	7.0
NH_3 oxidation	-	3.0	0.5 - 3	-	0.9
Lightning	5.0	7.0	3 - 13	3 - 5	5.0
Stratosphere	<0.5	0.15	0.1 - 0.6	-	0.6
Total	**51.9**	**44.6**			**44.3**



CO Sources

Adapted from Logan et al. (1981)

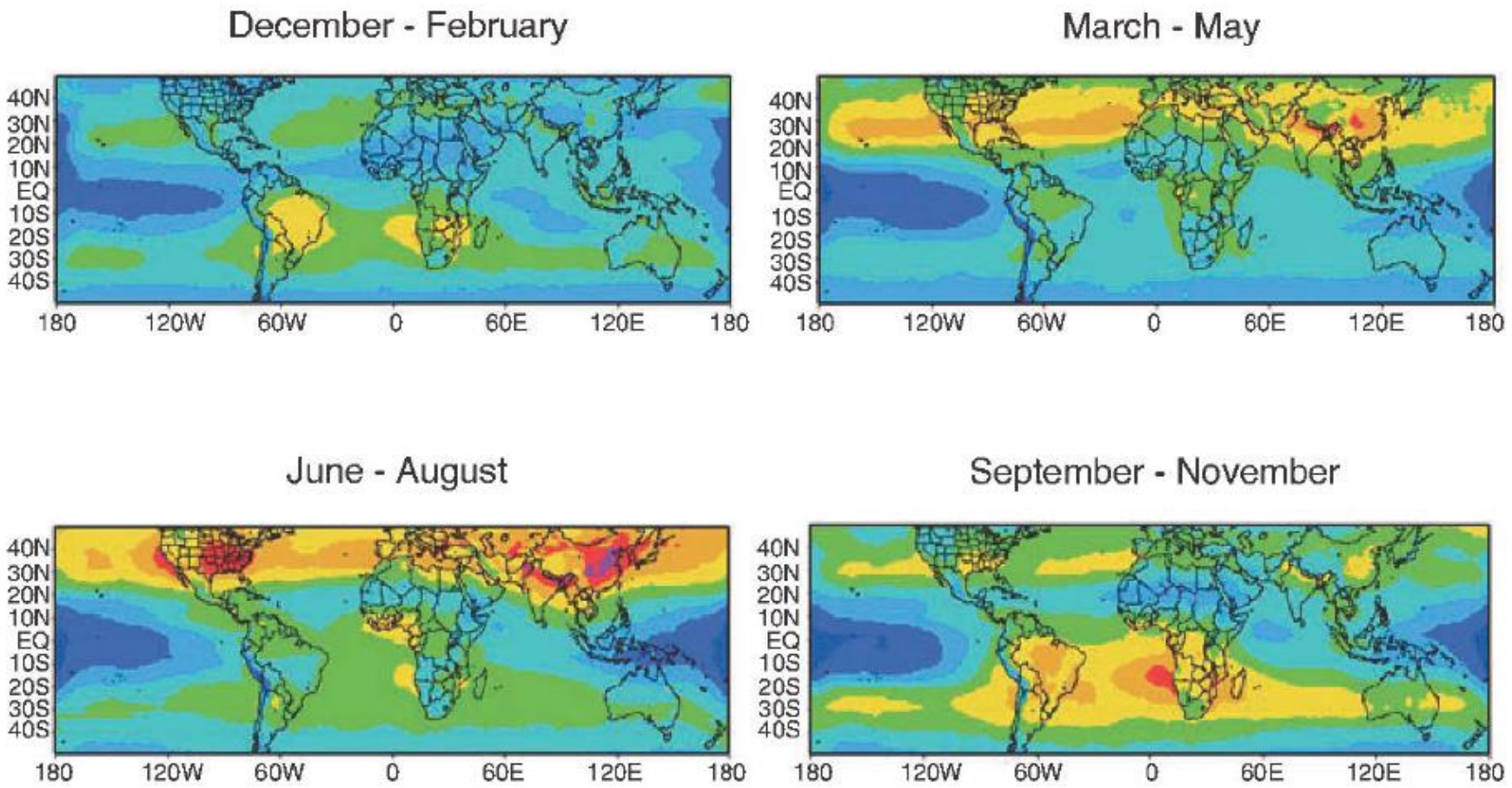
Global emissions of non-methane hydrocarbons

Human Sources		**~100 TgC/yr**
Energy use and transfer		43 TgC/yr
Biomass burning		45 TgC/yr
Organic solvents		15 TgC/yr
Natural Sources		**~1170 TgC/yr**
Emissions from vegetation		
异戊二烯	*isoprene (C_5H_8)*	*500 TgC/yr*
单萜烯	monoterpenes	125 TgC/yr
	other VOC	520 TgC/yr
Oceanic emissions		6-36 TgC/yr

Brasseur et al., 1998

Tropospheric ozone column seen from space

~ 30 DU on average



Meridional Distribution

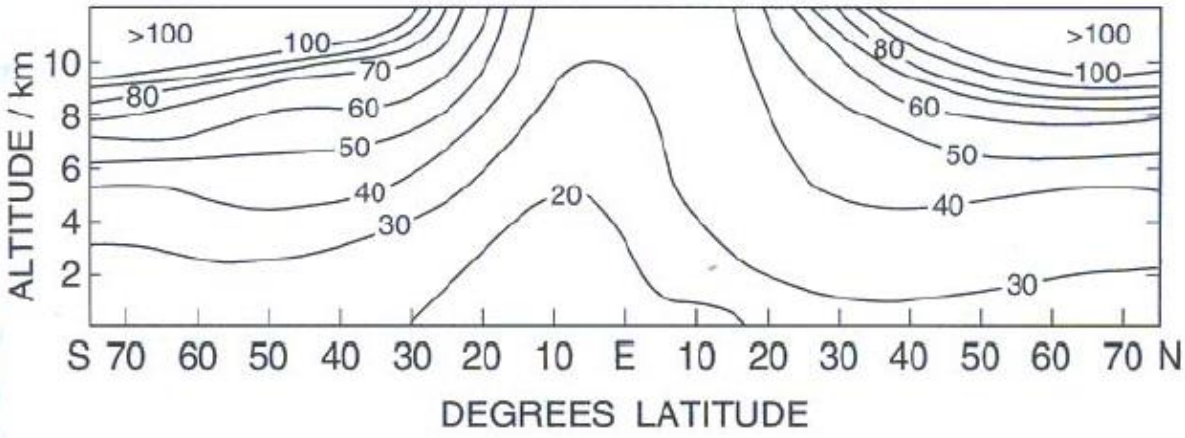
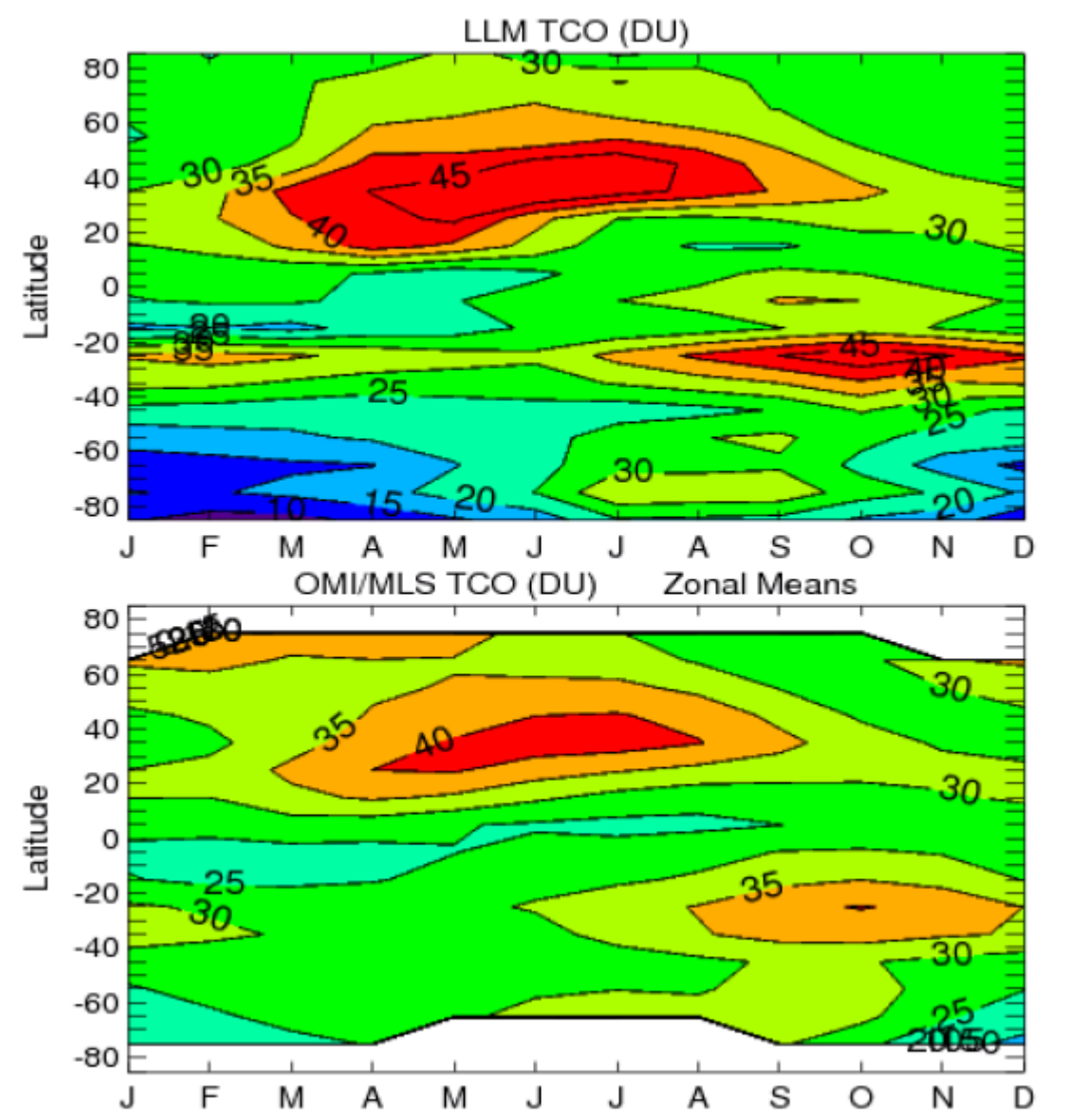


FIGURE 5.6 Seasonally averaged meridional distribution of ozone according to the analysis of Fishman and Crutzen (1978a, b). Contours indicate equal mixing ratios (unit: nmol mol^{-1}).

Fishman and Crutzen(1978)

- An excess of ozone in the Northern Hemisphere at altitudes below about 5 km
- Northern Hemisphere contains 40% more zone on average than the Southern Hemisphere
- The ozone concentrations in the Tropics are lower than at mid-latitudes

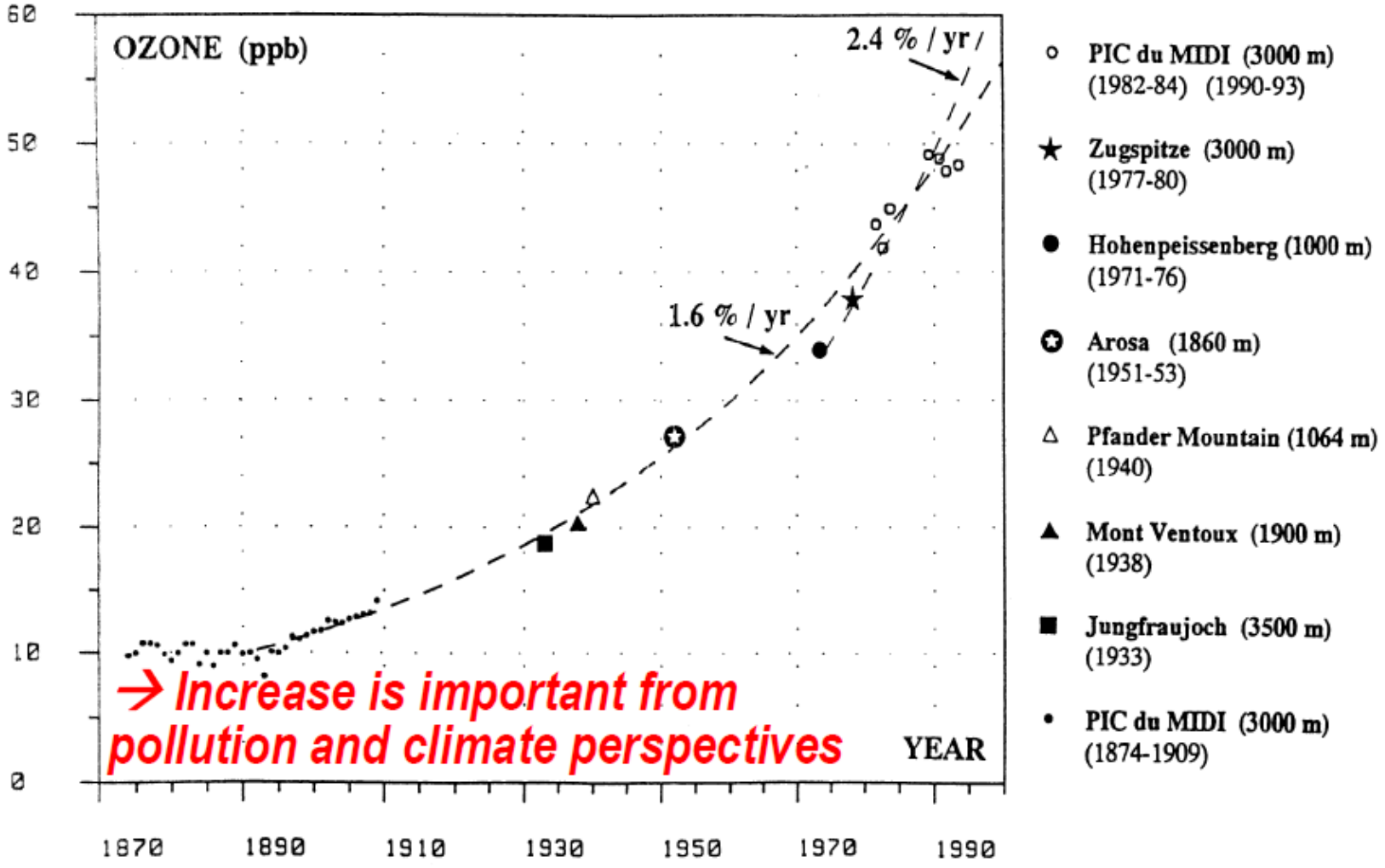
Meridional – Seasonal Cross Section



Ziemke et al., 2011

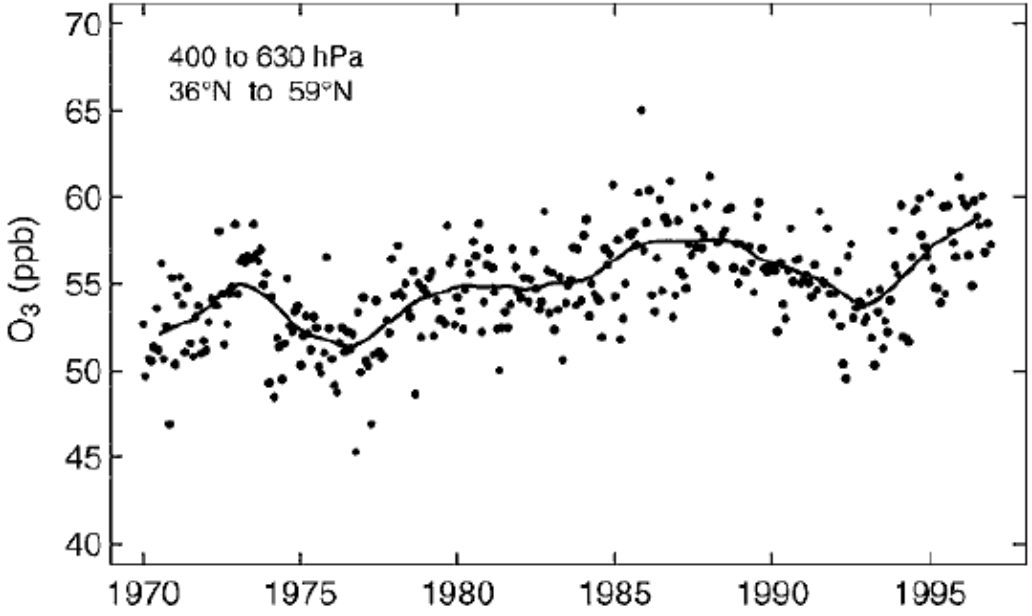
Historical records imply a large anthropogenic contribution to the present-day ozone background at northern midlatitudes

Ozone trend from European mountain observations, 1870-1990 [Marenco et al.,1994]



The more recent past

- Statistically significant negative trends of 1-2% per year found at several stations in Canada for 1980-1993 (Tarasick *et al.*, Geophys. Res. Lett., 409-412, 22, 1995)
- trends at most other stations in NH ambiguous



Monthly averaged O_3 concentration between 630 and 400 hPa from 9 ozonesonde stations located between 36 and 59N. From Logan *et al.* J. Geophys. Res., 104, 26373-26399, 1999.

Tropospheric OH: the cleanser (pacman)

Production:

- $O_3 + h\nu + H_2O \rightarrow O_2 + 2OH$ ($\lambda < 330$ nm)
- $HONO + h\nu \rightarrow OH + NO$
- VOC ozonolysis
- $NO + HO_2 \rightarrow OH$
- $NO + RO_2 \rightarrow OH$

Loss:

- $OH + CO \rightarrow HO_2$
- $OH + VOC \rightarrow RO_2$
- $OH + NO_2 + M \rightarrow HNO_3 + M$
- …

Sinks of OH

Dominant sinks of OH in the global troposphere:

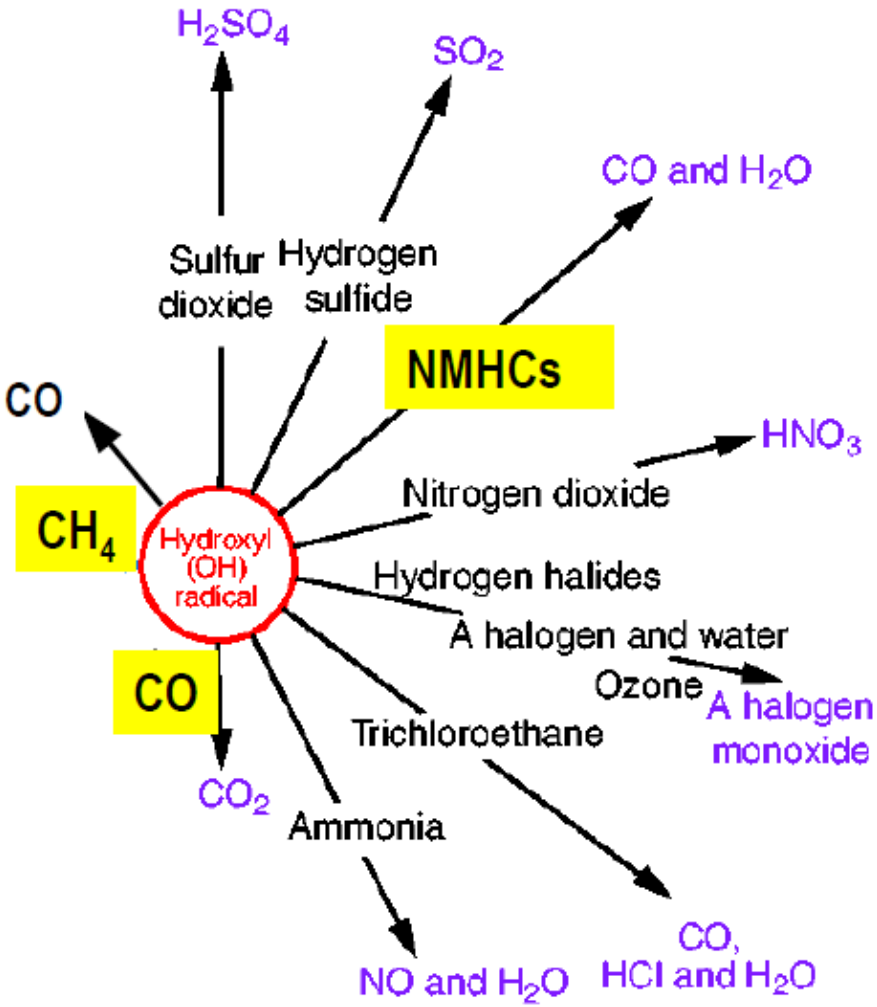
$CO + OH \rightarrow CO_2 + H$

$CH_4 + OH \rightarrow CH_3 + H_2O \rightarrow \ldots CO$

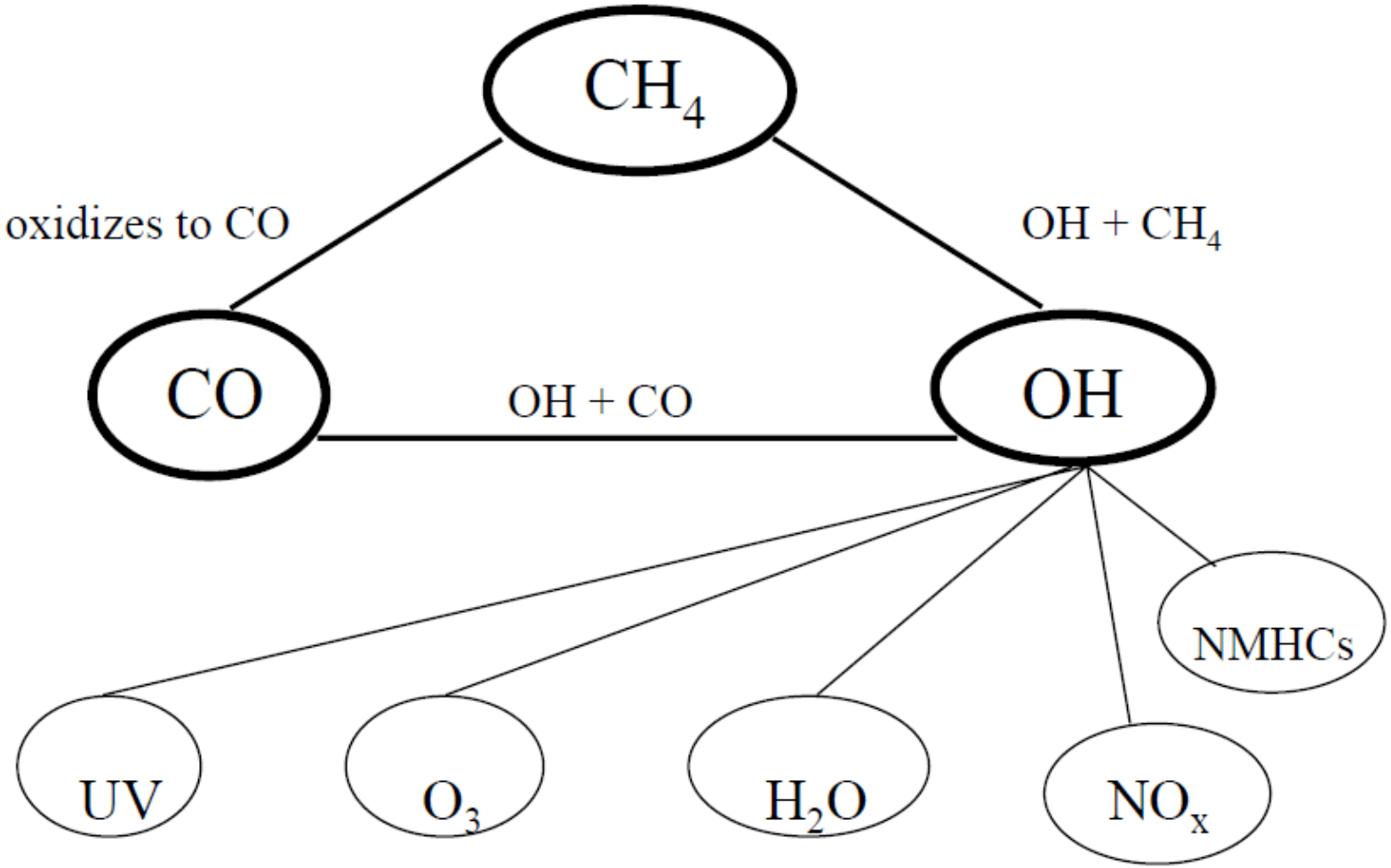
Over continents, reactions with non-methane hydrocarbons (NMHCs) dominates:

NMHC + OH → products

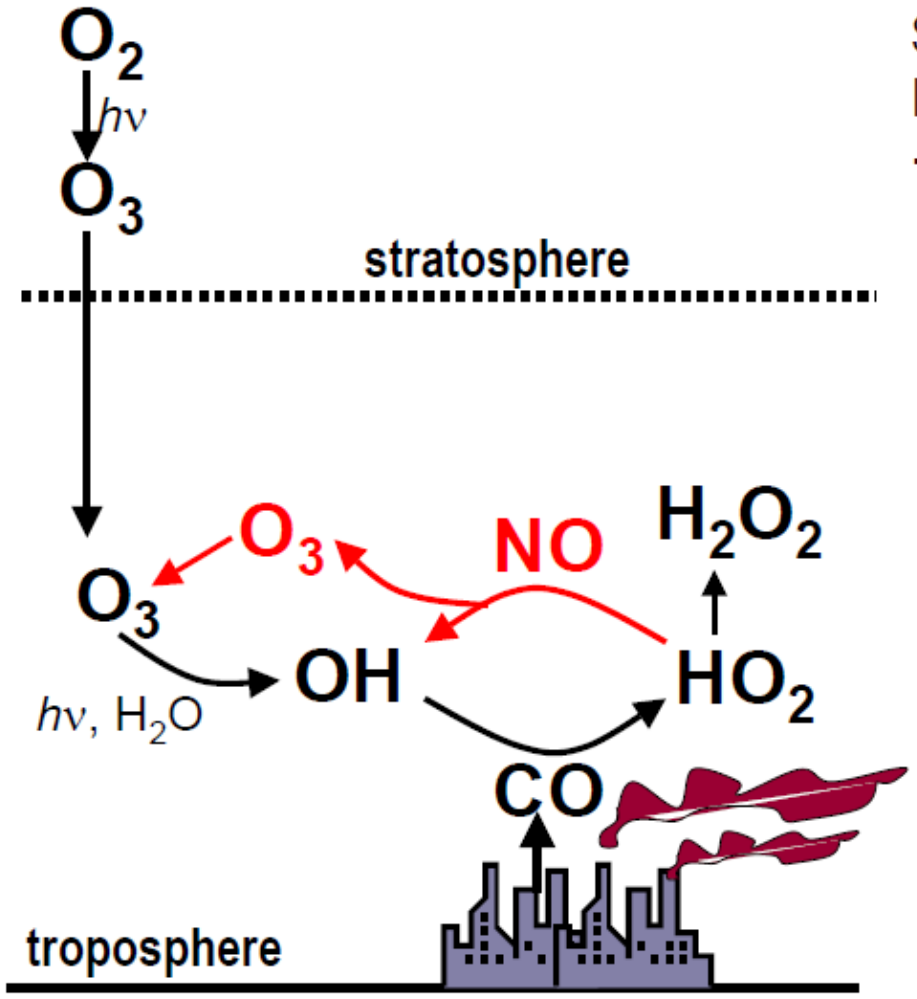
Lifetime of OH ~ 1 second!



Simplified CH_4/OH/CO Chemistry



The OH titration problem



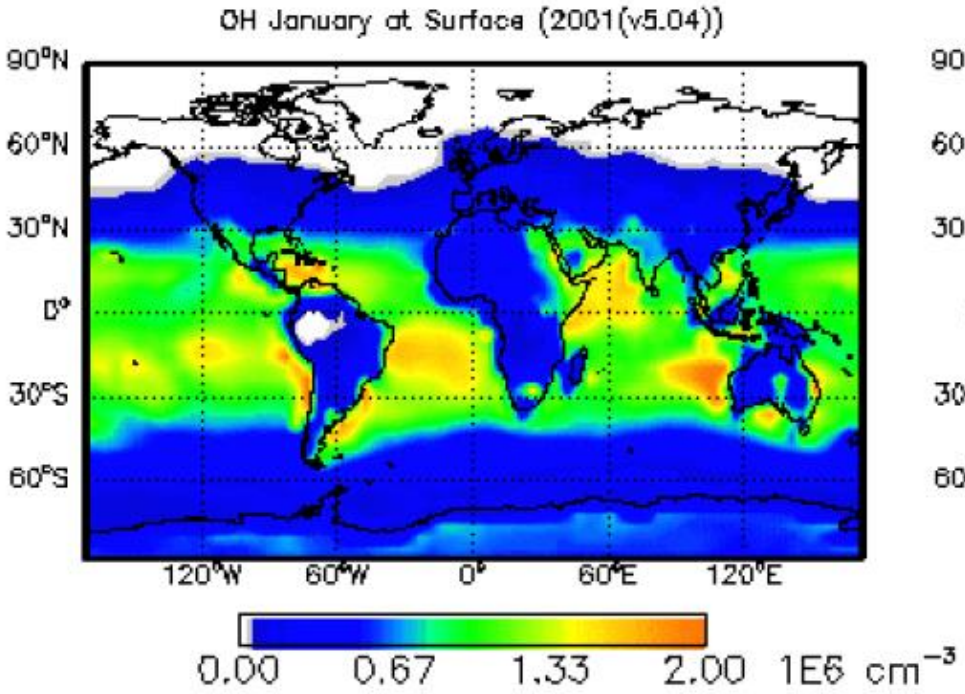
Source of $CO+CH_4$>> source of OH
If no other sources, OH would be **titrated**.
→ CO and CH_4 would accumulate to very high levels!!

→BUT, trace levels of NO_x allow the **chemical cycling** of OH and provides a **major source of tropospheric ozone** to generate additional OH

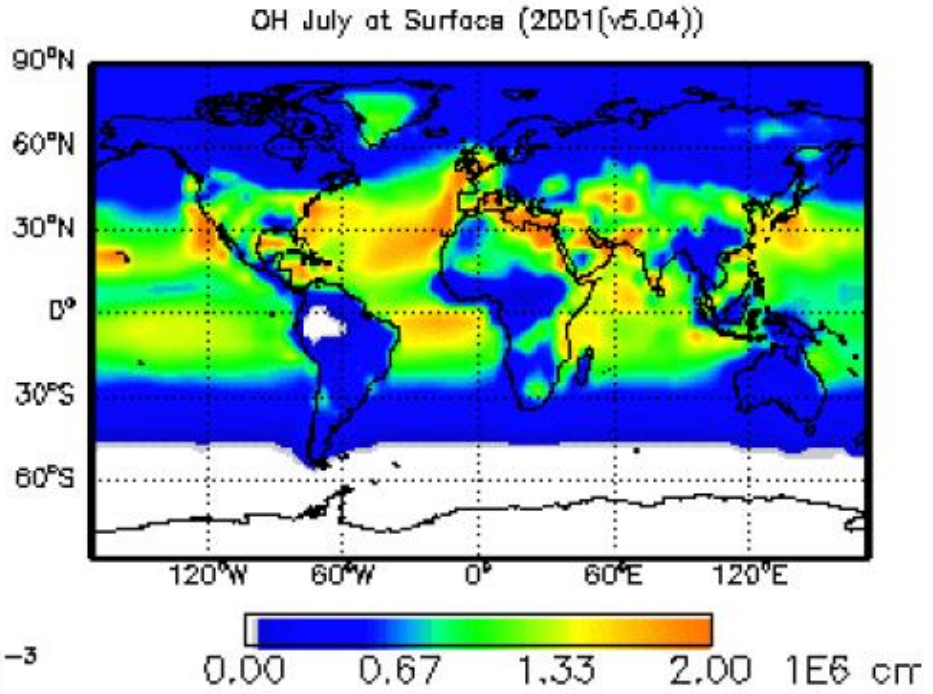
→[OH]~10^6 molecules/cm^3 (0.03 parts per trillion)

Global OH Concentrations: Model Calculations

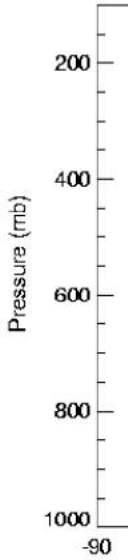
January



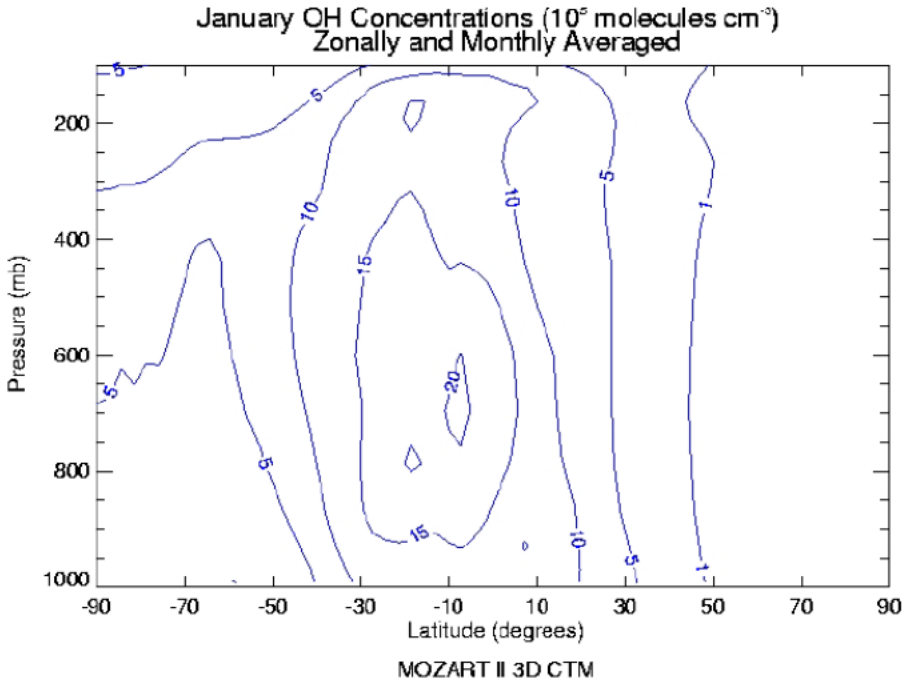
July



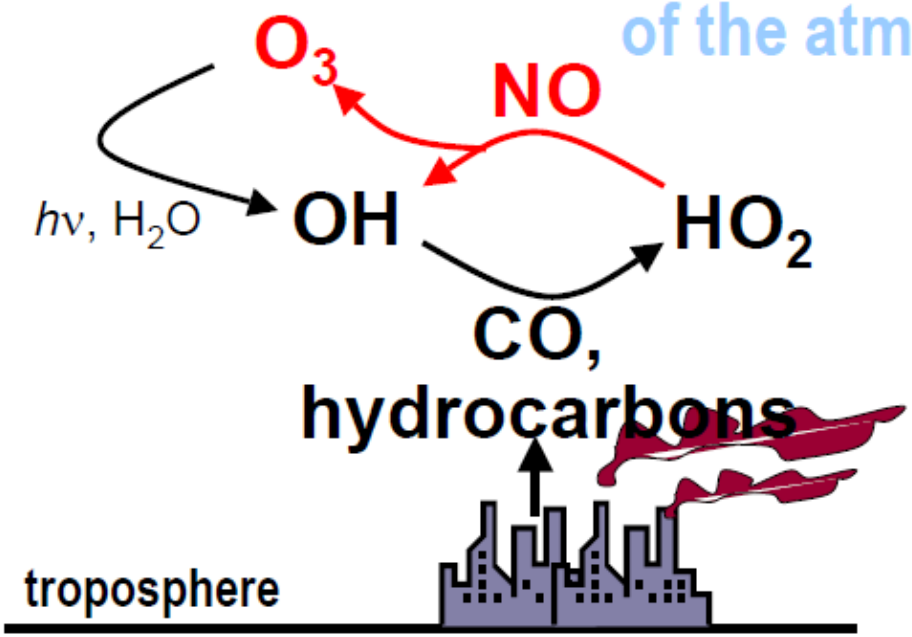
Tropospheric OH July -- MOZART2



Tropospheric OH (January) – MOZART2



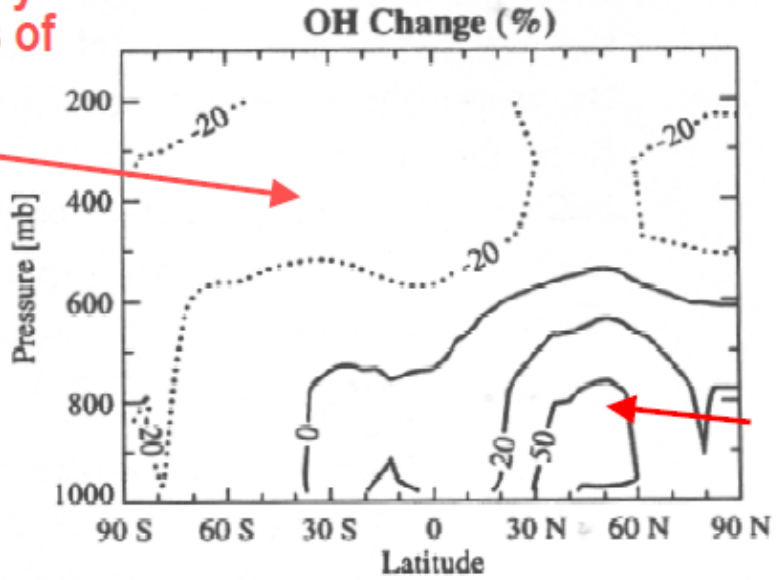
Have human activities changed the oxidizing capacity of the atmosphere?



→Since pre-industrial times CO has increased by factors of 3-4;
NO has increased by factors of 2-8
…. What has happened to OH?

NO ↑ → increase in OH
CO ↑ → decrease in OH

Decrease in OH away from sources driven by increases of CO (~months)

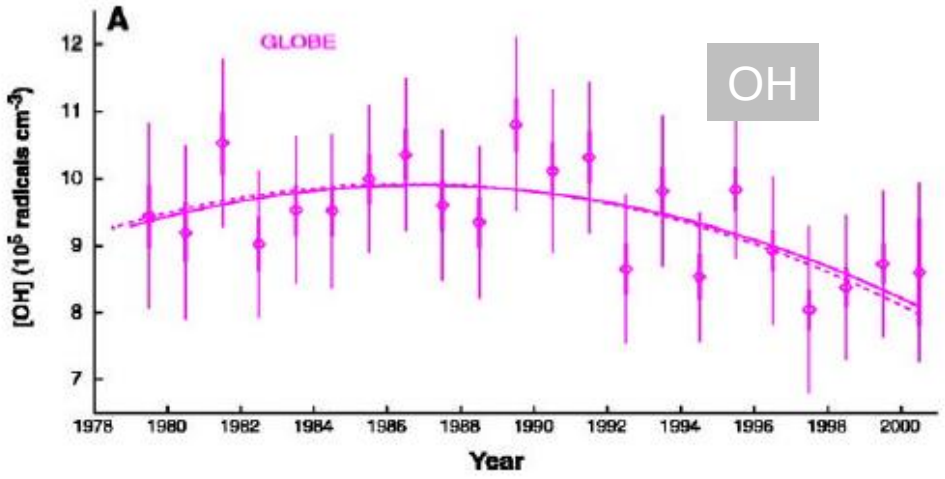


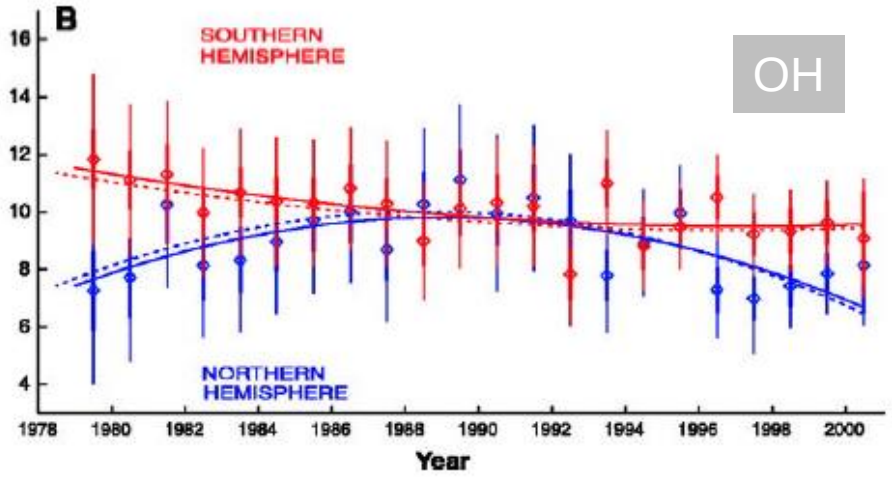
➔ ***Little change in OH globally (buffering)***

Increase in OH near sources driven by increases of NO_x (~days)

Wang & Jacob, 1999

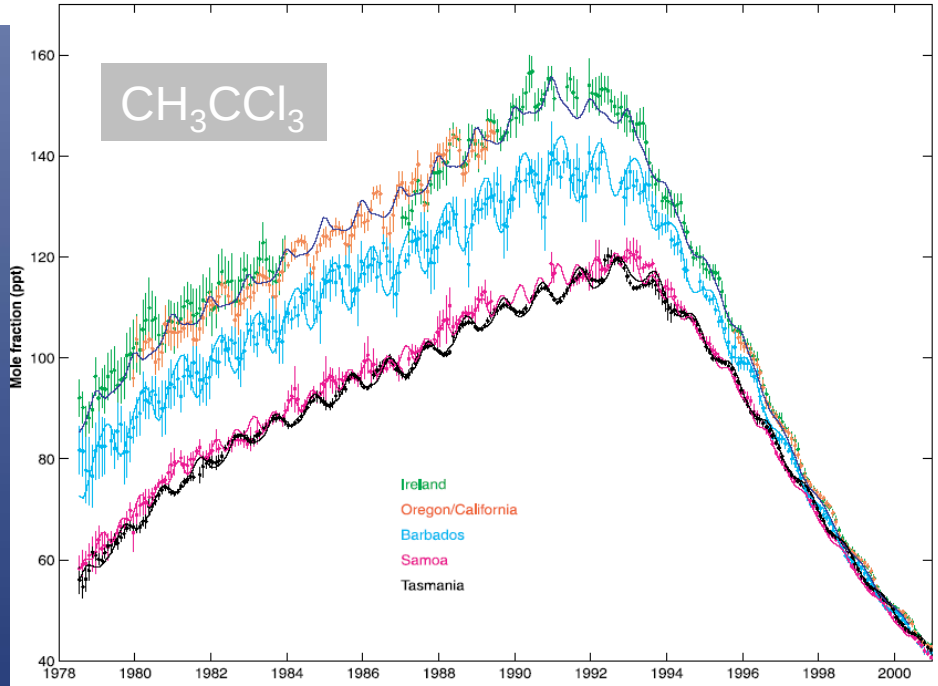
Global OH Trend: 1978 – 2000





甲基氯仿

Methyl chloroform (CH_3CCl_3) is an excellent tracer to study changes in OH



Prinn et al., 2001

Air Quality

What are the major issues in Air Quality?

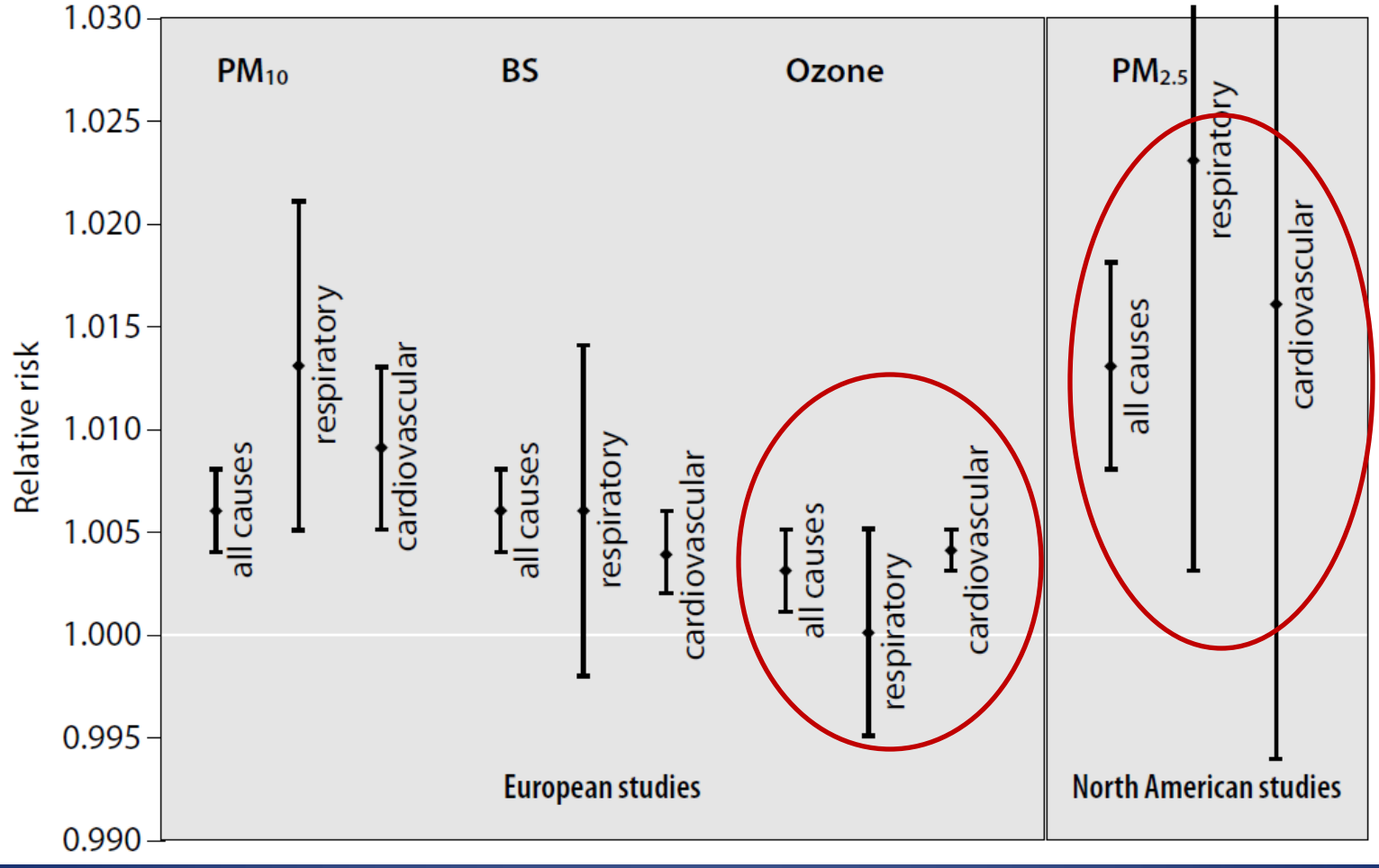
- Urban Air Pollution
  - Outdoor /indoor
- Acid deposition
- Particulate matter

Effects of air pollution:

- Visibility degradation
- Plants get damaged – UV radiation effect+ cell membrane can break down
- Material damage
- Health effects

Air Pollution: Health Impacts

Relative risks for mortality end-points related to a 10- µg/m^3 increase in pollution including 95% confidence intervals. *Left part:* PM_{10}, black smoke (BS) and ozone from European studies; *right part:* $PM_{2.5}$ from North American studies.



WHO Europe Report， 2004

Air Pollution: Impacts on Agriculture

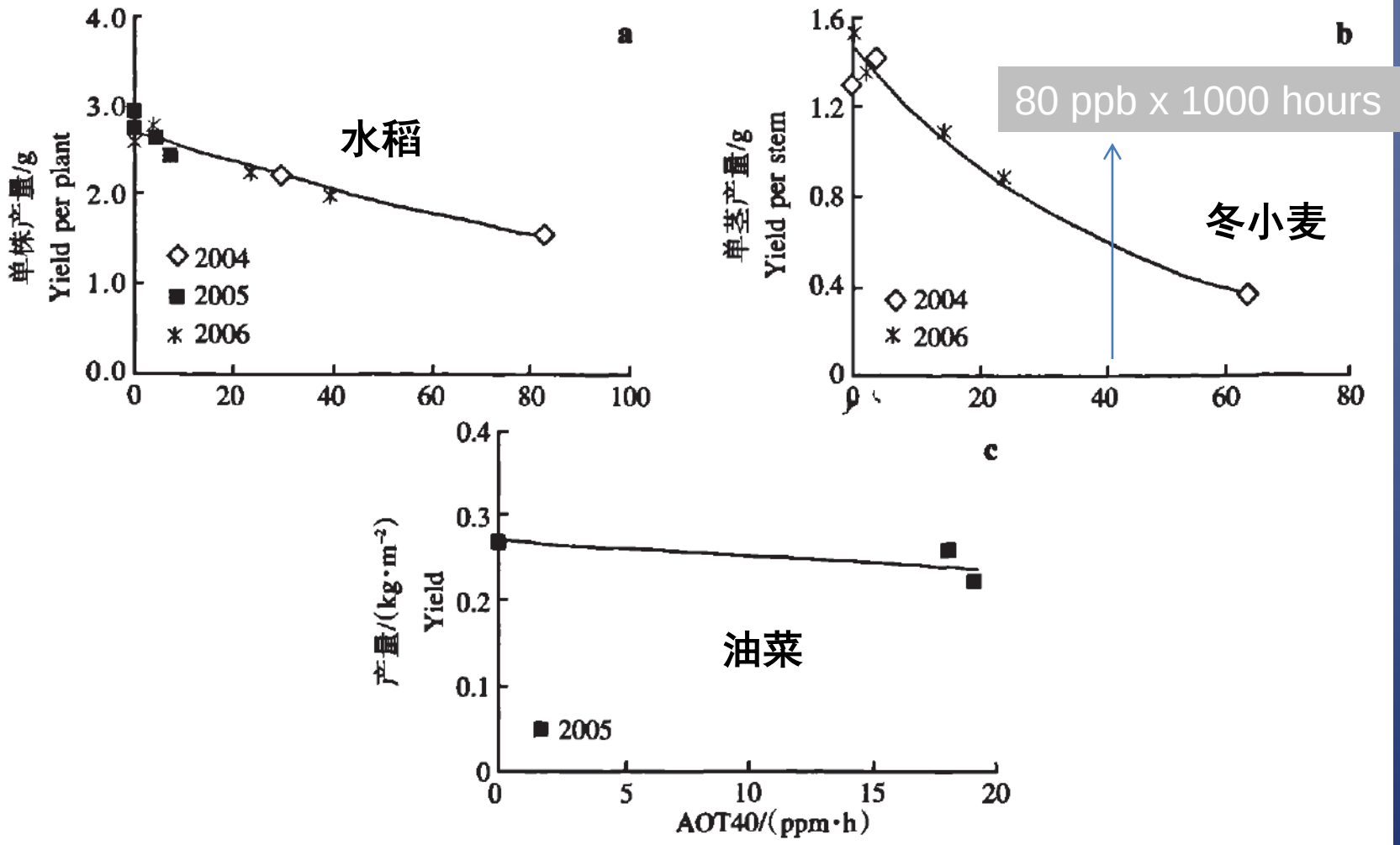


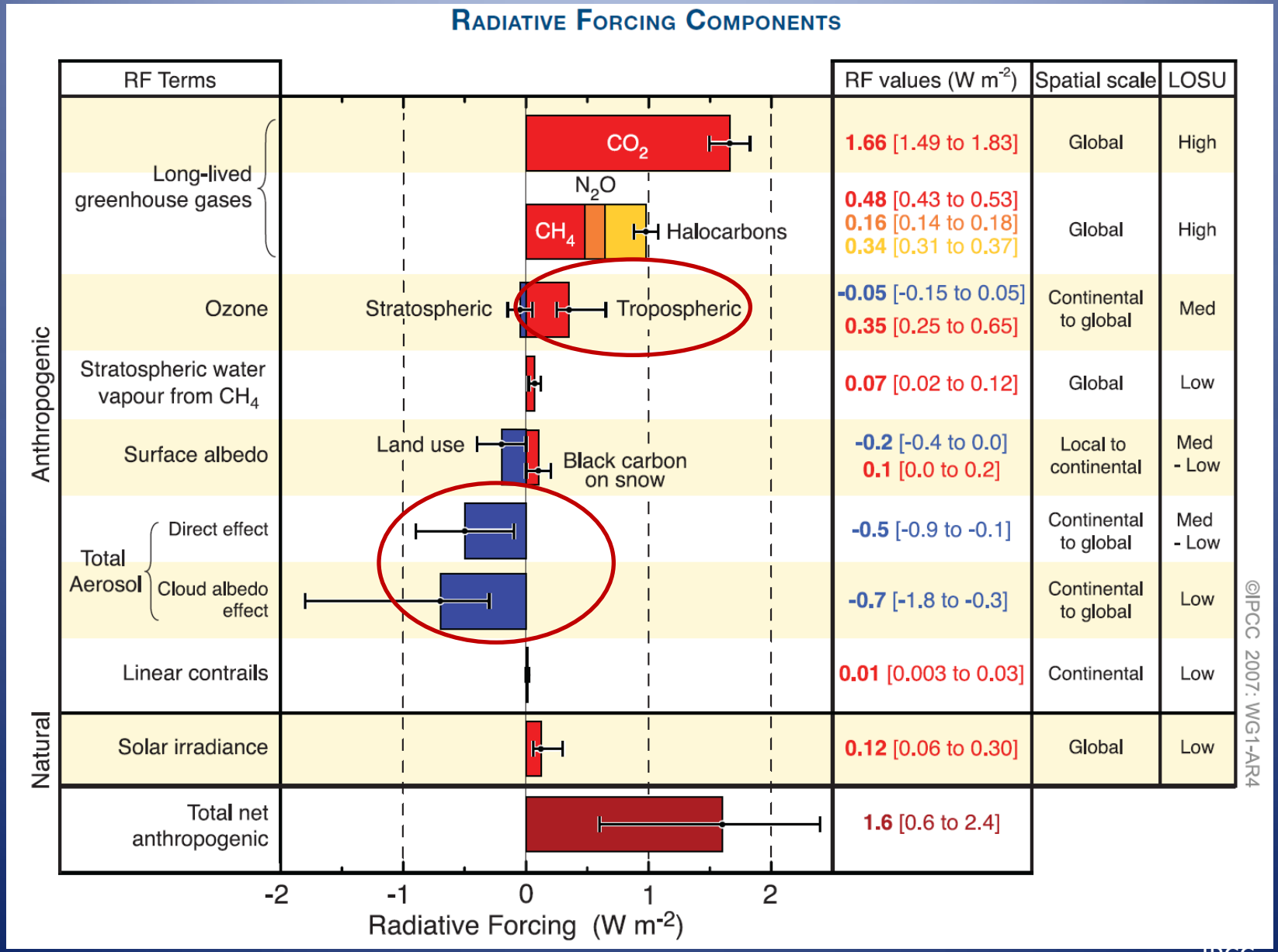
图 2　O_3 剂量与 3 种作物的剂量-响应模型(a: 水稻; b: 冬小麦; c: 油菜)

Fig.2　Dose-response models between O_3 dose and crop yield(a: rice; b: winter wheat; c: rape)

姚芳芳等人，2008

Effects of Acid Rain

Air Pollution: Impacts on Climate



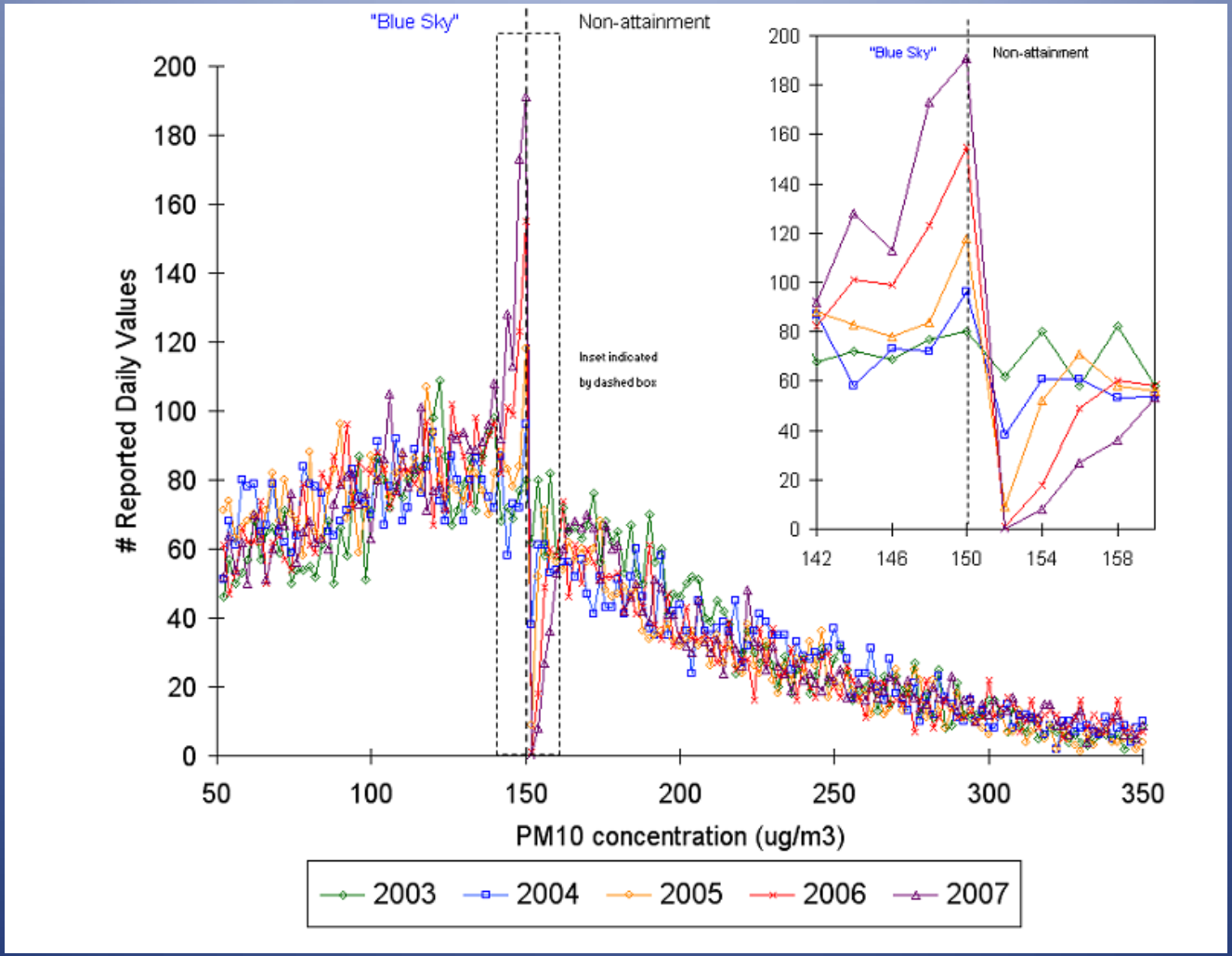
IPCC，2007

Ambient Air Quality Standards

	WHO	WHO IT-1	Europe	U.S.	China***
PM_{10} ($\mu g/m^3$)	20 (1-yr) 50 (24-h)	70 (1-yr) 150 (24-h)	40 (1-yr) 50 (24-h)	150 (24-h)	**70 (1-yr)** **150 (24-h)**
$PM_{2.5}$ ($\mu g/m^3$)	10 (1-yr) 25 (24-h)	35 (1-yr) 75 (24-h)	25 (1-yr)*	15 (1-yr) 35 (24-h)	**35 (1-yr)** **75 (24-h)**
O_3 ($\mu g/m^3$)	100 (8-h)	160 (8-h)	120 (8-h)	152 (8-h)** 243 (1-h)**	**160 (8-h)** **200 (1-h)**
SO_2 ($\mu g/m^3$)	20 (24-h) 500 (10-min)	125 (24-h)	125 (24-h) 350 (1-h)	81 (1-yr)** 378 (24-h)** 203 (1-h)**	150 (24-h) 500 (1-h)
NO_2 ($\mu g/m^3$)	40 (1-yr) 200 (1-h)		40 (1-yr) 200 (1-h)	103 (1-yr)** 194 (1-h)**	80 (24-h) 200 (1-h)
CO (mg/m^3)			10 (8-h)	10 (8-h) 40 (1-h)	4 (24-h) 10 (1-h)

* Fully enforced in Jan 01, 2015; ** Converted from mixing ratio assuming 15° C and 1 atm; *** For 2nd district

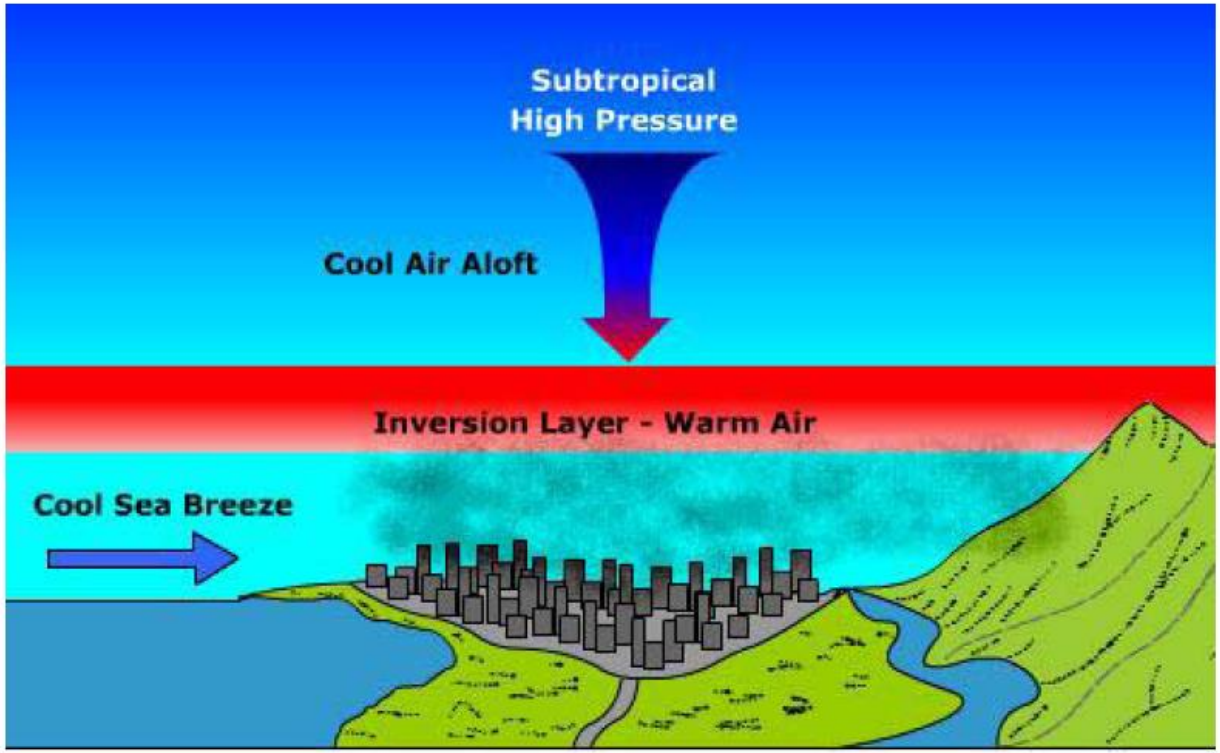
Ambient Air Quality Standards



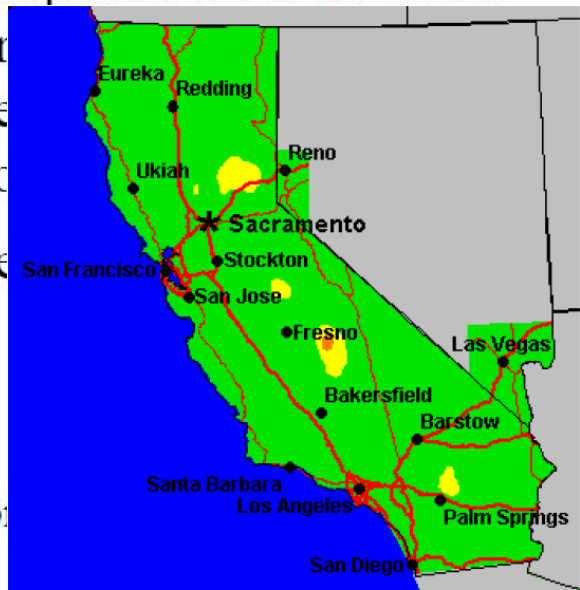
Photochemical 'Smog'

- Composition:
  Ozone, NOx, VOC, PANs, RCHO
- Conditions for ozone formation:
  Emissions of NOx and VOC
  Sunlight
  High temperature
  Stagnant atmosphere

Photochemical 'Smog' in Los Angeles



- LA sits on a basin with St. Gabriel Mountains to the east of the city
- Subtropical high pressure migrate
- subsiding air of the subtropical high compresses as it descends thr
cre
alc



- adiabatic heating that occurs lowers the relative humidity pre
of clouds
- Cool sea breeze – causes inversion – limits the mixing
- much insolation to penetrate to the surface – photochemical reactio

Photochemistry

Production

Initiation

$CO + OH (+ O_2) \rightarrow CO_2 + HO_2$

$RH + OH (+ O_2) \rightarrow RO_2 + H_2O$

VOC

Propagation

$NO + RO_2 (+ O_2) \rightarrow Carbonyl + NO_2 + HO_2$

$NO + HO_2 \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O(^3p)$ $(\lambda < 420\ nm)$

$O(^3p) + O_2 + M \rightarrow O_3 + M$

Termination

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$

$OH + NO_2 + M \rightarrow HNO_3 + M$

Destruction

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $(\lambda < 330\ nm)$

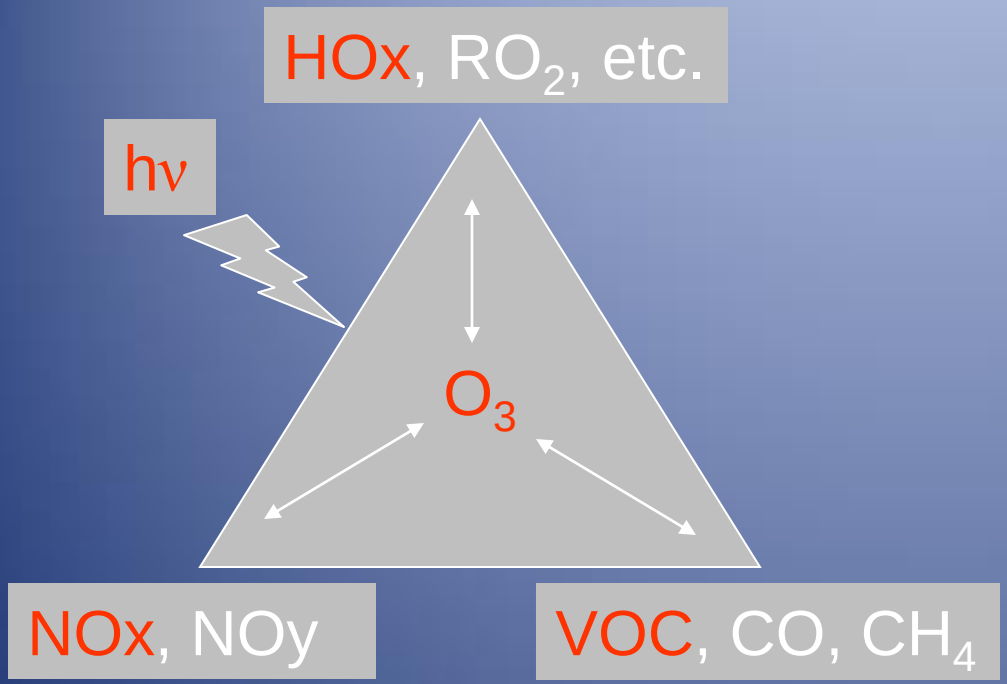
$O(^1D) + H_2O \rightarrow 2OH$

$OH + O_3 \rightarrow O_2 + HO_2$

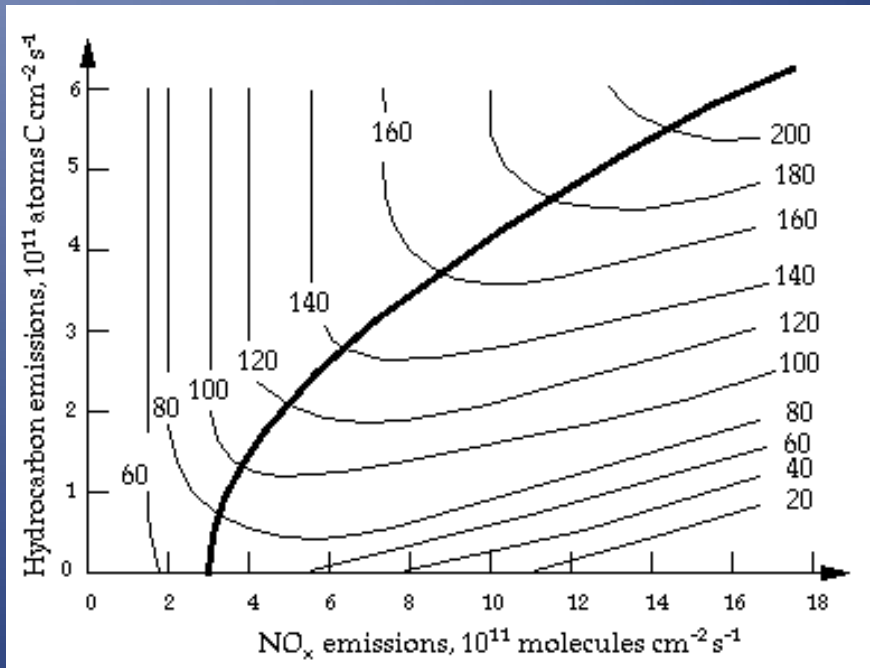
$HO_2 + O_3 \rightarrow 2O_2 + OH$

$NO + O_3 \rightarrow O_2 + NO_2$

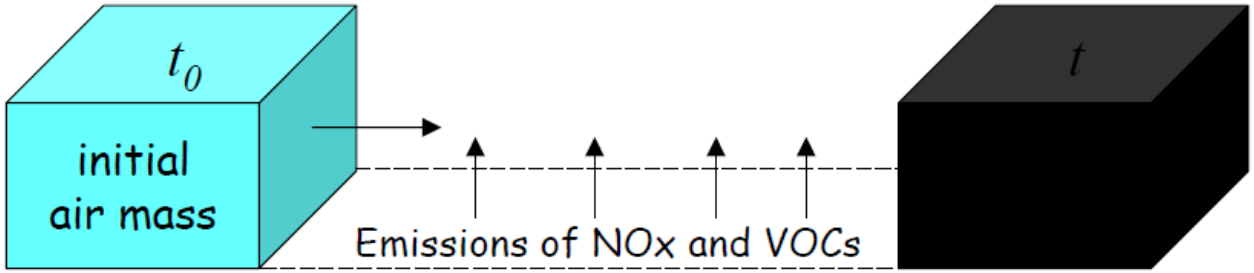
Ozone Formation: Sensitivity to NOx and VOC



- Oxidation of CO and CH_4 provides background
- Oxidation of VOC provides variability



Lagrangian OPE



- Lagrangian OPE

$$\text{Lagrangian OPE}(t) = \frac{\Delta[\text{O}_3(t)]_{\text{prod}}}{\Delta[\text{NO}_x(t)]_{\text{dest}}}$$

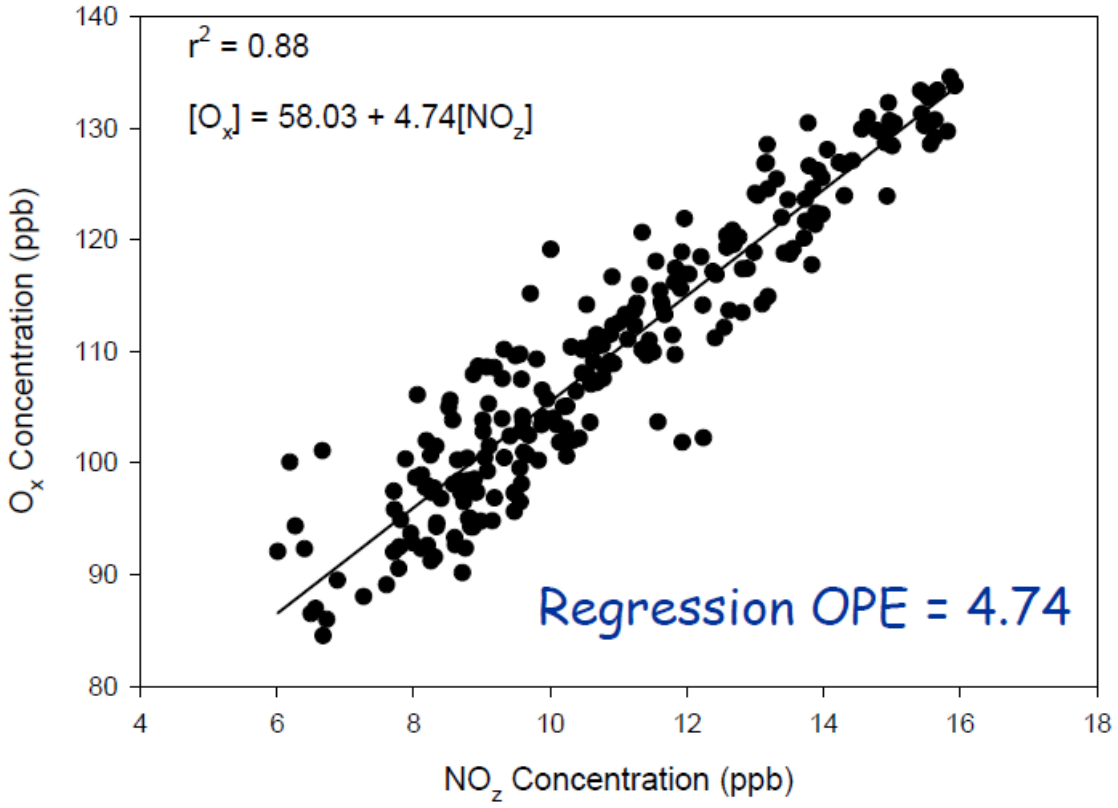
Where

$\Delta[\text{O}_3(t)]_{\text{prod}}$ is the cumulative net change in the amount of O_3 since t_0

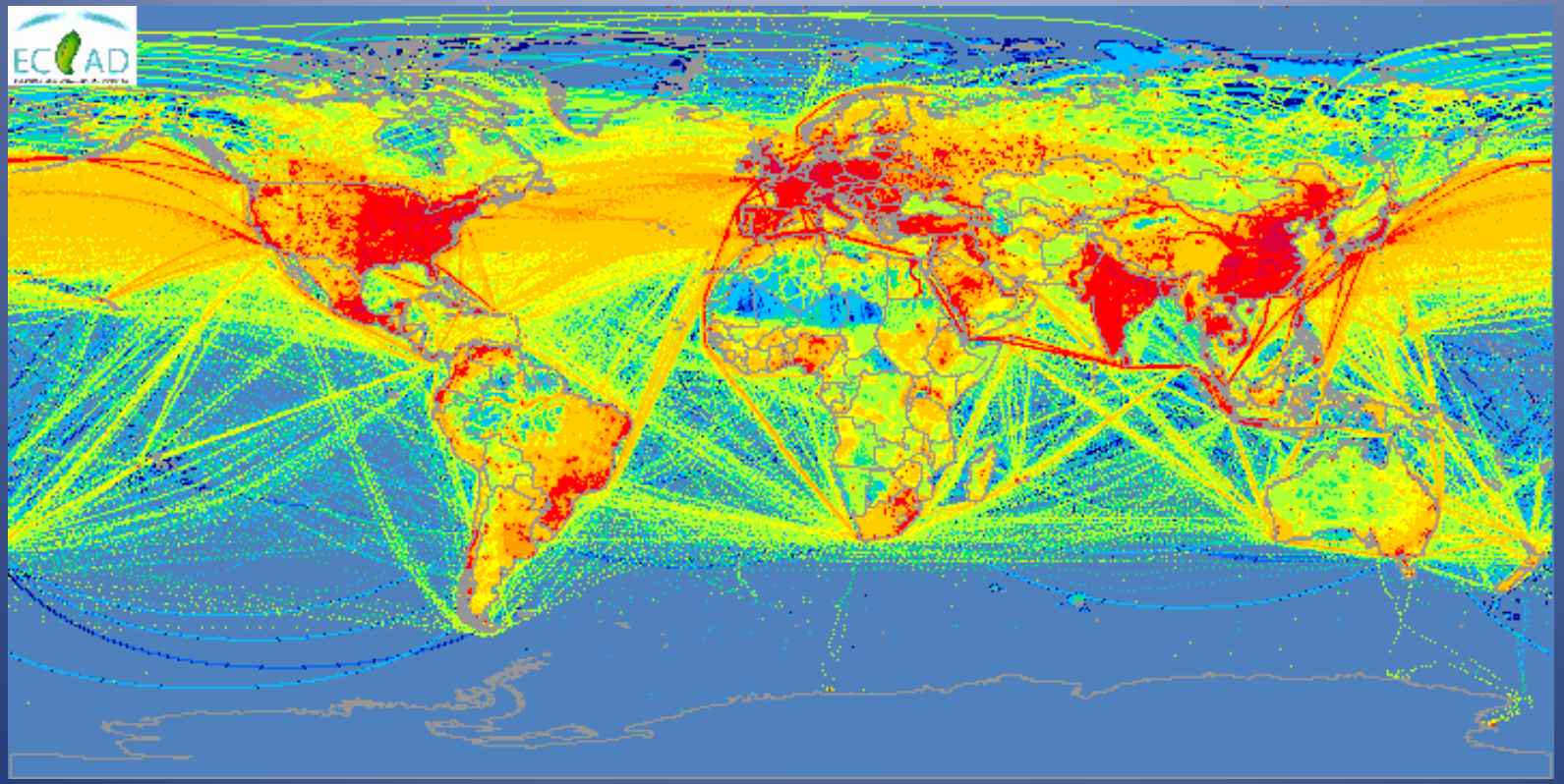
$\Delta[\text{NO}_x(t)]_{\text{dest}}$ is the cumulative amount of NO_x destroyed by oxidation and dry deposition since t_0

Regression OPE

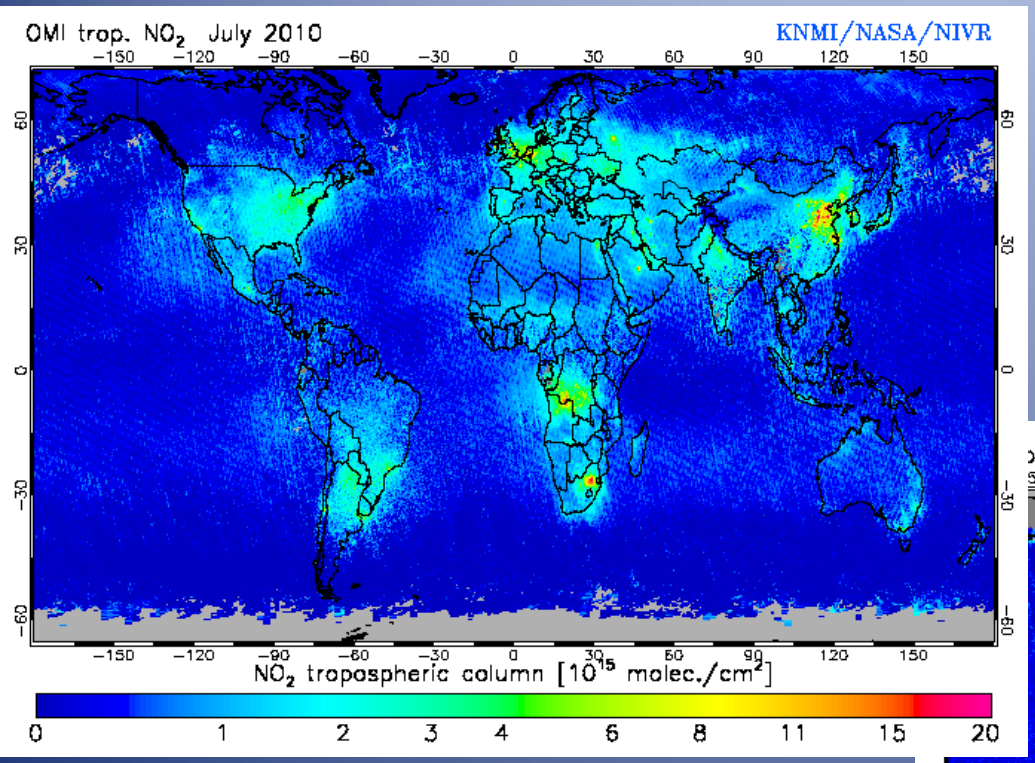
Plot O_x vs NO_z for the whole plume (including the background air)

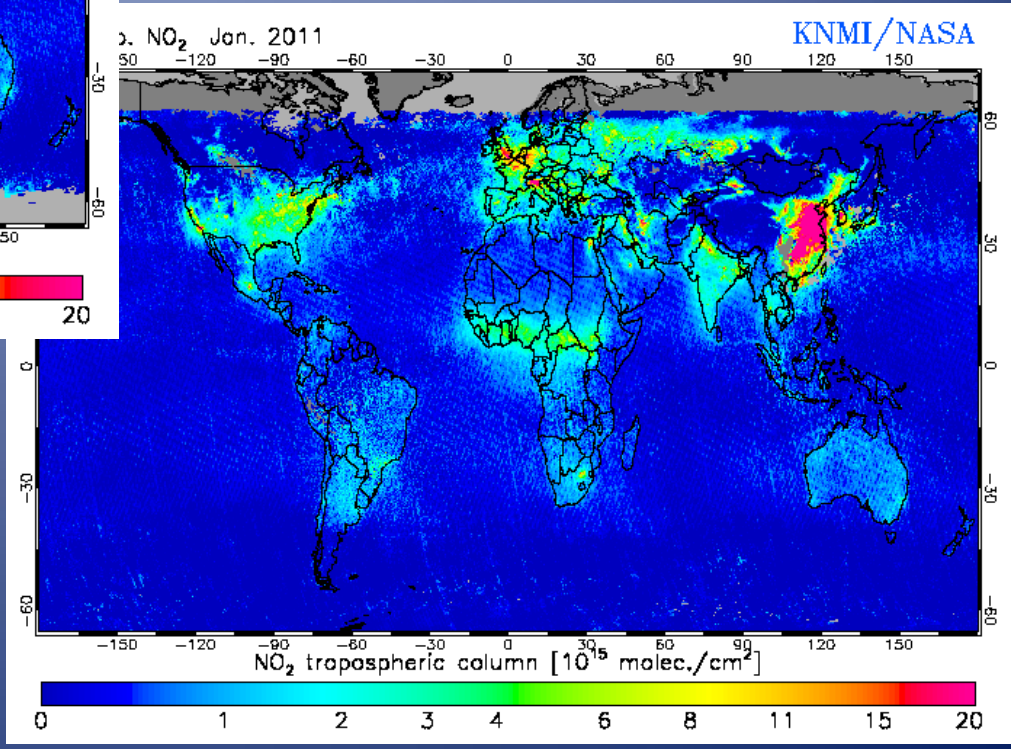


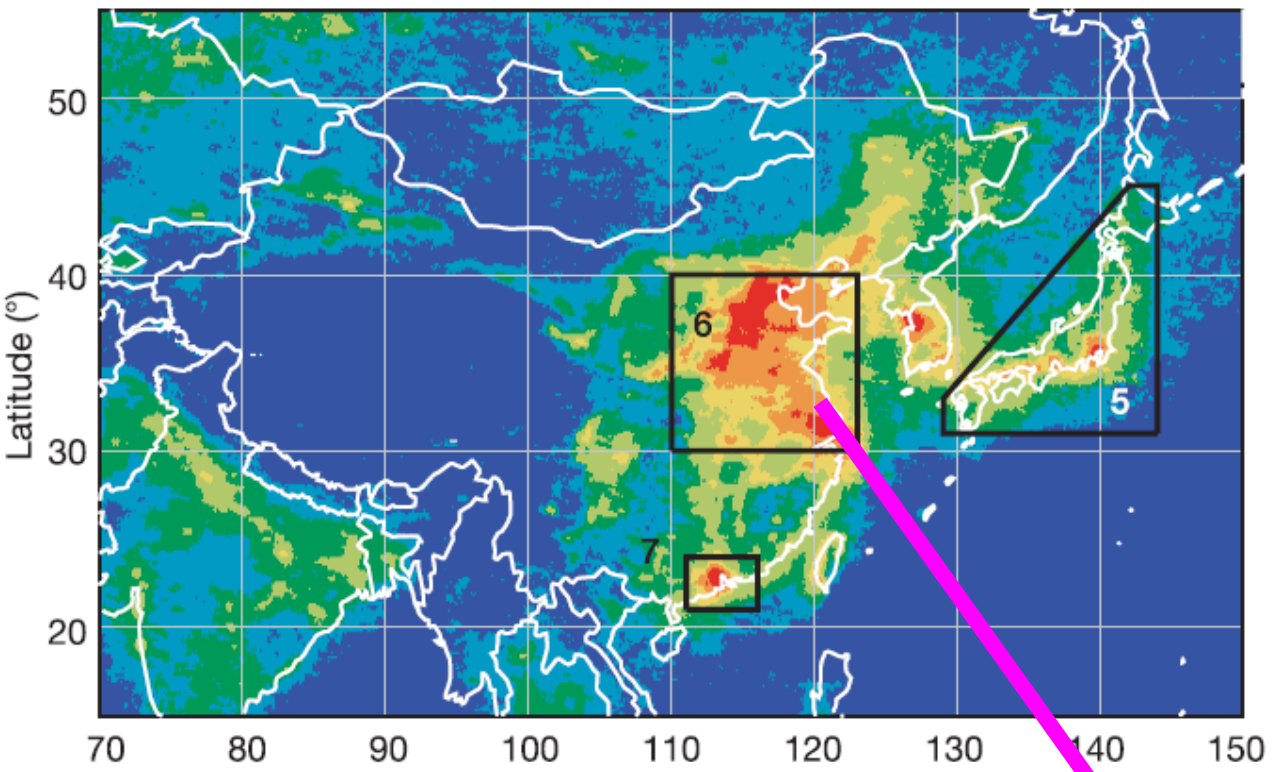
Anthropogenic NOx Emissions in 2008 (EDGAR v4.2)

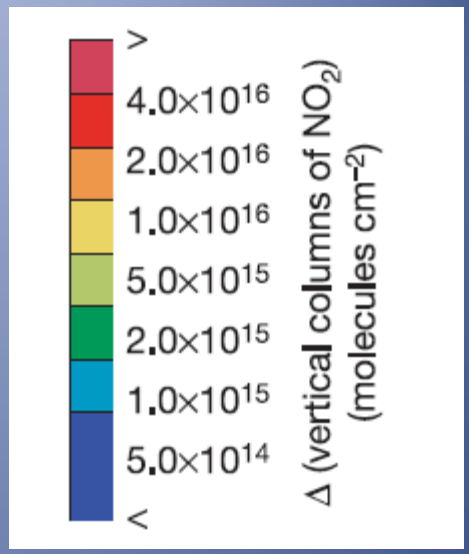


VCDs of Tropospheric NO_2



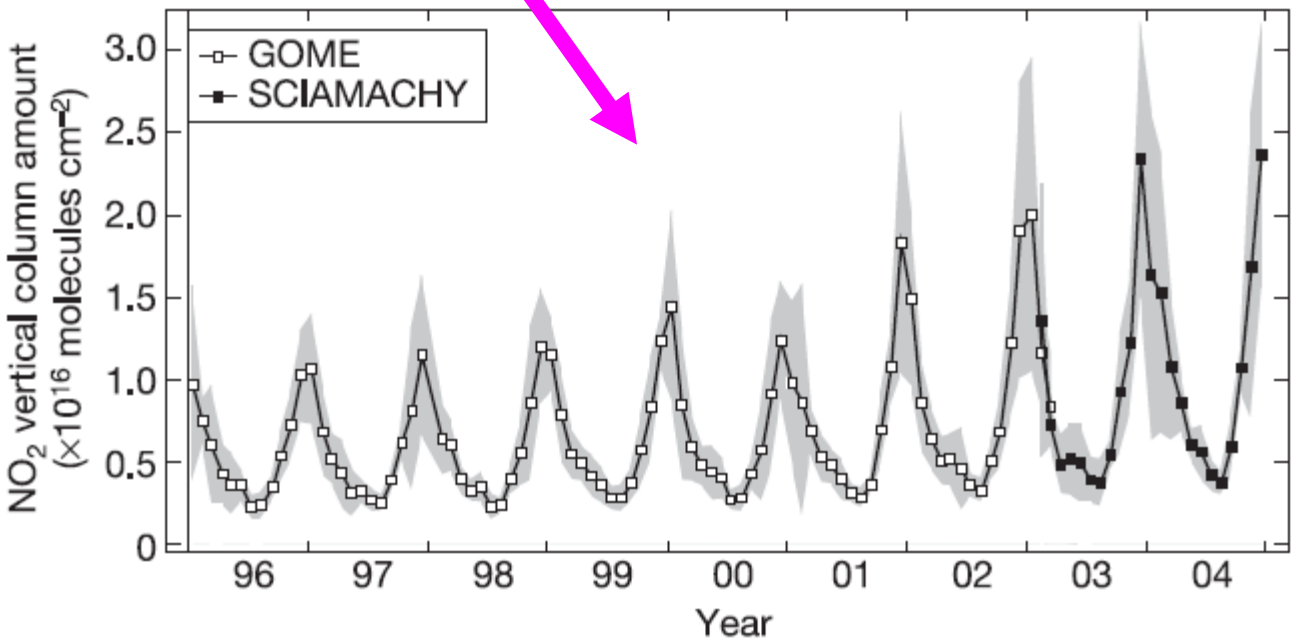




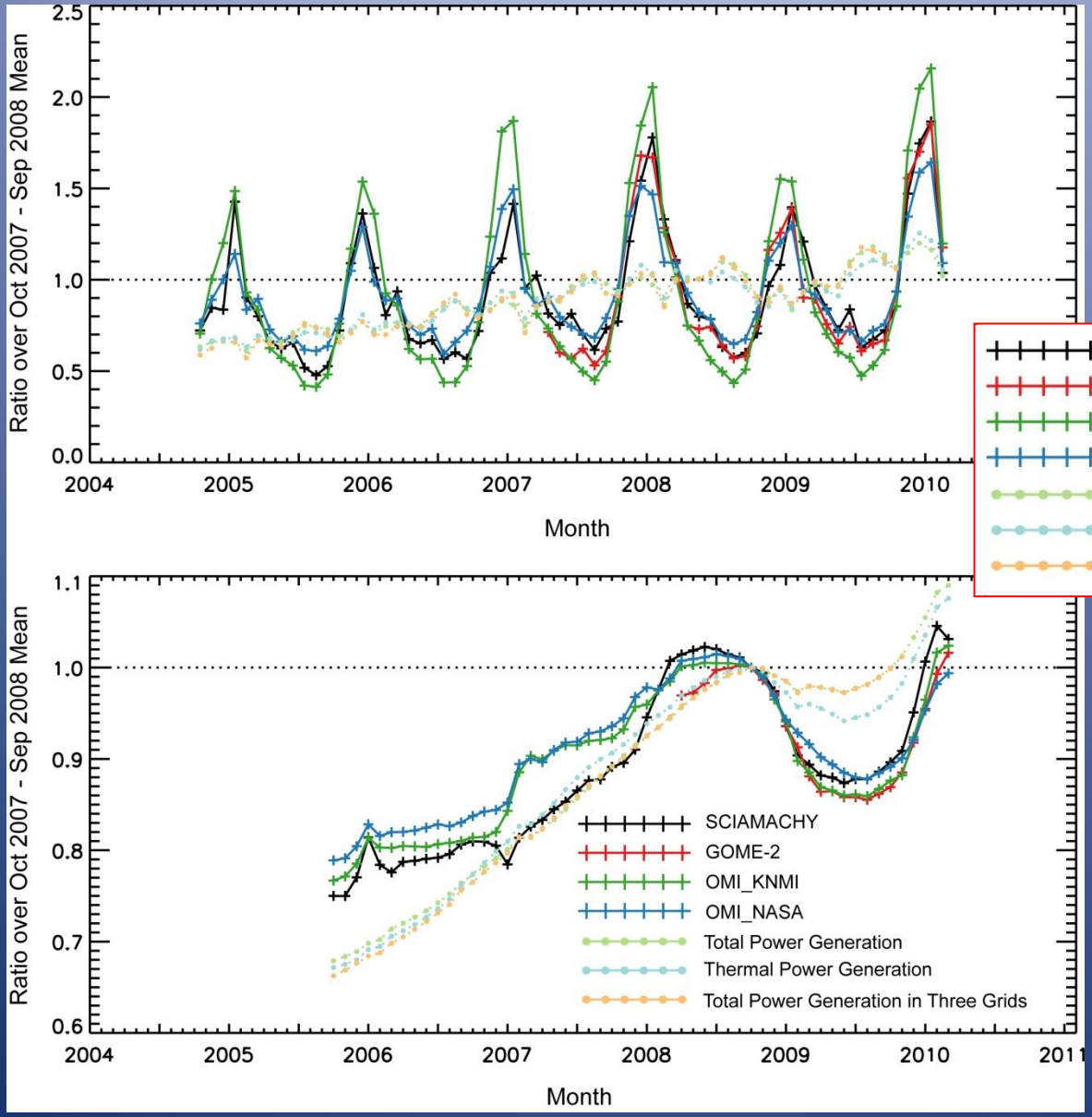


Tropospheric NO_2 vertical columns (2003,12~2004,11)

(Richter et al, 2005: Nature, 437:129-132)

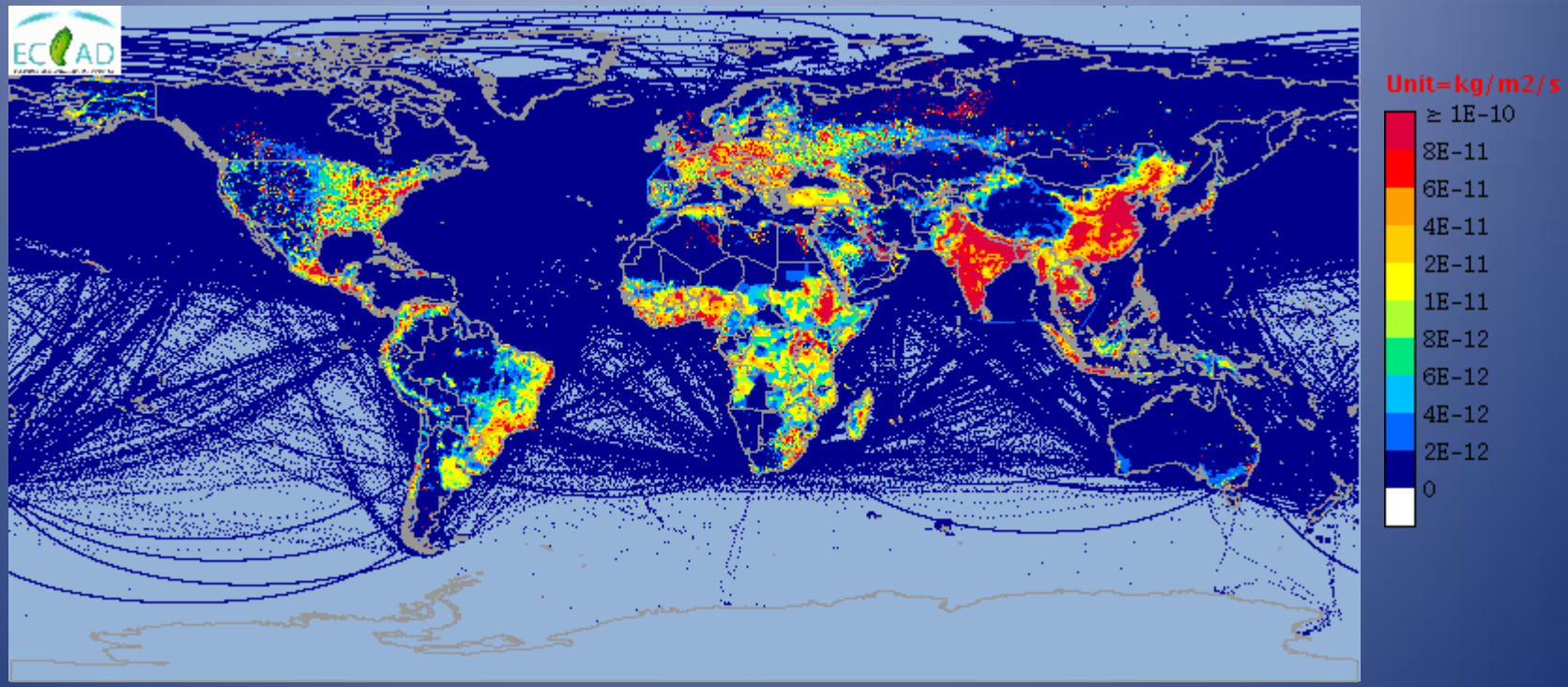


Increases of NO_2 VCD Observed from Space

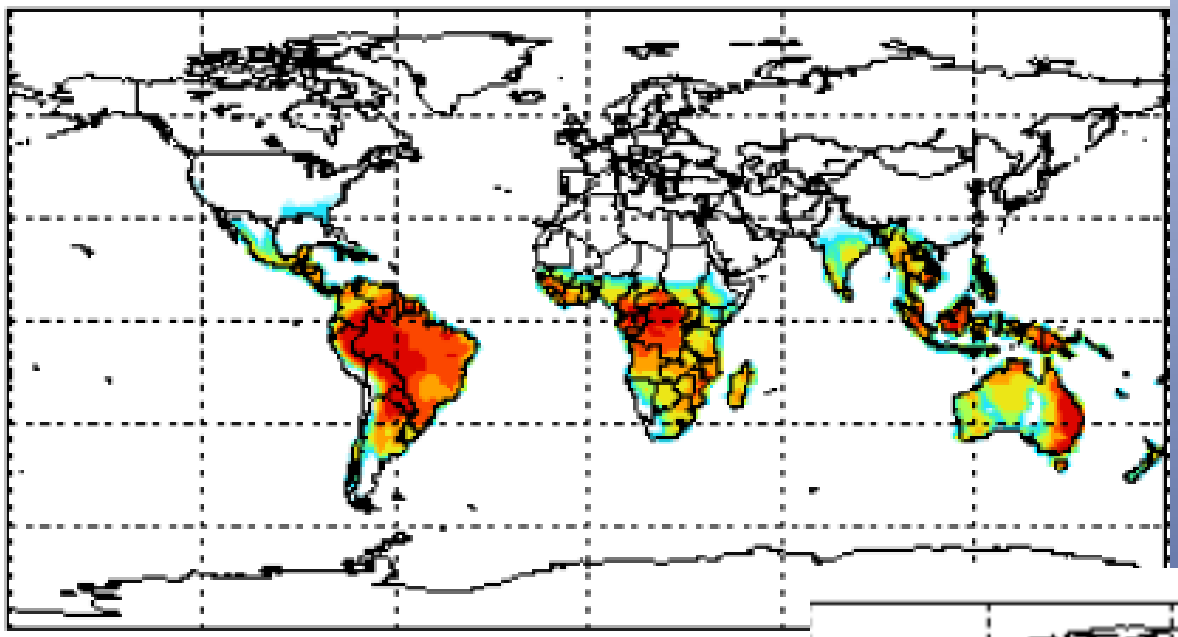


Lin and McElroy, 2011

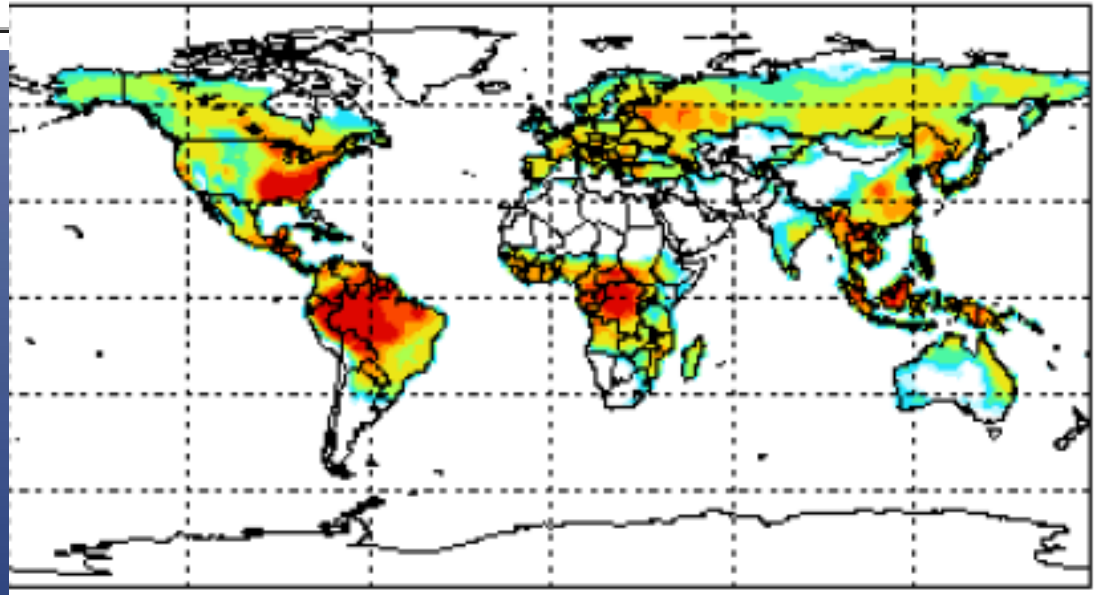
Anthropogenic VOC Emissions in 2008 (EDGAR v4.2)



Biogenic Emissions of Isoprene



July

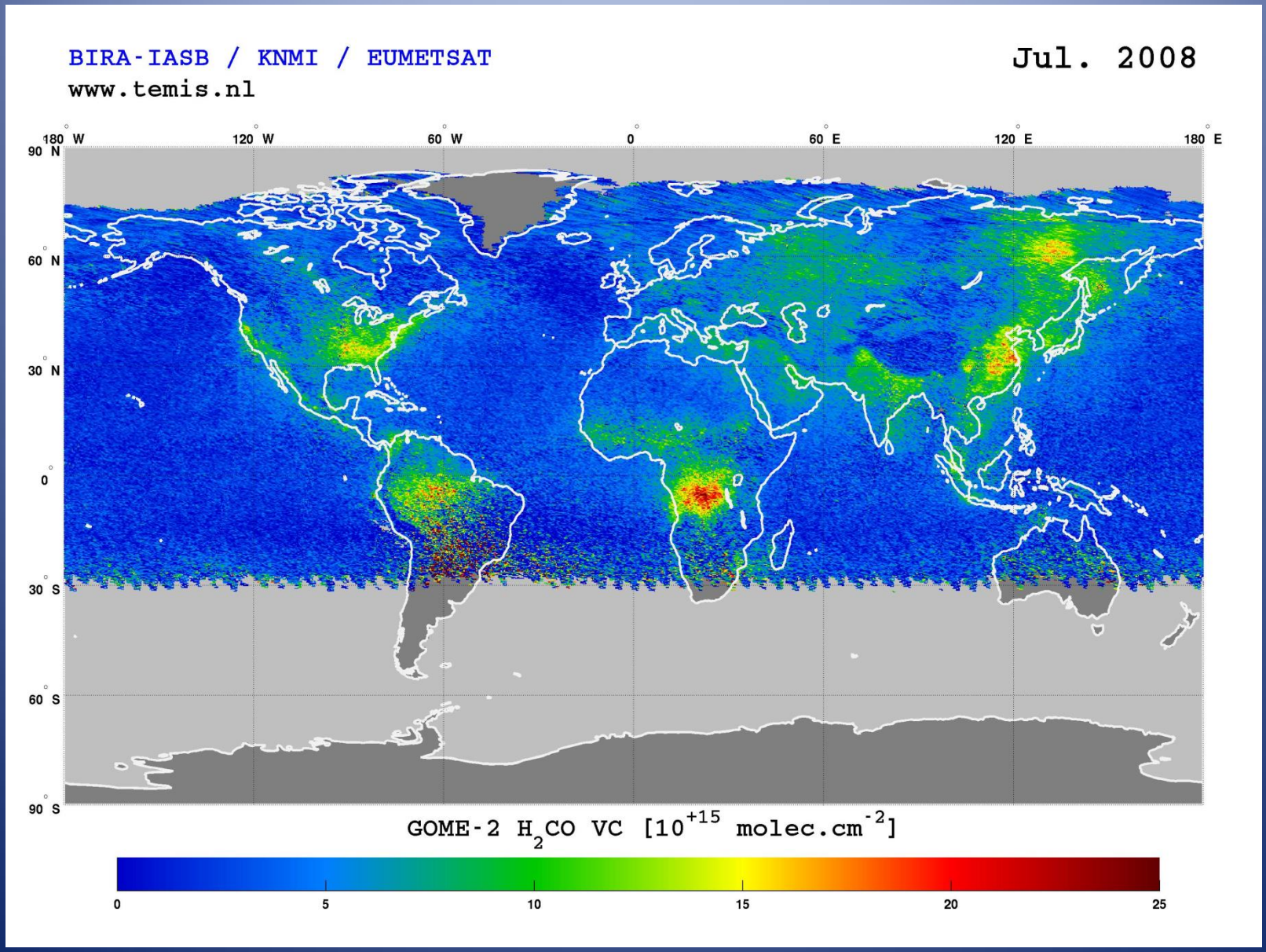


January

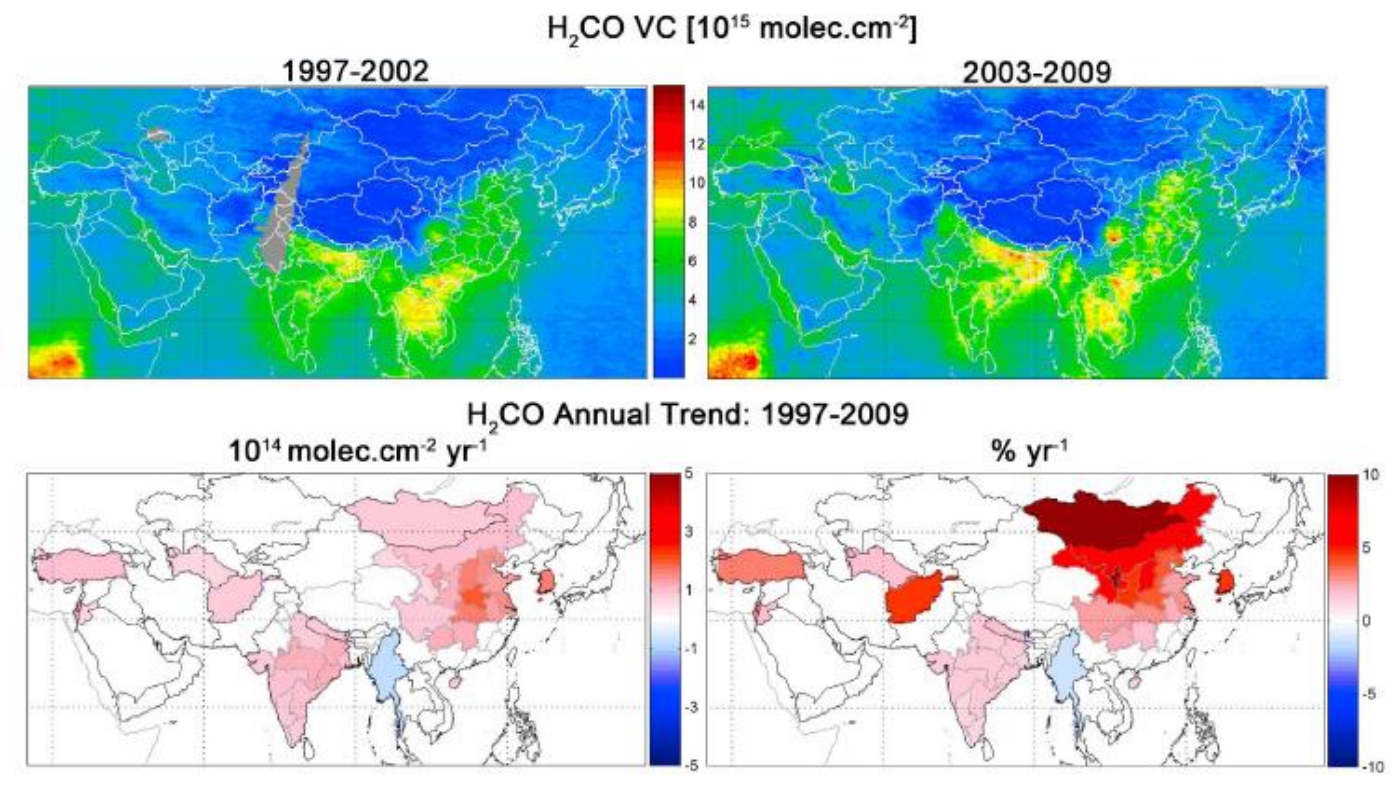
Isoprene:

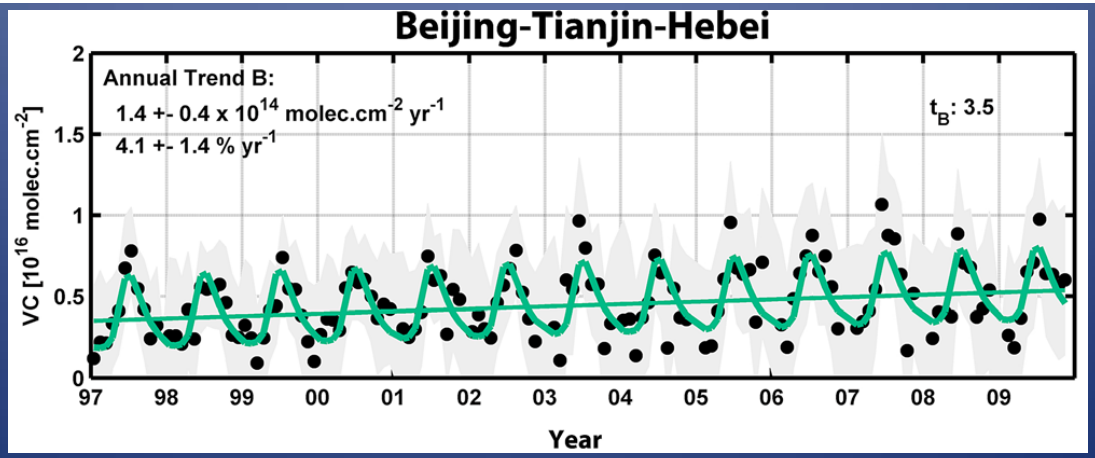
- Emissions: most abundant
- Reactivity: largest

VCDs of Tropospheric HCHO: July 2008



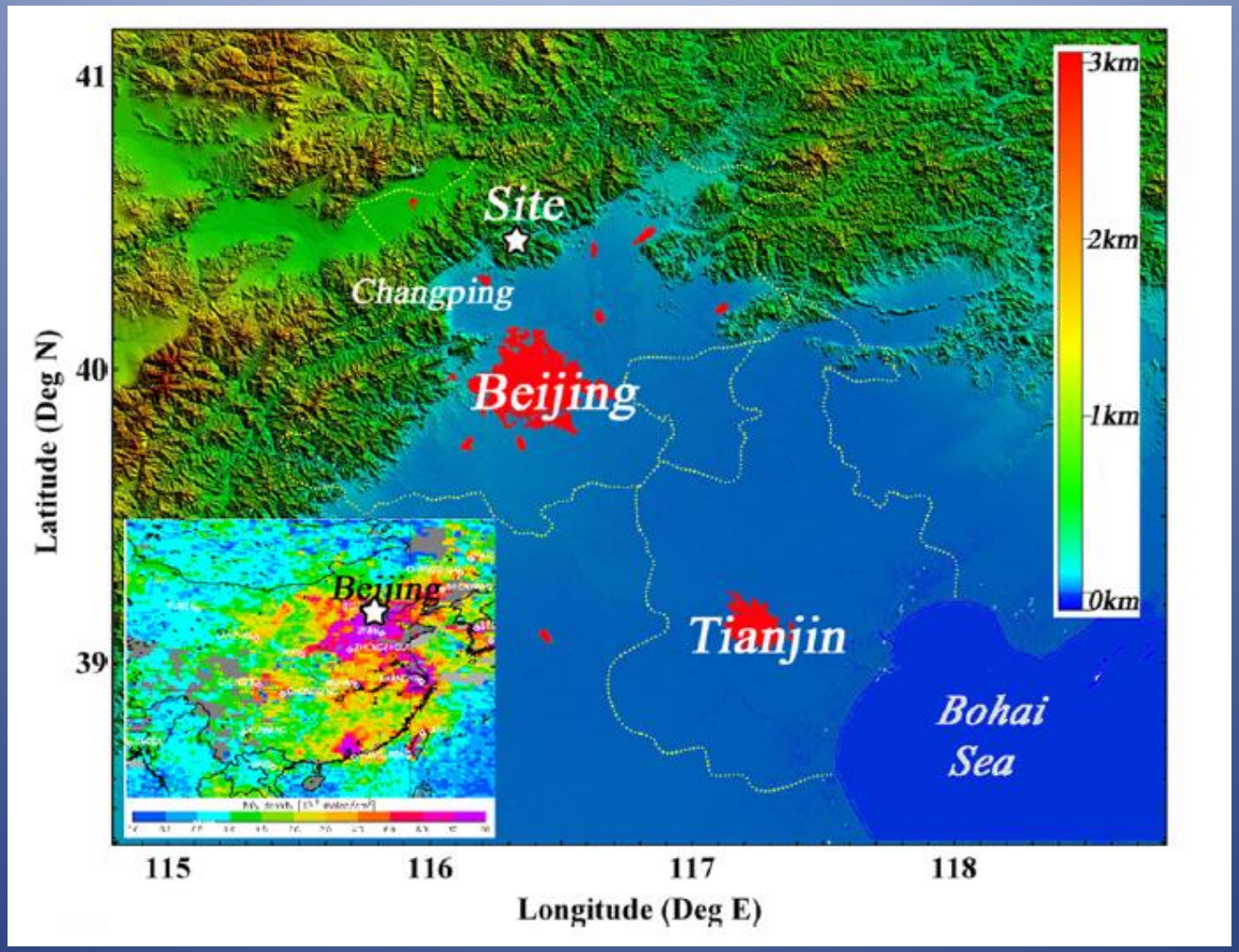
Trends of VCDs of HCHO in Asia: 1997 – 2009





De Smedt et al., 2010

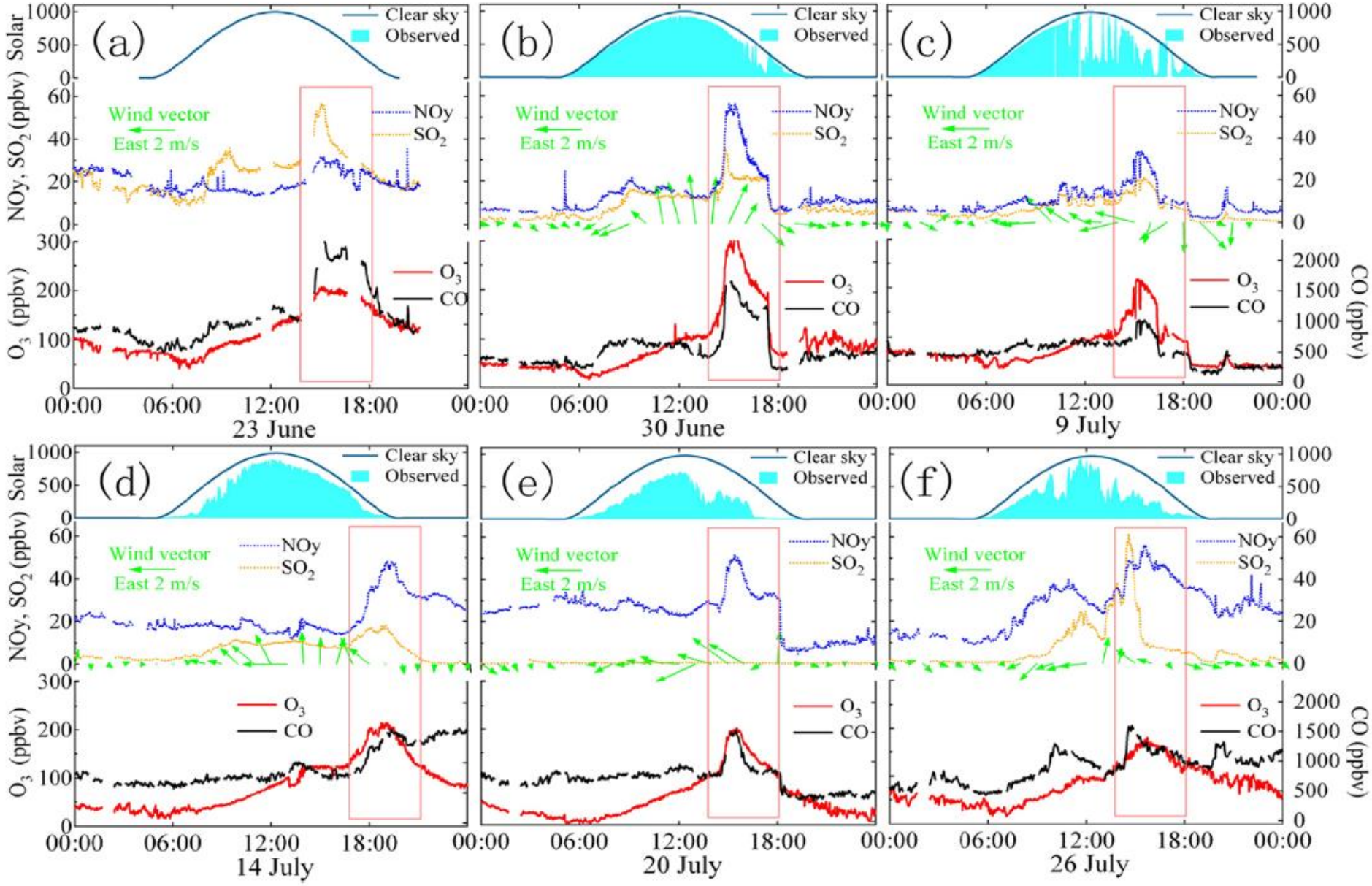
Ozone Air Pollution in Beijing



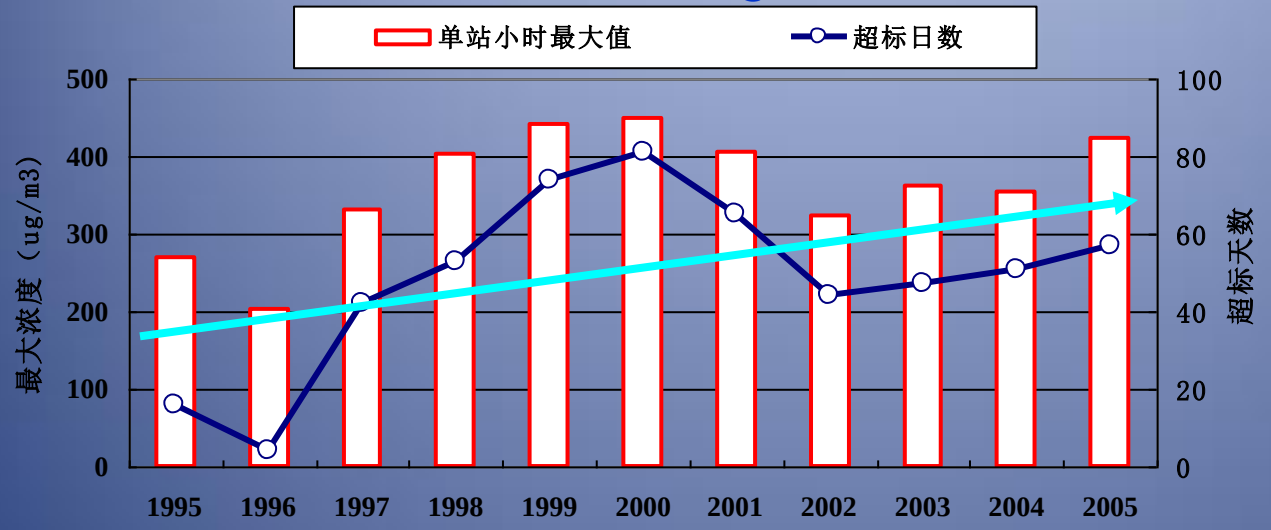
- Lots of emissions of NOx and VOC
- Wind direction/speed
- High temperature, clear sky

Wang et al., 2006

Severe Ozone Pollution in Miyun, Beijing, 2005

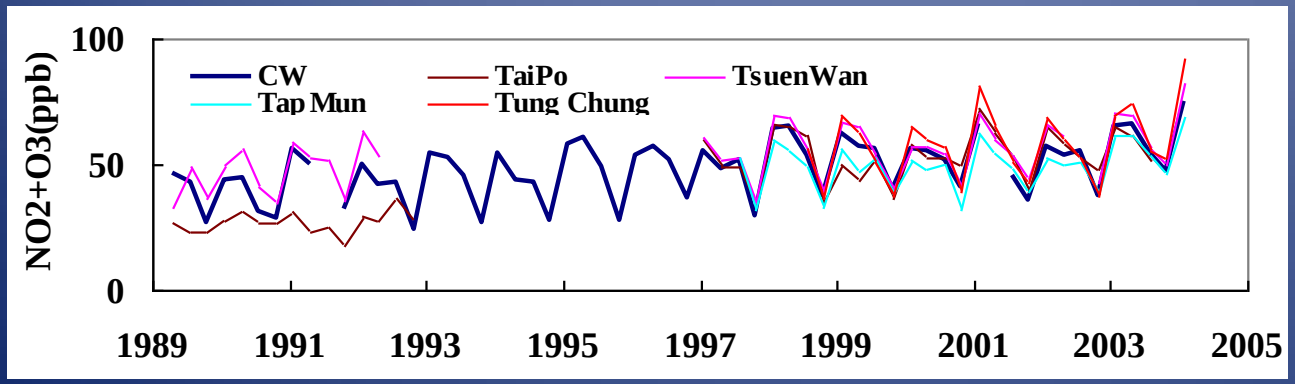


Trends of O_3 in Beijing and PRD



Beijing,

Max O_3 and days over STD



Hong Kong: Daytime O_3 concentration

O_3: 1ppb/yr

Background O_3 concentrations are increasing

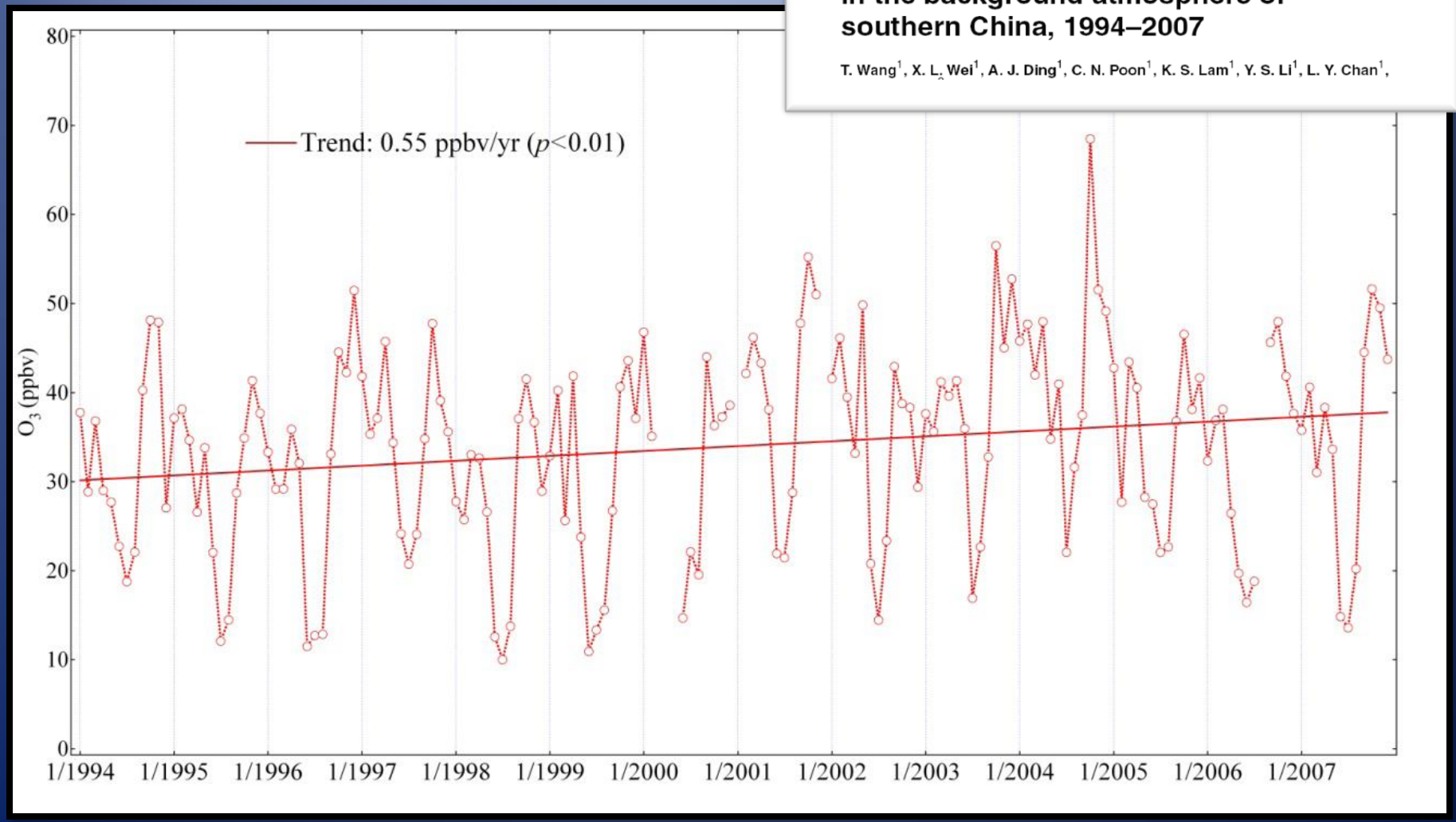
Atmos. Chem. Phys. Discuss., 9, 10429–10455, 2009
www.atmos-chem-phys-discuss.net/9/10429/2009/

Atmospheric Chemistry and Physics Discussions

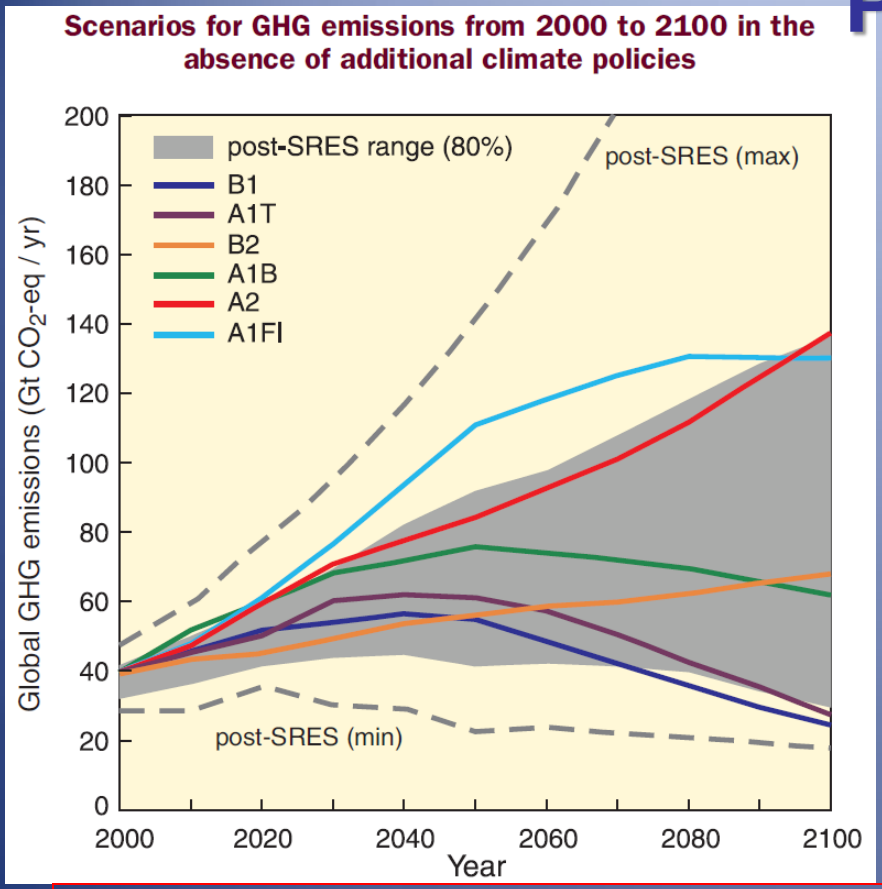
This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

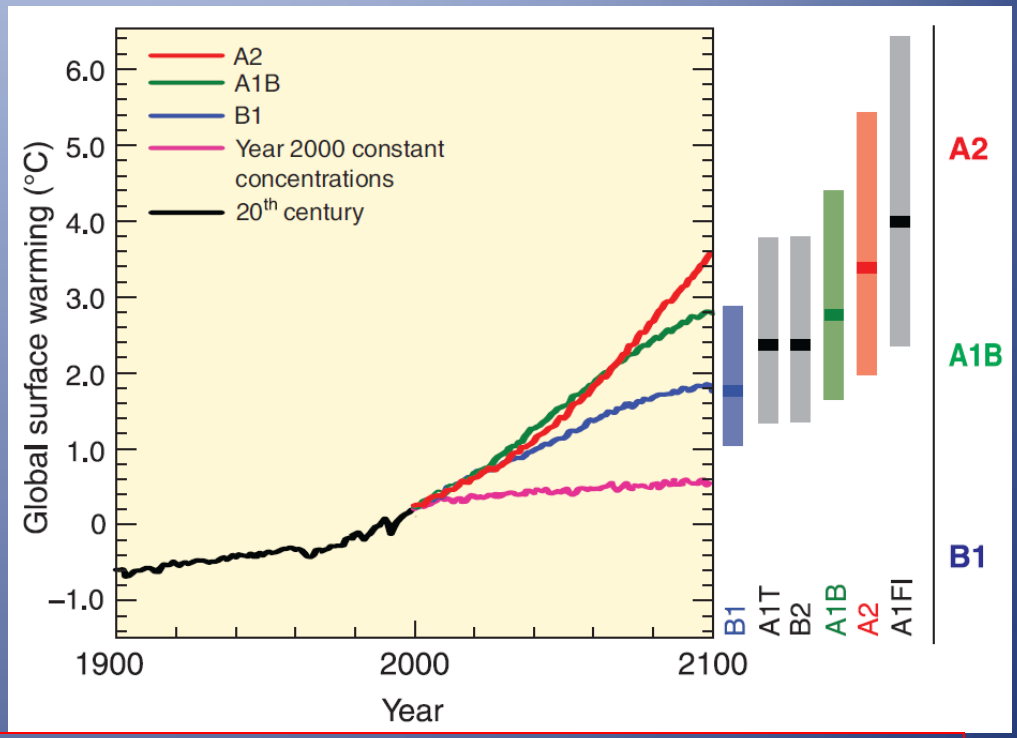
Increasing surface ozone concentrations in the background atmosphere of southern China, 1994–2007

T. Wang[1], X. L. Wei[1], A. J. Ding[1], C. N. Poon[1], K. S. Lam[1], Y. S. Li[1], L. Y. Chan[1],



Projected Climate Change

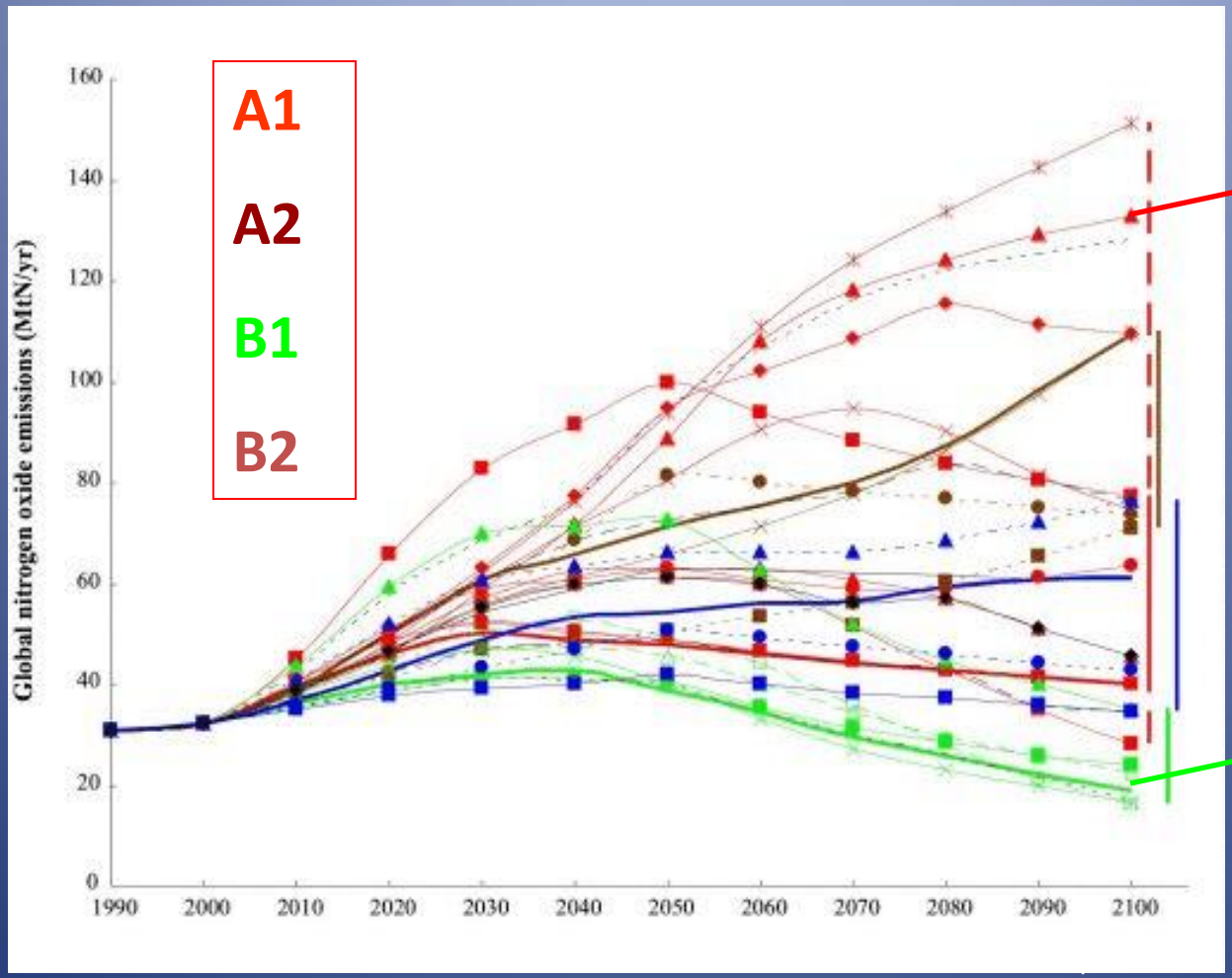




IPCC 2007: Potential changes in global mean air temperature currently assumed plausible are bounded roughly by the A1Fi (highly-warming) and B1 (less-warming) scenarios.

NOTE: The current rate of increase in GHG emissions exceeds A1Fi pathway.

Projected Anthropogenic Emissions: NOx

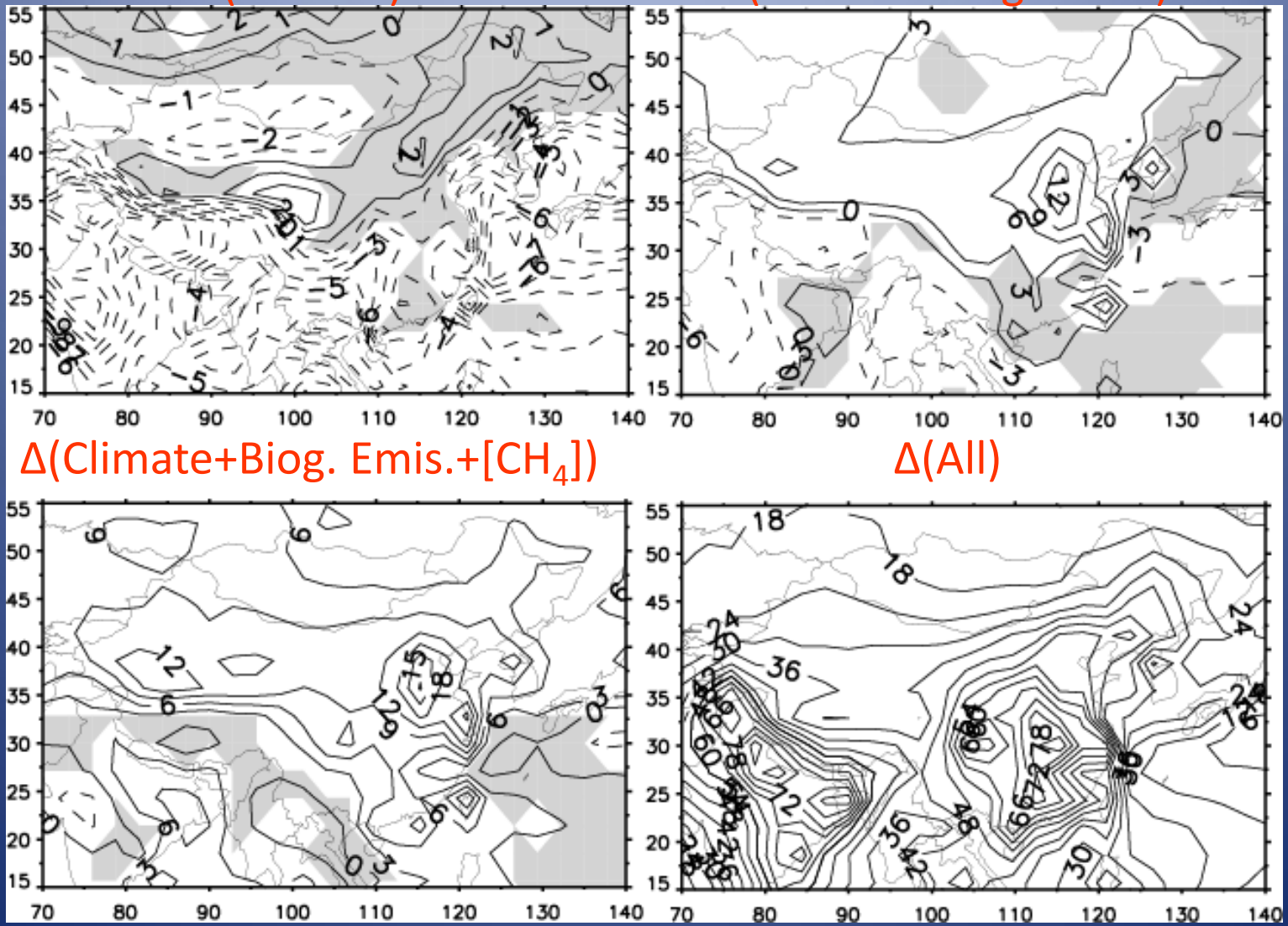


The A1Fi and B1 scenarios are amongst the highest and smallest precursor emissions scenarios for projected fossil fuel burning.

Ozone Changes in China: 2090s (A1fi)

Δ(Climate)

Δ(Climate+Biog. Emis.)



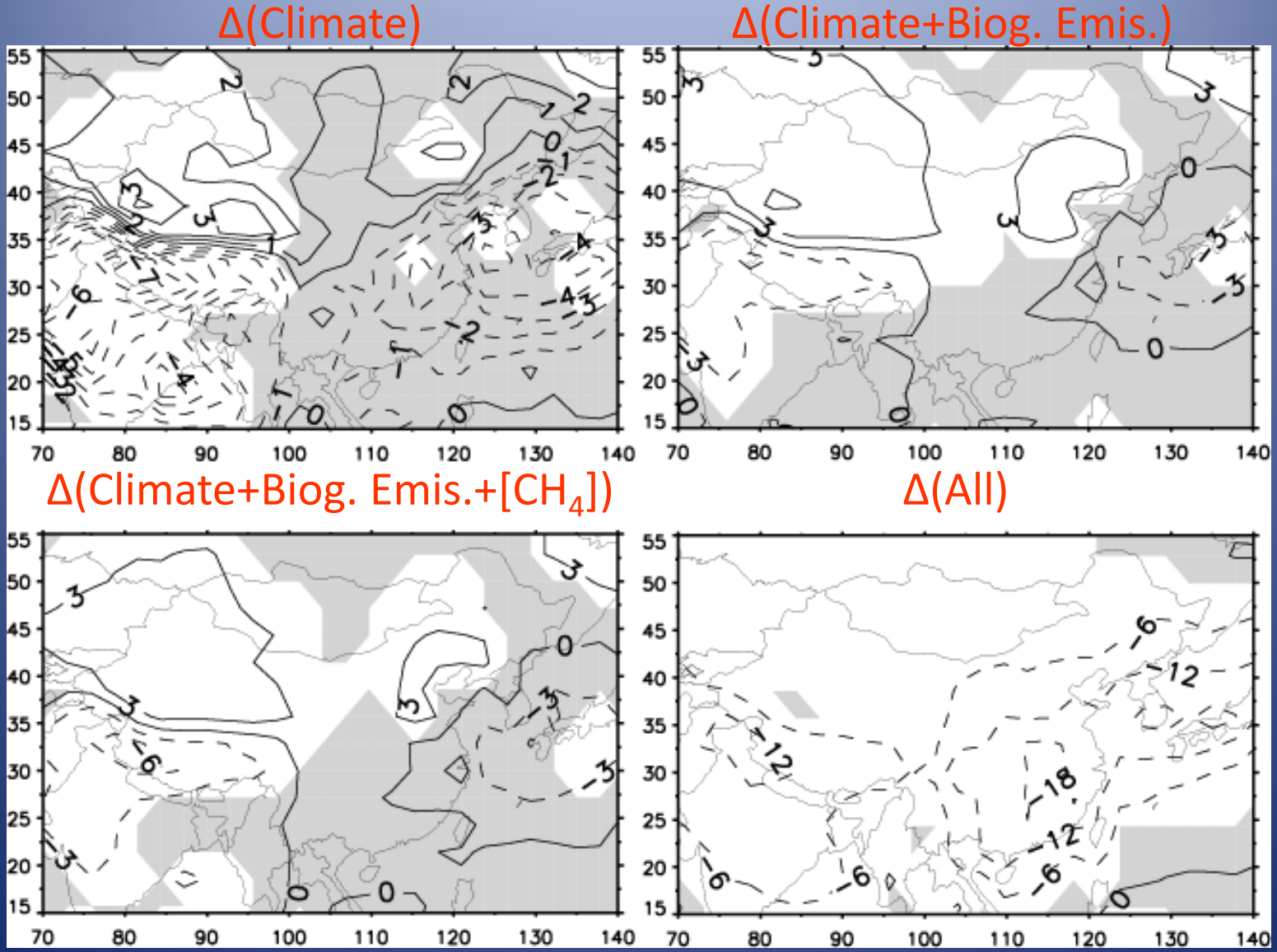
Δ(Climate+Biog. Emis.+[CH_4])

Δ(All)

ΔO_3 (ppb)

*** Changes are not statistically significant over shaded areas ***

Ozone Changes in China: 2090s (B1)

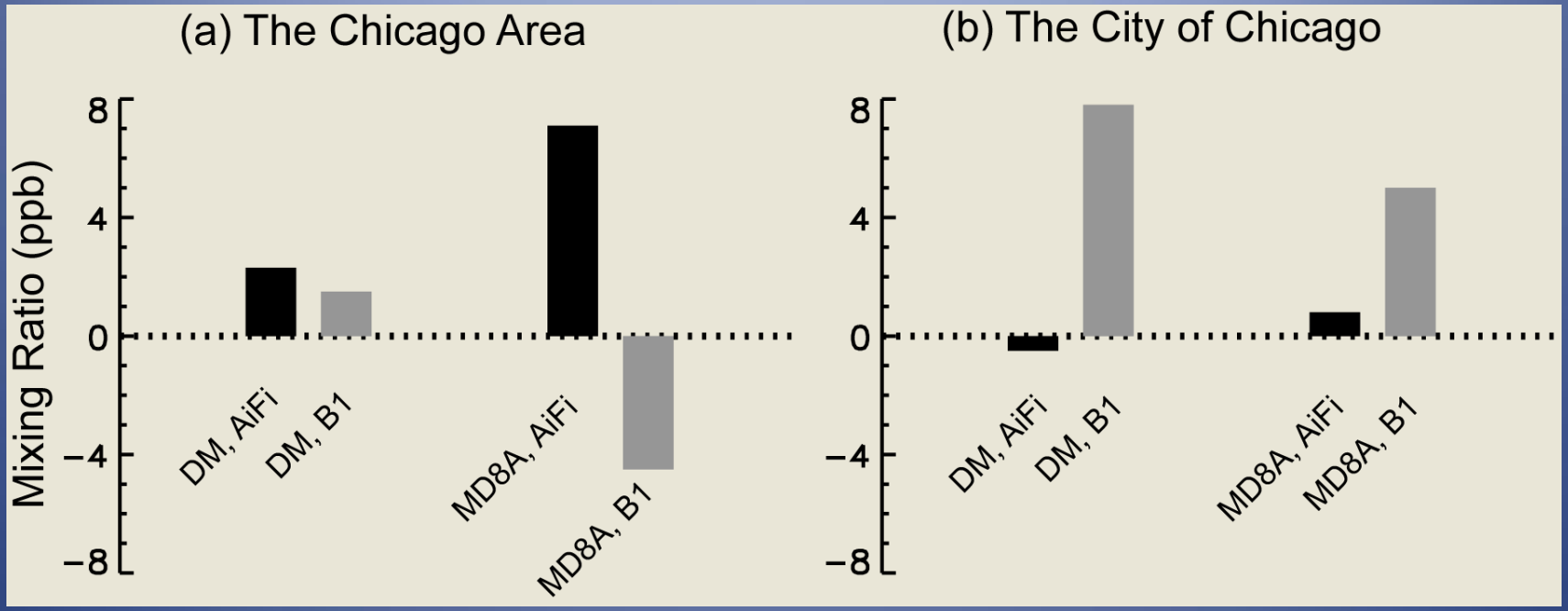


ΔO_3 (ppb)

*** Changes are not statistically significant over shaded areas ***

Ozone Change: Regional versus Urban

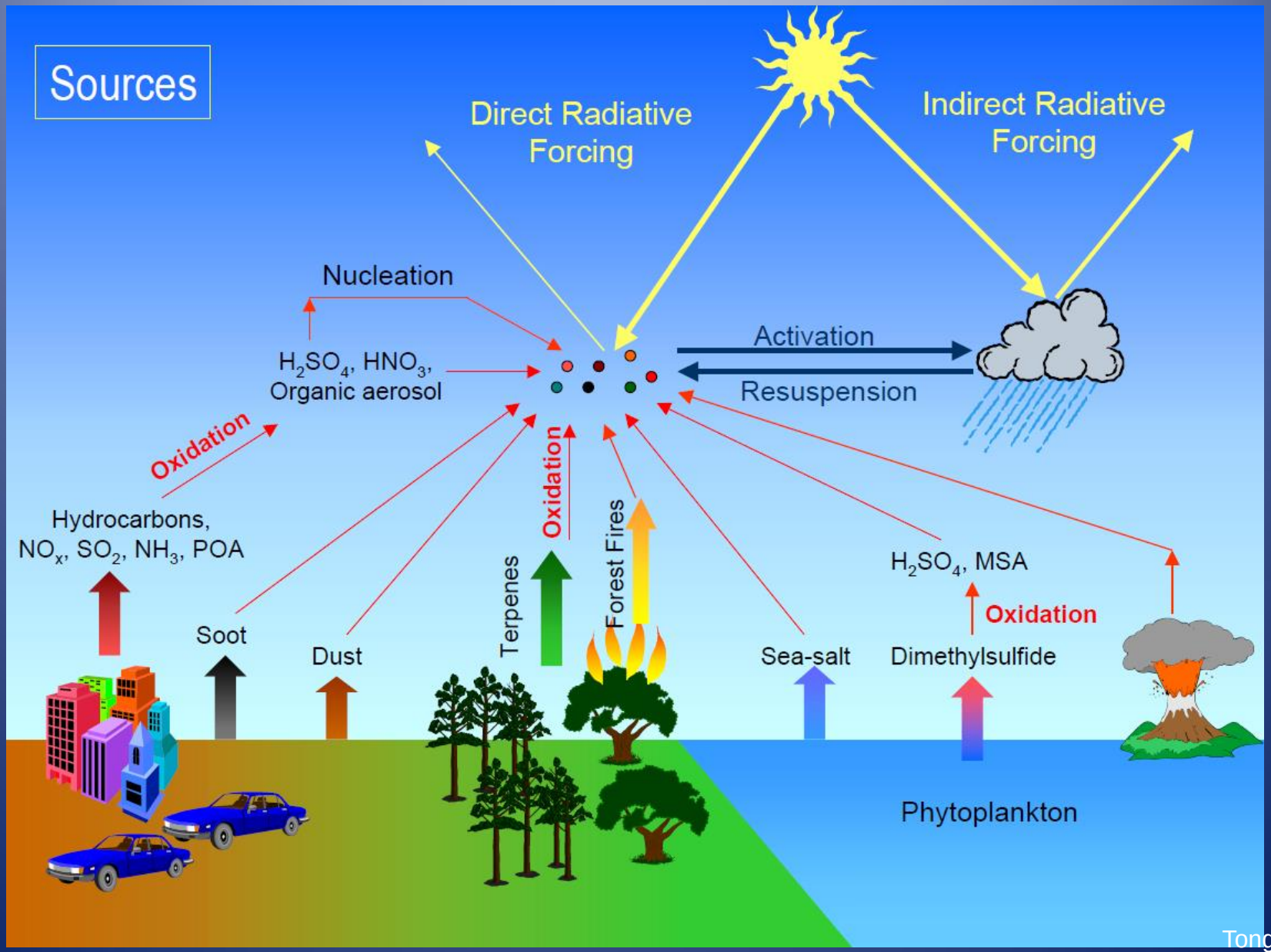
From 1990s to 2090s



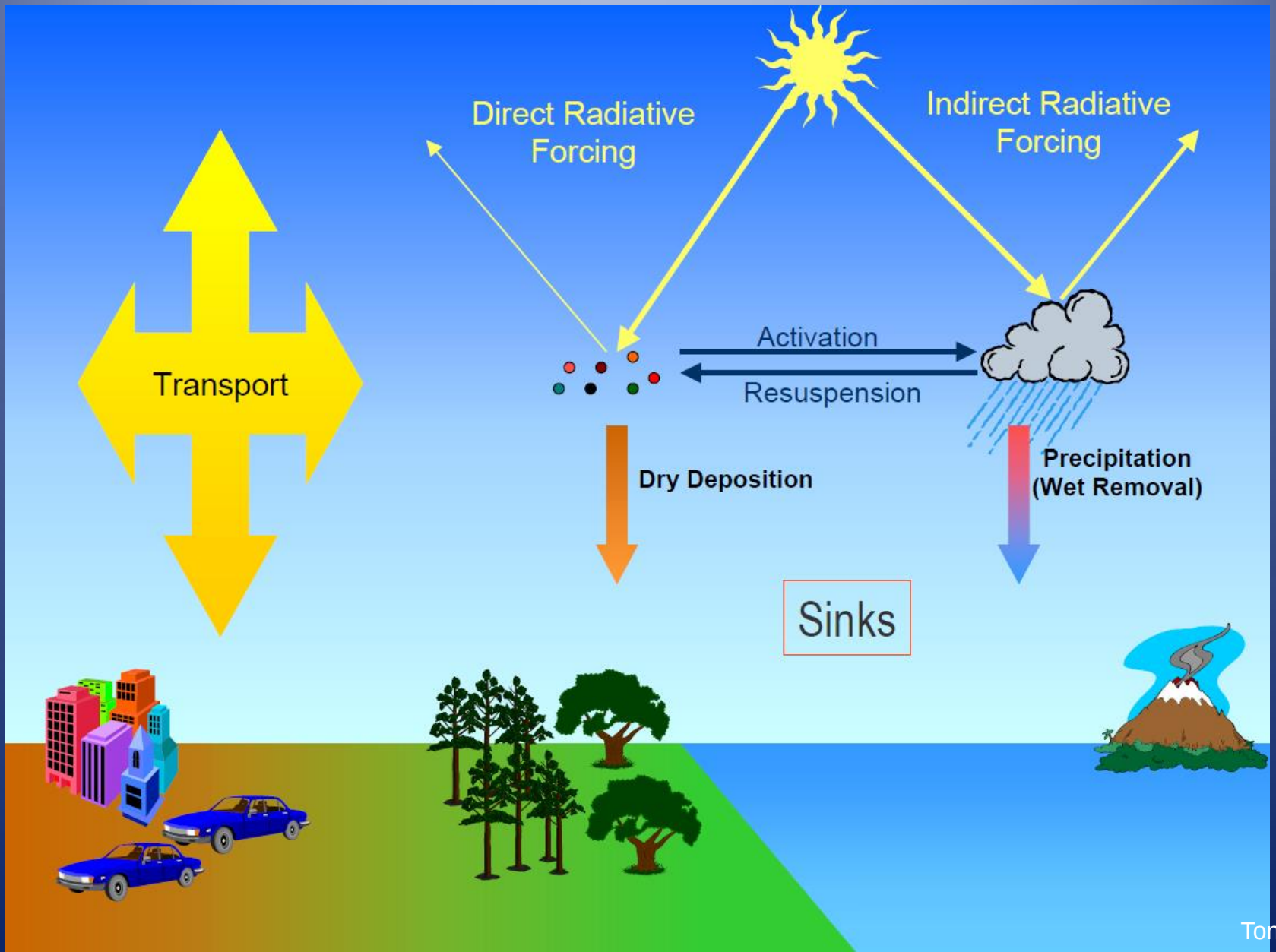
ΔO_3 as a result of Δ (precursor emissions) and Δ (climate):

- Chicago Area: Significant increases under A1Fi
- City of Chicago: Significant increases under B1 and minor changes for A1Fi

Particulate Matter (PM) Pollution



Particulate Matter (PM) Pollution



PM Air Pollution: Sources and Sizes

- Primary aerosols: anthropogenic and natural; small and large
  - BC, POC – anthropogenic; typically small, i.e., ≤ 2.5 µm
  - Industrial dust – anthropogenic; small and large
  - Fugitive dust – anthropogenic; small and large
  - Desert dust – natural; small and large; not important except in spring
  - Sea salt – natural; small and large; not important over non-coastal lands

- Secondary aerosols: mostly anthropogenic; mostly small
  - Sulfate – anthropogenic; small
  - Nitrate – anthropogenic; typically small
  - Ammonium – anthropogenic; small
  - SOA – anthropogenic and natural; typically small; natural sources important mainly in summertime

The Great Smog of London, Dec 1952

Cold and stagnant weather
Inversion
Burning of coal
12000+ people died

- Emissions of PM and precursors
- High humidity, sunlight
- Stagnant atmosphere
- Wind direction/speed

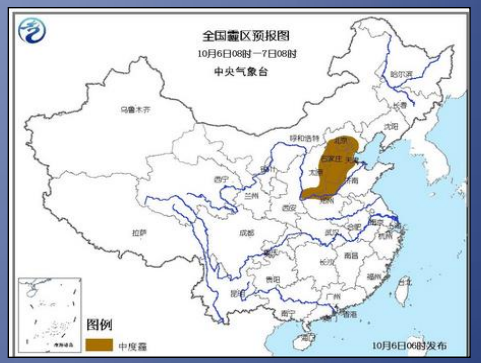
2013年全国主要雾霾重污染过程

每一次雾霾重污染过程都涉及到京津冀地区

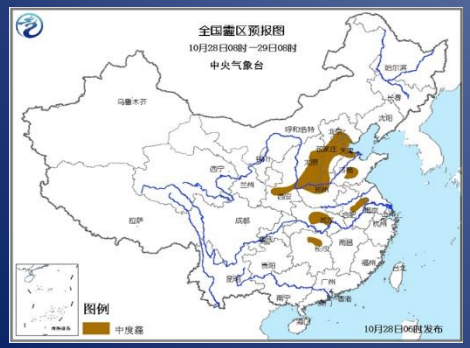
Jan 14-15, 2013

Jan 29, 2013

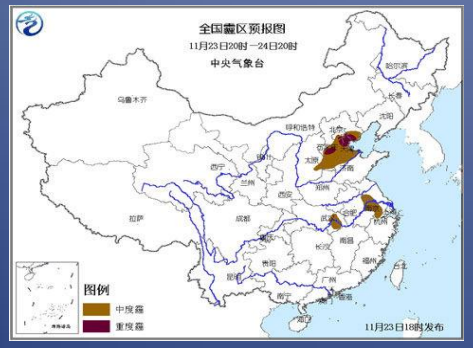
Feb 24-25, 2013



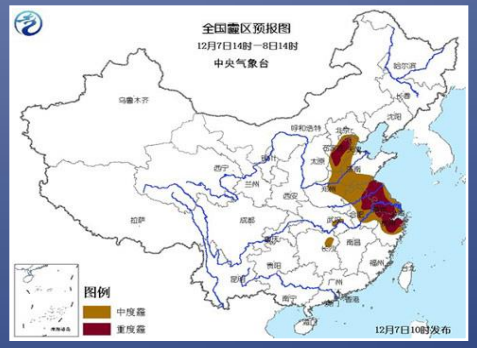
Oct 06-07, 2013



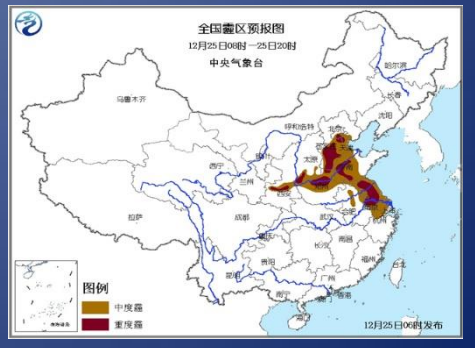
Oct 28-29, 2013



Nov 23-24, 2013



Dec 07-08, 2013

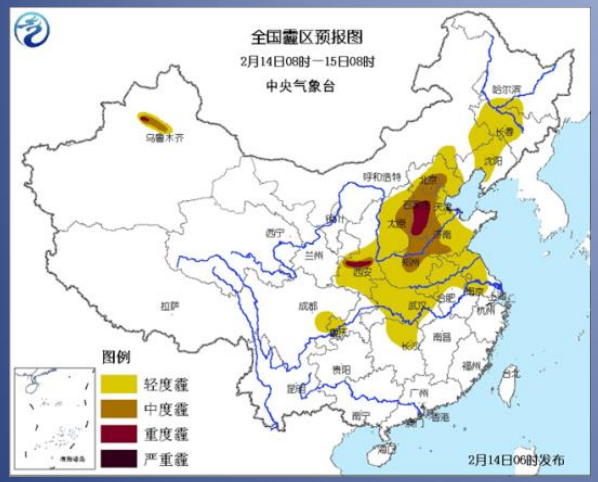


Dec 25, 2013

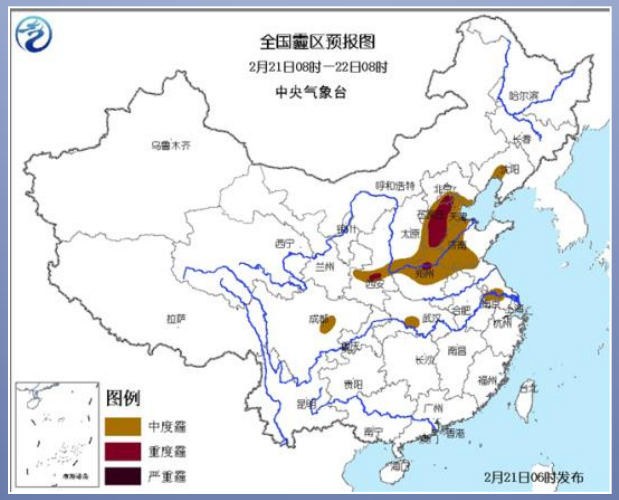
贺克斌，2014

2014年全国霾区分布图

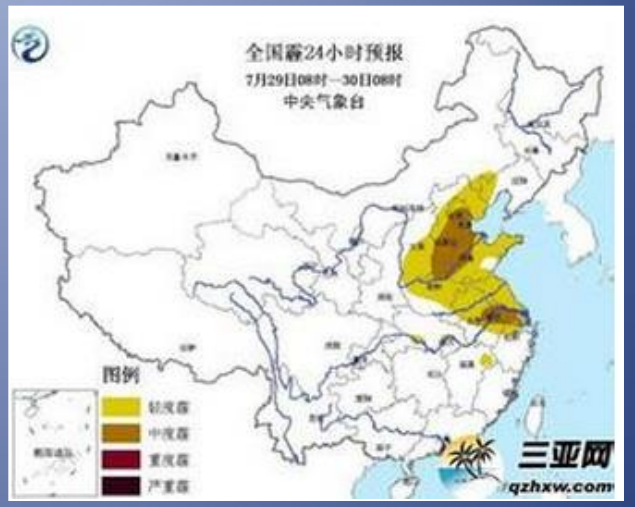
2月14日-2月16日



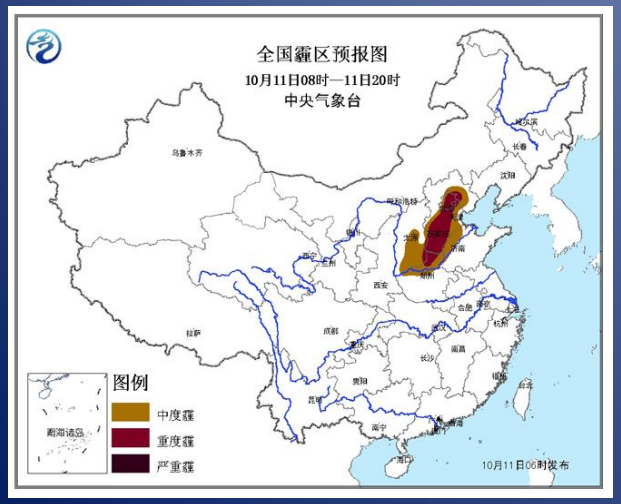
2月21日-2月24日



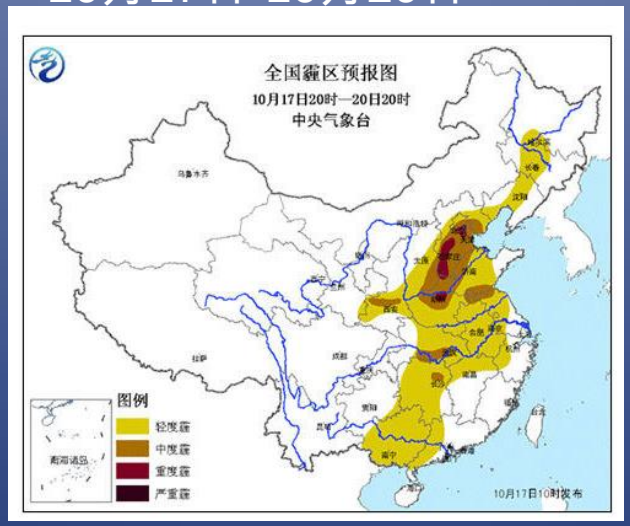
7月29日-7月30日



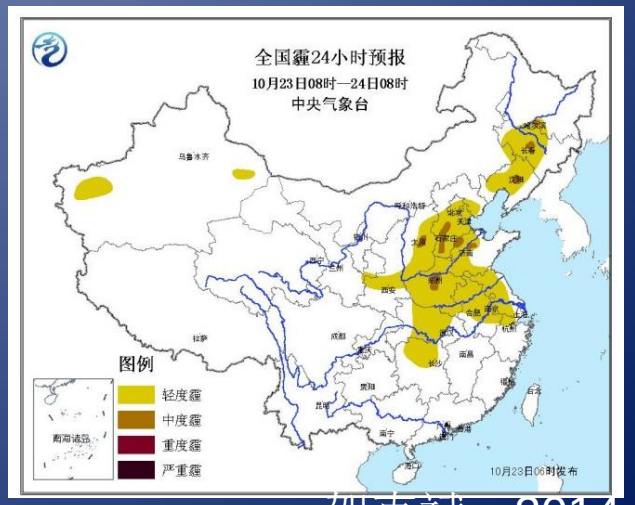
10月7日-10月11日



10月17日-10月20日

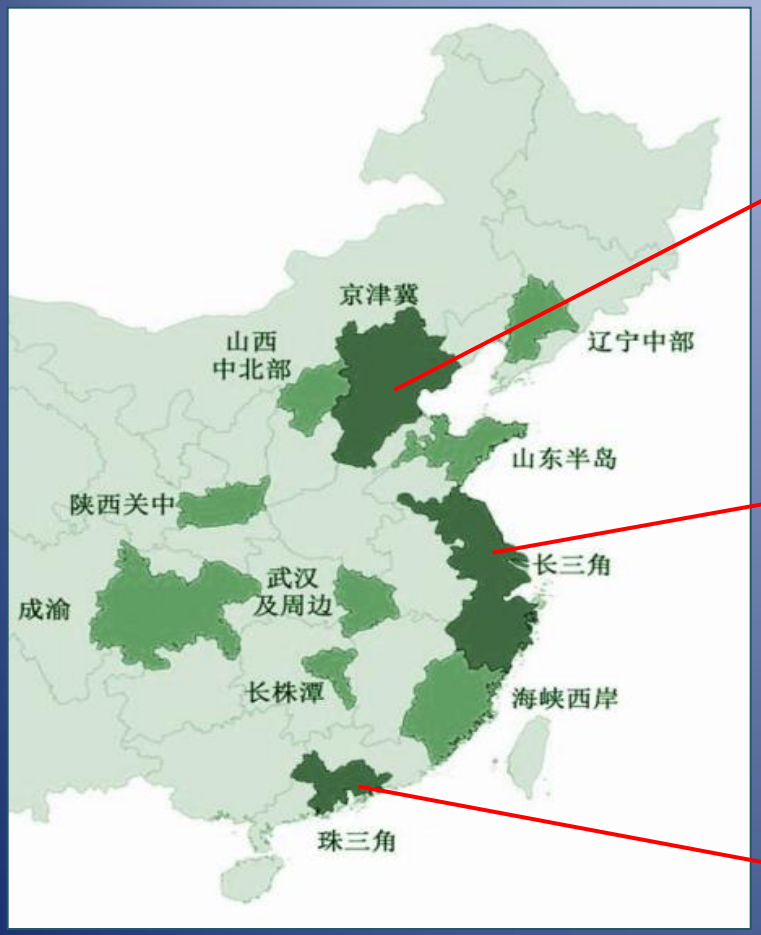


10月23日-10月26日



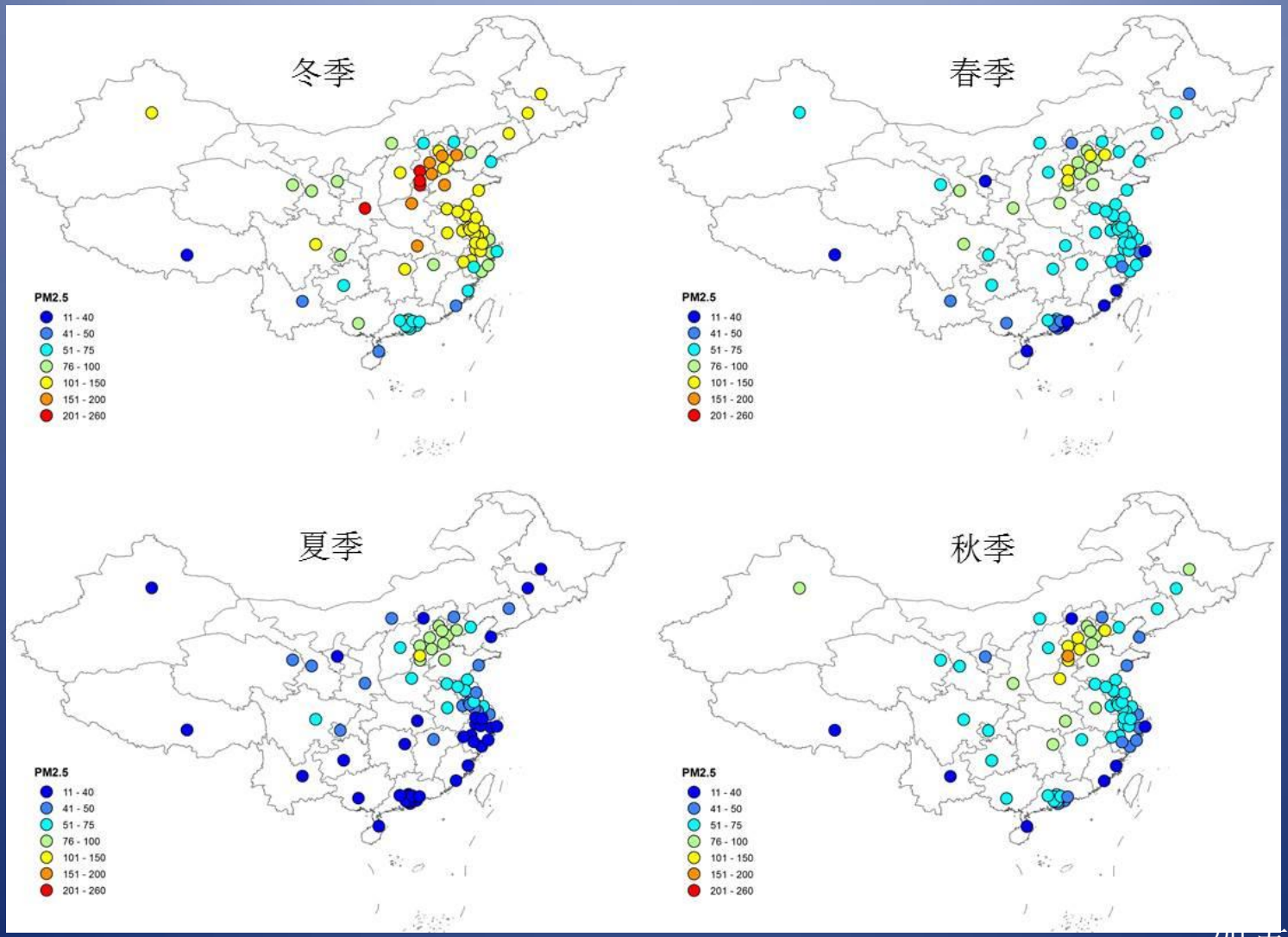
贺克斌，2014

Annual Average $PM_{2.5}$ in 74 cities, 2013



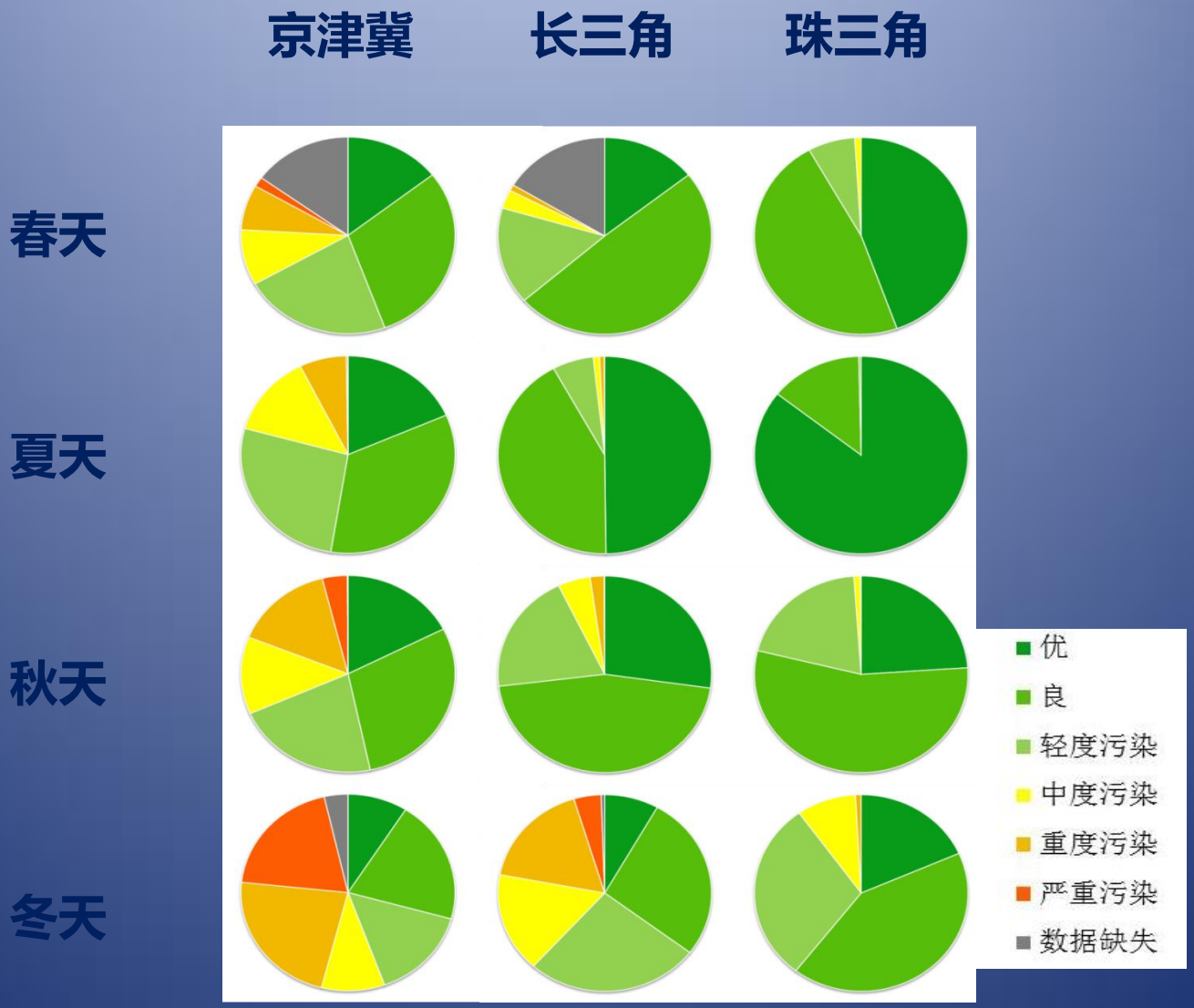
贺克斌，2014

$PM_{2.5}$浓度季节变化特征



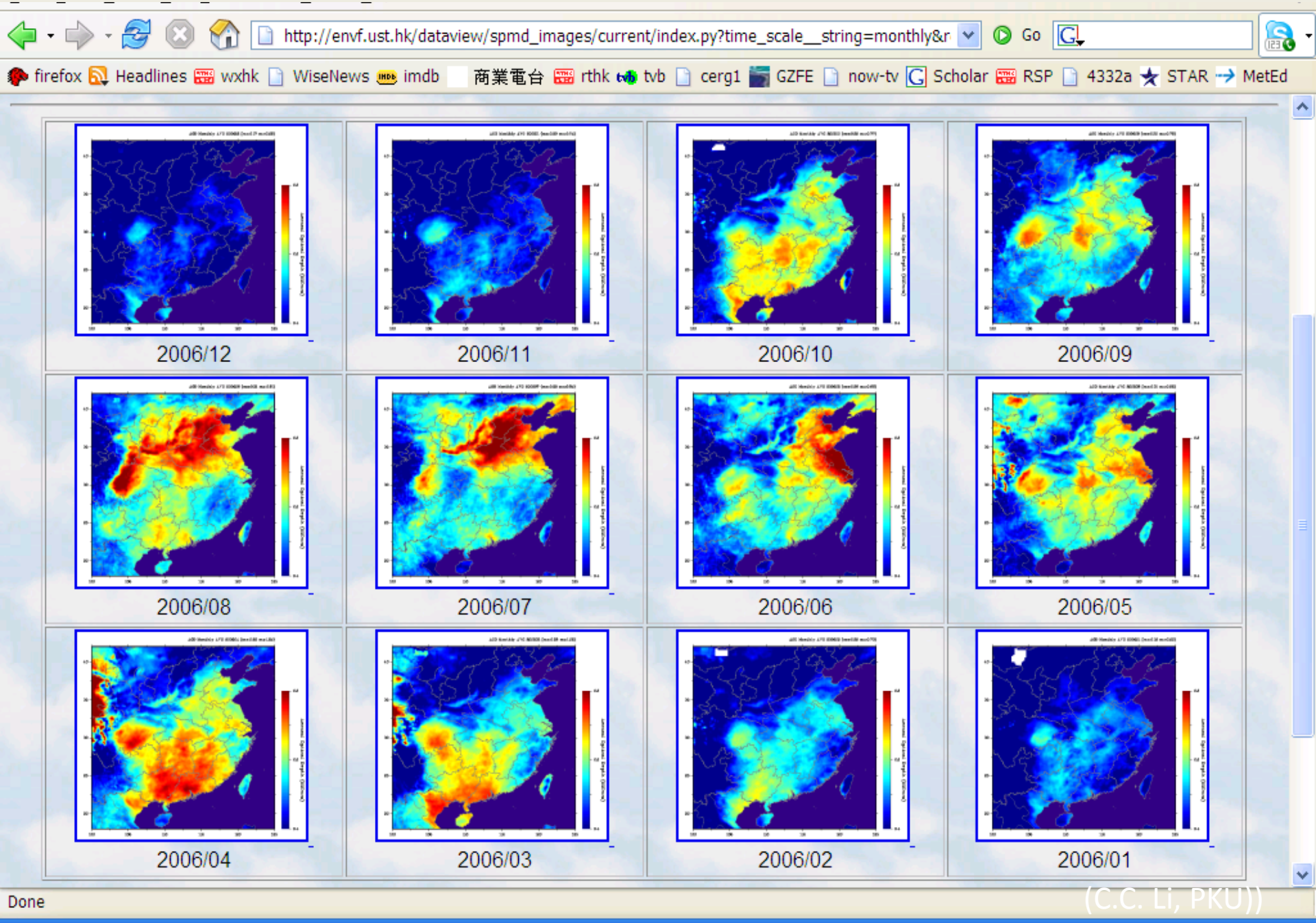
贺克斌，2014

基于地面监测评估我国$PM_{2.5}$变化特征



贺克斌，2014

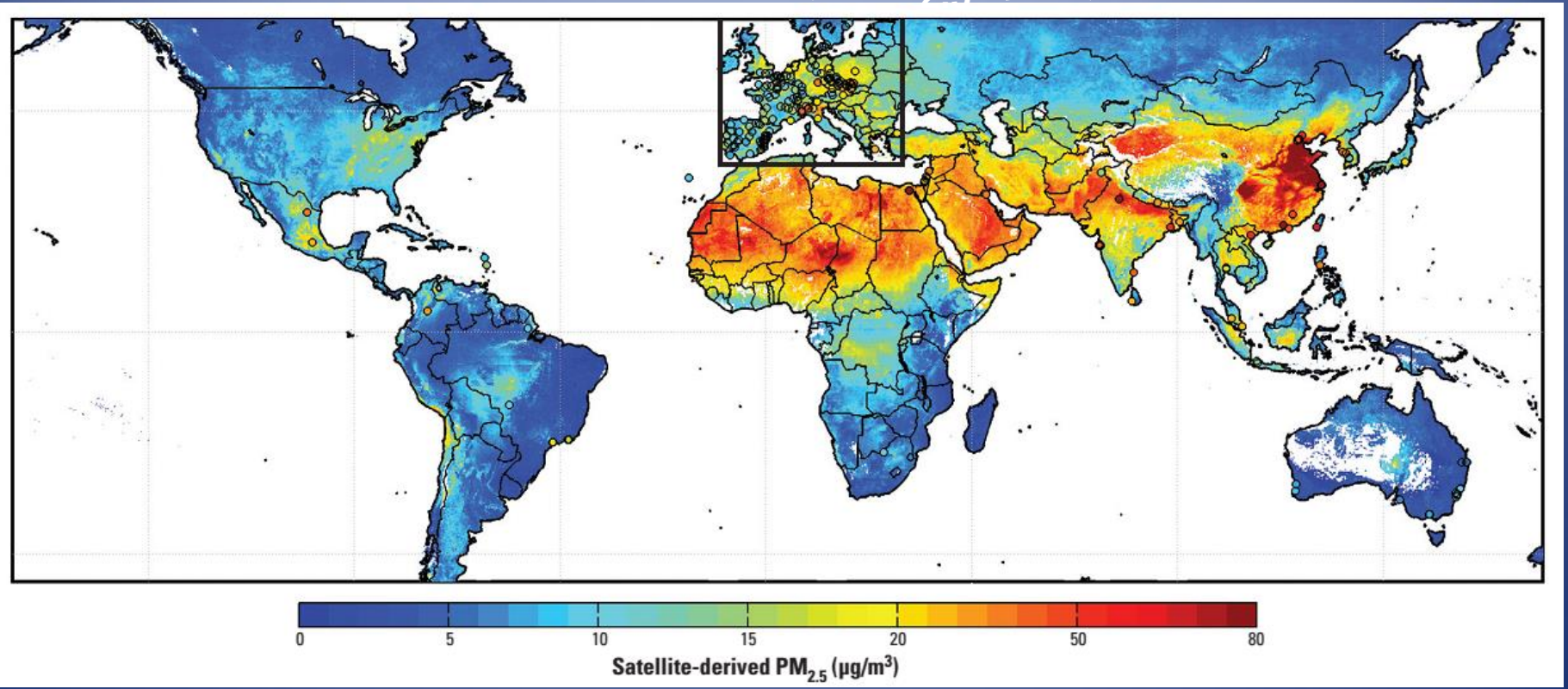
Monthly averaged Aerosol Optical Depth (AOD) -for 2006



(C.C. Li, PKU))

卫星观测：中国$PM_{2.5}$污染全世界最严重

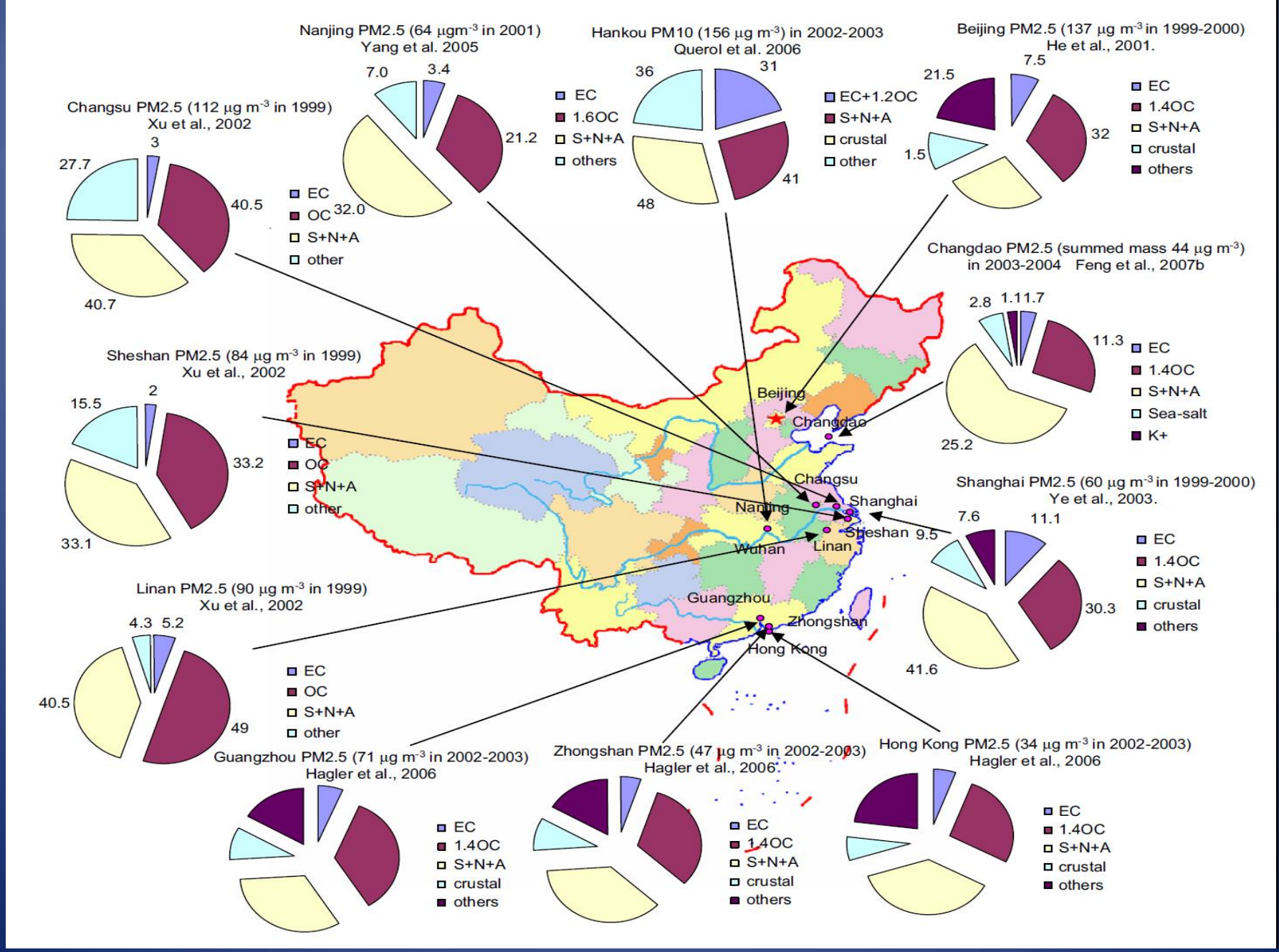
2000-2006年全球$PM_{2.5}$污染分布



中国有 2300万人 生活在 > 100 µg/m³的区域

北京2013：90 µg/m³

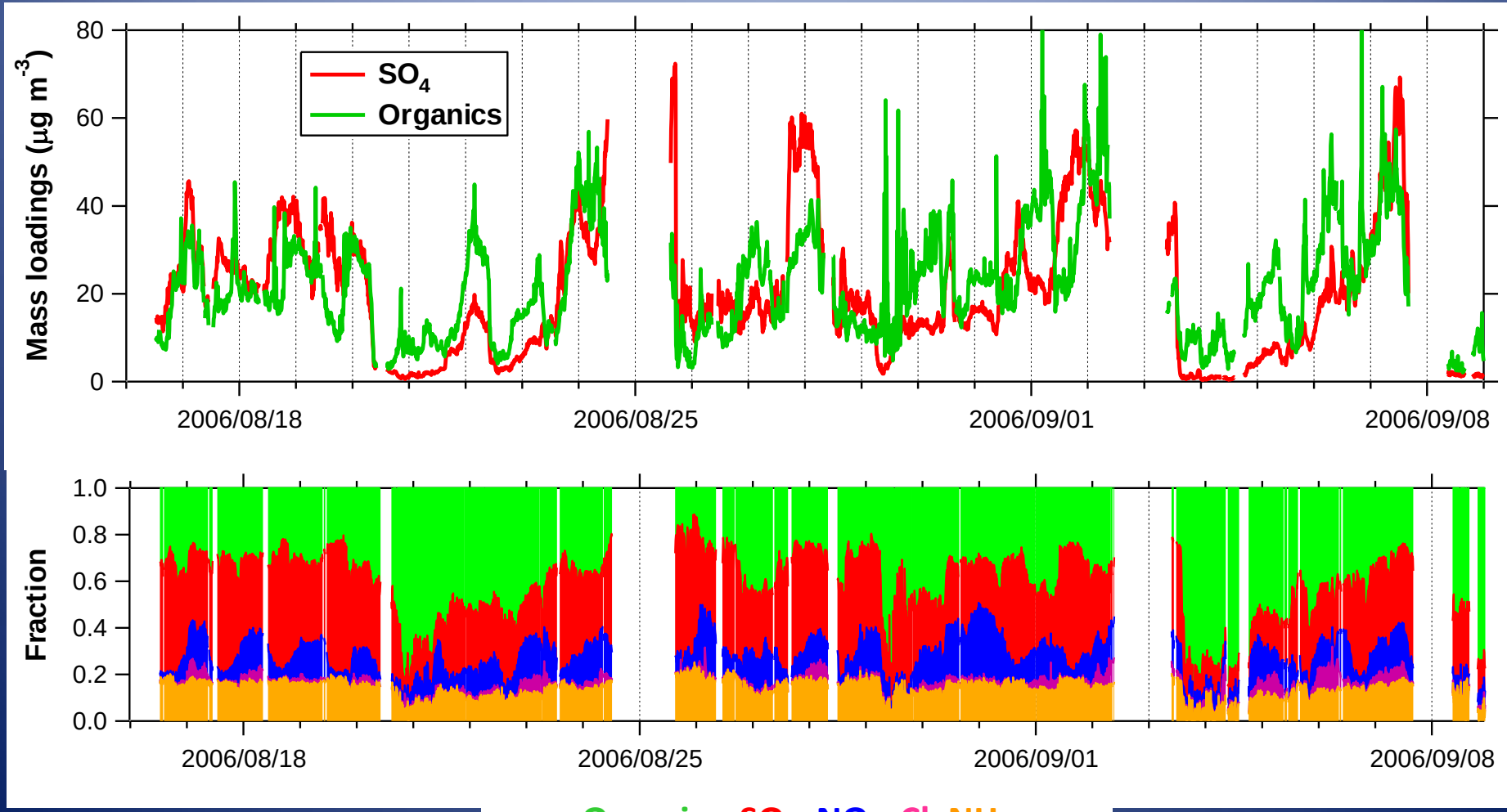
Van Donkelaar et al., 2010, EHP



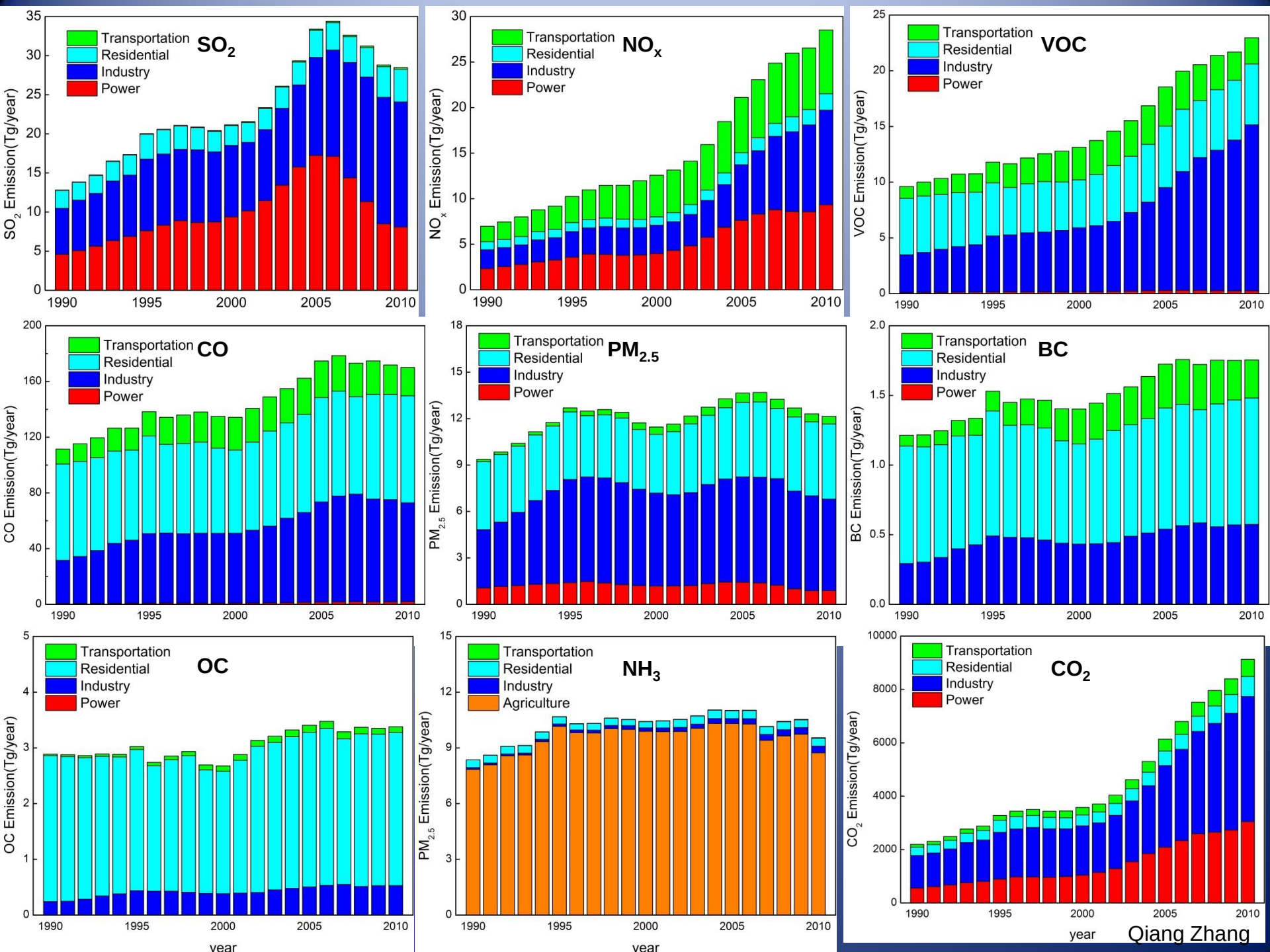
(Fang et al., 2009)

Compositions of PM1 in Beijing: Summer 2006

SO_4^{2-} and Organics are the major fraction of non-refractory PM_1 mass

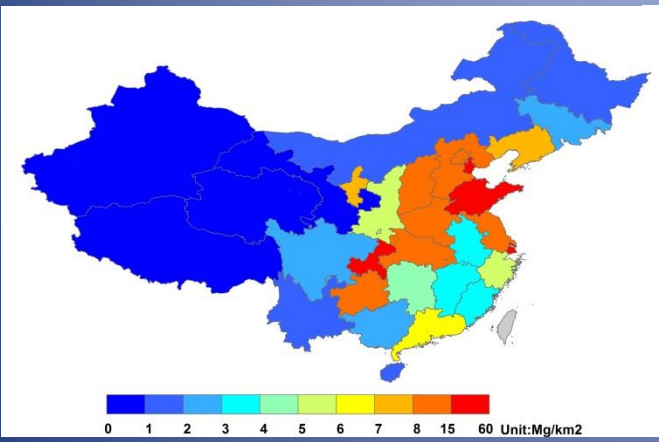


(Takegawa)

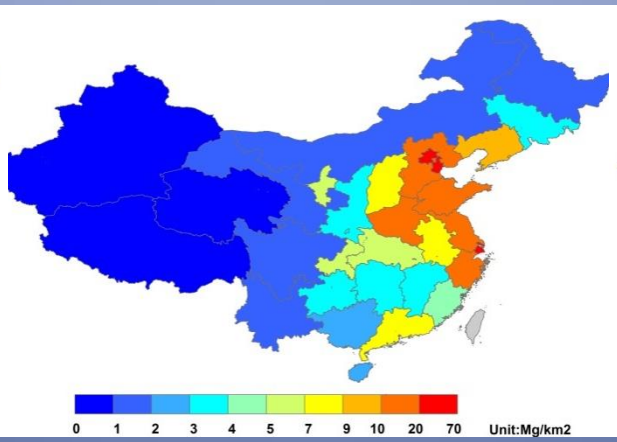

SO2
Transportation
Residential
Industry
Power
SO2 Emission(Tg/year)
NOx
NOx Emission(Tg/year)
VOC
VOC Emission(Tg/year)
CO
CO Emission(Tg/year)
PM2.5
PM2.5 Emission(Tg/year)
BC
BC Emission(Tg/year)
OC
OC Emission(Tg/year)
NH3
Agriculture
NH3 Emission(Tg/year)
CO2
CO2 Emission(Tg/year)
year
1990
1995
2000
2005
2010
Qiang Zhang

主要污染物排放强度高值区集中在华北地区

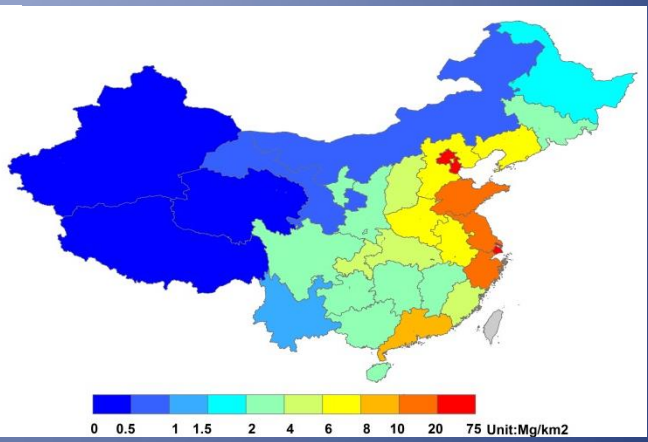
SO_2



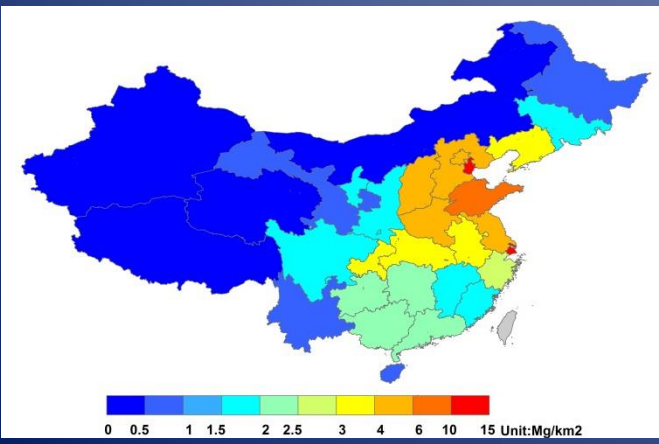
NO_x



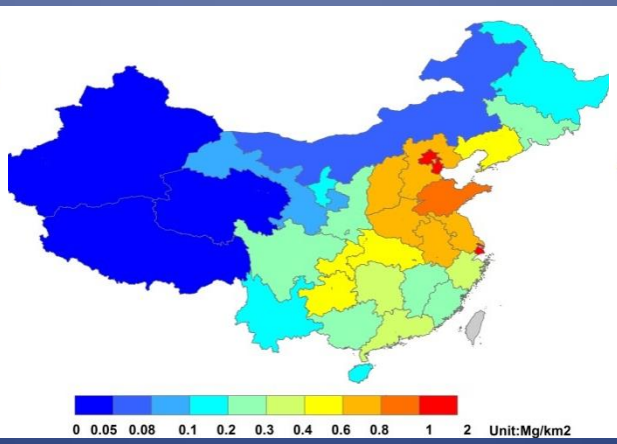
VOC



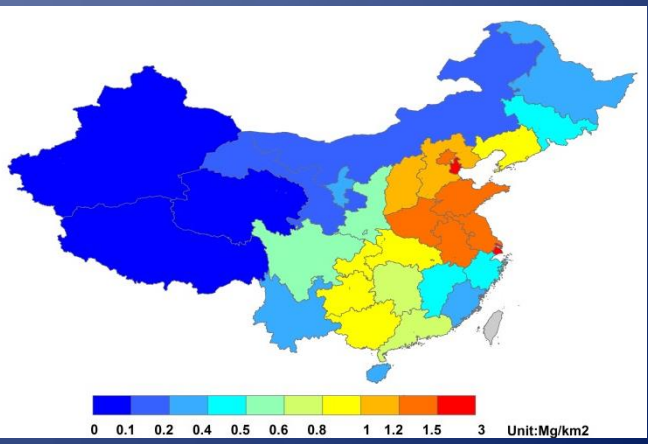
$PM_{2.5}$



BC

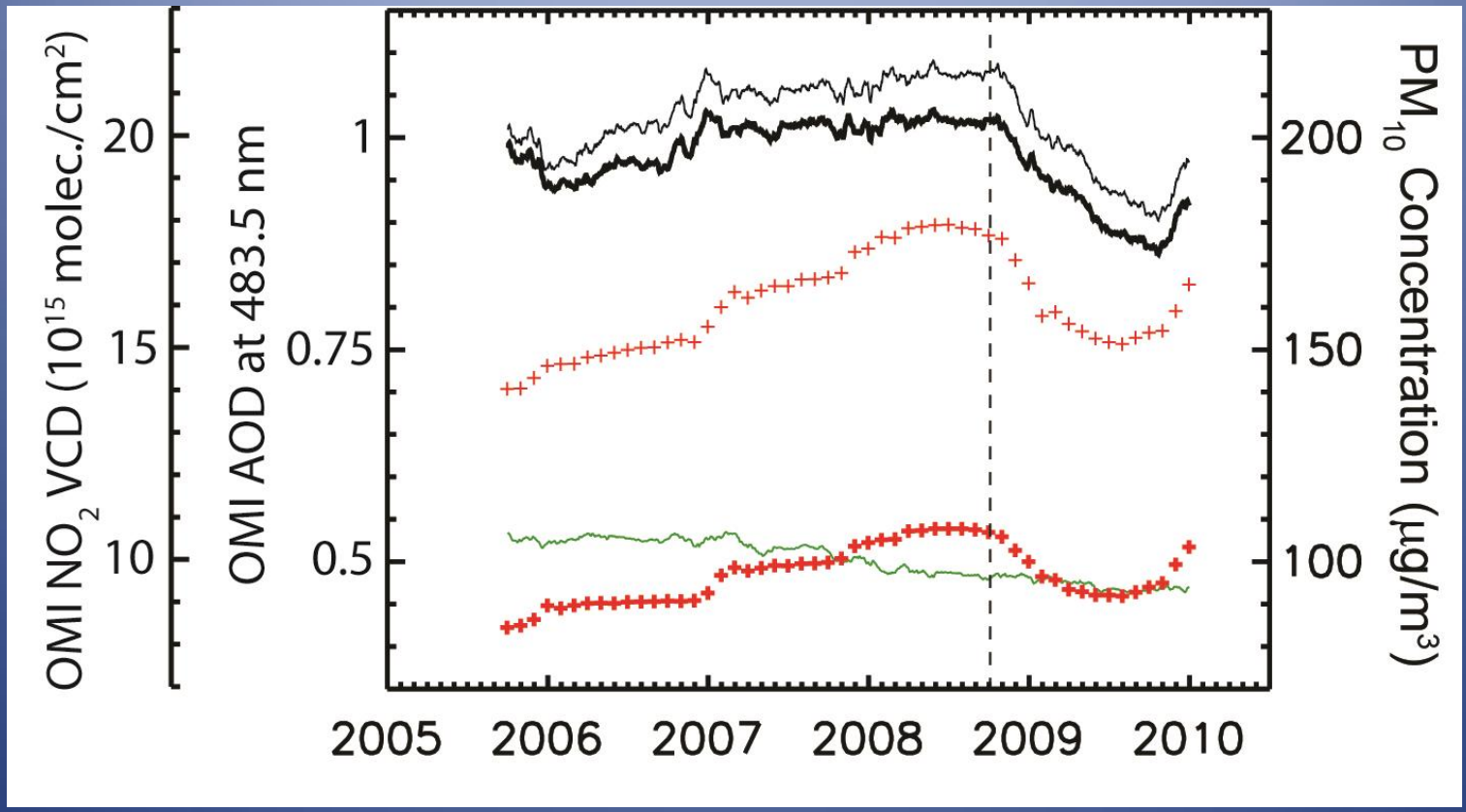


OC



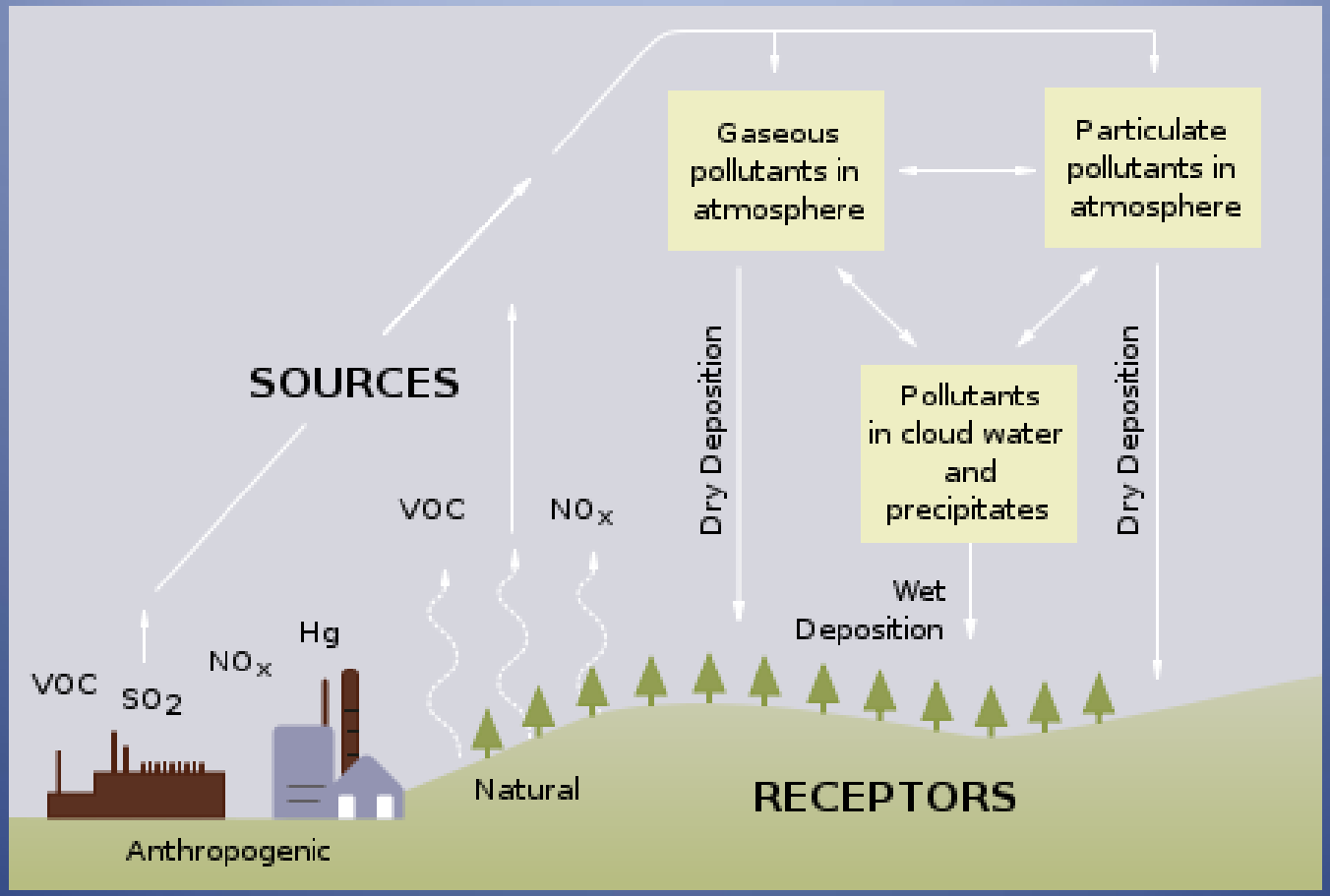
贺克斌，2014

Trends of PM_{10} and AOD: 2005 – 2010



Lin et al., 2010

Acid Deposition



$SO_2 + OH + H_2O \rightarrow H_2SO_4 + HO_2$

$SO_2 + O_3 \rightarrow \ldots \rightarrow H_2SO_4$

$SO_2 + H_2O_2 \rightarrow \ldots \rightarrow H_2SO_4$

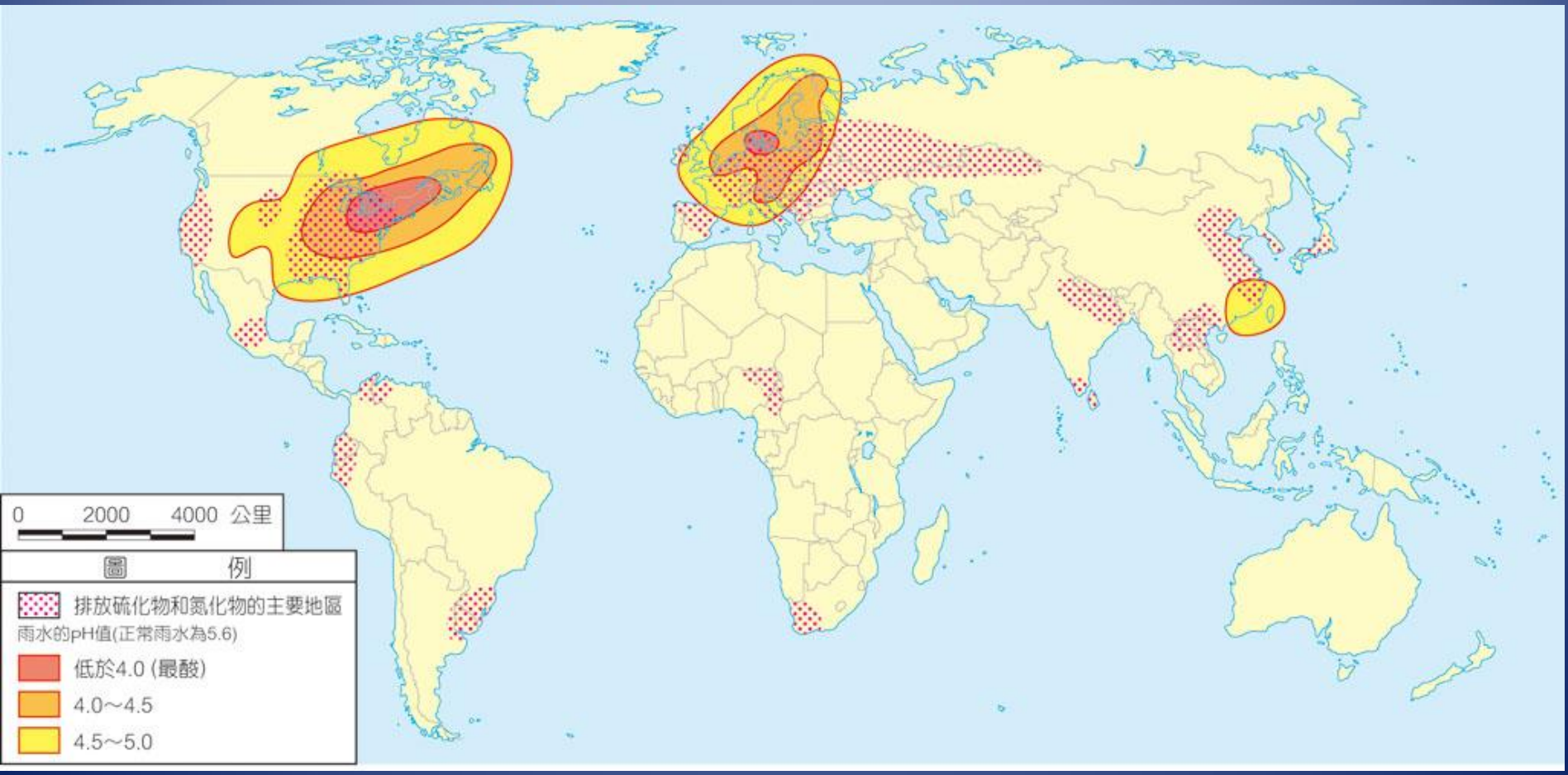
$NO_2 + OH + M \rightarrow HNO_3 + M$

$N_2O_5 + H_2O(l) + \text{aerosols} \rightarrow 2HNO_3 + \text{aerosols}$

VOC + OH (NO_3, O_3, H_2O_2) → … → organic acids

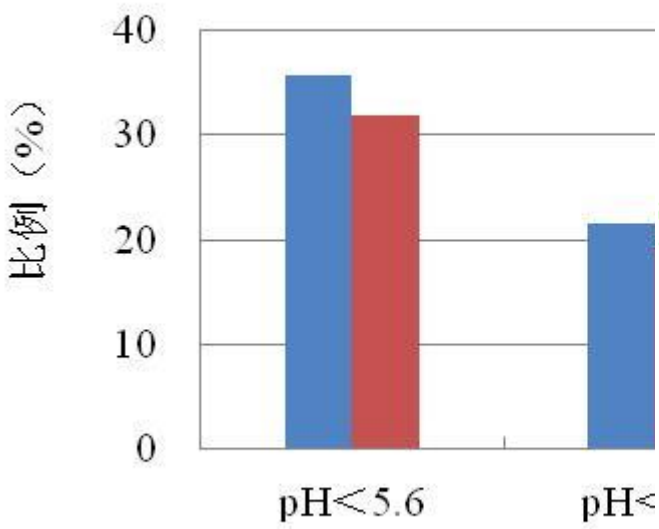
Acids are balanced by mineral or ammonium ions

Acid Deposition

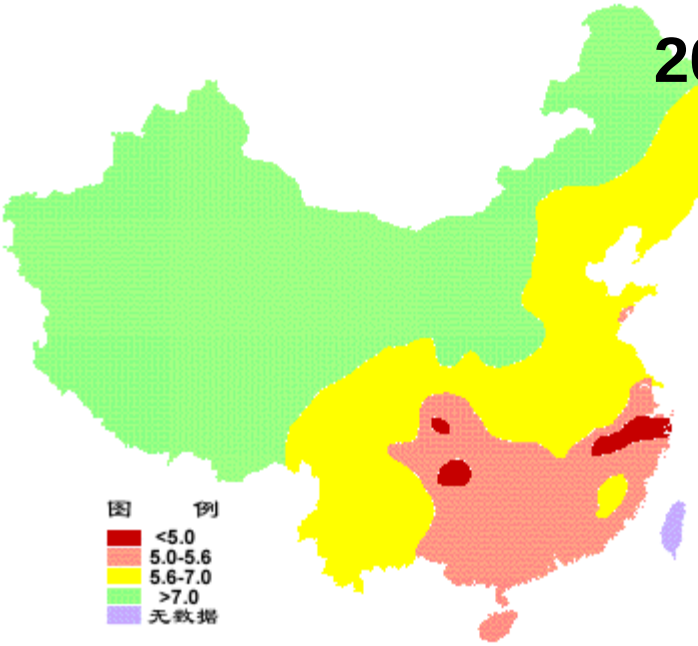


中国降水pH值分布

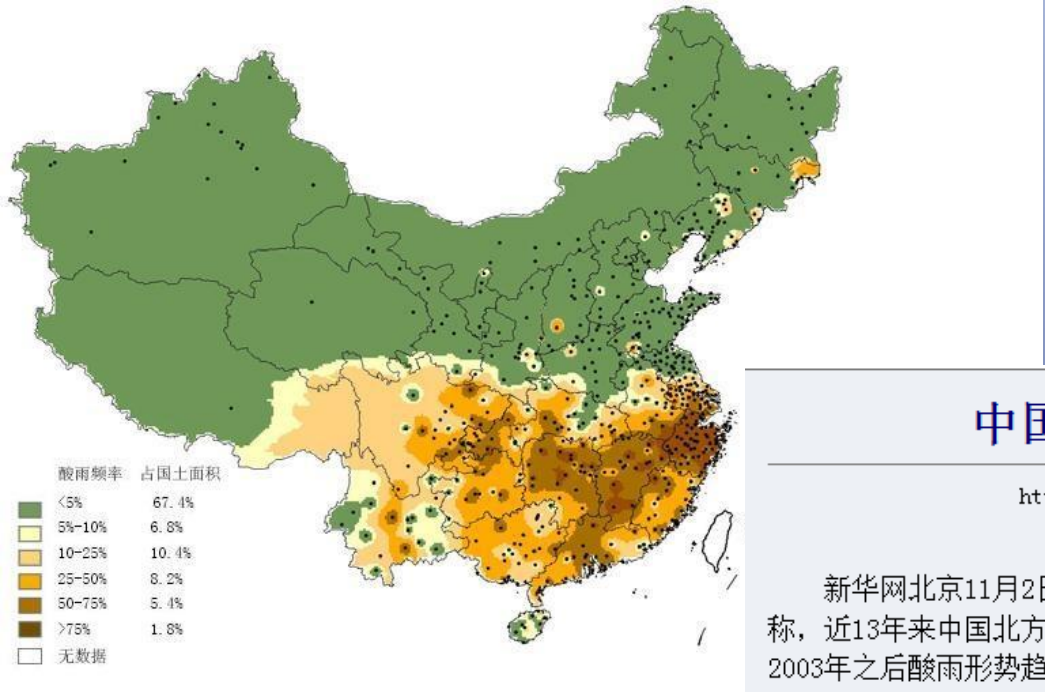
2011年：酸雨区面积约占国土面积的12.9%



2000年



中国酸雨分布



中国北方地区酸雨区有扩展趋势

http://www.sina.com.cn 2006年11月02日16:12 新华网

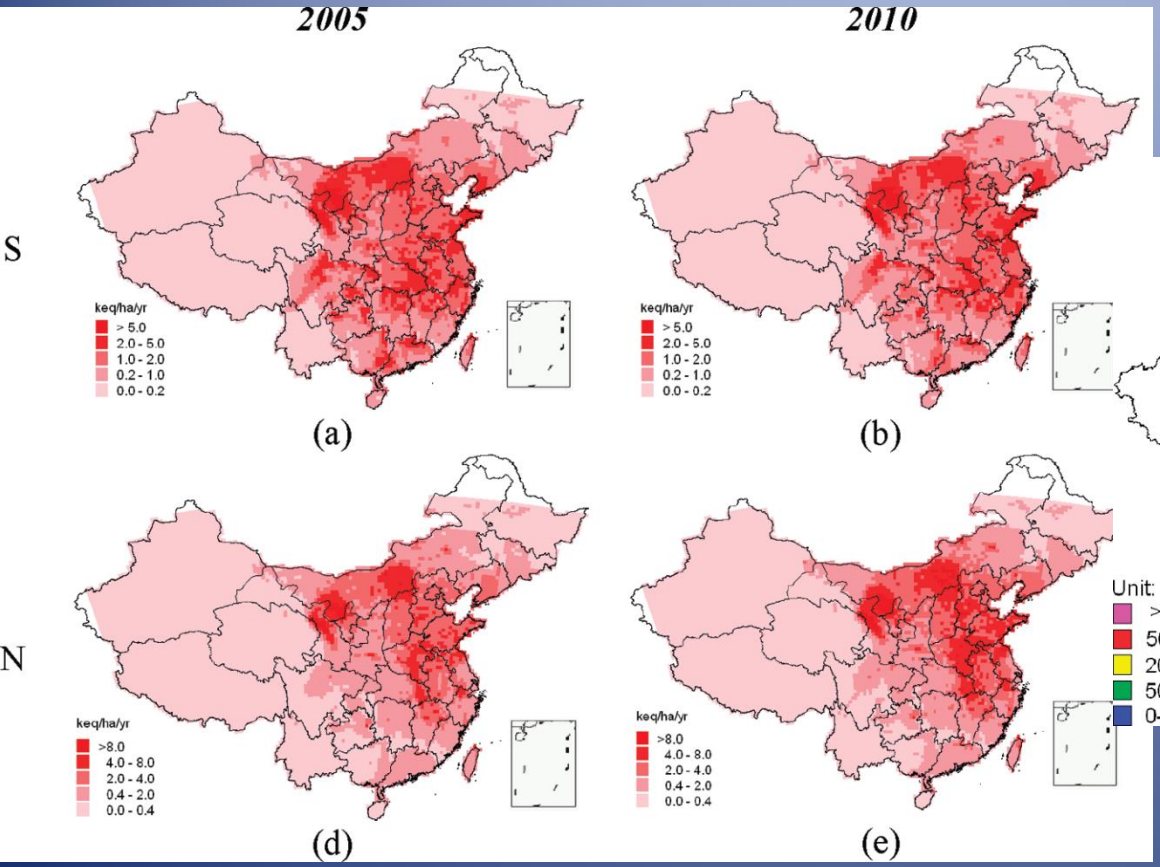
新华网北京11月2日电（记者陈玉明苏万明）中国气象局监测网络司副司长周恒2日称，近13年来中国北方地区酸雨区范围扩大明显；南方酸雨区范围基本保持不变，但2003年之后酸雨形势趋于严重。

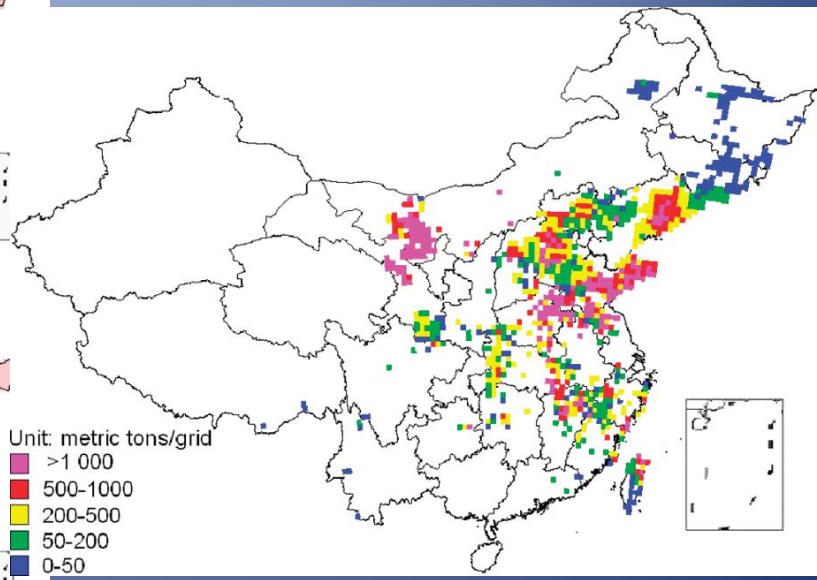
气象部门对酸雨的监测资料显示，中国酸雨区总的来说呈东北至西南走向，酸雨区主体位于长江以南的广大地区，另外，北方也存在小范围的酸雨区。从全国范围来看，近13 年，酸雨区总体上呈范围扩大、强度稍有减弱的趋势。北方酸雨区范围扩大明显，南方酸雨区范围基本保持不变。

据周恒介绍，中国南方酸雨区1993年至1998年期间酸雨问题严重，1999年至2002年期间总体来说酸雨高发区范围减小、强度减弱；2003年之后，酸雨形势又趋于严重。就北方酸雨区而言，酸雨发生频率一直维持在较低的水平，但自2003年开始，京津冀地区及河南部分地区的酸雨发生频率增加到20%甚至50%以上，山东省酸雨发生频率大于50%的区域面积也逐渐扩大。尤其值得注意的是，传统上为非酸雨区的北京地区近些年雨水酸化趋势十分明显。

气象专家认为，酸雨形势趋于严重的原因是2003年以后空气中二氧化硫和氮氧化物的含量在逐年增加，它们在空气中转化为硫酸和硝酸，随雨水降下而形成酸雨。（完）

Soil Acidification from 2005 to 2010





Extra S reduction to offset incr. NOx

- Sulfur emissions have reduced since 2006
- NOx emissions continue to increase significantly, offsetting the benefits of S reduction

Zhao et al., 2009

Regional and Megacity-City Air Pollution in China

- SO_2, PM_{10}, NOx: not solved
- O_3 and $PM_{2.5}$ pollution getting worse
  - Visibility degradation
  - Oxidative capacity enhanced
- Pollutions complex (Multi-pollutants Pollution)
  - Primary + secondary pollutants
  - Urban-Regional scale

Quiz

1. Impacts of NOx, CO and VOC on climate
2. Potential human influences on recent tropospheric OH trends
3. Ozone production is normally VOC-limited in urban areas and NOx-limited in surrounding rural areas. To control urban ozone pollution, should we control NOx or VOC emissions?
4. How can ozone and PM pollution affect each other?