Chapter 4

Tropospheric Chemistry and Air Pollution



北京大学
PEKING UNIVERSITY

Basic Concepts of Chemistry

- Source, sink, production, loss, destruction
- Mass, 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 Chemical Species in the Troposphere

- **Main pollutants:** O_3, PM, CO, NO_2, SO_2, NMVOC...
- **Oxygen family:** $O_x = O_3 + O\ (+ NO_2)$
- **Nitrogen family:** $NO_x = NO + NO_2$
- **Nitrogen family:** $NO_y = NO_x + NO_z = NO_x + NO_3 + 2N_2O_5 + HONO + HNO_3 + PANs + \ldots$
- **Ammonia species:** $NH_x = NH_3 + NH_4$
- **Carbon species:** CO, CH_4, NMVOC
- **Sulfur species:** SO_2, SO_4, SO_3, …
- **Radicals:** $HO_x = OH + HO_2$; RO, RO_2, NO_3, Halogen
- **GHGs:** H_2O, CO_2, O_3, CH_4, N_2O, CFCs, HCFCs, HFCs, SF_6
- **PM species:** SO_4+NO_3+NH_4,, POA+SOA, BC, sea salts, dusts

Lifetime (Residence Time)

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

F_{out}, L and D:

- **Is often proportional to m, thus τ is an e-folding time**
- **Can depend on m in high orders (e.g., for CH_4, CO…)**
- **Can vary complexly in time, so does τ (e.g., for CO_2)**

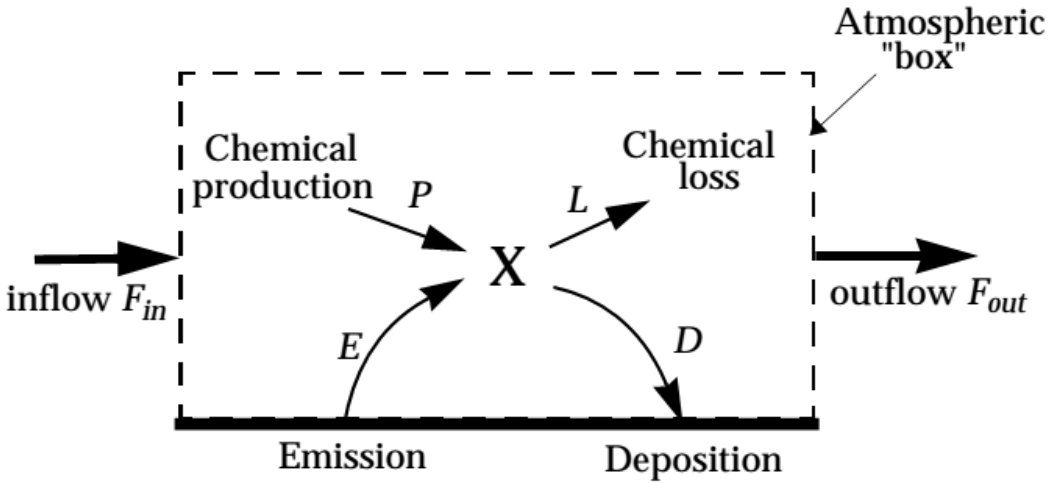
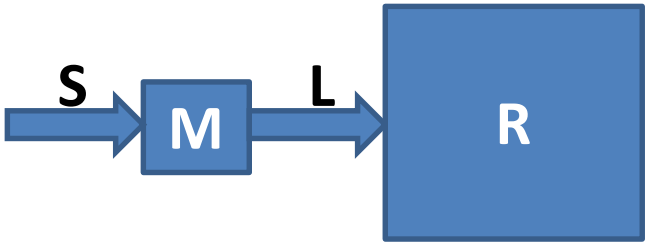


Figure 3-1 One-box model for an atmospheric species X

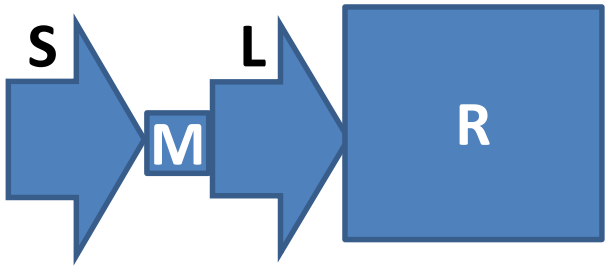
Jacob, 1999

Mass, Reservoir, and Lifetime

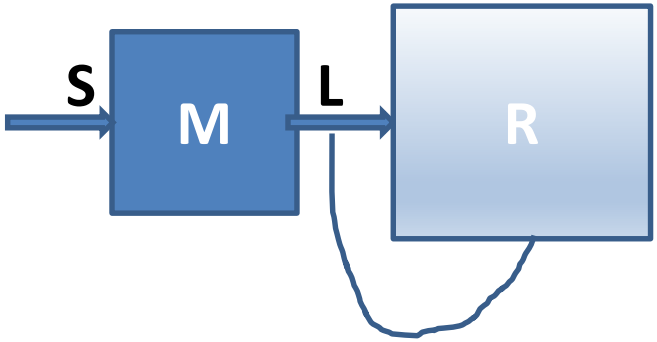
Normal M, τ, R, S & L



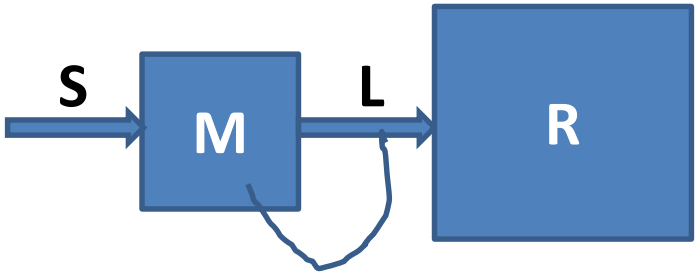
Small M, small τ, large S & L
(e.g., radicals)



Large M, variable τ, R & L,
R-dependent L
(e.g., CO_2)



Large M, M-dependent τ
(e.g., CH_4)



Basic Concepts of Chemistry

- **Photolysis: $A + h\nu \rightarrow B + C$**

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

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

- **Reaction: $A + B \rightarrow C + D$**

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

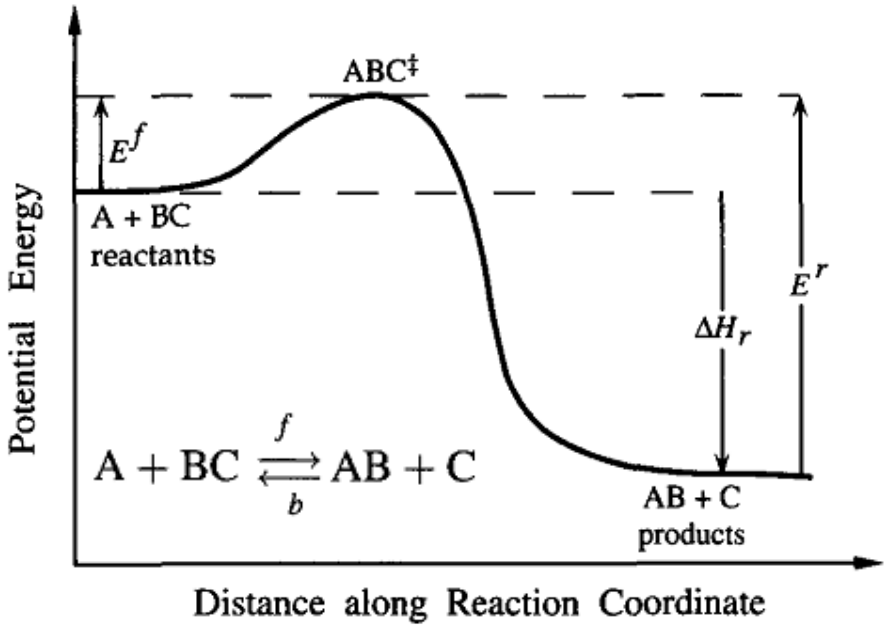
  lifetime of A: $1 / (k * [B])$

- **Equilibrium: $A + B \leftrightarrow C + D$**

  $d[A]/dt = -k_f * [A] * [B] + k_b * [C] * [D] = 0$

Bimolecular Reactions: Increase with T

- **Collision theory**
- **Transition state theory**
- **Potential energy surface**



- **Collision-like**
- **Electronic rearrangement**
- **Time to re-distribute energy**

Arrhenius Form:

$$k = A \cdot e^{-\frac{E/R}{T}}$$

Collision theory:

$$A = \pi d^2 \left(\frac{8k_B T}{\pi \mu}\right)^{\frac{1}{2}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$d = r_A + r_B$$

Most bimolecular reactions are fastened by increasing T, but some exhibit the opposite.

Seinfeld and Pandis, 2006

Pseudo-Steady-State Approximation (PSSA)

Form: $\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}$

Truth: $\mathrm{A} + \mathrm{M} \underset{1b}{\overset{1f}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M}$

$$\mathrm{A}^* \xrightarrow{2} \mathrm{B} + \mathrm{C}$$

$$\frac{d[\mathrm{A}]}{dt} = -k_{1f}[\mathrm{A}][\mathrm{M}] + k_{1b}[\mathrm{A}^*][\mathrm{M}]$$

$$\frac{d[\mathrm{A}^*]}{dt} = k_{1f}[\mathrm{A}][\mathrm{M}] - k_{1b}[\mathrm{A}^*][\mathrm{M}] - k_2[\mathrm{A}^*]$$

A* is in PSS:

$$\frac{d[\mathrm{A}^*]}{dt} = k_{1f}[\mathrm{A}][\mathrm{M}] - k_{1b}[\mathrm{A}^*][\mathrm{M}] - k_2[\mathrm{A}^*] = 0$$

$$[\mathrm{A}^*] = \frac{k_{1f}[\mathrm{A}][\mathrm{M}]}{k_{1b}[\mathrm{M}] + k_2}$$

Therefore:

$$\frac{d[\mathrm{A}]}{dt} = -\frac{k_{1f}k_2[\mathrm{M}][\mathrm{A}]}{k_{1b}[\mathrm{M}] + k_2}$$

And:

$$\frac{d[\mathrm{A}^*]}{dt} = \frac{d}{dt}\frac{k_{1f}[\mathrm{A}][\mathrm{M}]}{k_{1b}[\mathrm{M}] + k_2}$$

?

If [M] is constant:

$$\frac{d[\mathrm{A}^*]}{dt} = -\frac{k_{1f}^2 k_2[\mathrm{M}]^2[\mathrm{A}]}{(k_{1b}[\mathrm{M}] + k_2)^2}$$

Seinfeld and Pandis, 2006

Termolecular Reactions: Decrease with T

Lindemann–Hinshelwood theory

Form: $A + B + M \rightarrow AB + M$

Truth:

$$A + B \underset{r}{\overset{a}{\rightleftharpoons}} AB^{\dagger}$$

$$AB^{\dagger} + M \xrightarrow{s} AB + M$$

$$\frac{d[AB]}{dt} = \frac{k_a k_s [A][B][M]}{k_s[M] + k_r}$$

Where: $AB^{\dagger}$ is in Pseudo-Steady-State

if $k_r \gg k_s[M]$ $\quad \frac{d[AB]}{dt} = \frac{k_a k_s}{k_r}[A][B][M]$

$k_r \ll k_s[M]$ $\quad \frac{d[AB]}{dt} = k_a[A][B]$

Seinfeld and Pandis, 2006

Pseudo-Second-Order:

$$\frac{d[AB]}{dt} = k[A][B]$$

$$k = \frac{k_0[M]k_\infty}{k_0[M] + k_\infty} \qquad k_\infty = k_a \qquad k_0 = \frac{k_a k_s}{k_r}$$

Troe (1983):

$$k(T) = \left\{ \frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)}} \right\} F \left\{ \left(1 + \left[\log_{10} \left(\frac{k_0(T)[M]}{k_\infty(T)} \right) \right]^2 \right)^{-1} \right\}$$

$$k_0(T) = k_0^{300} \quad (T/300)^{-n} \quad \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

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

F = 0.6

Basic Chemistry

- $NO + O_3 \rightarrow NO_2$ (R1)
- $NO_2 + h\nu \rightarrow NO + O$ (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 伪稳态
- Without perturbation, this is a null cycle

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

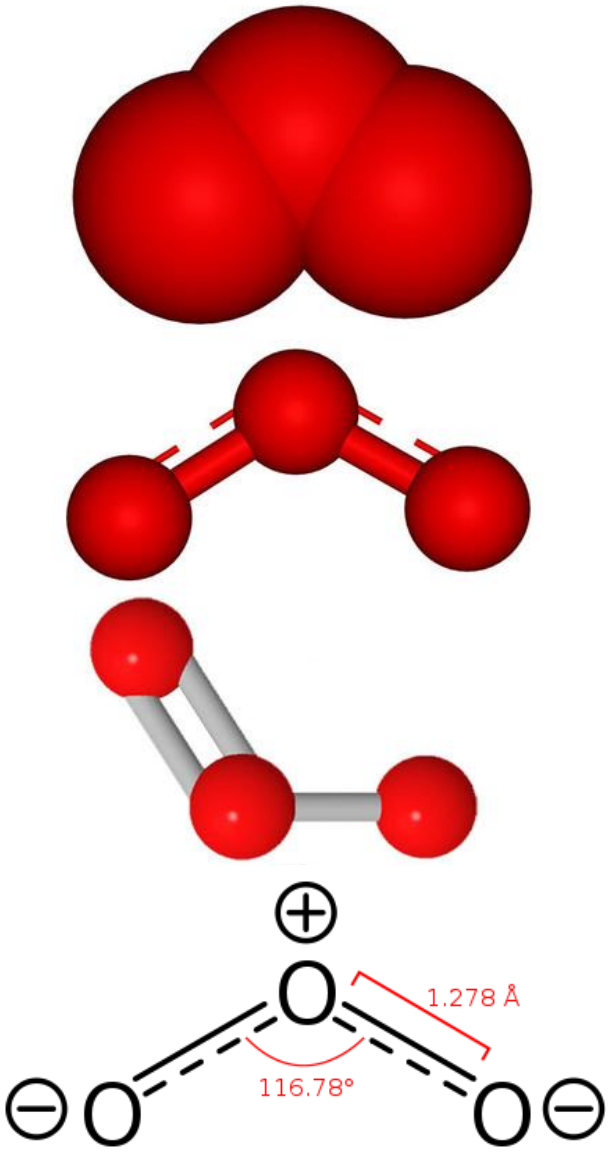
➢ It leads to the chemical family of NOx = NO + NO_2

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, $[OH] / [HO_2] = k_3 * [NO] / (k_1 * [CO] + k_2 * [VOC])$

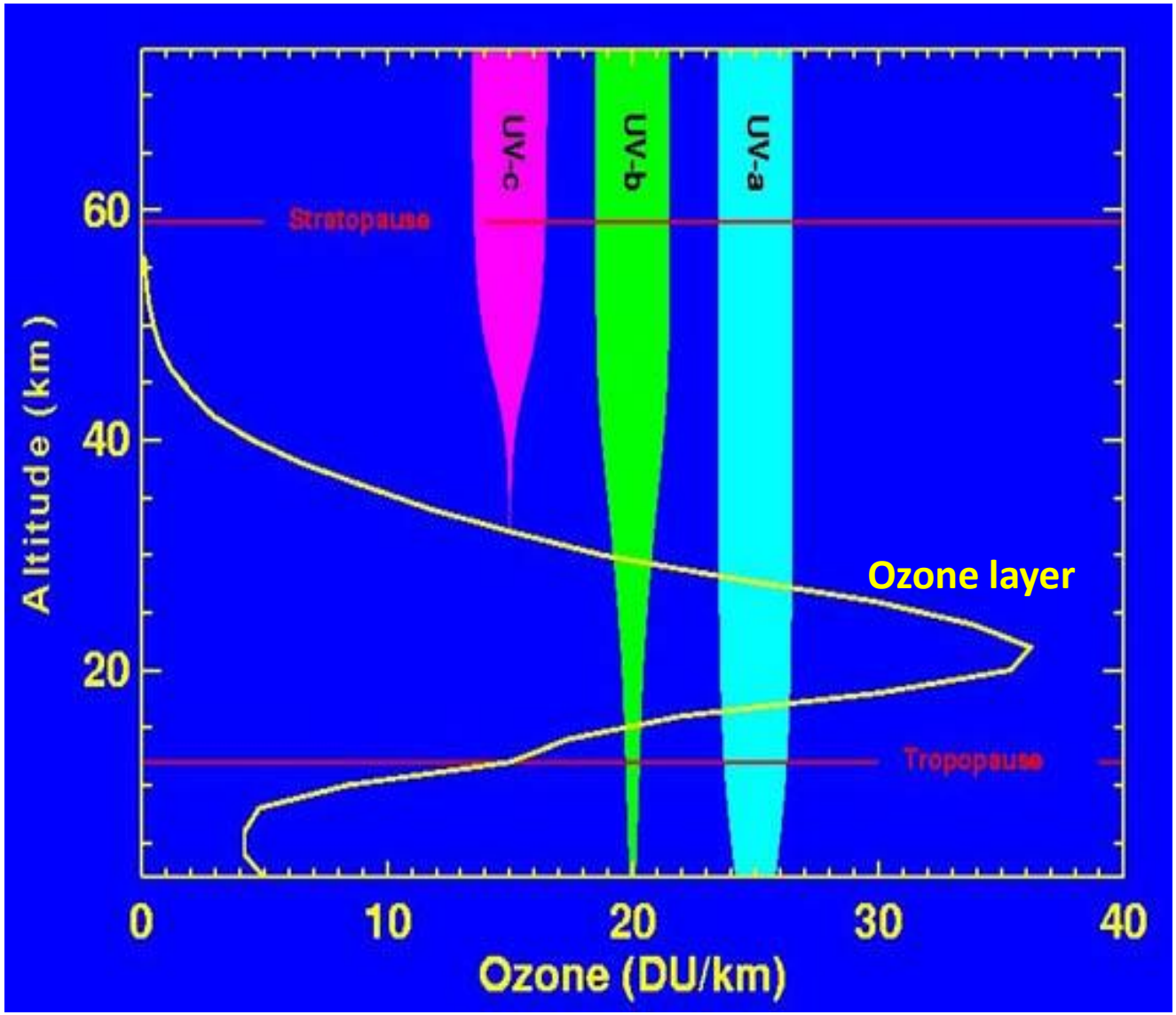
- This is one of the most important relations regulating concentrations of OH and HO_2 in the troposphere.
- It leads to the chemical family of HOx = OH + HO_2

臭氧 Ozone

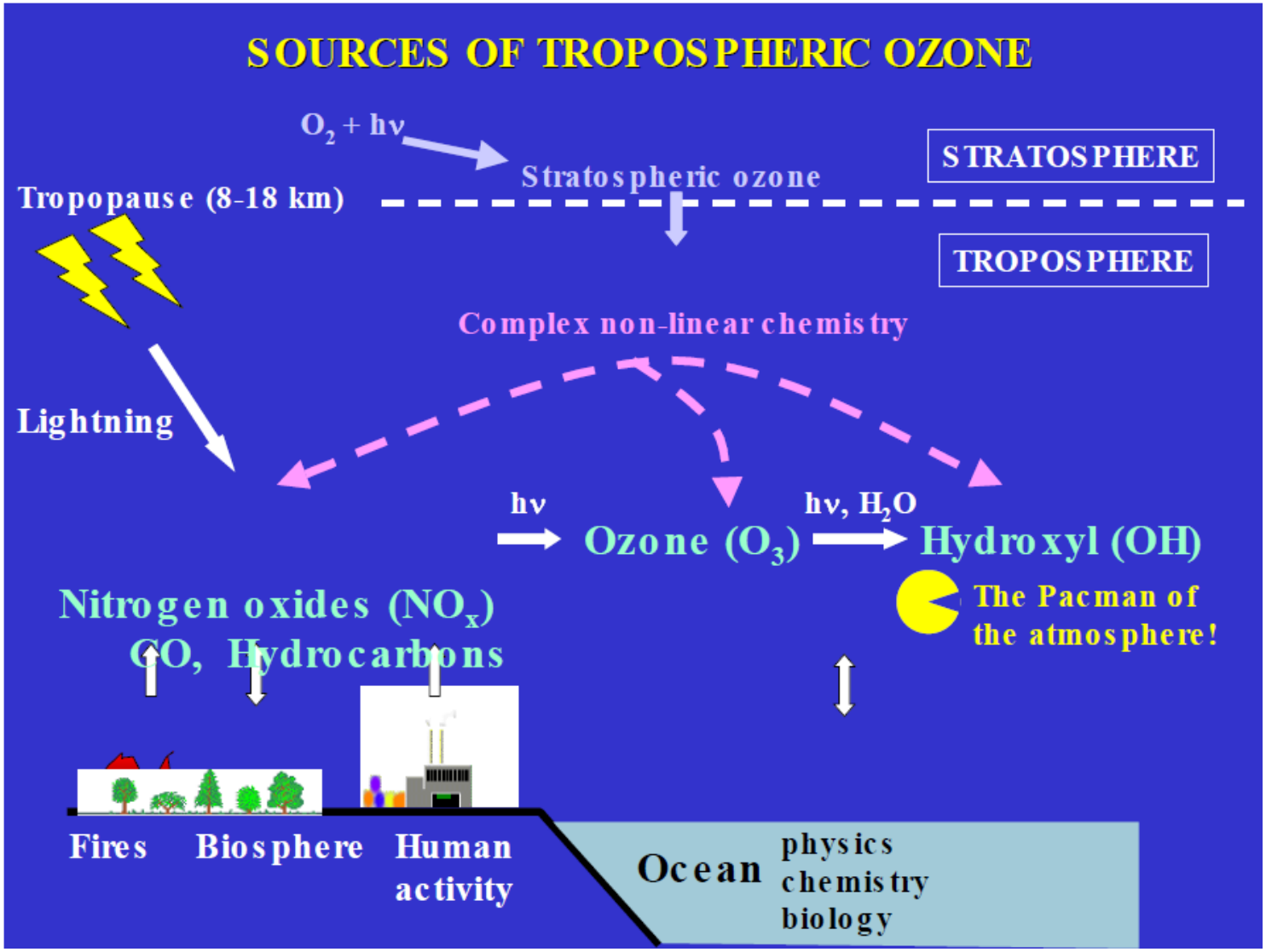


- 臭氧是氧气的同素异形体，淡蓝色气体，液态为深蓝色，固态为紫黑色。气味类似鱼腥味，浓度过高时类似于氯气的气味。
- 1840年，由Schonbein发现。由于它的令人讨厌的气味， Schonbein 将其命名为Ozein, the Greek word for ‘to smell’，英语是 Ozone。
- 1881年，Hartley第一个推测地面太阳光谱在300 nm处截断的原因是大气中臭氧吸收造成的。
- 1917年，Fowler和Strutt以及1921年Fabry和Buisson用光谱分析方法验证了这一点。
- 1925年，Cabannes和Dufay指出了臭氧层大约在地表以上几十公里的高度而不是在大气低层。
- 这些发现为上世纪30年代Sidney Chapman的理论工作和Dobson的观测工作奠定了基础。

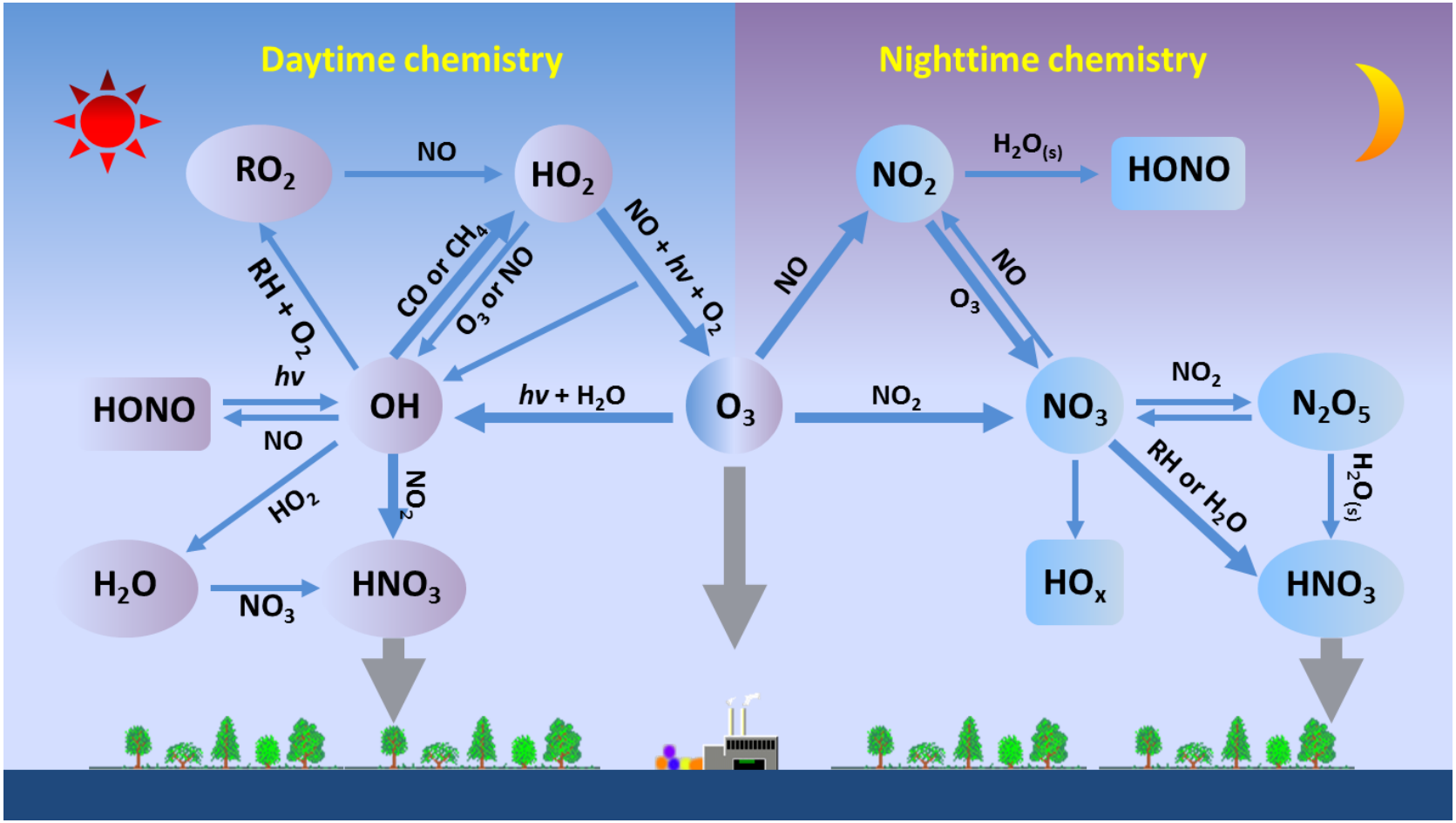
Stratospheric and Tropospheric Ozone



Sources of Tropospheric Ozone



Daytime versus Nighttime Chemistry of Ozone



Yan et al., 2018, ACP

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

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

$NO + HO_2 \rightarrow OH + NO_2$

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

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

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

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

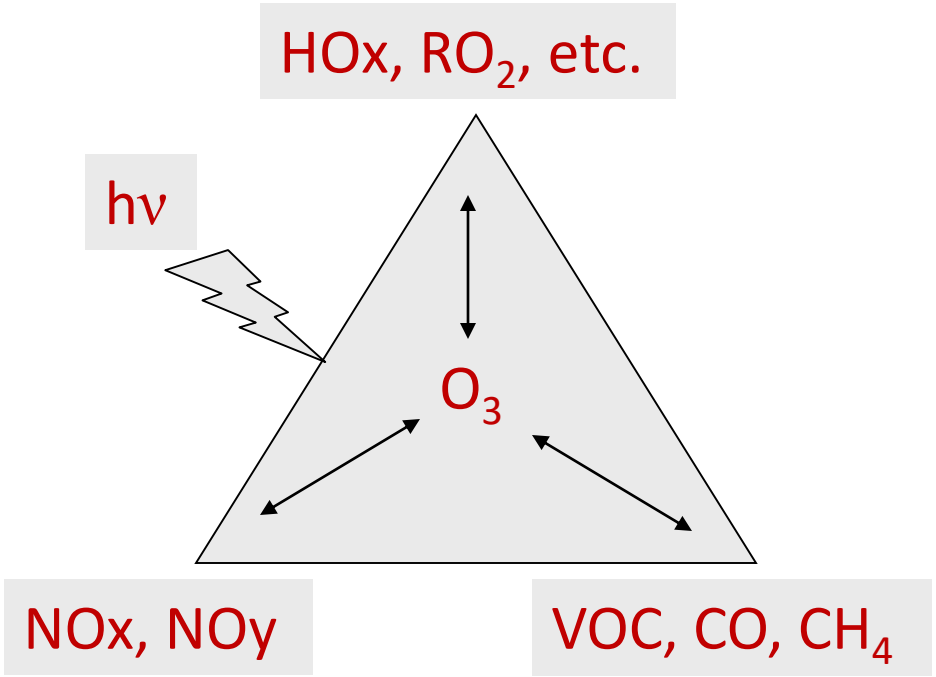
$O(^1D) + H_2O \rightarrow 2OH$

$OH + O_3 \rightarrow O_2 + HO_2$

$HO_2 + O_3 \rightarrow 2O_2 + OH$

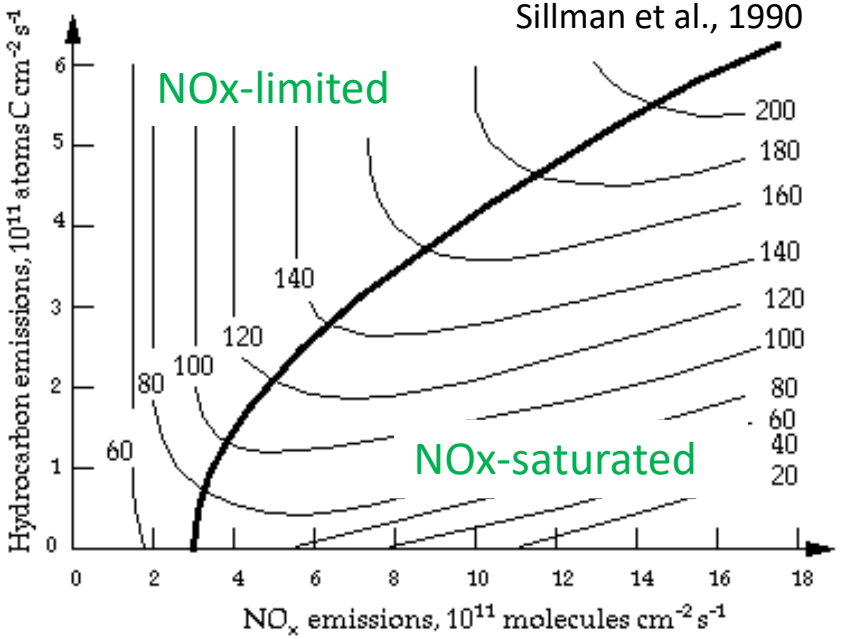
$NO + O_3 \rightarrow O_2 + NO_2$

Ozone Formation: Sensitivity to NOx and VOC



Ozone mixing ratio as a function of NOx and NMVOC emissions

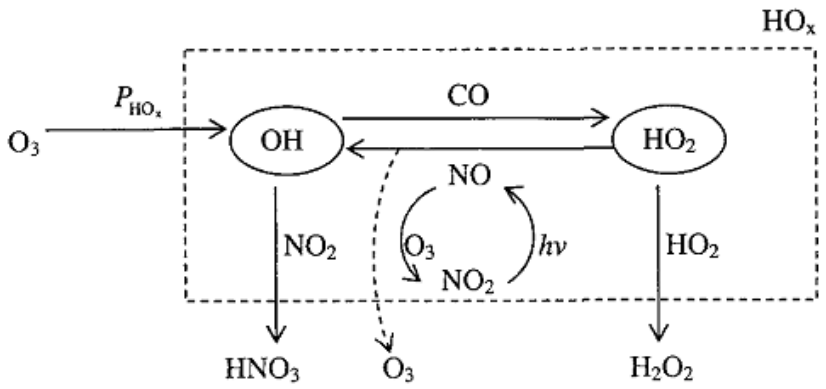
Sillman et al., 1990



Ozone Production in a CO-NOx-HOx System

$$P_{O_3} = k_{HO_2+NO}[HO_2][NO]$$

$$P_{HO_x} = 2\,k_{HO_2+HO_2}[HO_2]^2 + k_{OH+NO_2}[OH][NO_2]$$



Low-NOx limit

$$P_{HOx} \cong 2\,k_{HO_2+HO_2}[HO_2]^2$$

$$[HO_2] \cong \left(\frac{P_{HO_x}}{2\,k_{HO_2+HO_2}}\right)^{1/2}$$

$$P_{O_3} = k_{HO_2+NO}\left(\frac{P_{HO_x}}{2\,k_{HO_2+HO_2}}\right)^{1/2}[NO]$$

High-NOx limit

$$P_{HO_x} \cong k_{OH+NO_2}[OH][NO_2]$$

$$[OH] = \frac{P_{HO_x}}{k_{OH+NO_2}[NO_2]}$$

$$k_{CO+OH}[CO][OH] = k_{HO_2+NO}[HO_2][NO]$$

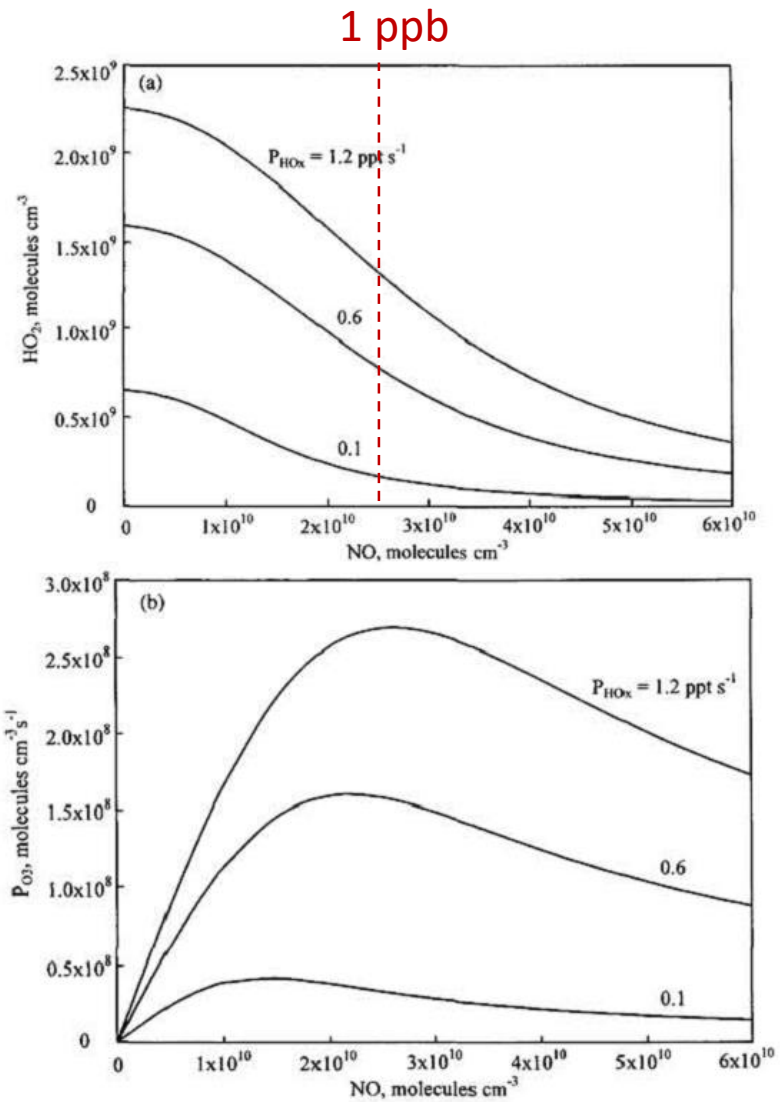
$$[HO_2] = \frac{k_{CO+OH}[CO][OH]}{k_{HO_2+NO}[NO]}$$

$$[HO_2] = \frac{k_{CO+OH}P_{HO_x}[CO]}{k_{HO_2+NO}k_{OH+NO_2}[NO][NO_2]}$$

$$P_{O_3} = \frac{k_{CO+OH}P_{HO_x}[CO]}{k_{OH+NO_2}[NO_2]}$$

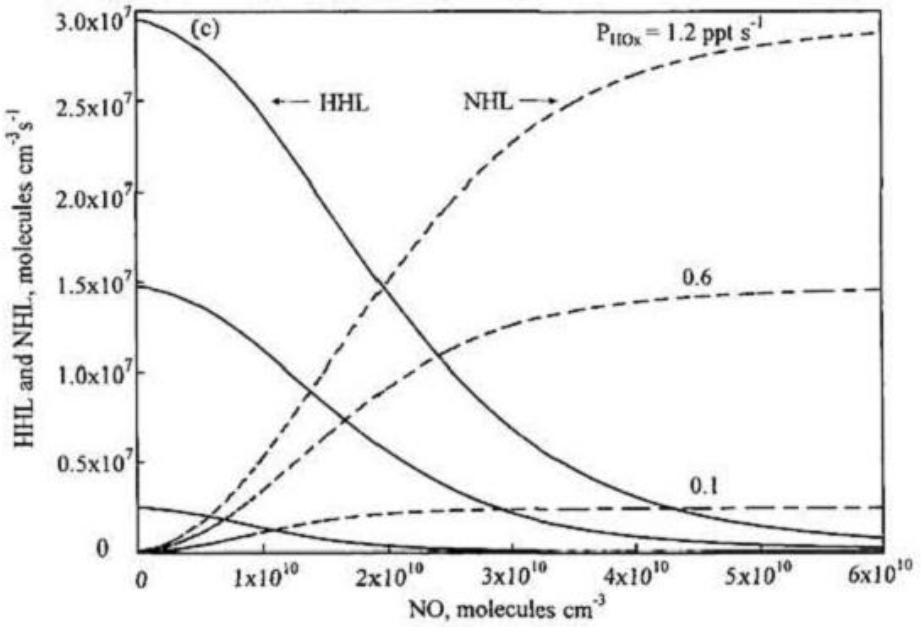
Seinfeld and Pandis, 2006

CO-led Ozone Production As a Function of NOx



$$HHL = 2\,k_{HO_2+HO_2}[HO_2]^2$$

$$NHL = k_{OH+NO_2}[OH][NO_2]$$



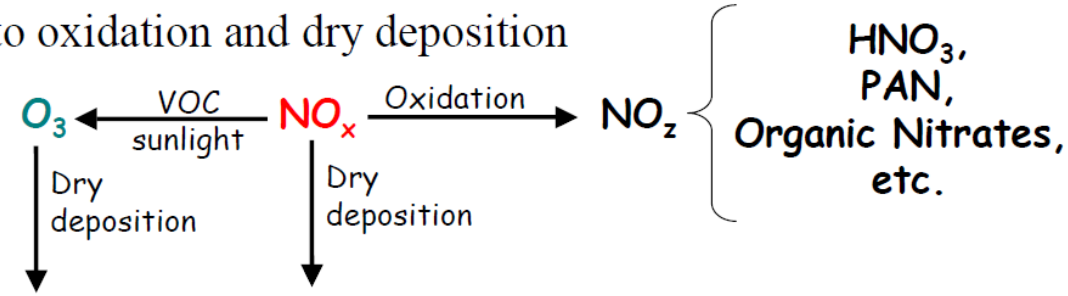
At Earth surface
T = 298 K
CO = 200 ppb ?
NO_2 / NO = 7
$\rho = 2.5 \times 10^{19}$ molecules/cm^3

Seinfeld and Pandis, 2006

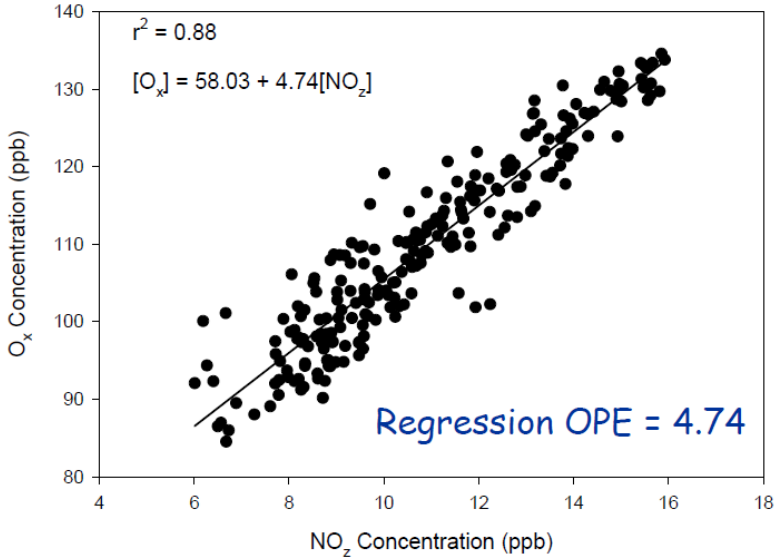
Ozone Production Efficiency (OPE)

General definition (Sillman, 2000, JGR)

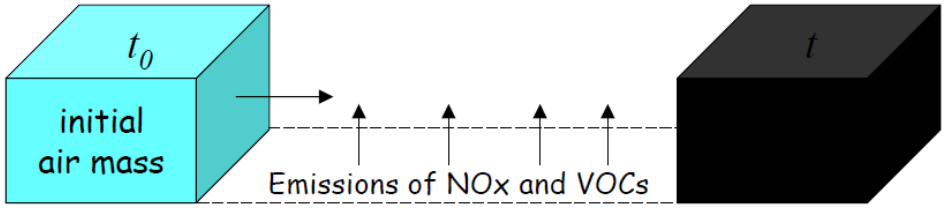
Number of O_3 molecules produced by a molecule of NO_x before it is lost from the $NO_x - O_3$ cycle due to oxidation and dry deposition



Regression OPE



Lagrangian OPE



Lagrangian OPE

$$\text{Lagrangian OPE}(t) = \frac{\Delta[O_3(t)]_{prod}}{\Delta[NO_x(t)]_{dest}}$$

More Chemistry

Gaseous chemistry (important in weak hv):

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

Heterogeneous chemistry (important in high-aerosol cases):

- $N_2O_5 + H_2O(s) \rightarrow 2\ HNO_3$
- $NO_2 + H_2O(s) \rightarrow HONO$ (important source of HONO and OH)
- $NO_2 + H_2O(s) \rightarrow NO_3^-$ (important in China ?)
- $NO_2 + SO_2 + H_2O(s) \rightarrow SO_4^{-2}$ (important in China ?, in high pH env.?)
- $HO_2 + H_2O(s) \rightarrow 0.5\ H_2O_2$ (important in China ?)
- TMI catalyzed processes ??? (HO_2, SO_2; in low pH env.)

Budget of Tropospheric Ozone in 2009

	Global model	Two-way model	Percentage difference
Tropospheric budget of ozone[a]			
Chemical loss of O_x (Tg)	4491	4537	1.0 %
Chemical production of O_x (Tg)	4885	4928	0.9 %
Dry deposition of O_x (Tg)	909	894	−1.7 %
STE of O_x (Tg)[b]	515	503	−2.3 %
Dry deposition of O_3 (Tg)	882	867	−1.7 %
STE of O_3 (Tg)[b]	488	478	−2.0 %
O_3 burden (Tg)	384	348	−9.5 %
Mean TCO (DU)	34.5	31.5	−8.7 %
O_3 lifetime (days)	26.1	23.5	−9.9 %
Tropospheric burdens and lifetimes of other species			
NO_x burden (TgN)	0.169	0.176	4.1 %
NMVOCs burden (TgC)[c]	10.1	10.2	1.0 %
CO burden (Tg)	359	398	10.8 %
OH number concentration (10^6 cm^{-3})	1.18	1.12	−5.0 %
OH-related MCF lifetime (yr)[d]	5.58	5.87	5.2 %
OH-related methane lifetime (yr)[d]	9.63	10.12	5.1 %

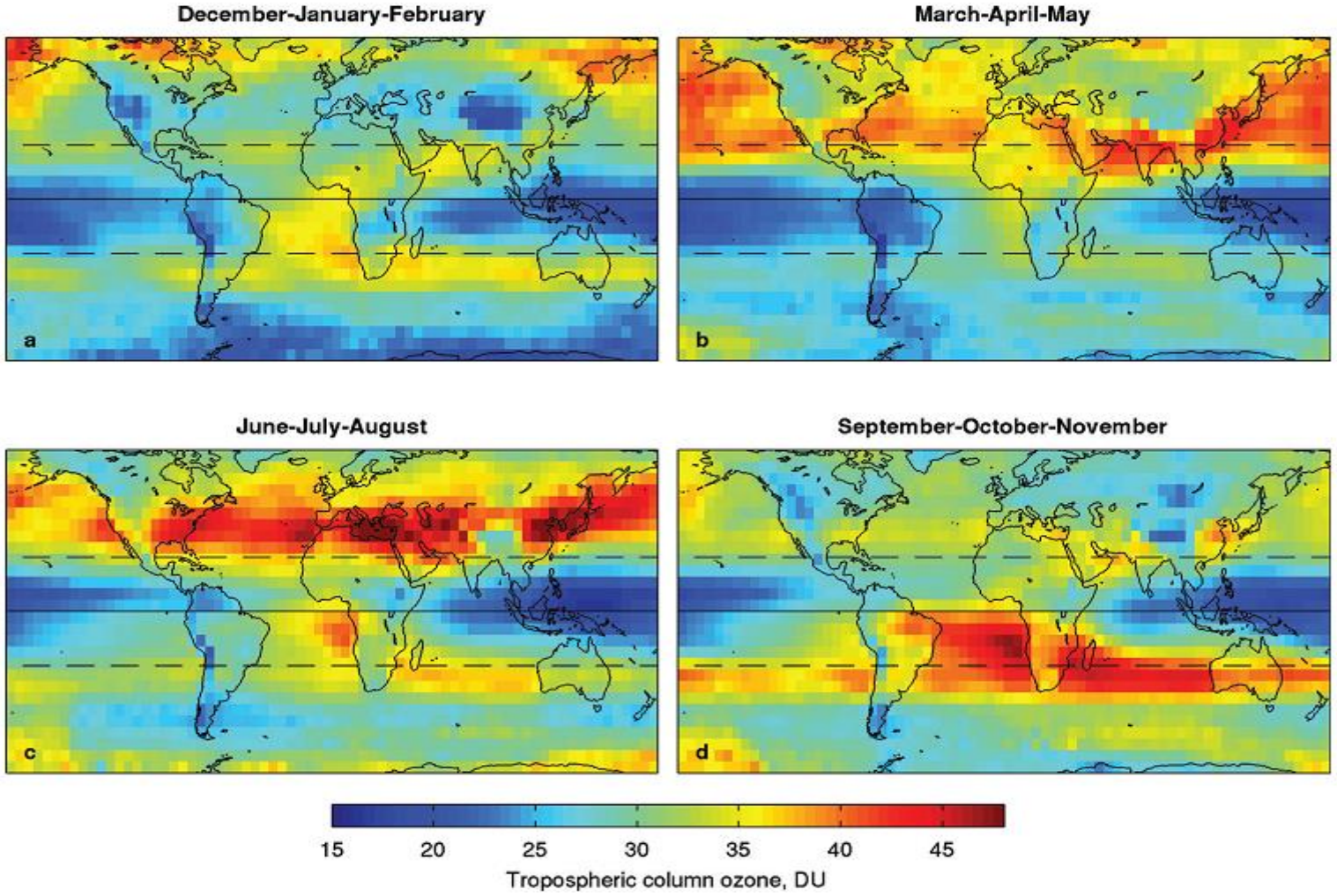
	MAM			JJA			SON			DJF		
	GB	TW	Diff. (%)	GB	TW	Diff. (%)	GB	TW	Diff. (%)	GB	TW	Diff. (%)
Chemical loss of O_x (Tg)	1087	1099	1.1 %	1252	1237	−1.2 %	1116	1141	2.2 %	1036	1060	2.3 %
Chemical production of O_x (Tg)	1197	1213	1.3 %	1446	1460	1.0 %	1199	1211	1.0 %	1042	1045	0.3 %
O_3 burden (Tg)	374	340	−9.1 %	394	362	−8.0 %	370	339	−8.4 %	399	352	−11.7 %
Lifetime against chemical loss (O_3 burden / O_x loss)	31.4	28.3	−9.8 %	28.7	26.7	−6.9 %	30.3	27.1	−10.5 %	35.1	30.3	−13.6 %

$O_x = O_3 + O + NO_2 + 2NO_3 + 3N_2O_5 + PANs + HNO_3 + HNO_4$ (Wu et al., 2007)

Yan et al., 2016

Tropospheric Ozone Column Detected From Space

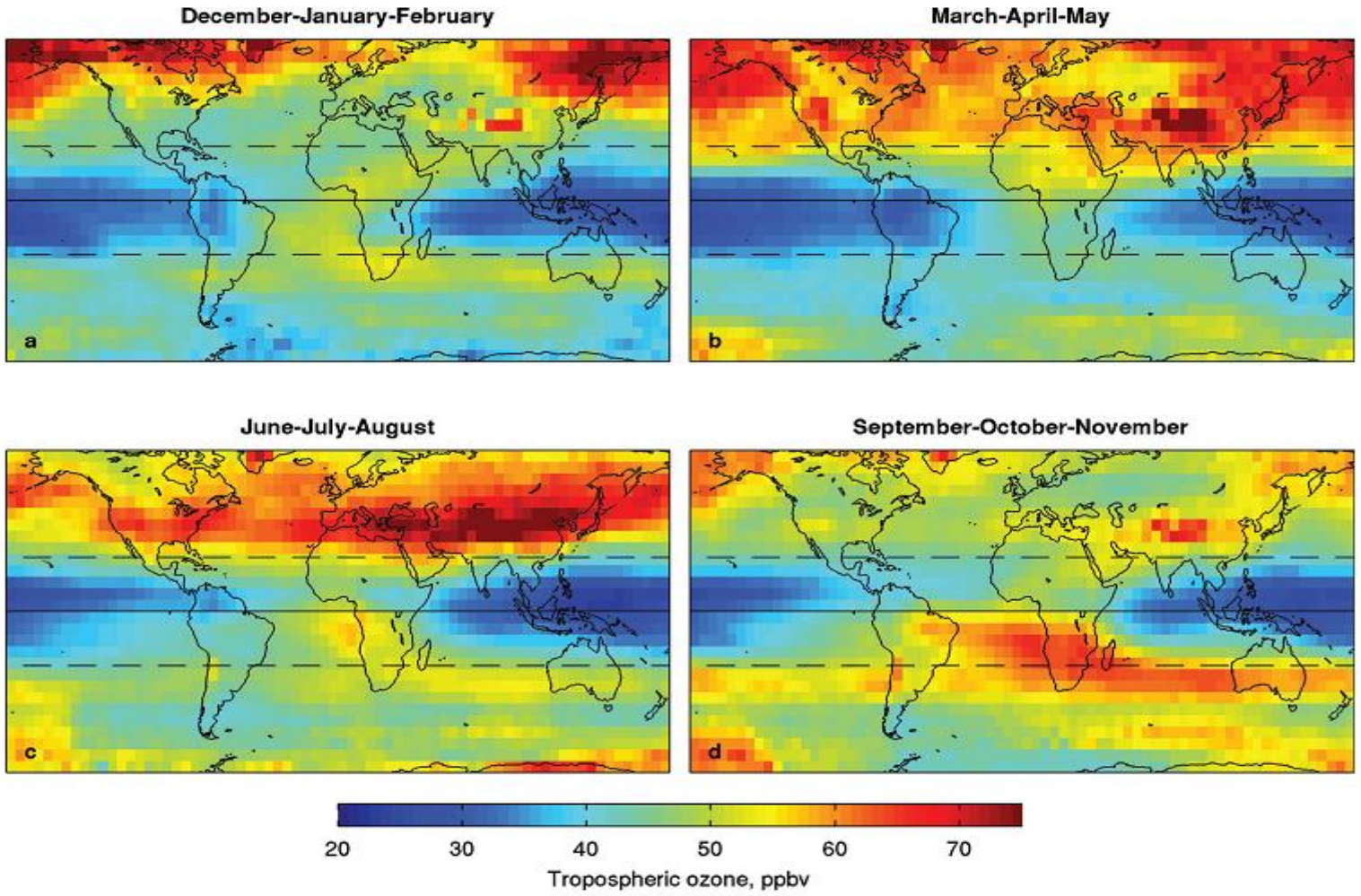
2004/10–2010/12 mean; ~ 31 DU on average



Cooper et al., 2014, Elementa; OMI/MLS data from Ziemke et al.

Tropospheric Ozone Mixing Ratio Detected From Space

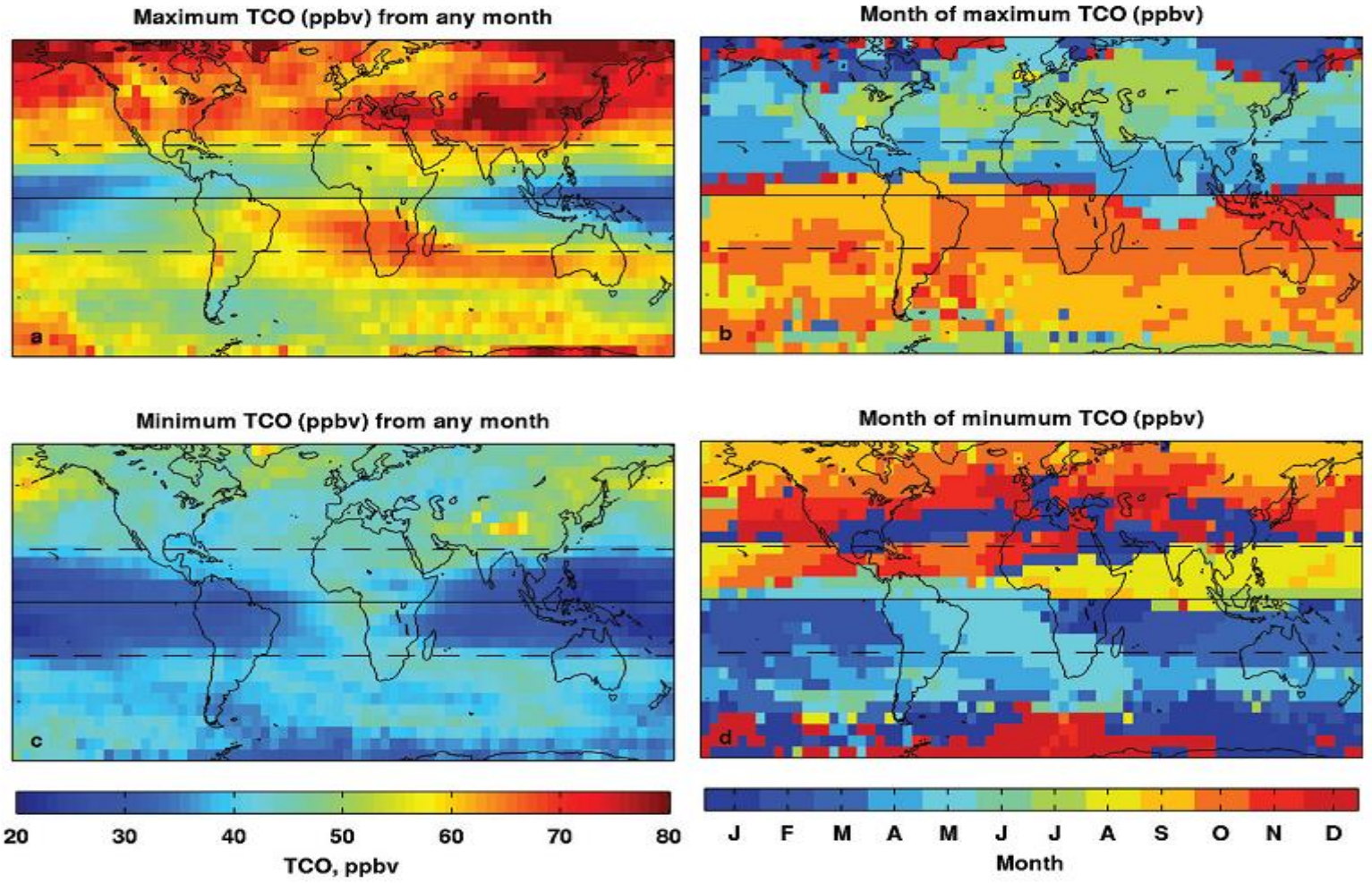
2004/10–2010/12 mean; in ppbv



Cooper et al., 2014, Elementa; OMI/MLS data from Ziemke et al.

Tropospheric Ozone Mixing Ratio Detected From Space

2004/10–2010/12 data; in ppbv

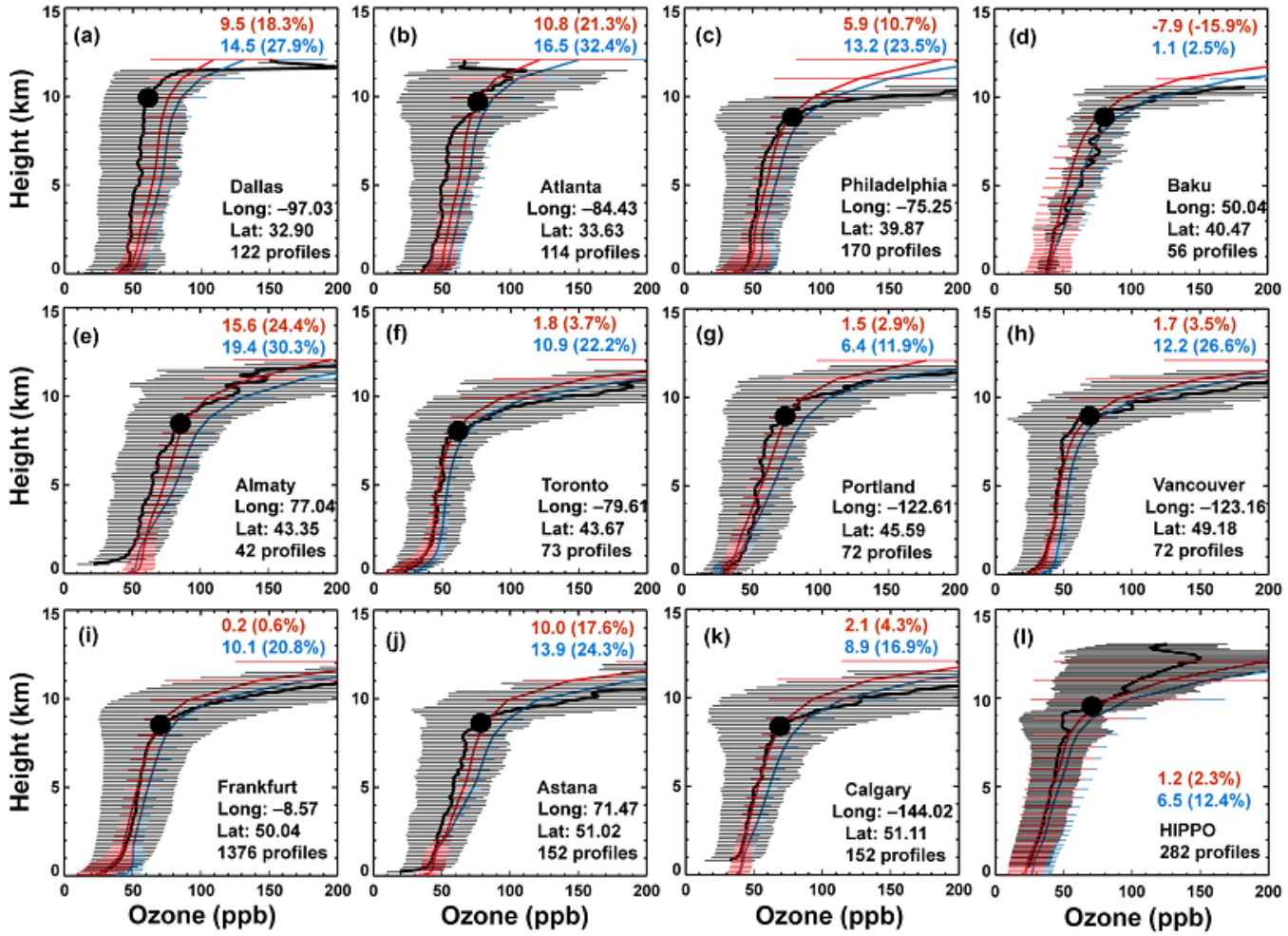


Cooper et al., 2014, Elementa; OMI/MLS data from Ziemke et al.

Vertical Profile of O_3 in the Troposphere

Comparisons with MOZIAC and HIPPO profiles

Obs
Two-way
Global

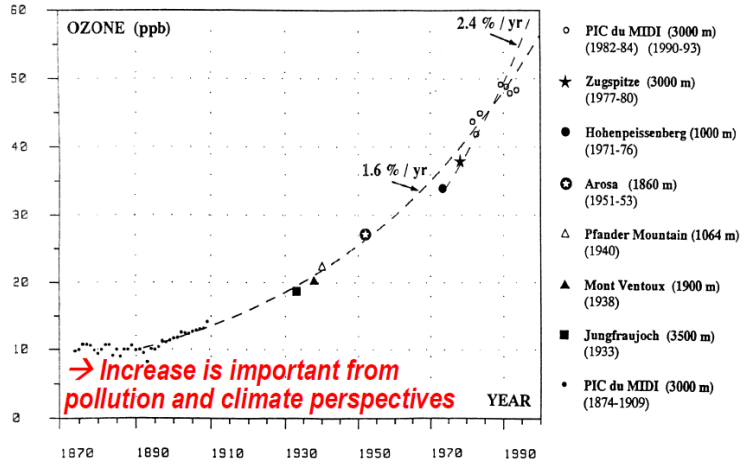


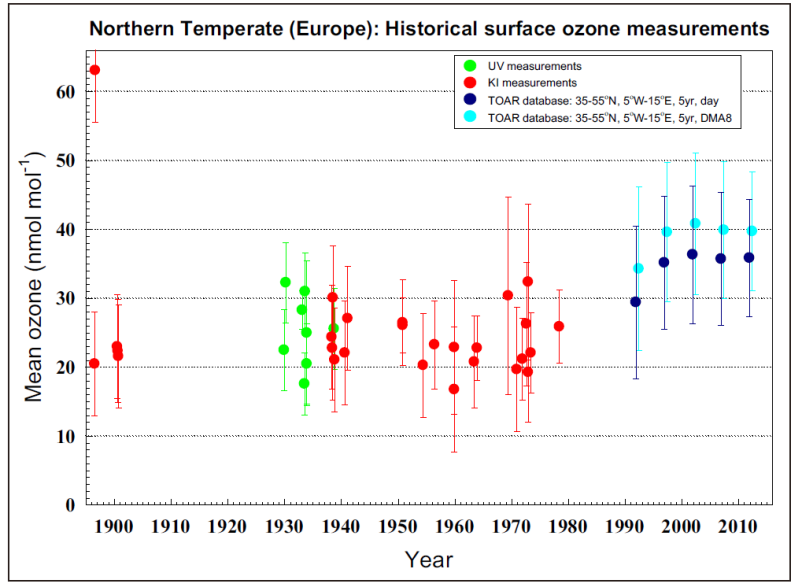
Yan Y.-Y. et al., ACP, 2014, 2016

Long-term Trends of Near-Surface Ozone

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

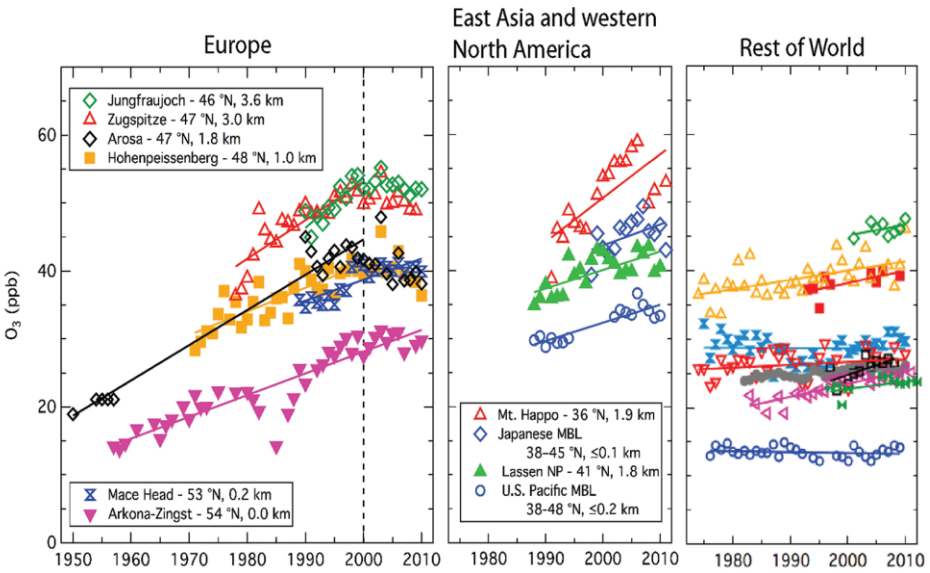
Ozone trend from European mountain observations, 1870-1990 [Marenco et al.,1994]



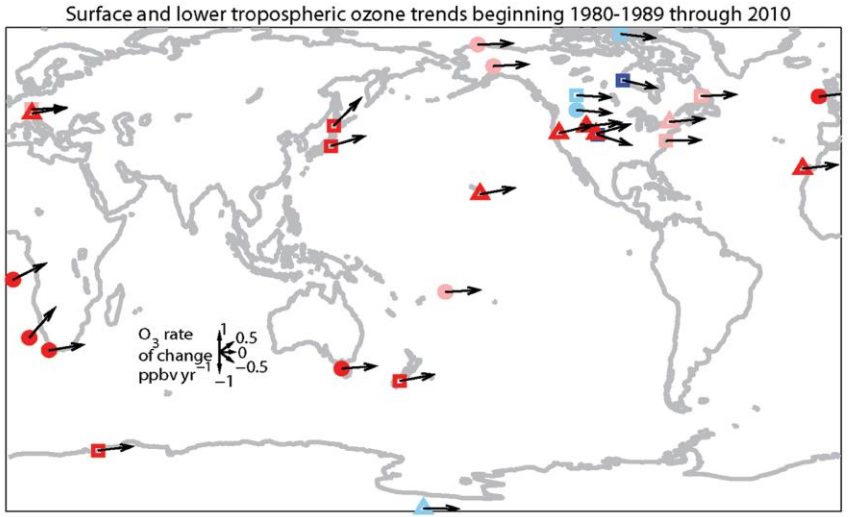


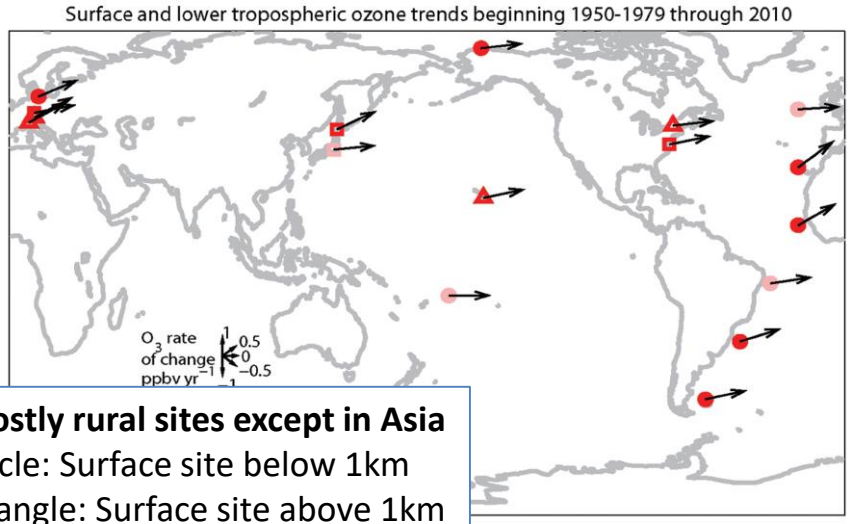
Tarasick et al., 2019 Elementa

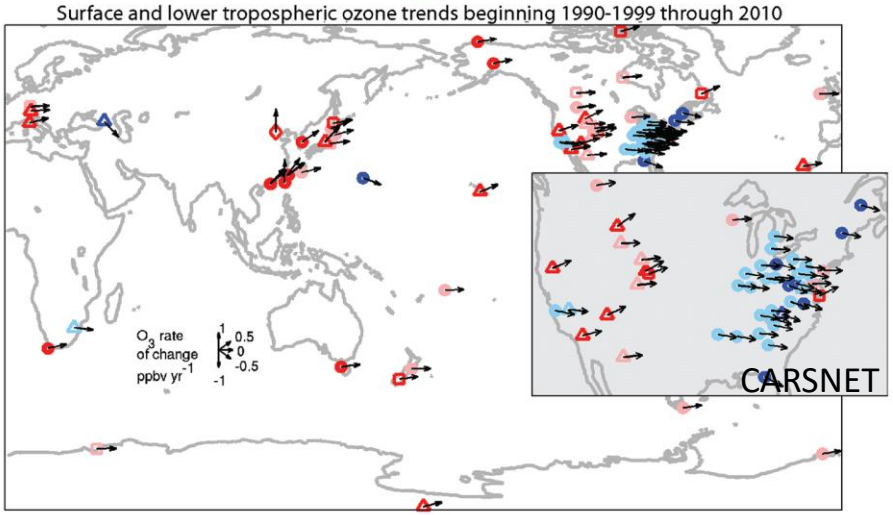
Long-term Trends of Near-Surface Ozone



Trends in annual average ozone
(mostly rural sites except in Asia)





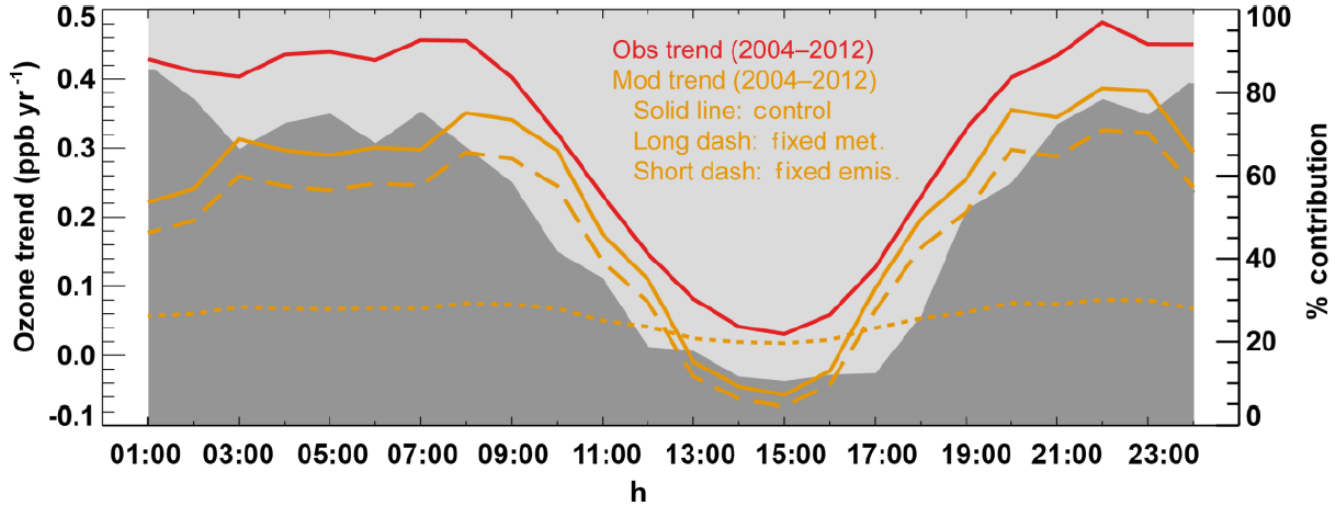


Mostly rural sites except in Asia
Circle: Surface site below 1km
Triangle: Surface site above 1km
Square: Ozonesonde
Diamond: Aircraft

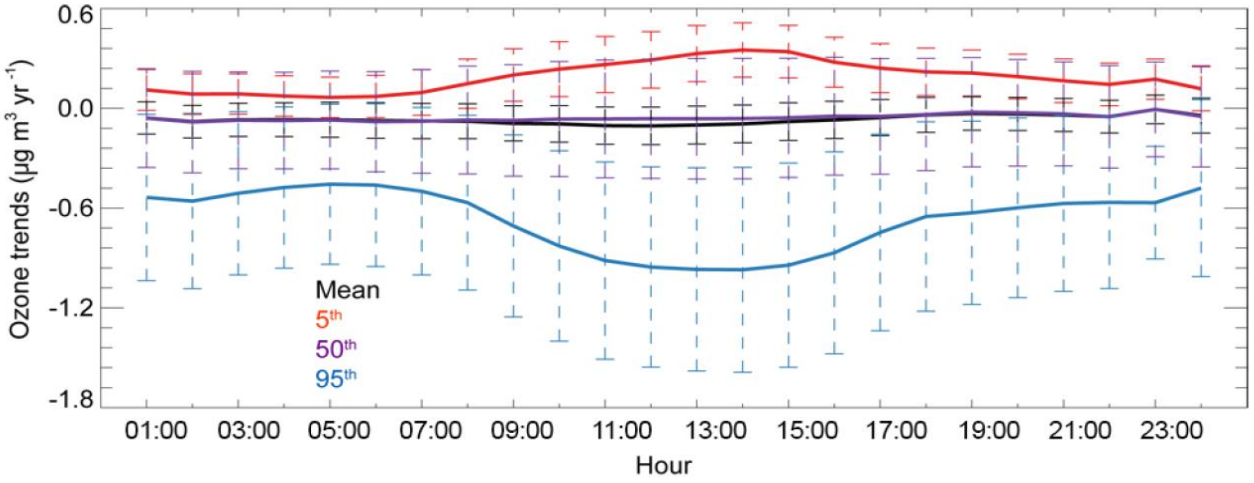
Cooper et al., 2014, Elementa

Contrasting Tends of O_3 at Different Times of Day

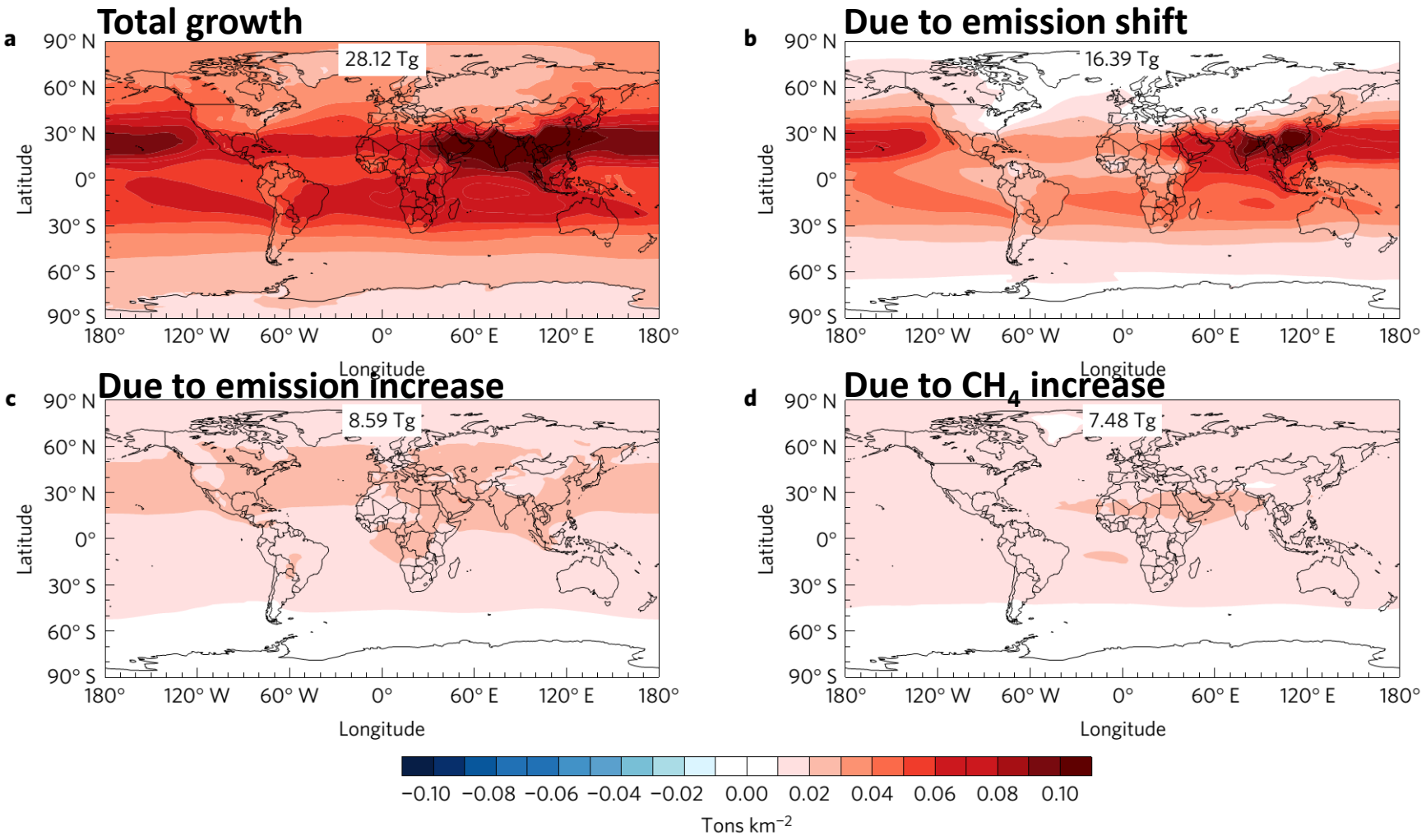
2004-2012 trends of O_3 at 1000 US EPA AQS sites (Yan et al., 2018a, ACP)



1995-2014 trends of O_3 at 93 EU EMEP sites (Yan et al., 2018b, ACP)



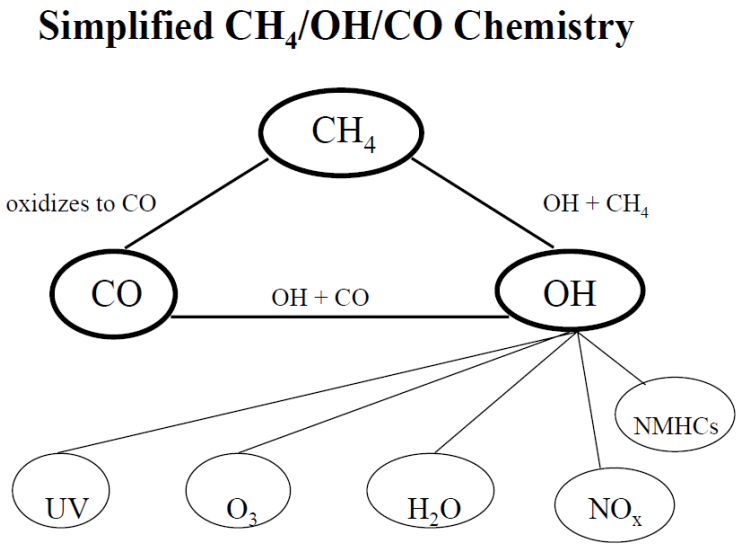
Factoring Affecting O_3 Growth between 1980 and 2010



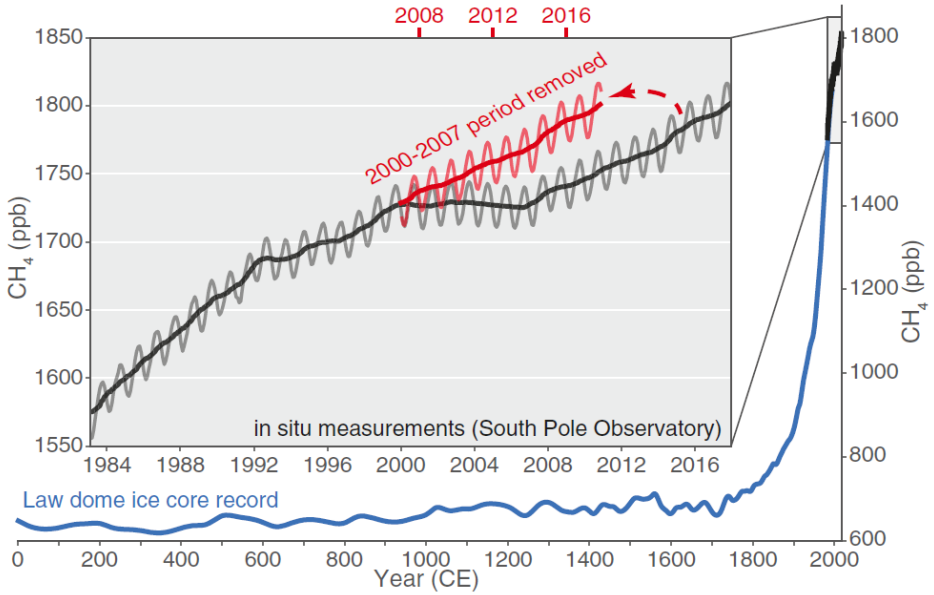
Zhang et al., 2016, Nature Geoscience

Atmospheric OH

- OH sources: O_3 photolysis, HONO photolysis, VOC ozonolysis, NO+HO_2, NO+RO_2…
- OH sinks: OH+CO, OH+CH_4, OH+NMVOC, OH+NO_2, etc.
- OH lifetime: ≤ 1s
- HO_2 lifetime: 1-2 mins



Changes in CH_4

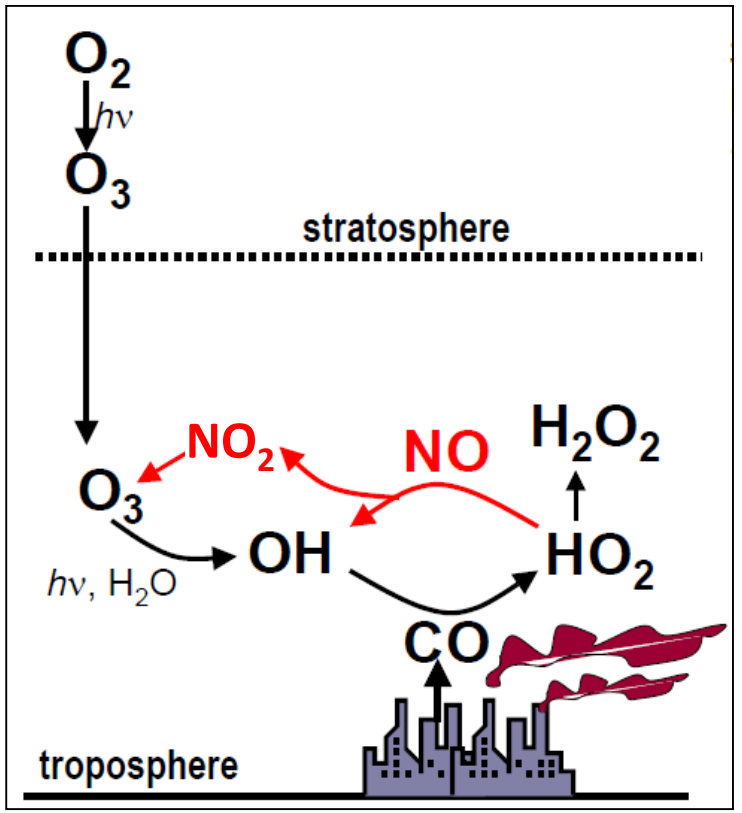


Turner et al., 2019, PNAS

Tropospheric OH: The Cleanser (pacman)

Production:

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



Loss:

- $OH + CO \rightarrow HO_2$
- $OH + VOC \rightarrow RO_2$
- $OH + O_3 \rightarrow O_2 + HO_2$
- $OH + NO_2 + M \rightarrow HNO_3 + M$
- …

Budget of Tropospheric OH

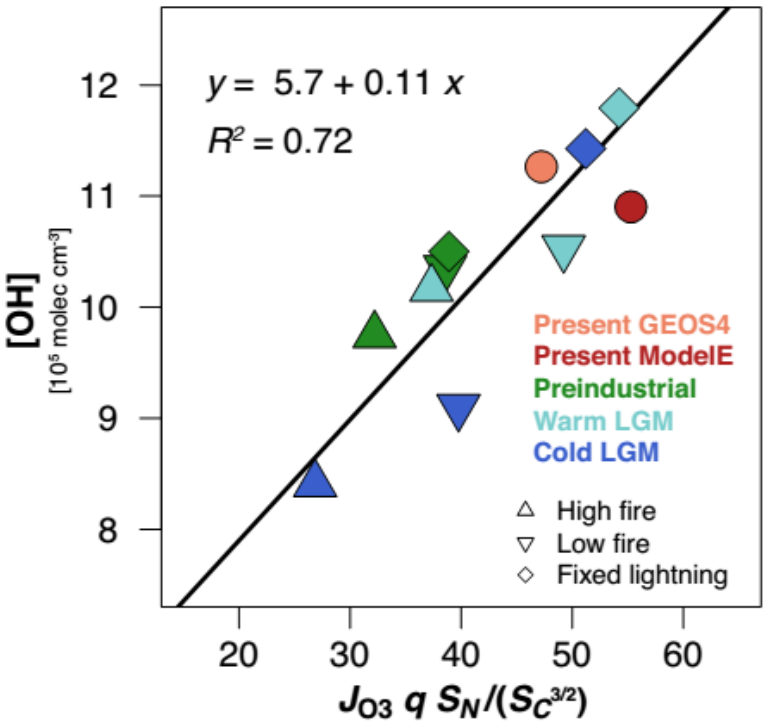
	Global model[1]	Two-way coupled model[1]
Total loss ($Tg\,yr^{-1}$)	3780	3756
$OH + CO$	1440 (38 %)	1452 (38 %)
$OH + CH_4^2$	540 (14 %)	516 (14 %)
$OH + NMVOCs$	840 (22 %)	852 (23 %)
$OH + O_3$	204 (5 %)	204 (5 %)
$OH + HO_y$	396 (10 %)	384 (10 %)
$OH + NO_y$	72 (2 %)	60 (2 %)
$OH + H_2$, SO_2, etc.	132 (9 %)	132 (8 %)
Total production ($Tg\,yr^{-1}$)	3780	3756
Photolysis of O_3	1608 (43 %)	1584 (42 %)
Photolysis of other species	480 (12 %)	504 (14 %)
Reactions	1692 (45 %)	1668 (44 %)
Air mass weighted mean concentration ($10^5\ cm^{-3}$)	12.4	11.9
MCF loss rate weighted mean concentration ($10^5\ cm^{-3}$)	12.5	12.1
Methyl chloroform lifetime (yr)[3]	5.3	5.5

甲基氯仿 MCF: Methyl chloroform (CH_3CCl_3) is an excellent tracer to study changes in OH

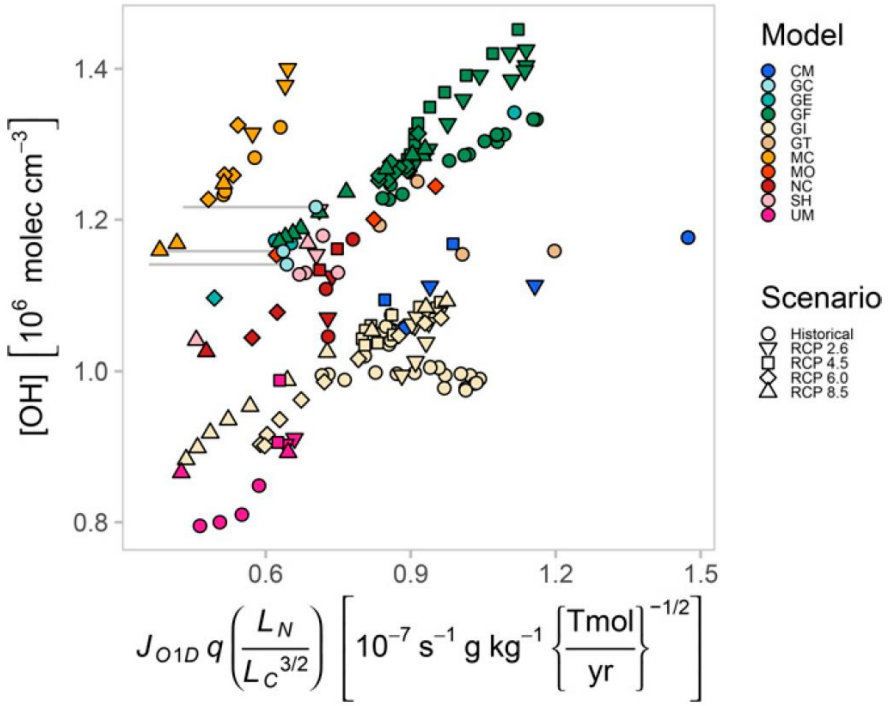
$$[\mathrm{OH}] \propto k_G = \frac{E}{G} - \frac{dG/dt}{G}$$

Yan et al., 2014, ACP

Factors Determining Tropospheric OH



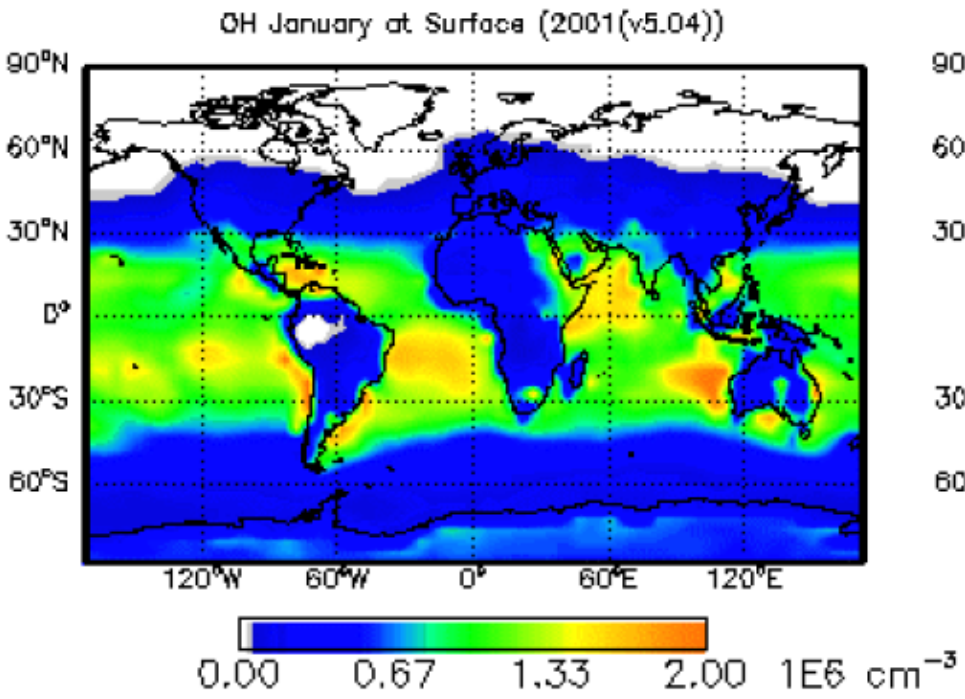
Murray et al., 2014, ACP



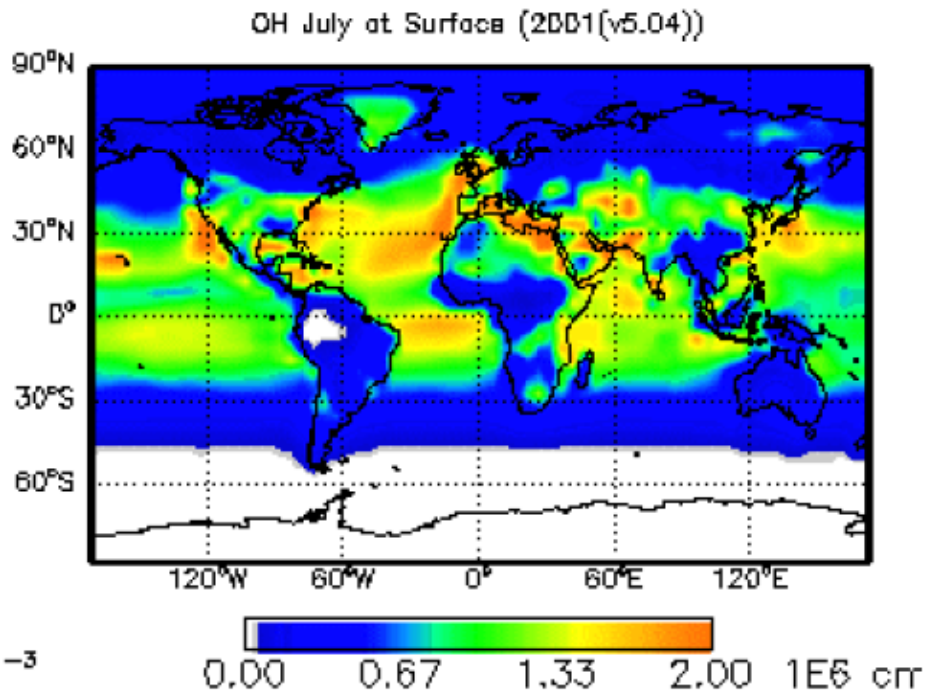
Murray et al., 2021, PNAS

Global OH Concentrations Near the Surface

January

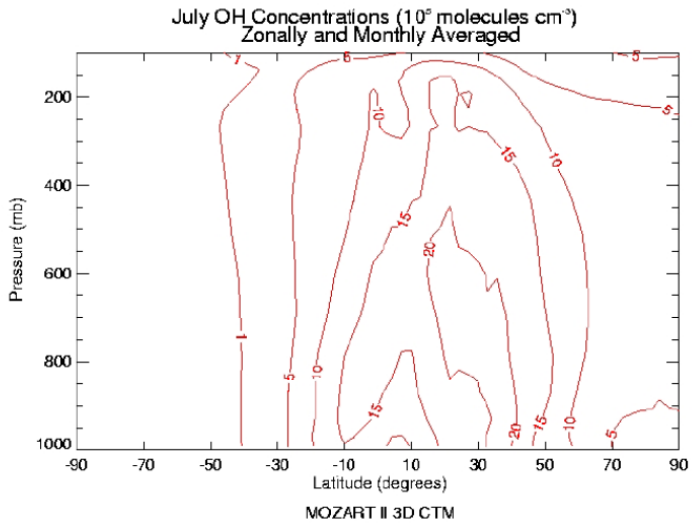


July

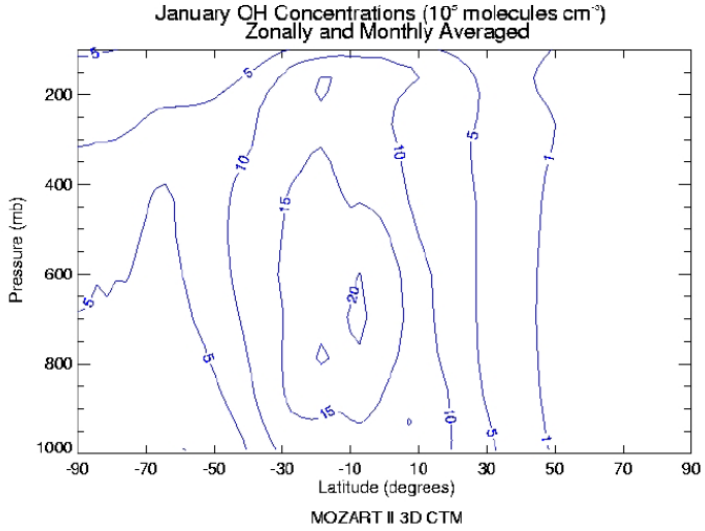


Tropospheric OH: Meridional-Vertical Cross Section

Tropospheric OH July -- MOZART2

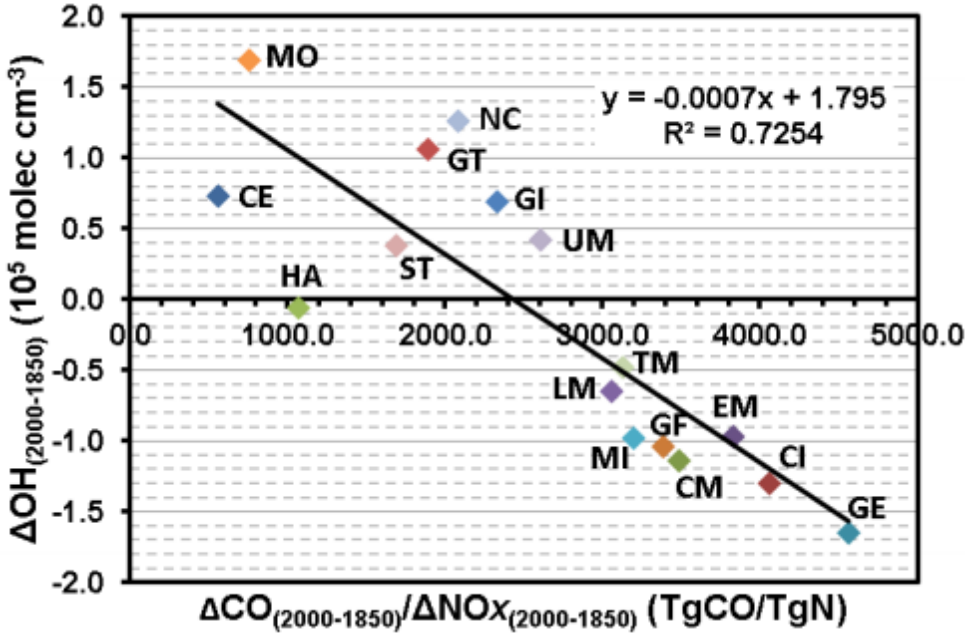


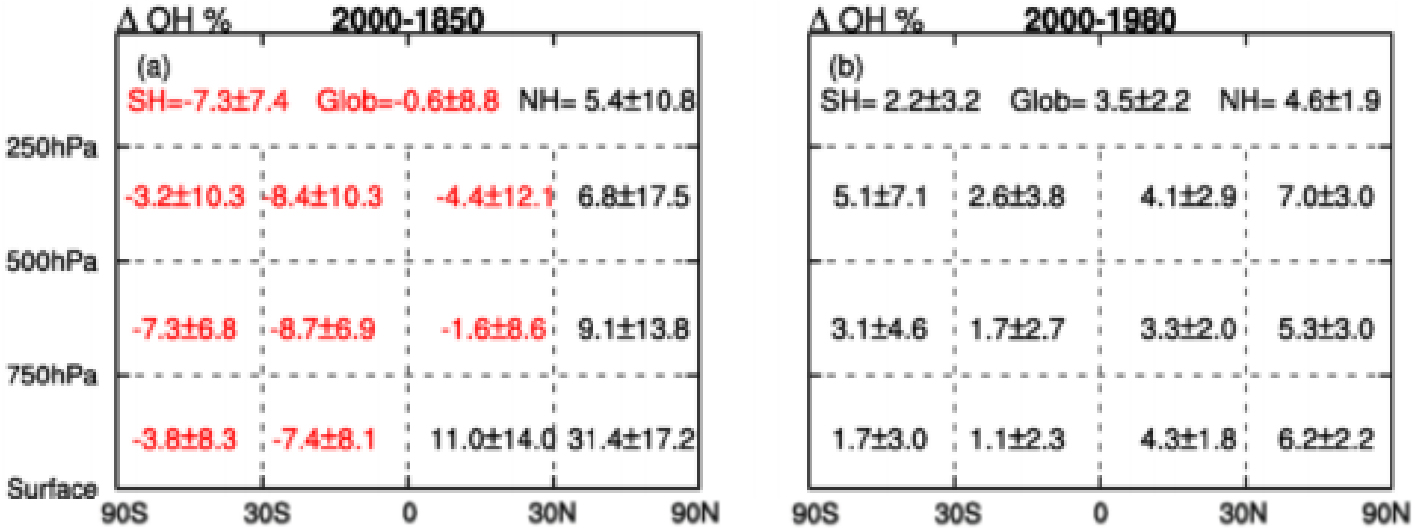
Tropospheric OH (January) – MOZART2



Modeled Change in Tropospheric OH: 1850-2000

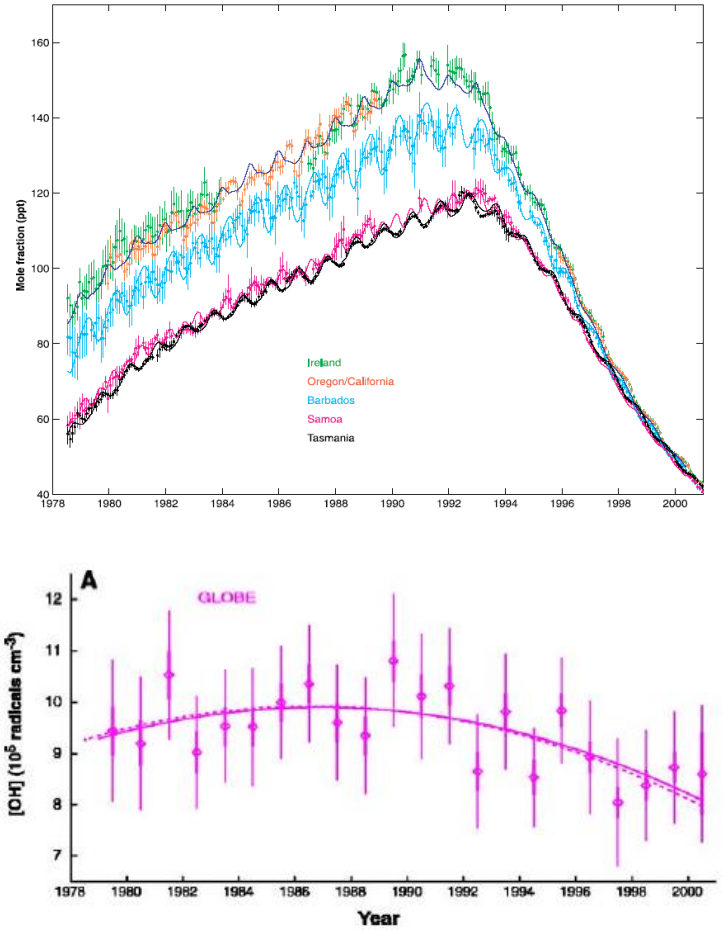
Naik et al., 2013, ACP





Obs-based Estimate of OH Temporal Variation

CH_3CCl_3甲基氯仿

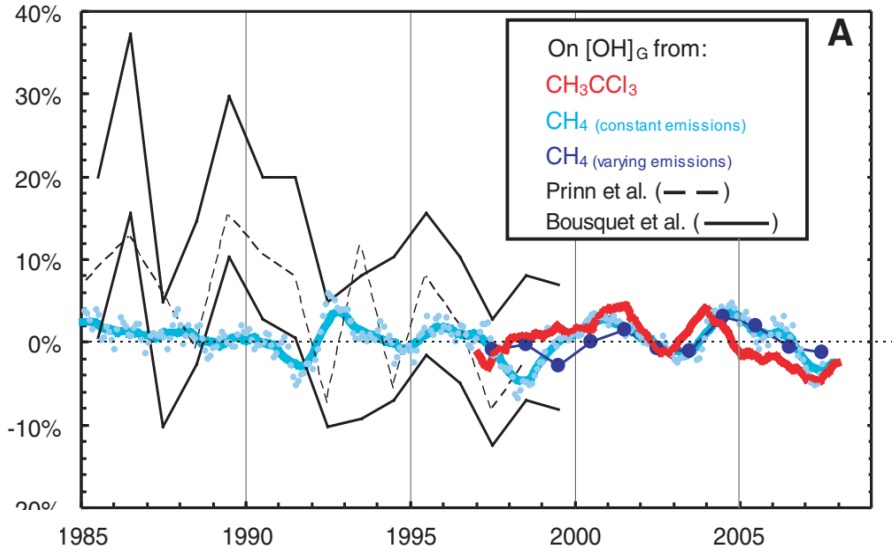


Prinn et al., 2001

Emis Obs. change

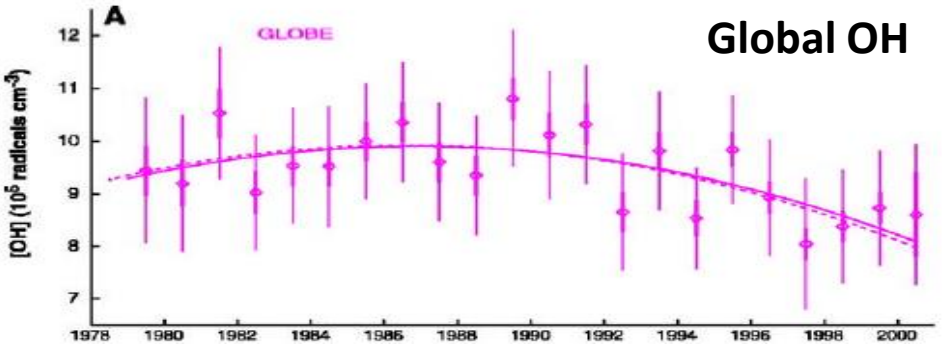
$$[\mathrm{OH}] \propto k_G = \frac{E}{G} - \frac{dG/dt}{G}$$

Loss coef. Global mass

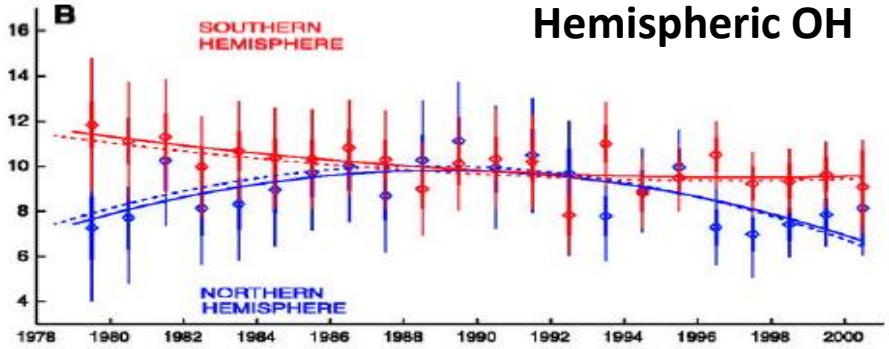


Montzka et al., Science, 2011

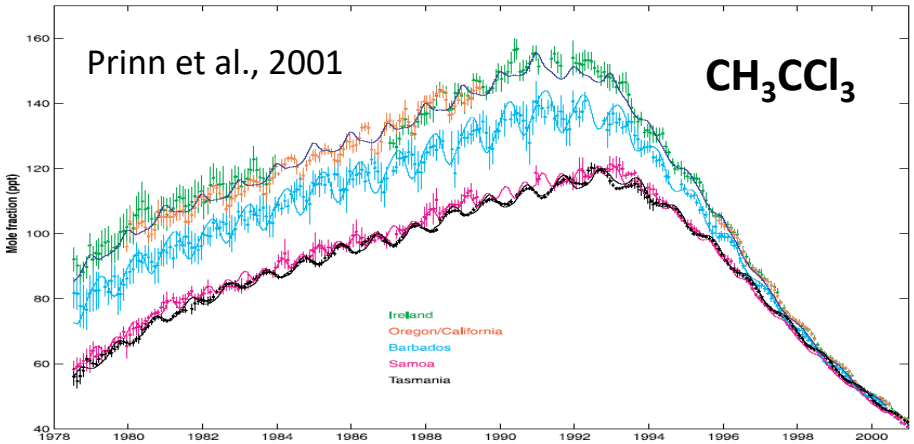
Obs-based Estimate of Trop. OH Interannual Variability



Global OH

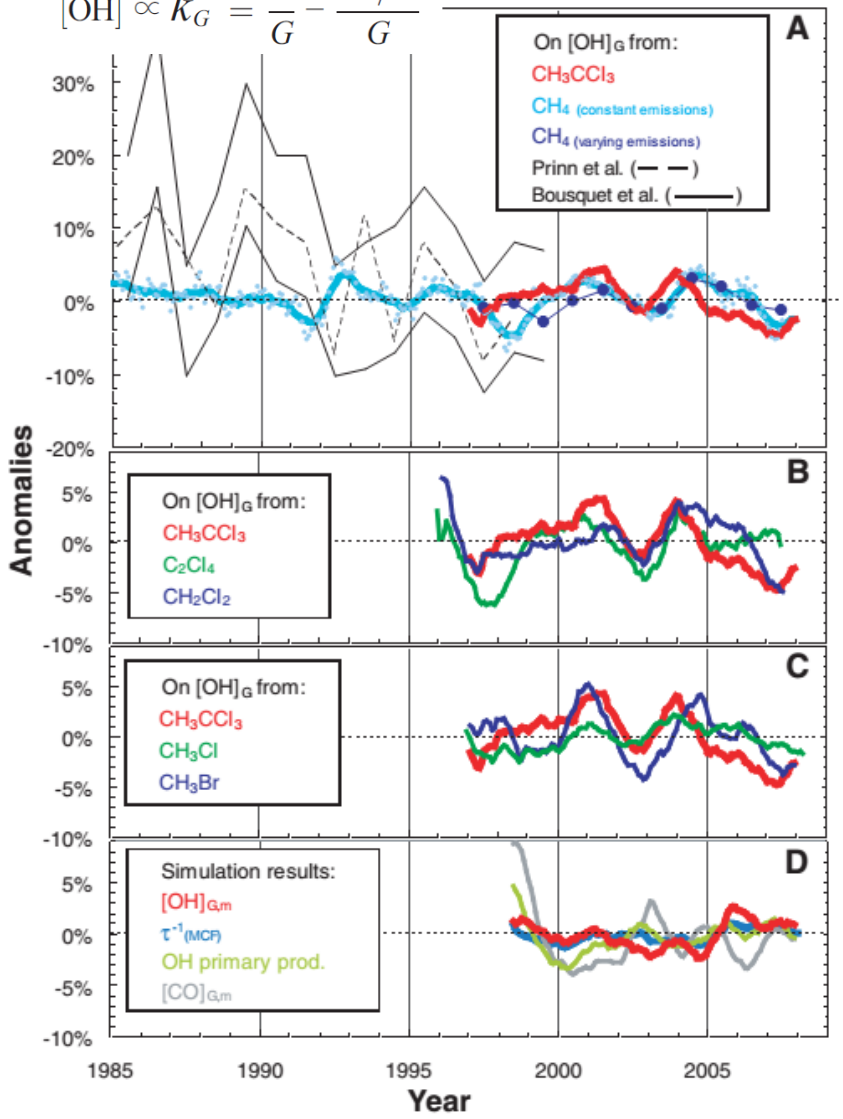


Hemispheric OH



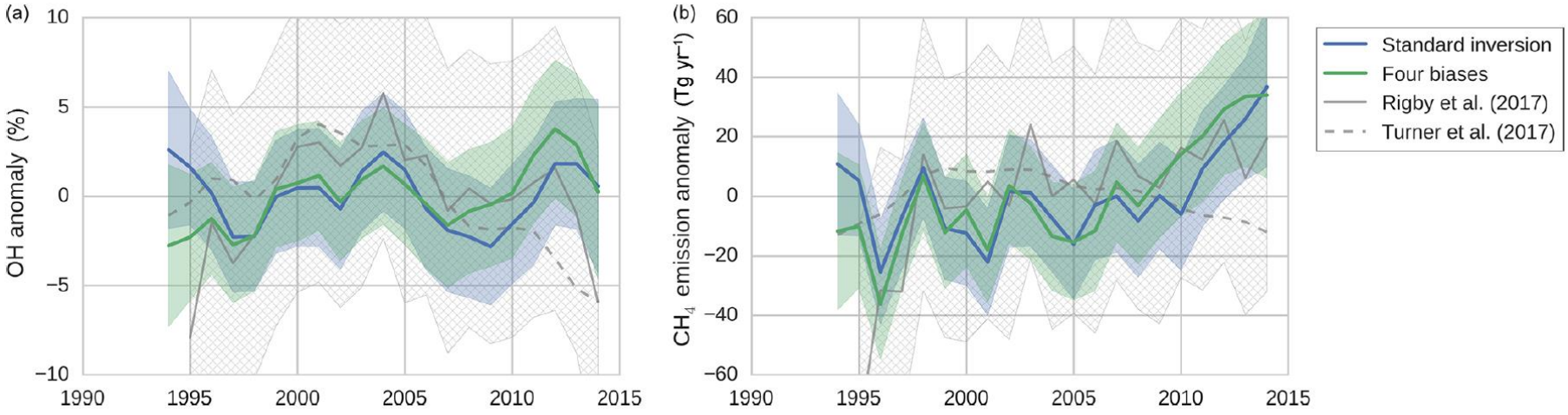
1978 1982 1986 1990 1994 1998

$$[\mathrm{OH}] \propto k_G = \frac{E}{G} - \frac{dG/dt}{G}$$



Montzka et al., 2011, Science

Unclear Recent Trend of OH Related to CH_4 Growth



Bias in box modeling affecting MCF-based OH estimate:

1. **Inter-hemispheric transport**
2. **Sampling bias**
3. **N/S OH ratio**
4. **MCF loss to stratosphere**

$$\frac{dX_{NH}}{dt} = E_{NH} - (k_{OH}[OH]_{NH} + l_{strat} + l_{other})X_{NH} - k_{IH}(X_{NH} - X_{SH}),$$

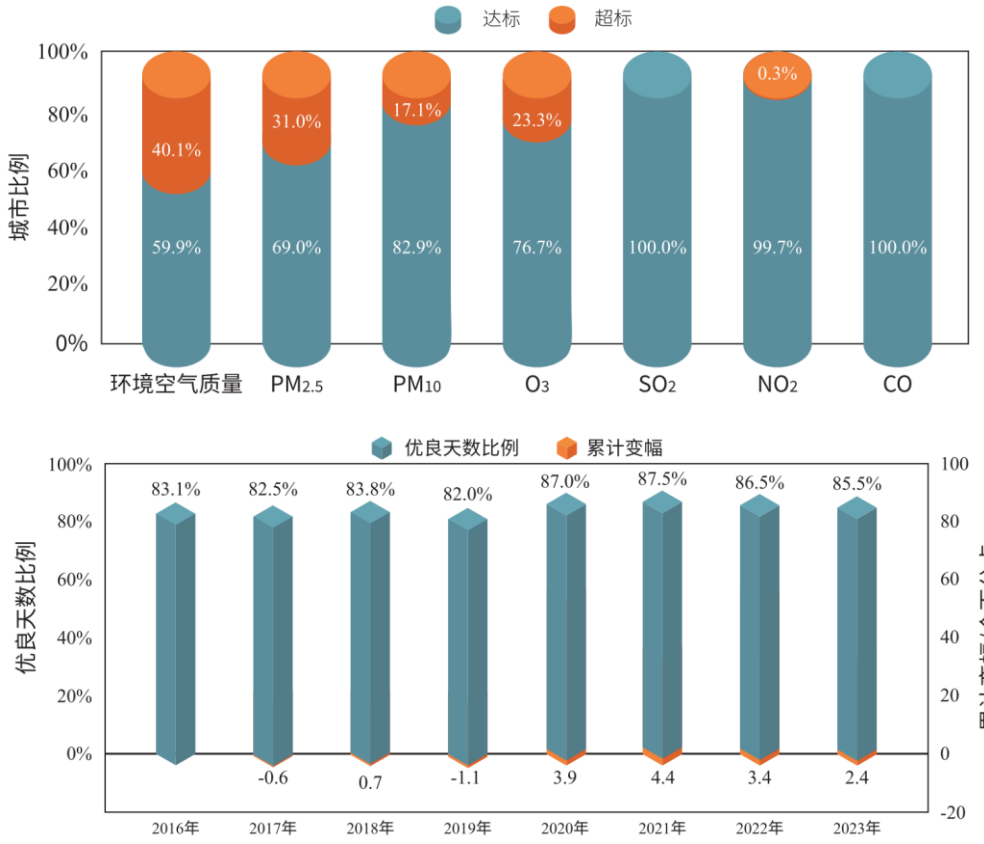
$$\frac{dX_{SH}}{dt} = E_{SH} - (k_{OH}[OH]_{SH} + l_{strat} + l_{other})X_{SH} + k_{IH}(X_{NH} - X_{SH}).$$

Naus et al., 2019, ACP

Near-Surface Air Pollution

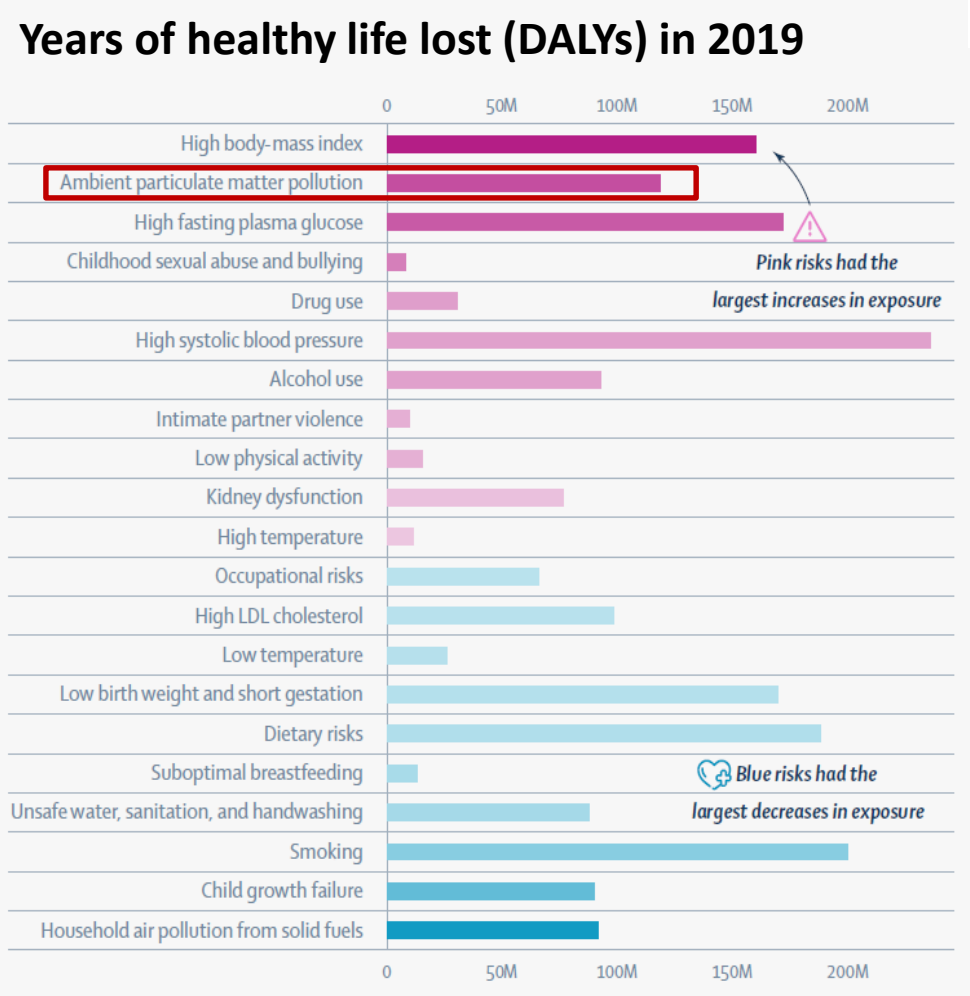
- **Outdoor Air Pollution**
  - ✓ **Ozone**
  - ✓ **$PM_{2.5}$**
  - ✓ **Acid deposition**
- **Consequences**
  - ✓ **Health impacts**
  - ✓ **Agriculture**
  - ✓ **Ecosystems**

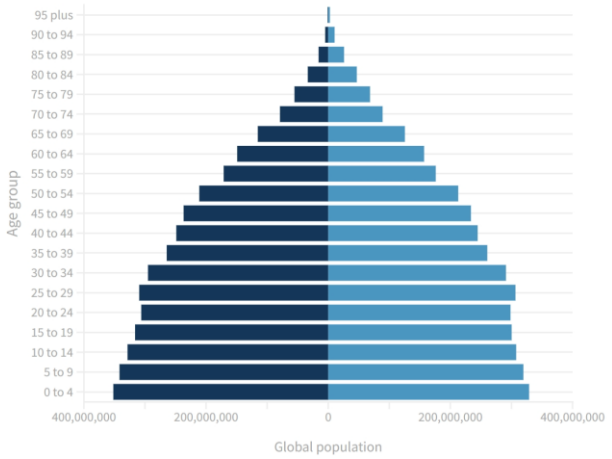
Chinese Air Quality Status



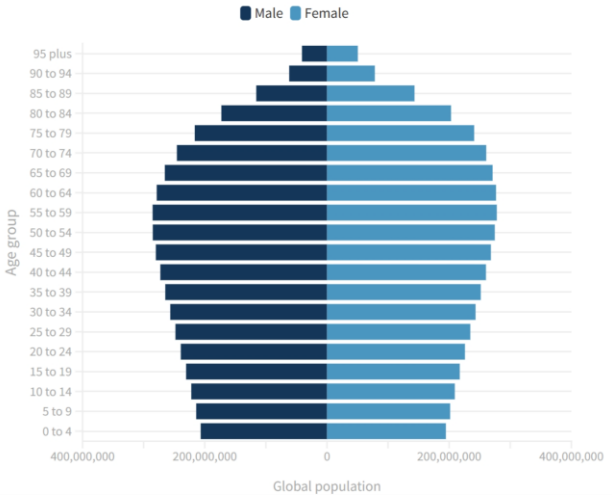
中国生态环境公报2023

Health Impacts of Air Pollution

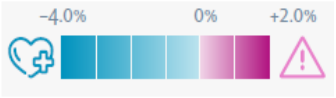




Population in 2017



Population in 2100

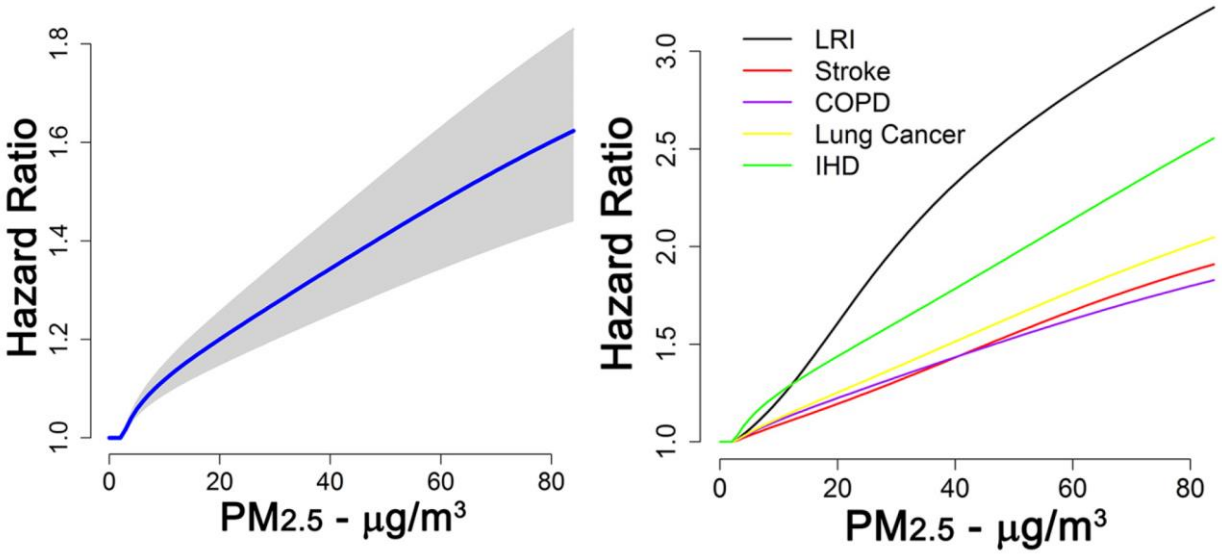


% change from 2010

https://www.thelancet.com/infographics-do/gbd-2019

Health Impacts of Air Pollution

Burnett et al., 2018 PNAS

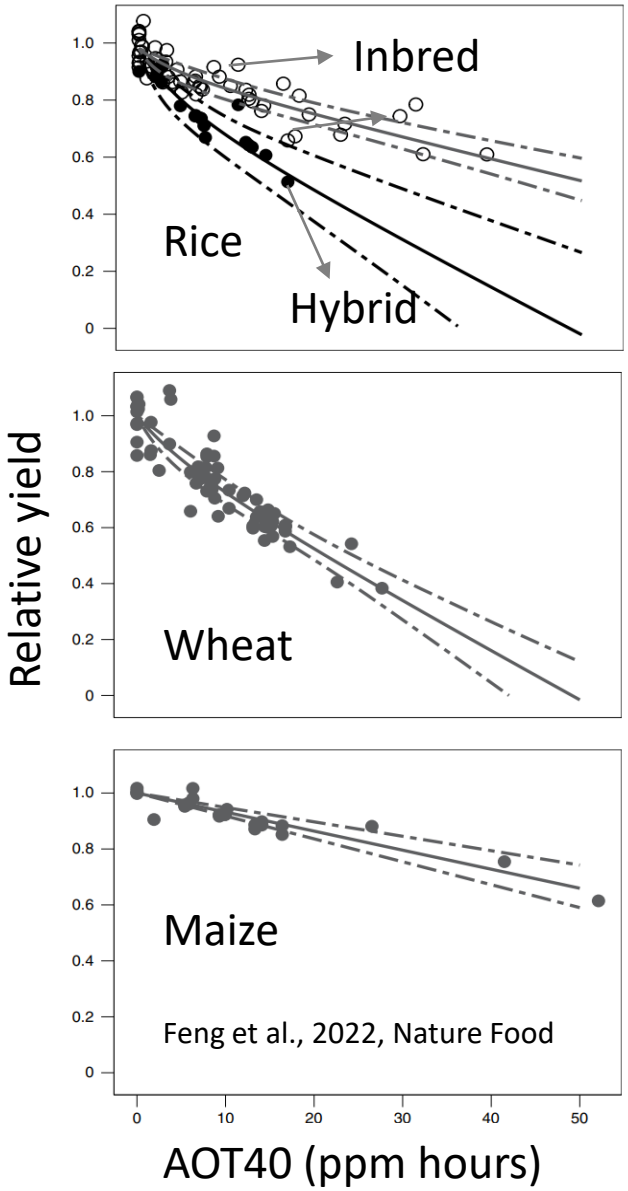


Di et al., 2017 NEJM

Table 2. Risk of Death Associated with an Increase of 10 µg per Cubic Meter in $PM_{2.5}$ or an Increase of 10 ppb in Ozone Concentration.*

Model	$PM_{2.5}$	Ozone
	hazard ratio (95% CI)	
Two-pollutant analysis		
Main analysis	1.073 (1.071–1.075)	1.011 (1.010–1.012)
Low-exposure analysis	1.136 (1.131–1.141)	1.010 (1.009–1.011)
Analysis based on data from nearest monitoring site (nearest-monitor analysis)†	1.061 (1.059–1.063)	1.001 (1.000–1.002)
Single-pollutant analysis‡	1.084 (1.081–1.086)	1.023 (1.022–1.024)

Ozone Exposure Can Lead to Reduced Crop Yields



Crop	Country		Yield loss (%)	95% confidence	
				Upper boundary (%)	Lower boundary (%)
Wheat	China		32.8	36.9	28.2
	Japan		15.8	19.5	12.2
	South Korea		27.8	32.2	23.3
Rice	China	All	23.0	30.3	17.4
		Inbred	12.2	15.9	9.2
		Hybrid	29.8	38.6	23.0
	Japan		5.1	8.1	3.2
	South Korea		10.7	14.9	7.7
Maize	China		8.6	10.4	6.4
	South Korea		4.7	5.6	3.5

Dose-response Functions :

$$AOT40 = \sum_{i=1}^{n} \left([O_3]_i - 0.04\right), \; for \; o_3 \geq 0.04ppm$$

$$RY \; (relative \; yield) = a \times AOT40 + b$$

WHO Air Quality Guidelines

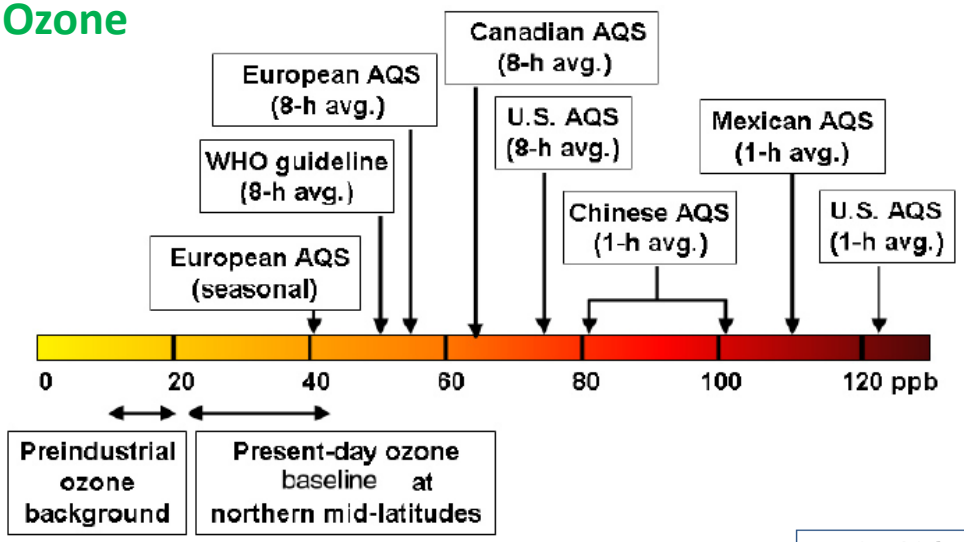
污染物	取值时间	2005 AQG	2021 AQG
$PM_{2.5}$, μg/m³	Annual	10	5
	24-hour[a]	25	15
PM_{10}, μg/m³	Annual	20	15
	24-hour[a]	50	45
O_3, μg/m³	Peak season[b]	–	60
	8-hour[a]	100	100
NO_2, μg/m³	Annual	40	10
	24-hour[a]	–	25
SO_2, μg/m³	24-hour[a]	20	40
CO , mg/m³	24-hour[a]	–	4

WHO, 2021

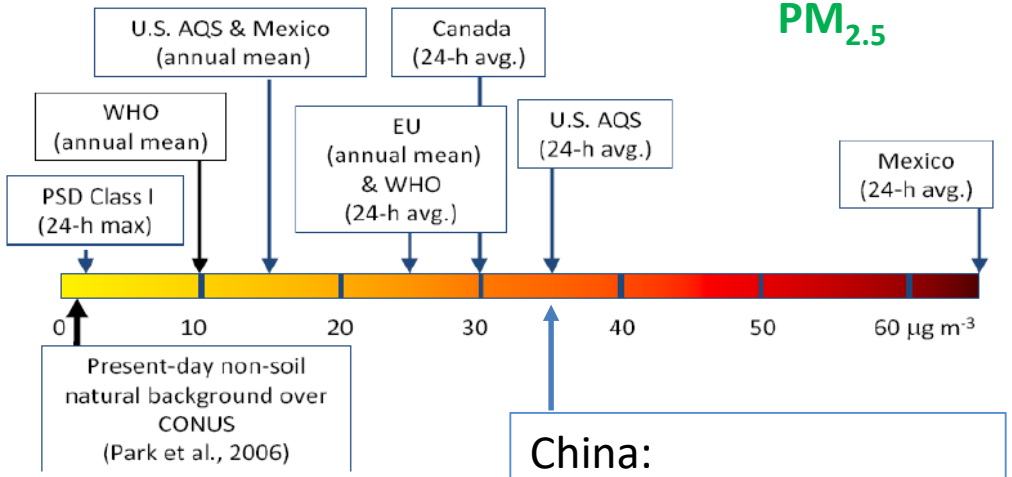
表格来自https://cese.pku.edu.cn/kycg/131451.htm

Ambient Air Quality Standards

Ozone



$PM_{2.5}$



China:
75 µg m^{-3} for 24-h avg.
35 µg m^{-3} for 1-yr avg.

HTAP, 2010

Air Quality Index (China)

表 1　空气质量分指数及对应的污染物项目浓度限值

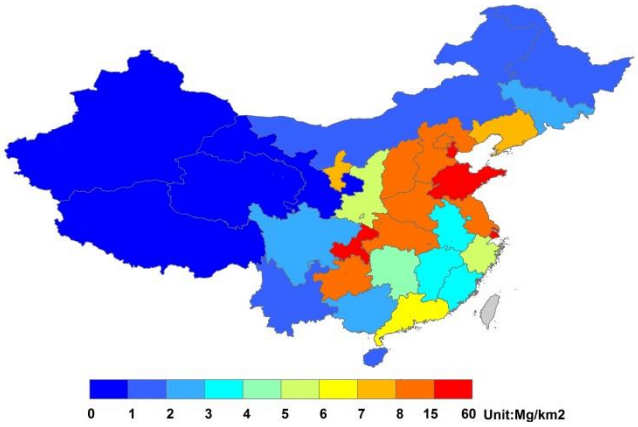
空气质量分指数（IAQI）	污染物项目浓度限值									
	二氧化硫（SO_2）24 小时平均/（$\mu g/m^3$）	二氧化硫（SO_2）1 小时平均/（$\mu g/m^3$）(1)	二氧化氮（NO_2）24 小时平均/（$\mu g/m^3$）	二氧化氮（NO_2）1 小时平均/（$\mu g/m^3$）(1)	颗粒物（粒径小于等于10μm）24 小时平均/（$\mu g/m^3$）	一氧化碳（CO）24 小时平均/（mg/m^3）	一氧化碳（CO）1 小时平均/（mg/m^3）(1)	臭氧（O_3）1 小时平均/（$\mu g/m^3$）	臭氧（O_3）8 小时滑动平均/（$\mu g/m^3$）	颗粒物（粒径小于等于2.5μm）24 小时平均/（$\mu g/m^3$）
0	0	0	0	0	0	0	0	0	0	0
50	50	150	40	100	50	2	5	160	100	35
100	150	500	80	200	150	4	10	200	160	75
150	475	650	180	700	250	14	35	300	215	115
200	800	800	280	1 200	350	24	60	400	265	150
300	1 600	(2)	565	2 340	420	36	90	800	800	250
400	2 100	(2)	750	3 090	500	48	120	1 000	(3)	350
500	2 620	(2)	940	3 840	600	60	150	1 200	(3)	500

优
良
轻度
中度
重度
严重

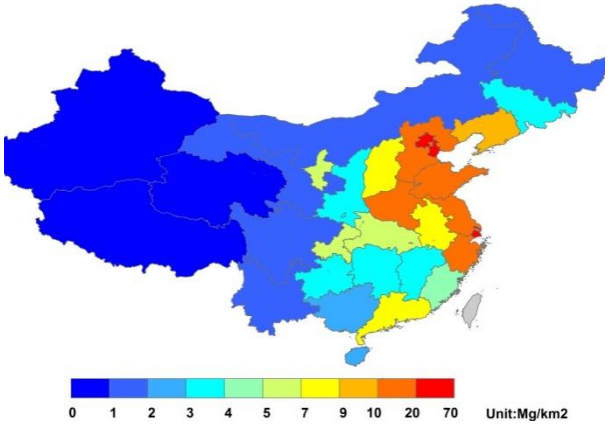
2018年9月1日前：参比状态为1atm、273K（气体和颗粒物）
2018年9月1日后：参比状态为1atm、298K（气体）；环境状况（颗粒物）

Anthropogenic Emissions in China

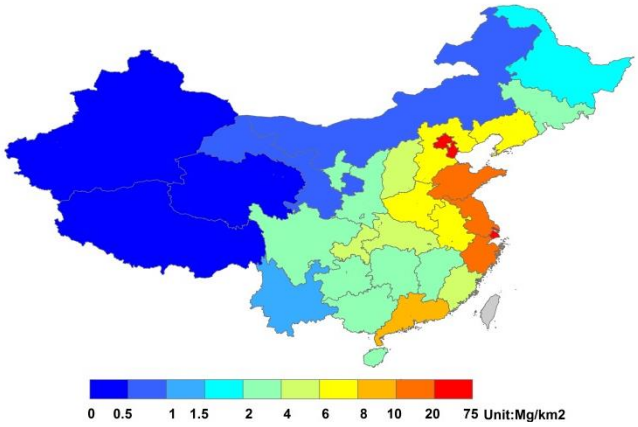
SO_2



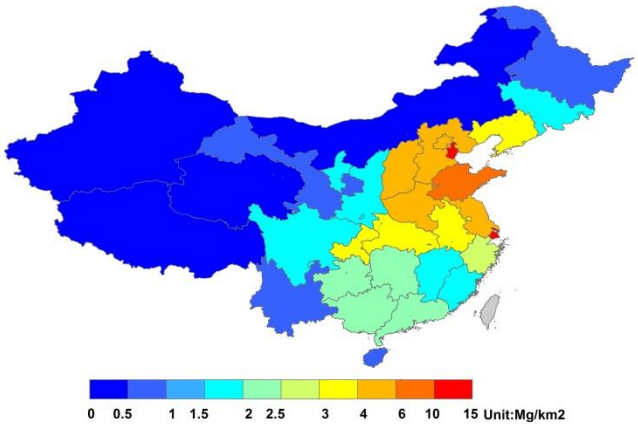
NO_x



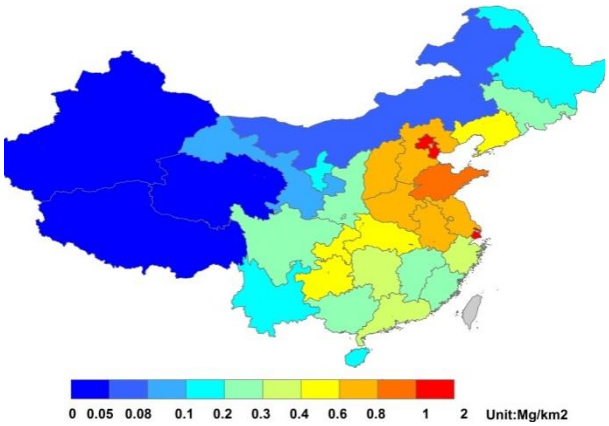
VOC



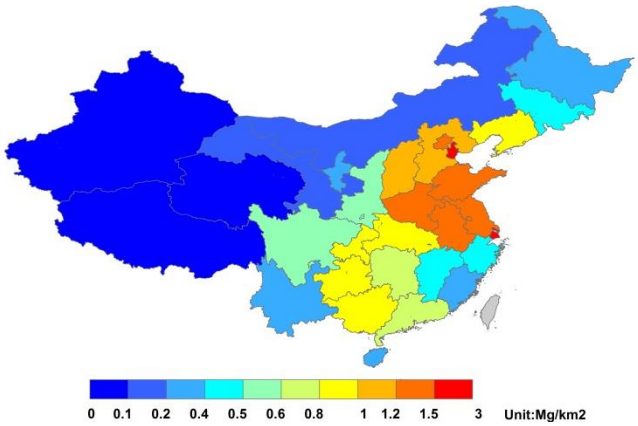
$PM_{2.5}$



BC

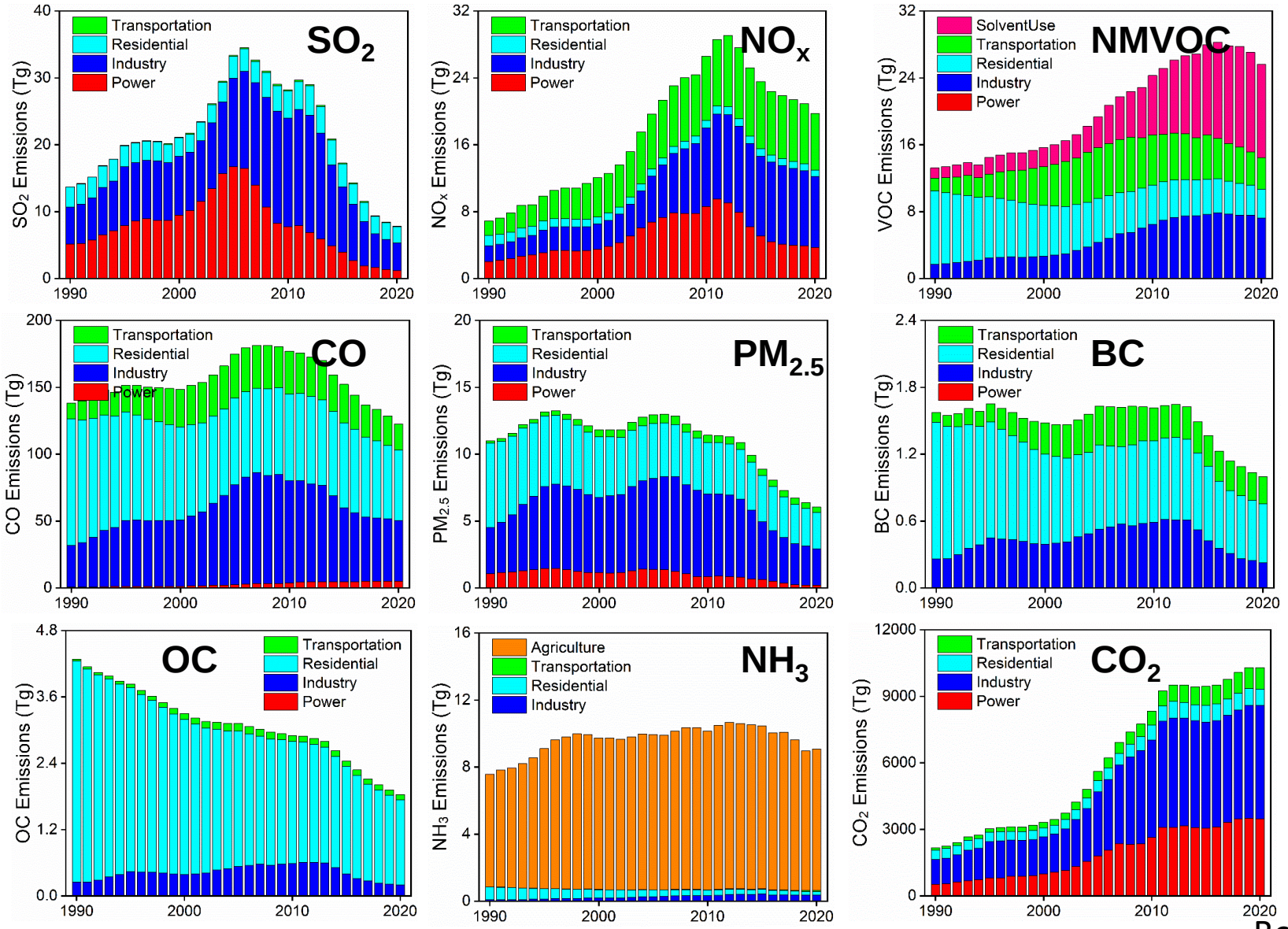


OC



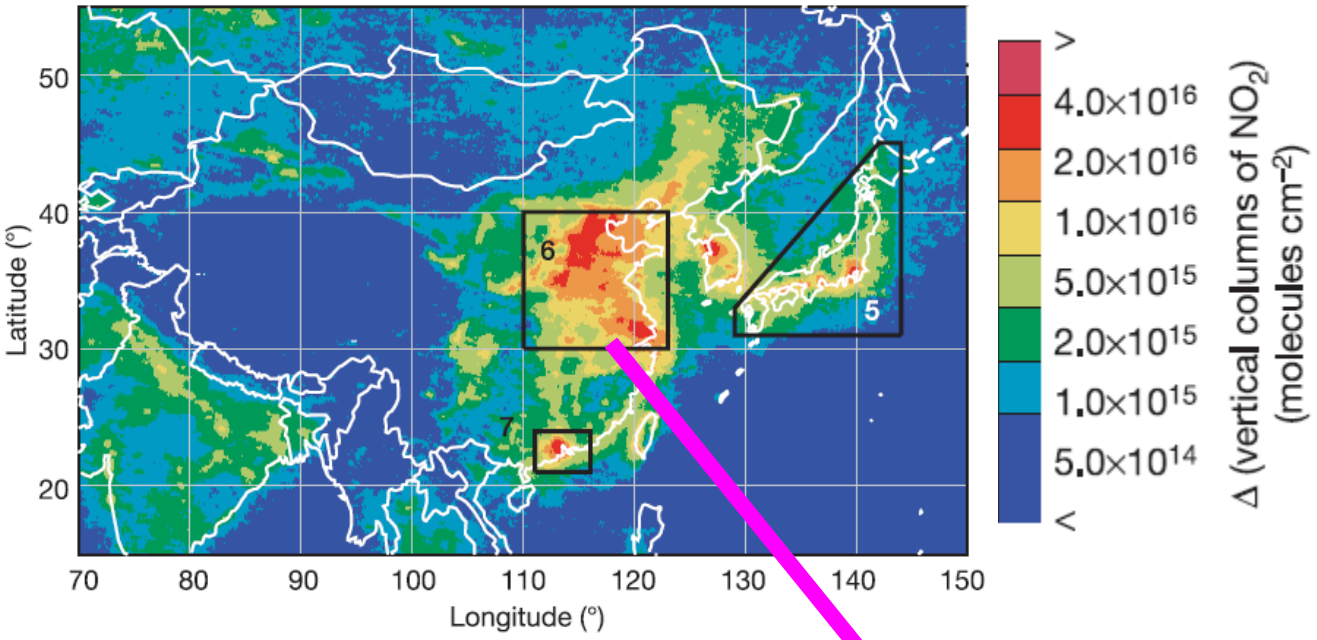
贺克斌，2014

Anthropogenic Emissions in China: 1990-2020



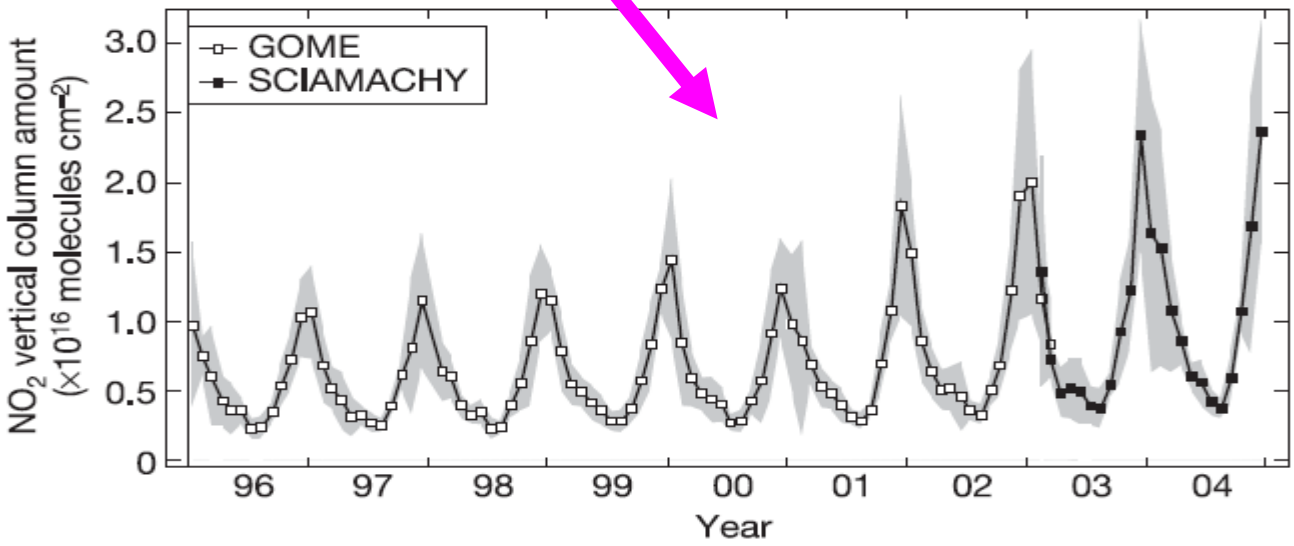
Bo Zheng

Increases of NO_2 VCD Observed from Space

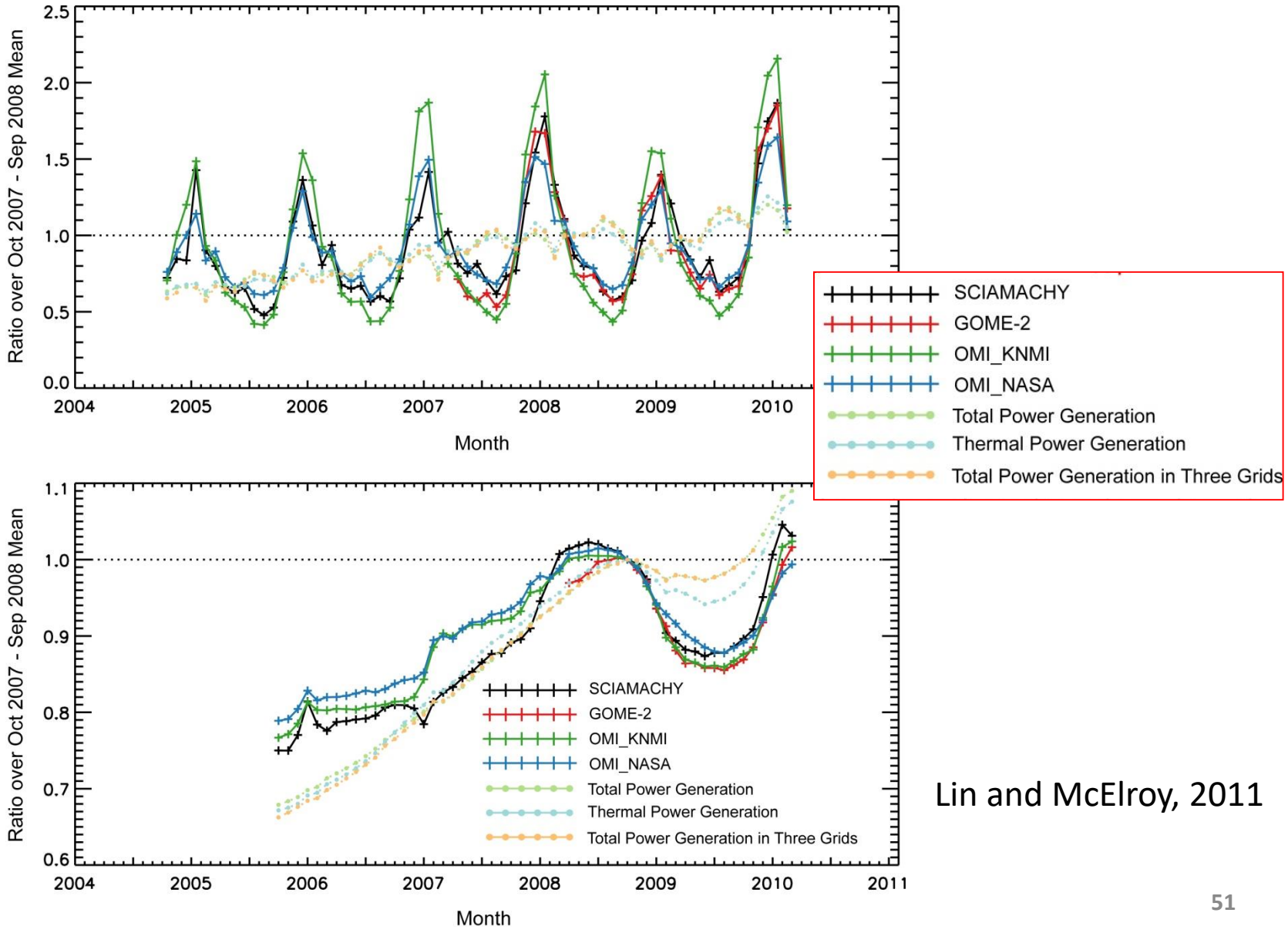


Tropospheric NO_2 vertical columns (2003,12~2004,11)

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

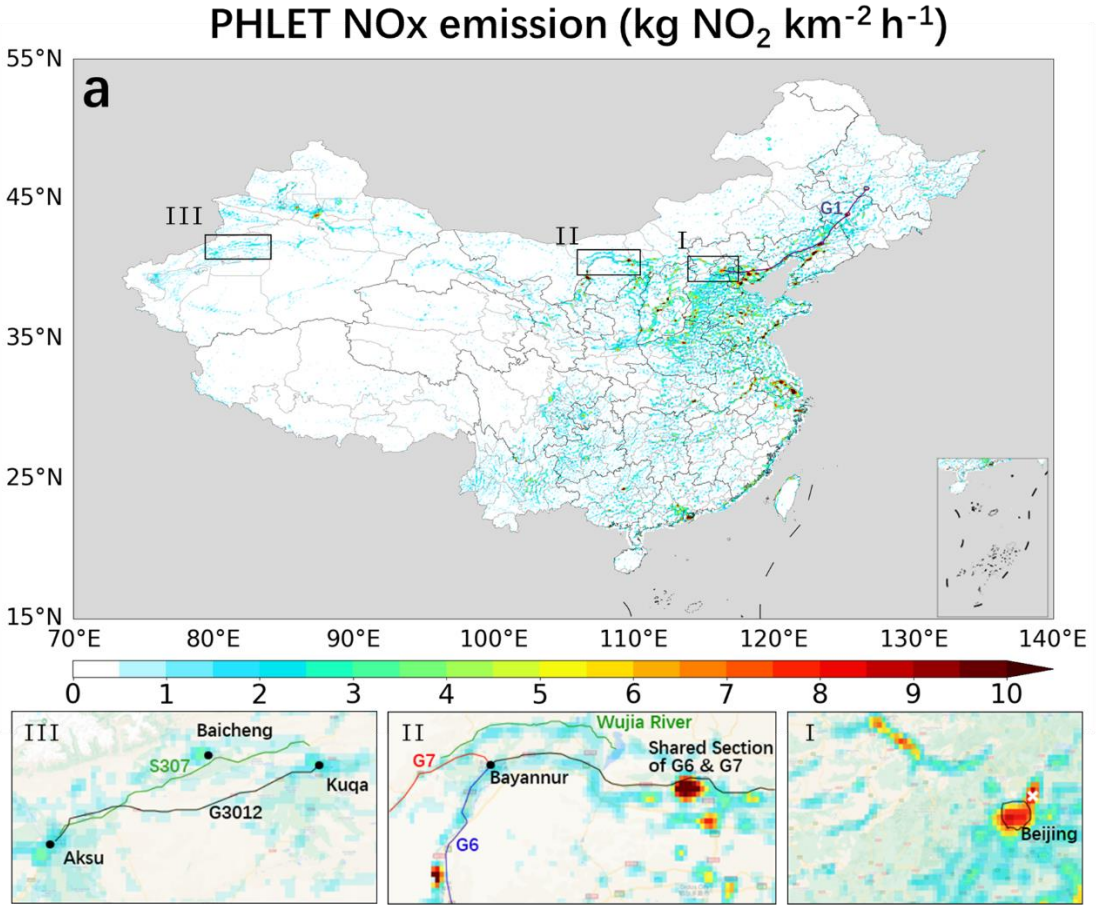


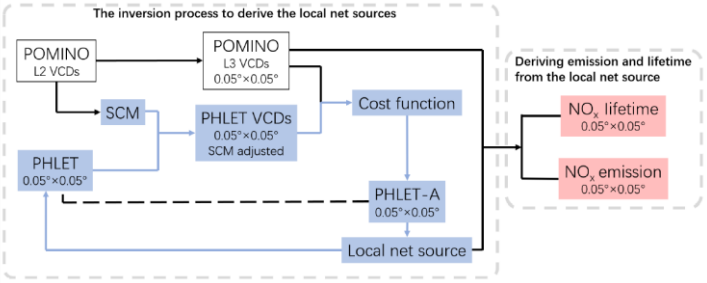
Increases of NO_2 VCD Observed from Space



Lin and McElroy, 2011

Satellite+Model Derived High-res (5 km) Emissions Reveal Biases in Bottom-up Inventories

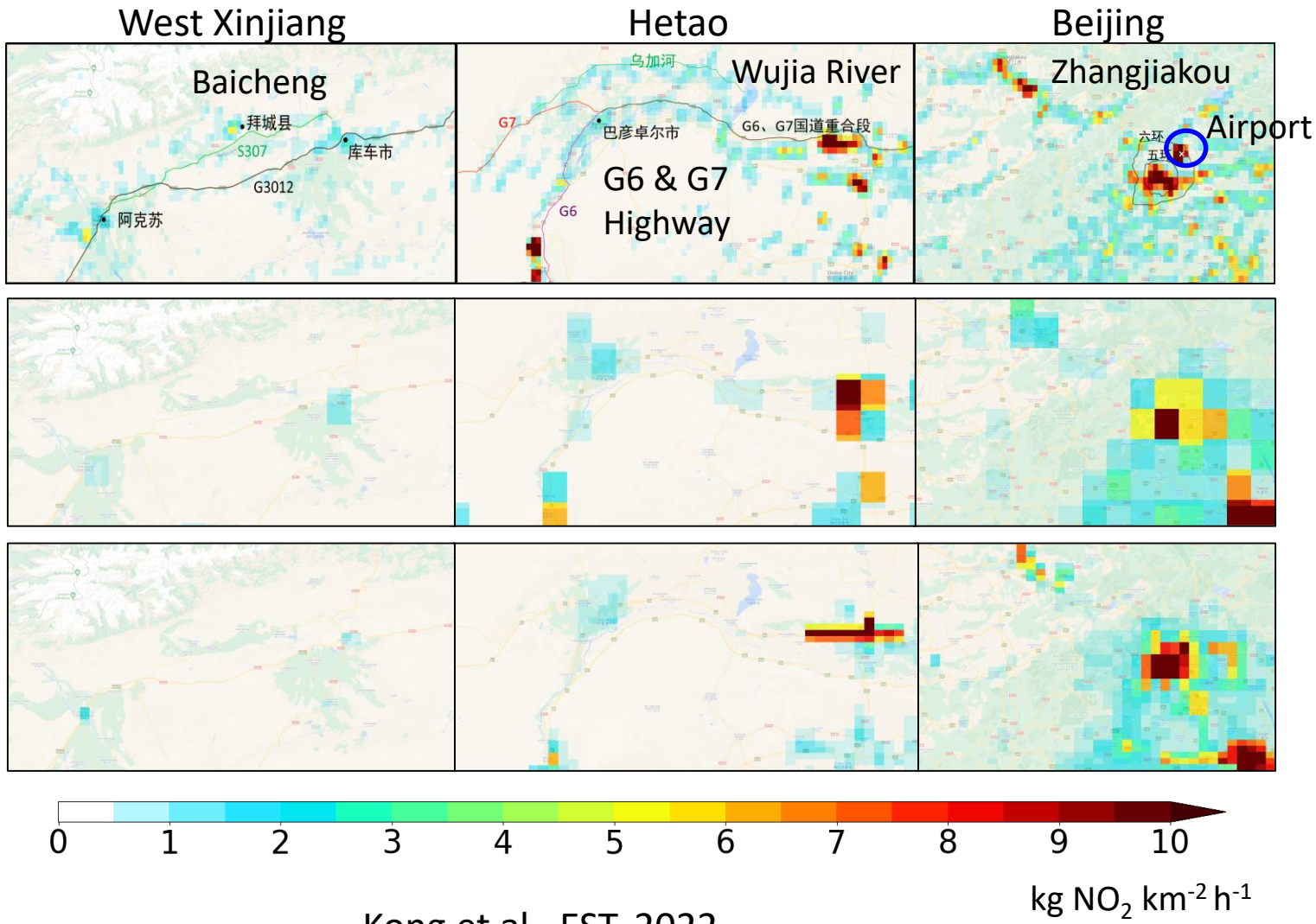




- Inversion model built from scratch
- Transport and nonlinear chemistry accounted for in emission estimate

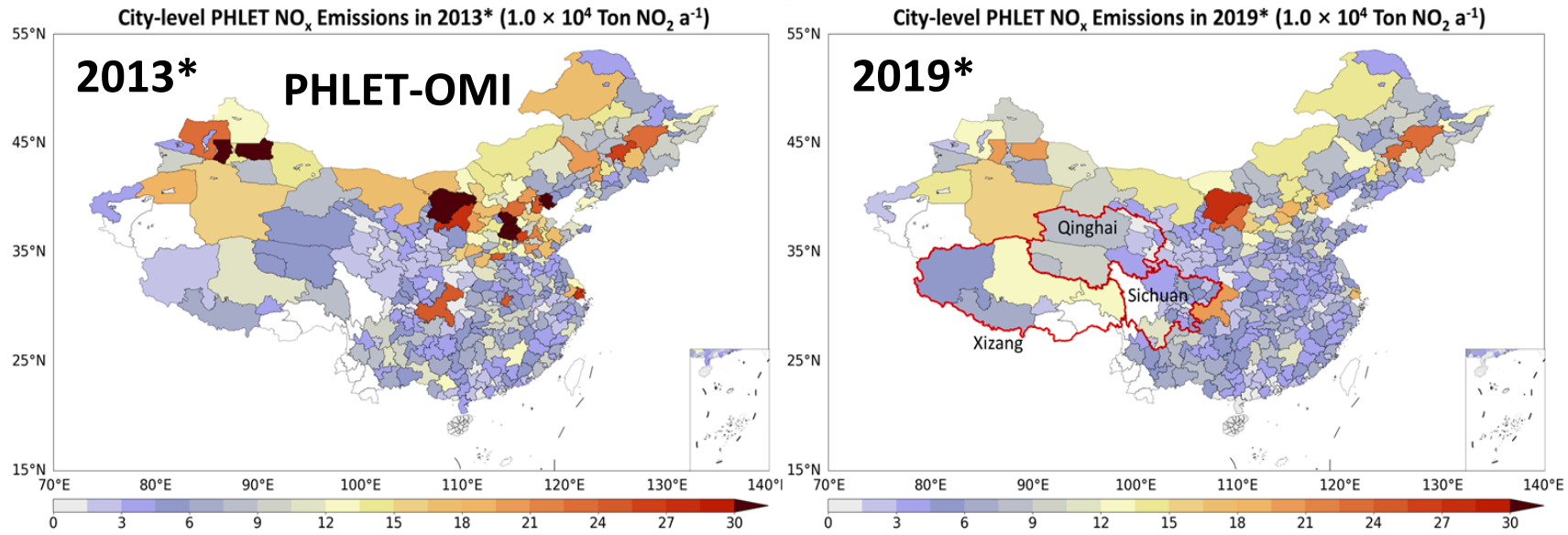
Kong et al., 2019, ACP; Kong et al., 2022, EST

High-Resolution NOx Emission Data Reveal Anthropogenic Sources Missing in Inventories

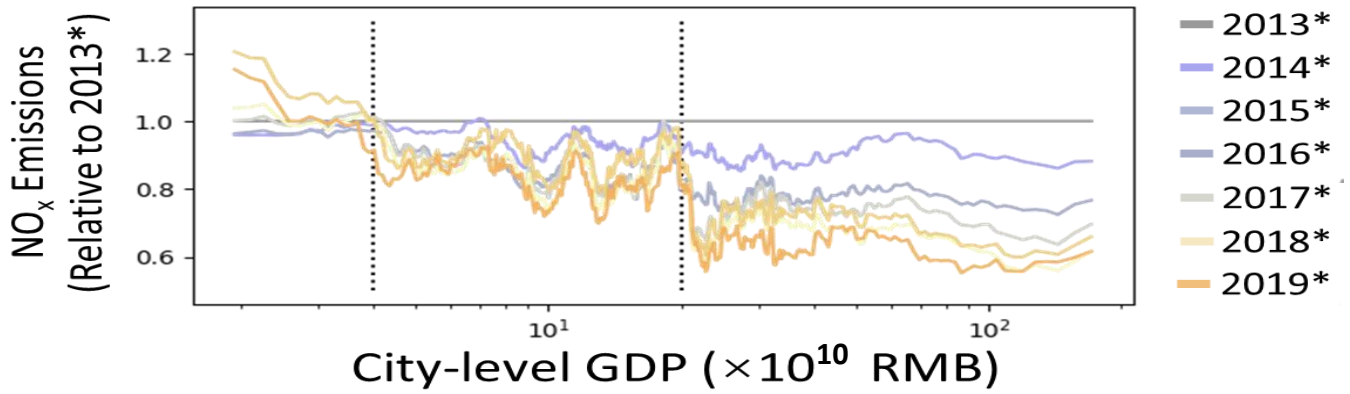


Kong et al., EST, 2022

High-Resolution NOx Emission Retrieval Data Reveal Large Inter-City Disparity in Anthro. Emis. Trends

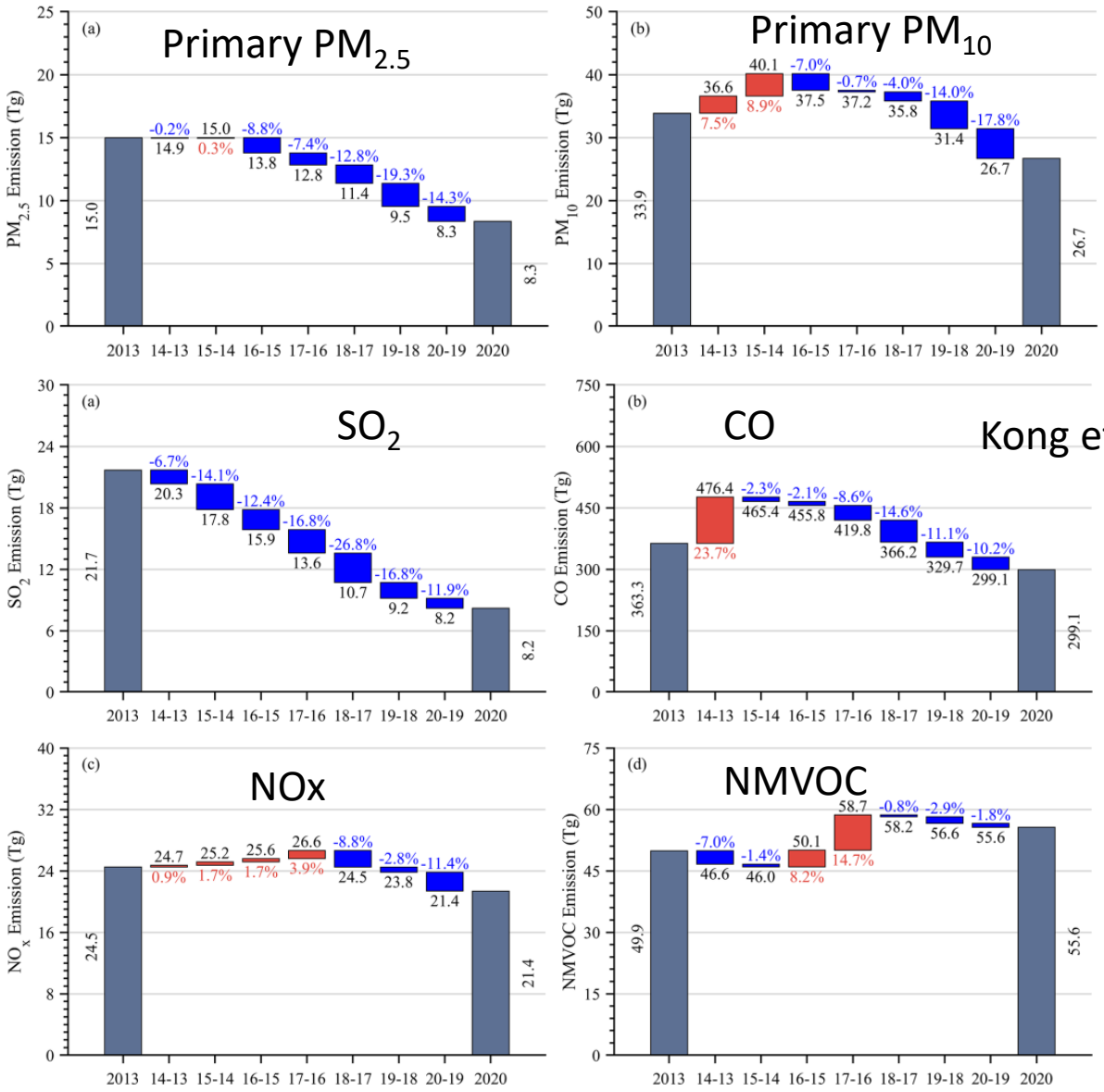


Emission change versus Economic volume



Kong et al., submitted

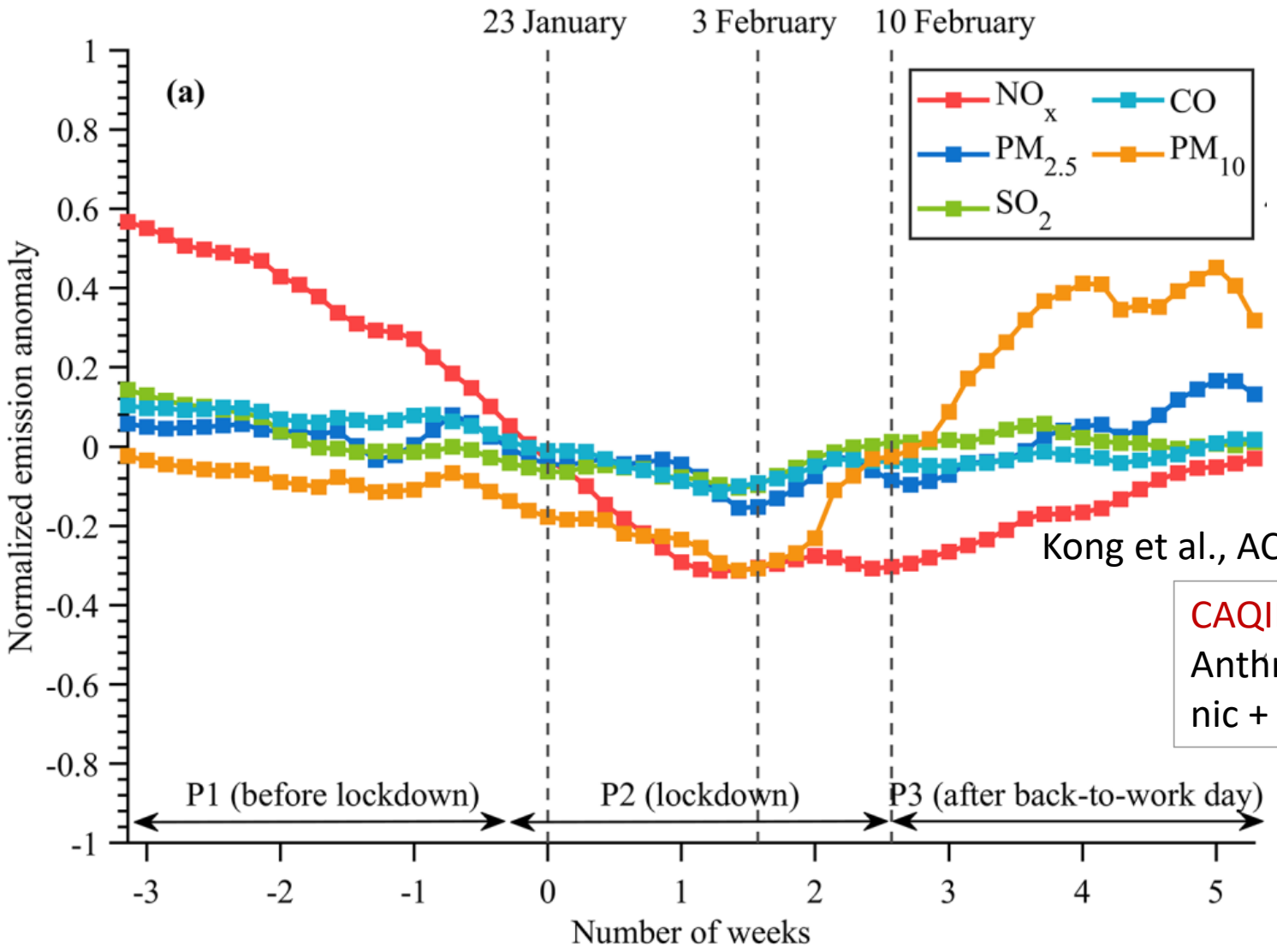
Chinese Emission Trends over 2013–2020 Constrained from Near Surface Concentration Measurements



Kong et al., ESSD, 2024

CAQIEI data: Anthropogenic + natural

Impacts of COVID-19 on Chinese Emissions Constrained from Surface Concentration Measurements

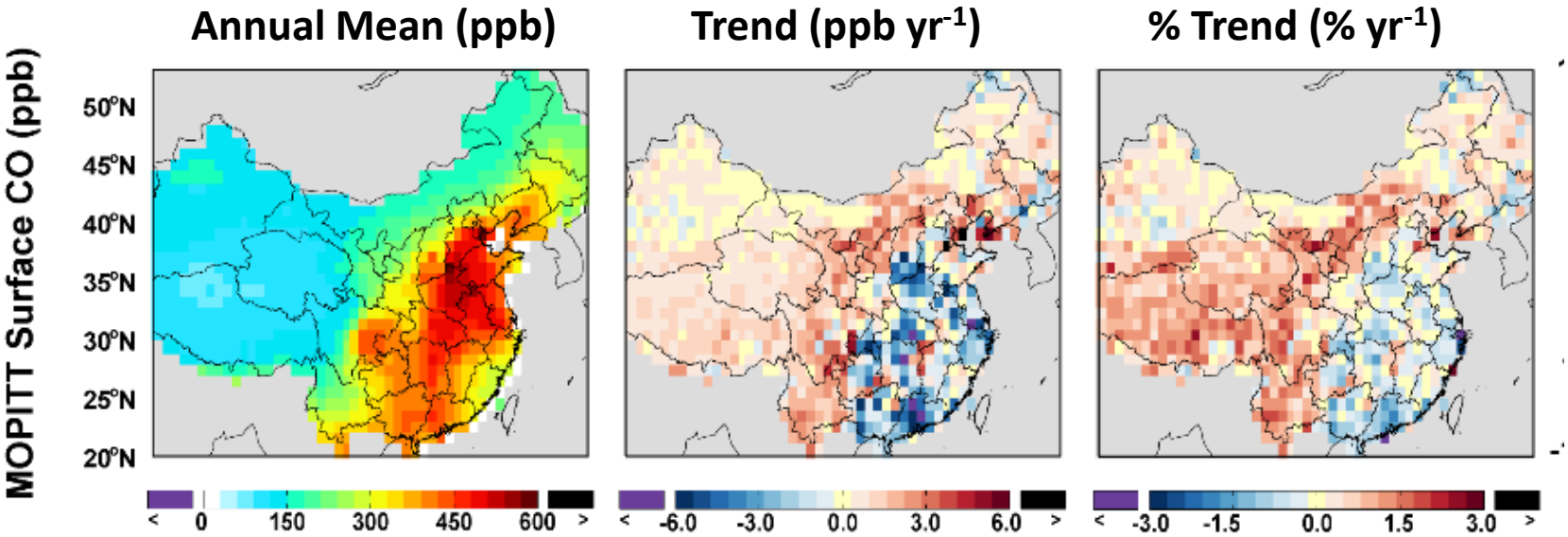


Kong et al., ACP, 2023

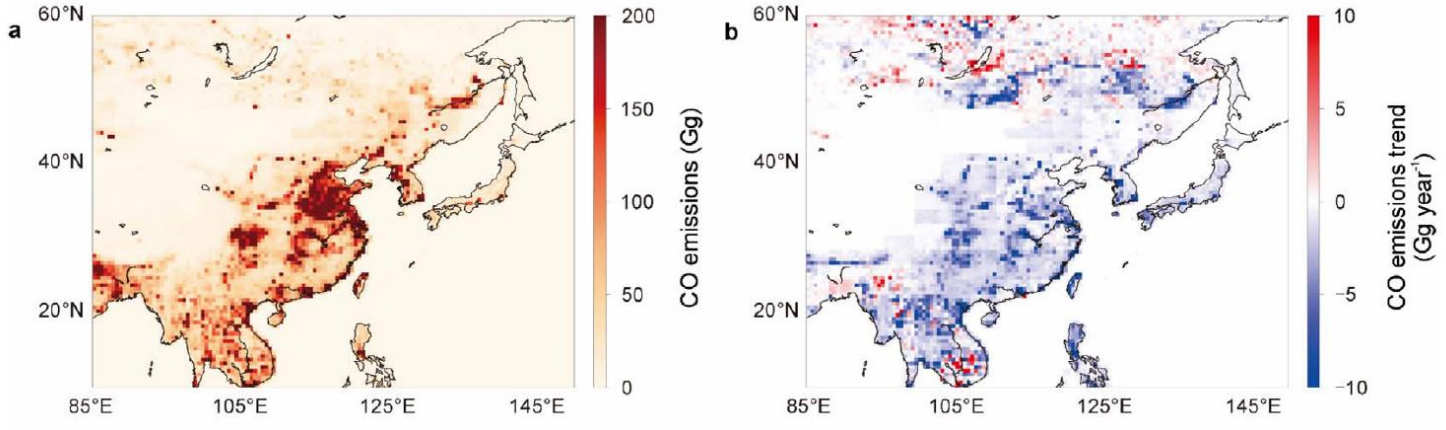
CAQIEI data: Anthropogenic + natural

Changes in CO over East Asia

CO mixing ratio over 2004-2012 (Yan et al., in prep)

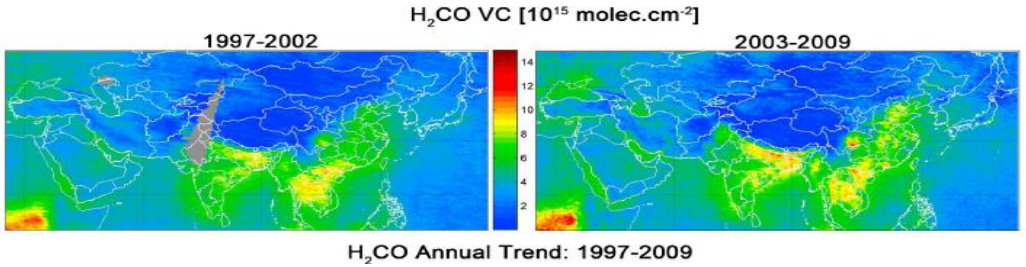


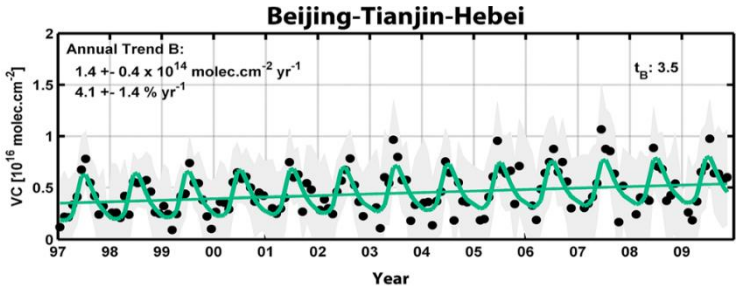
CO emissions over 2005-2016 based on MOPITT v7 (Zheng et al., ERL, 2018)



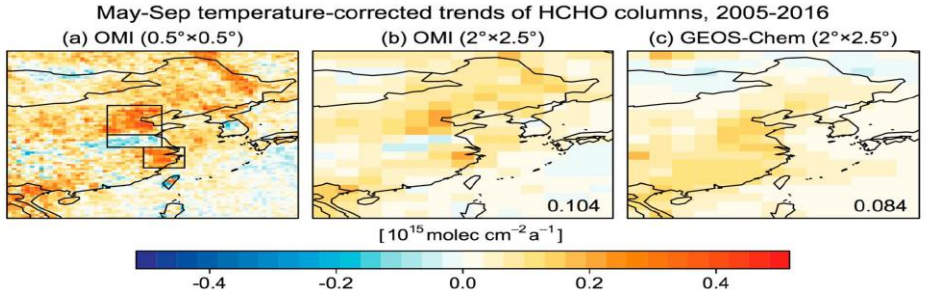
Trends of VCDs of HCHO in Asia: 1997 – 2009

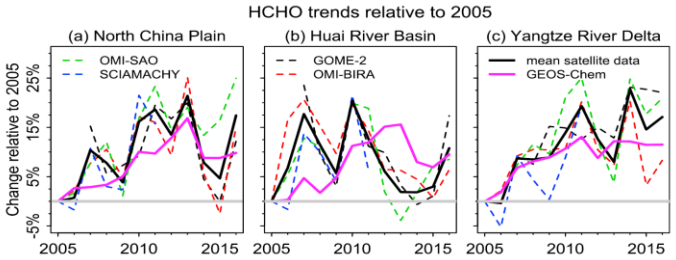
OMI VCD by BIRA (De Smedt et al., 2010 ACP)



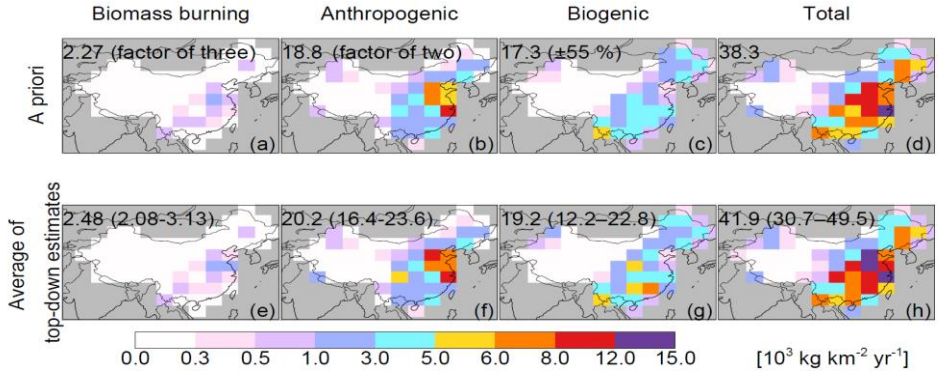


Multiple VCD products (Shen et al., 2019 GRL)





Emission constraint for 2007 based on OMI & GOME-2A HCHO and CHOCHO data (Cao et al., 2018 ACP)

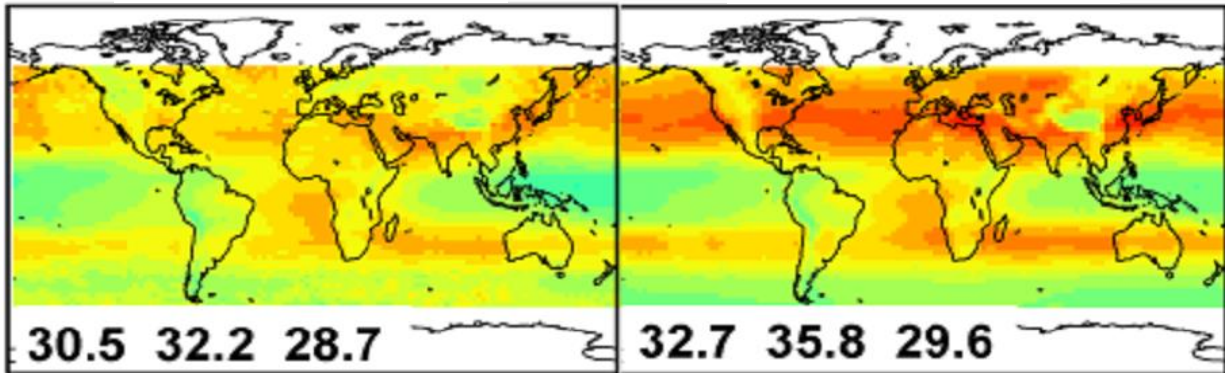


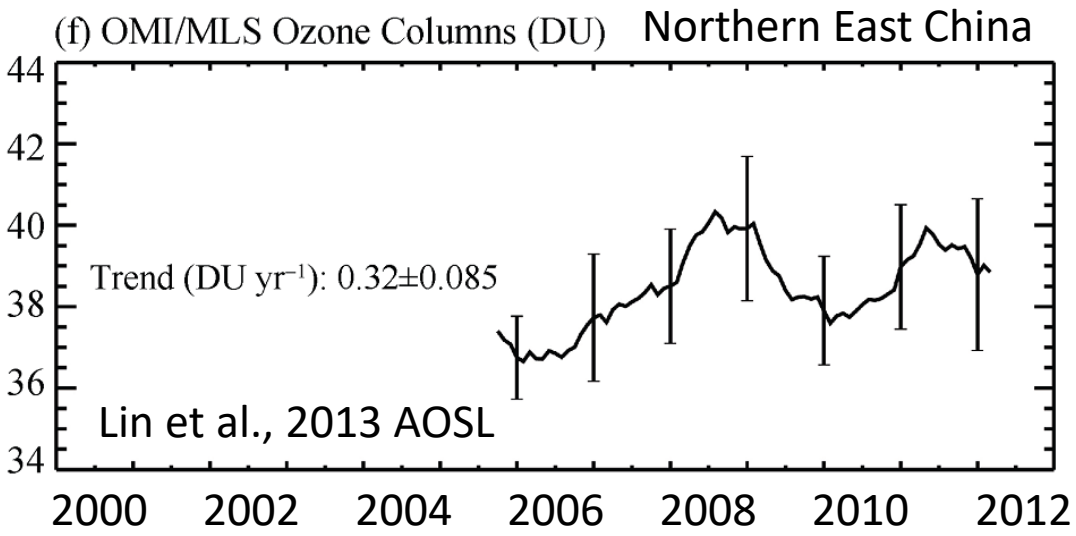
OMI-retrieved VCDs of Tropospheric Ozone

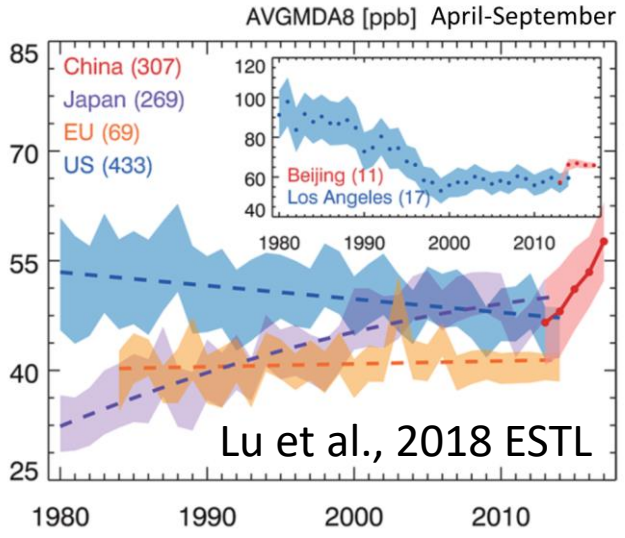
Annual mean in 2009 (DU) (Yan et al., 2016 ACP)

TCO, OMI/MLS

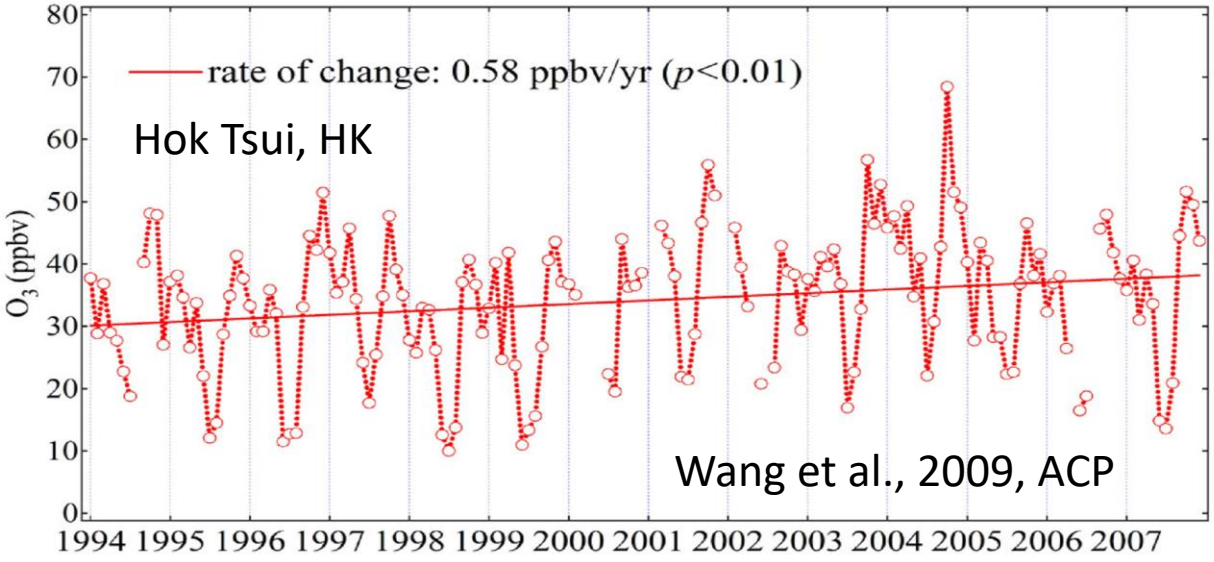
TCO, OMI/Liu

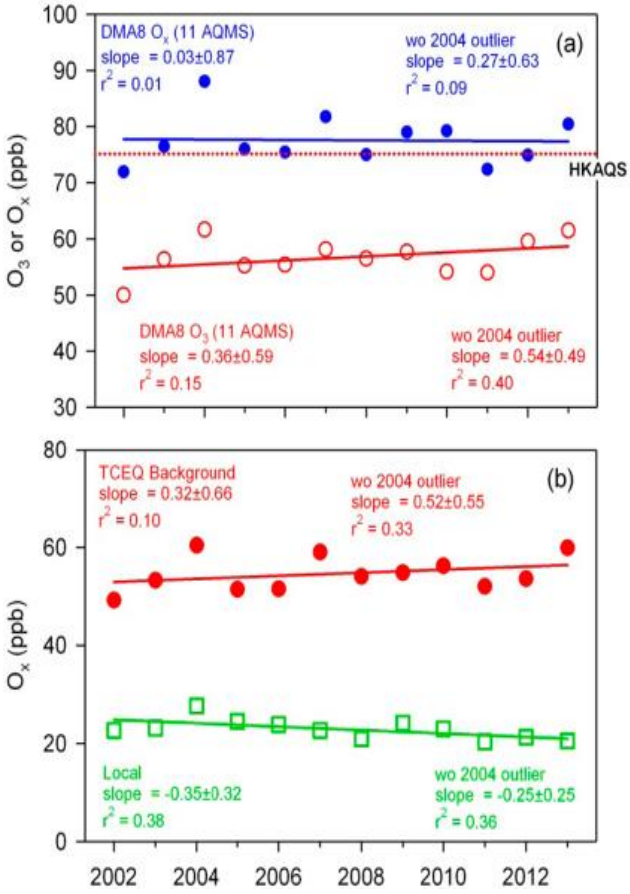






Background O_3 Concentrations are Increasing

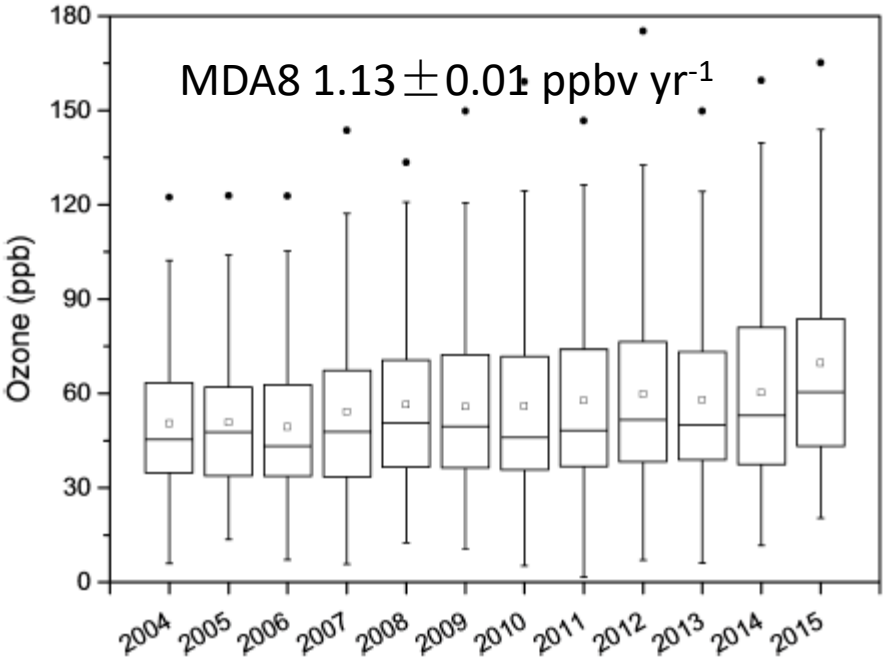




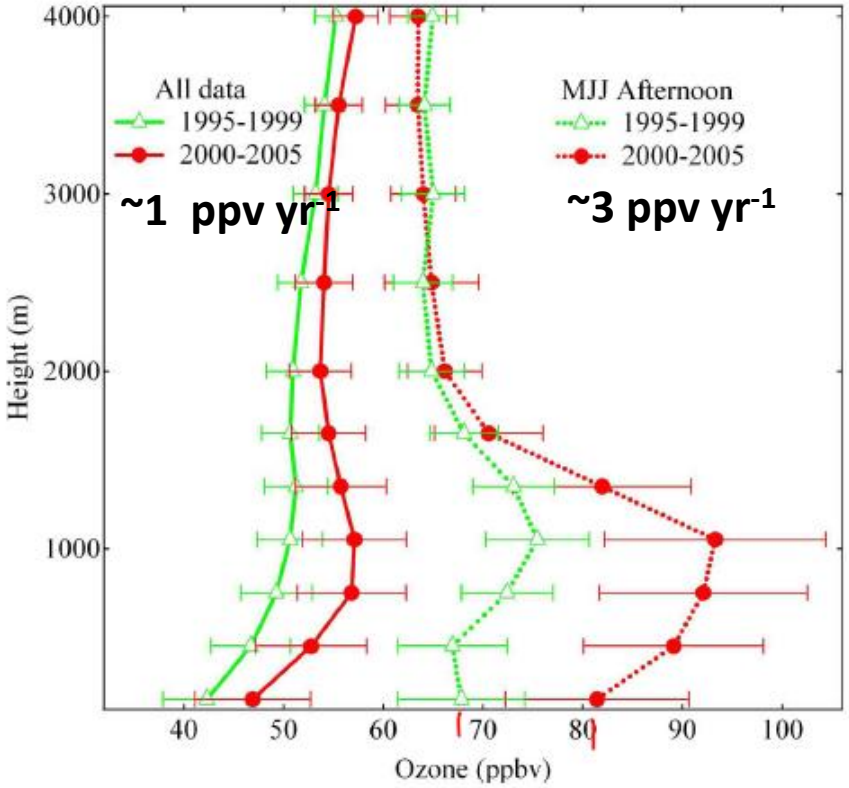
Xue et al., 2014, EST

Growing O_3 Pollution over Beijing

Shangdianzi, regional background



Beijing airport, MOZAIC

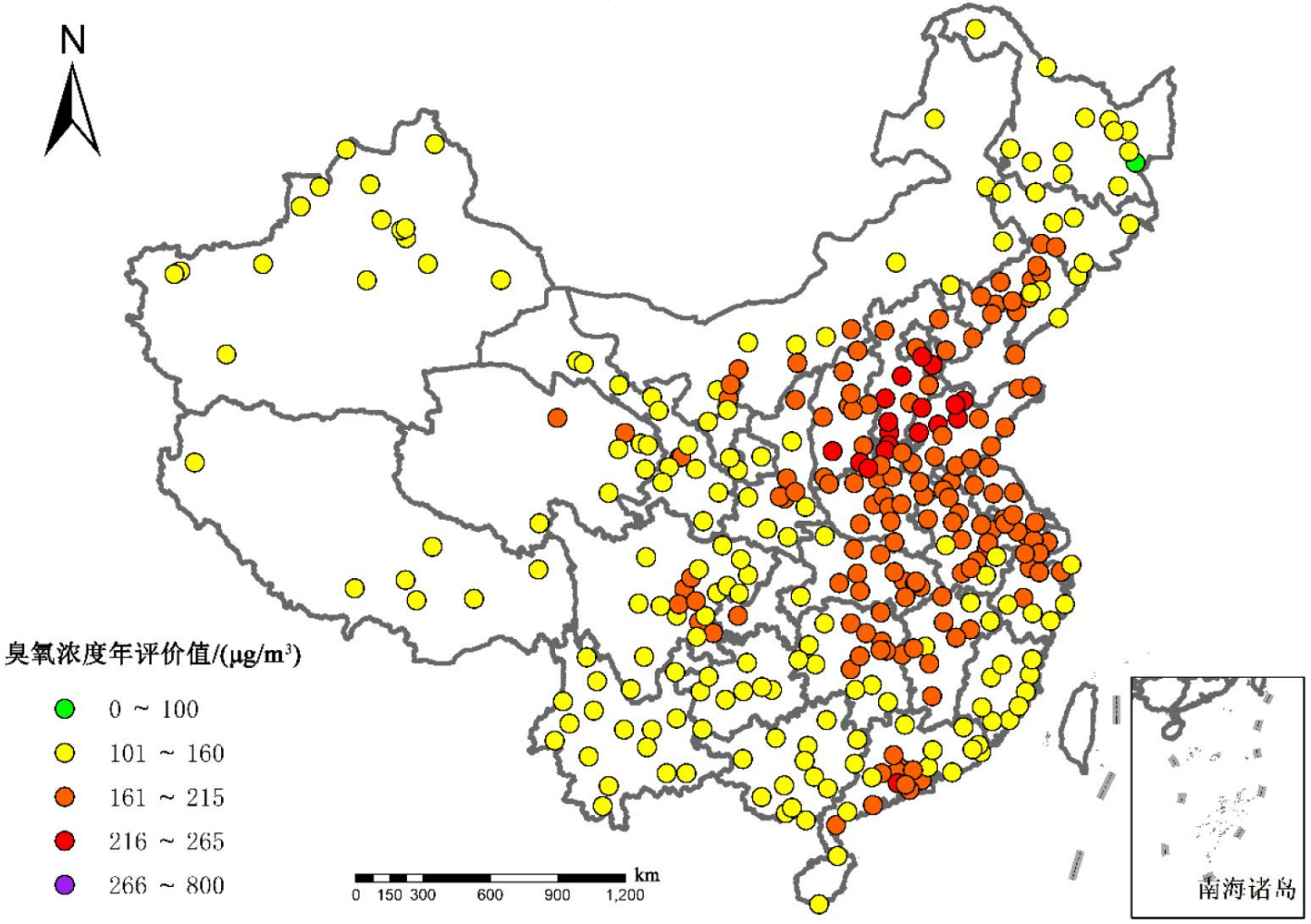


Emission changes in VOCs dominated

Ma et al., 2016; Ding et al., 2008, ACP

Severe Ozone Pollution over China

2019年，337个城市，MDA8臭氧年评价值



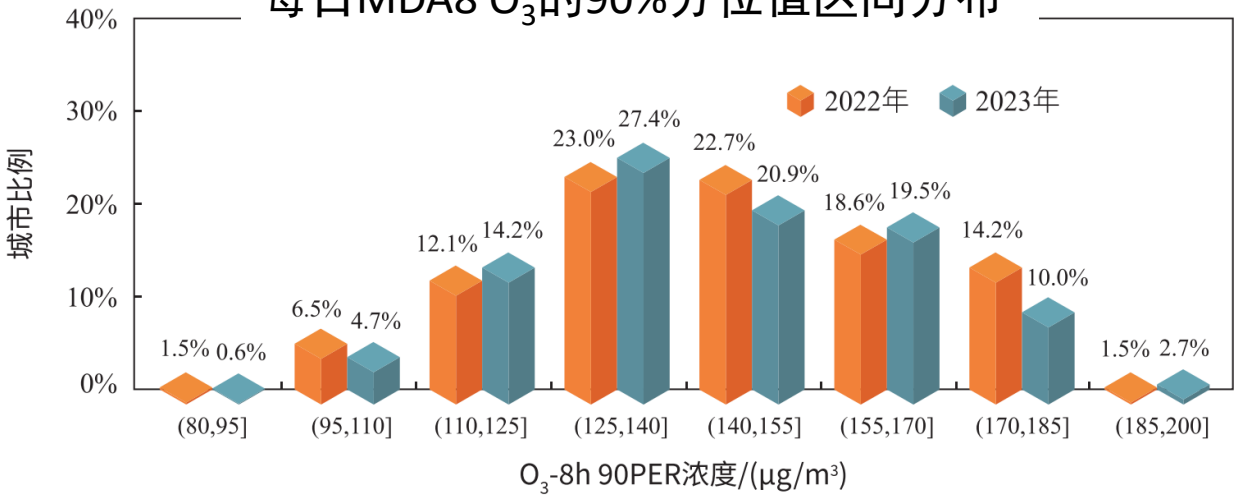
中国大气臭氧污染防治蓝皮书（2020）

Severe Ozone Pollution over China

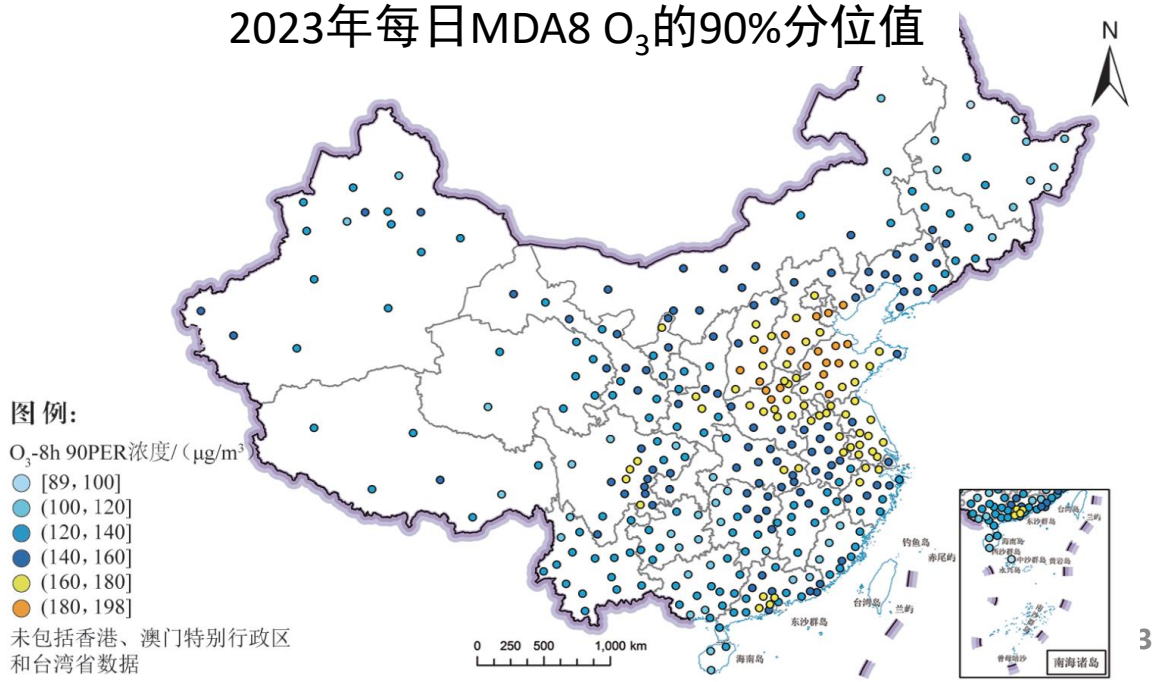
中国生态环境公报2023

- 2023年每日MDA8 O_3的90%分位值的平均值为144 μg/m³，比2022年降低0.7%
- 2022-2024年稳定在144-145 μg/m³
- 华北、长三角、珠三角、成渝地区、关中平原的污染状况尤其突出
- 现有观测数据主要覆盖城镇区域

每日MDA8 O_3的90%分位值区间分布

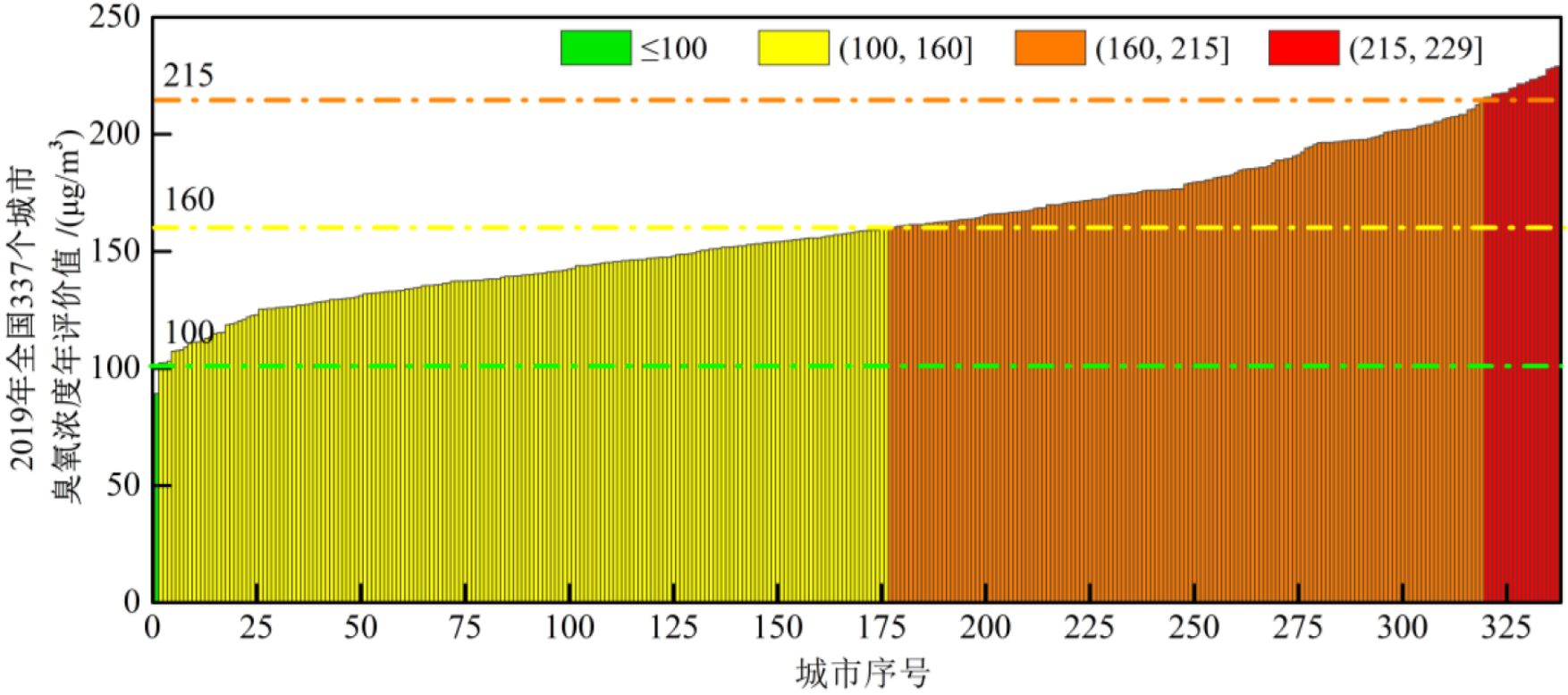


2023年每日MDA8 O_3的90%分位值



Severe Ozone Pollution over China

2019年，337个城市，MDA8臭氧年评价值

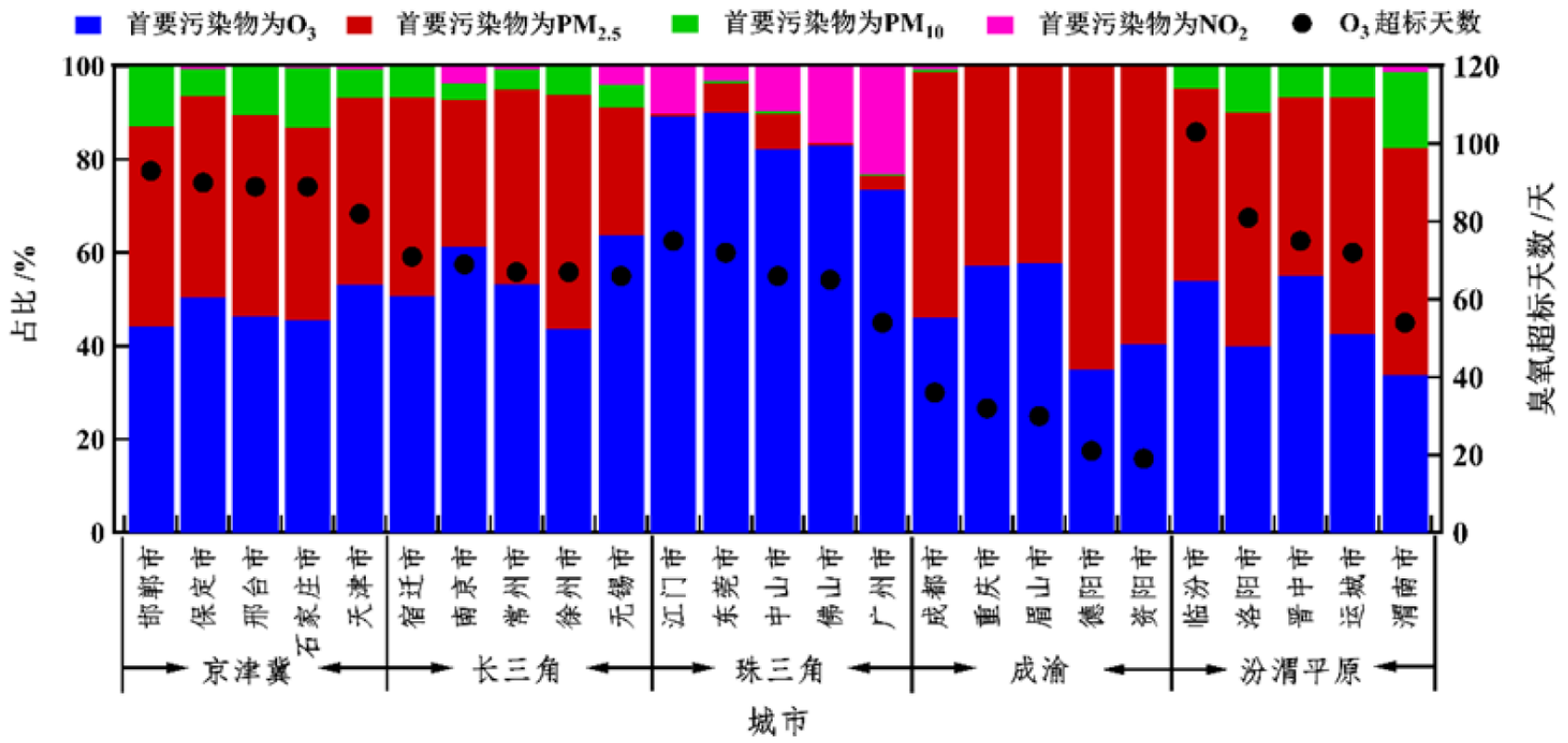


按照我国《环境空气质量评 价 技 术 规 范 （ 试 行 ） 》（HJ663—2013），采用臭氧日最大 8 小时滑动平均值的第 90百分位数（MDA8-90）进行臭氧年评价。

中国大气臭氧污染防治蓝皮书（2020）

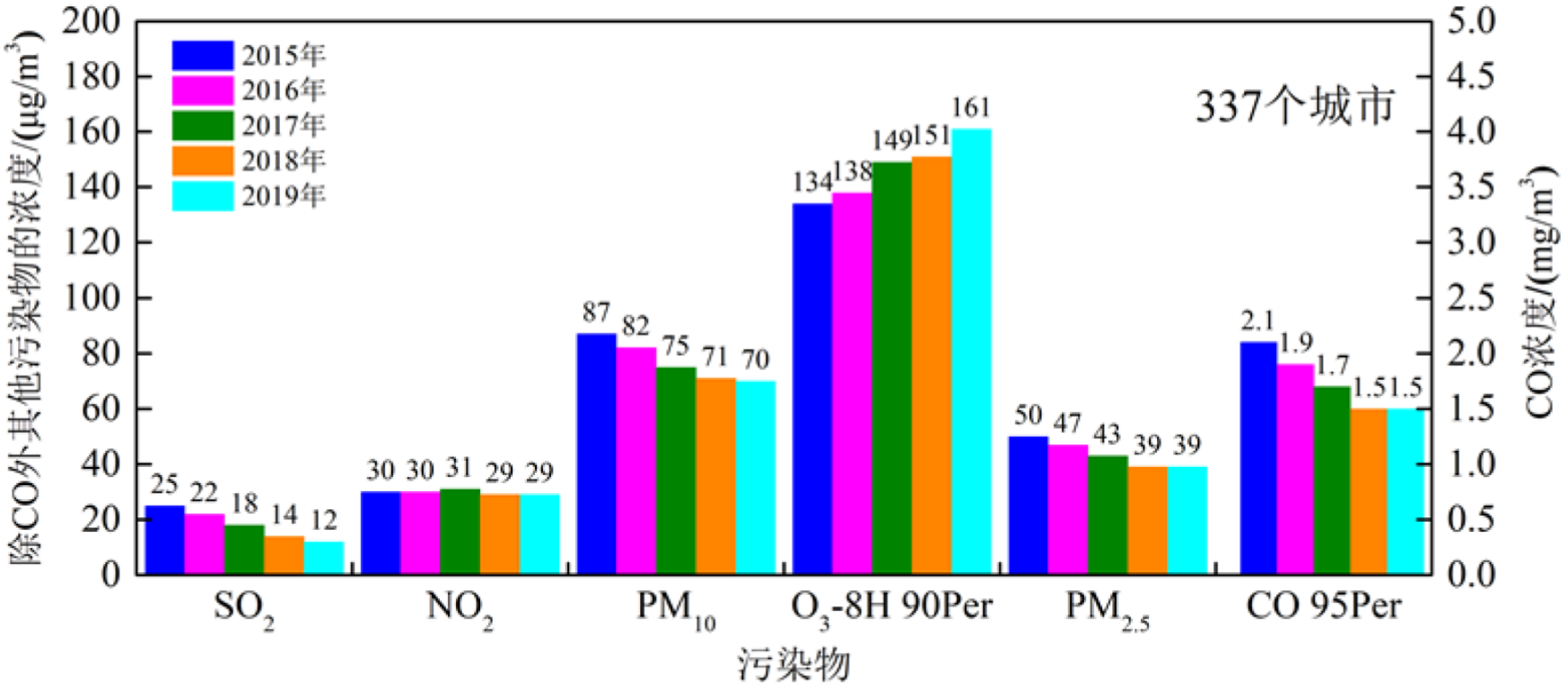
Severe Ozone Pollution over China

2019年，337个城市，首要污染物



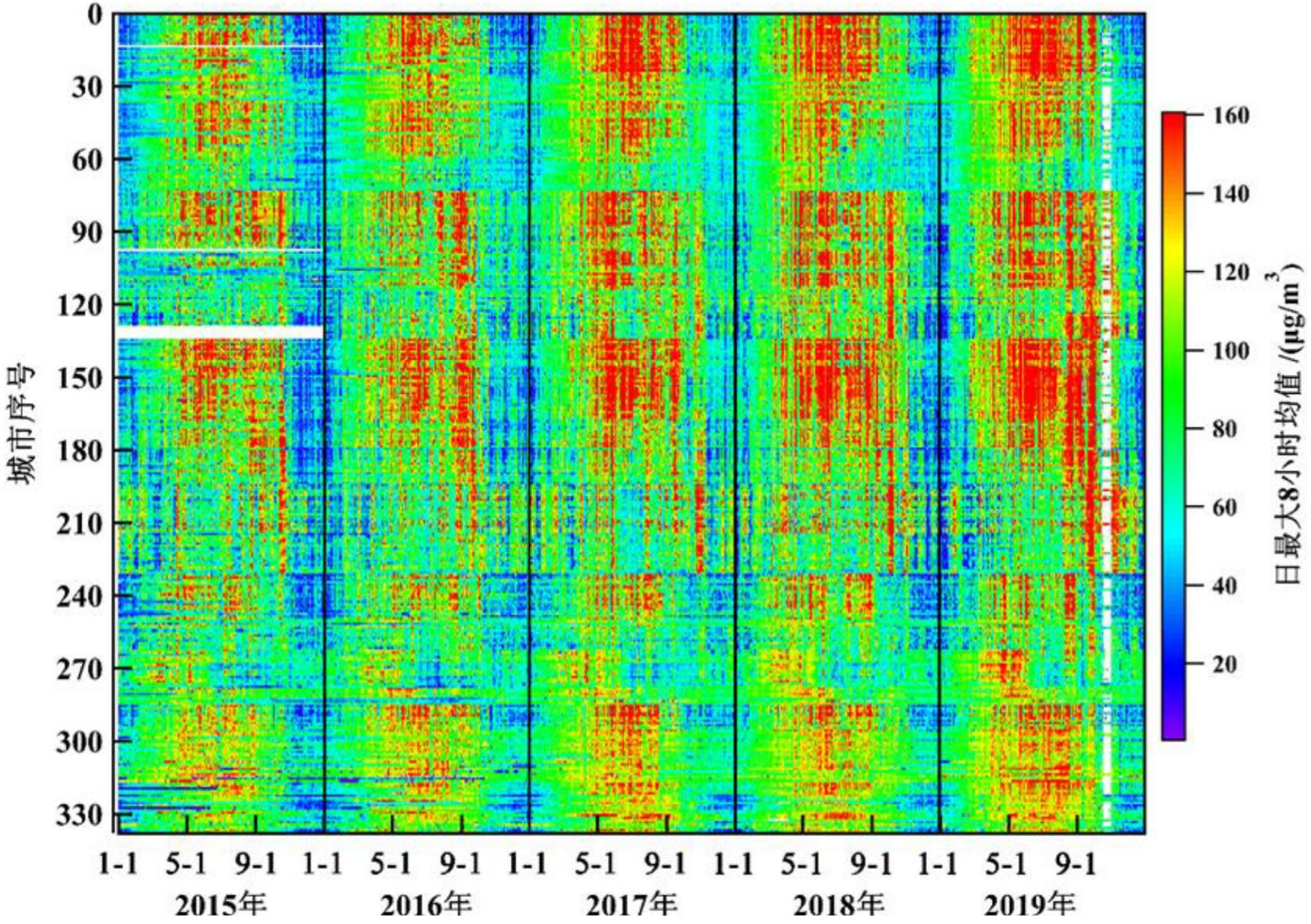
中国大气臭氧污染防治蓝皮书（2020）

China's Ozone Pollution Trend: 2015-2019



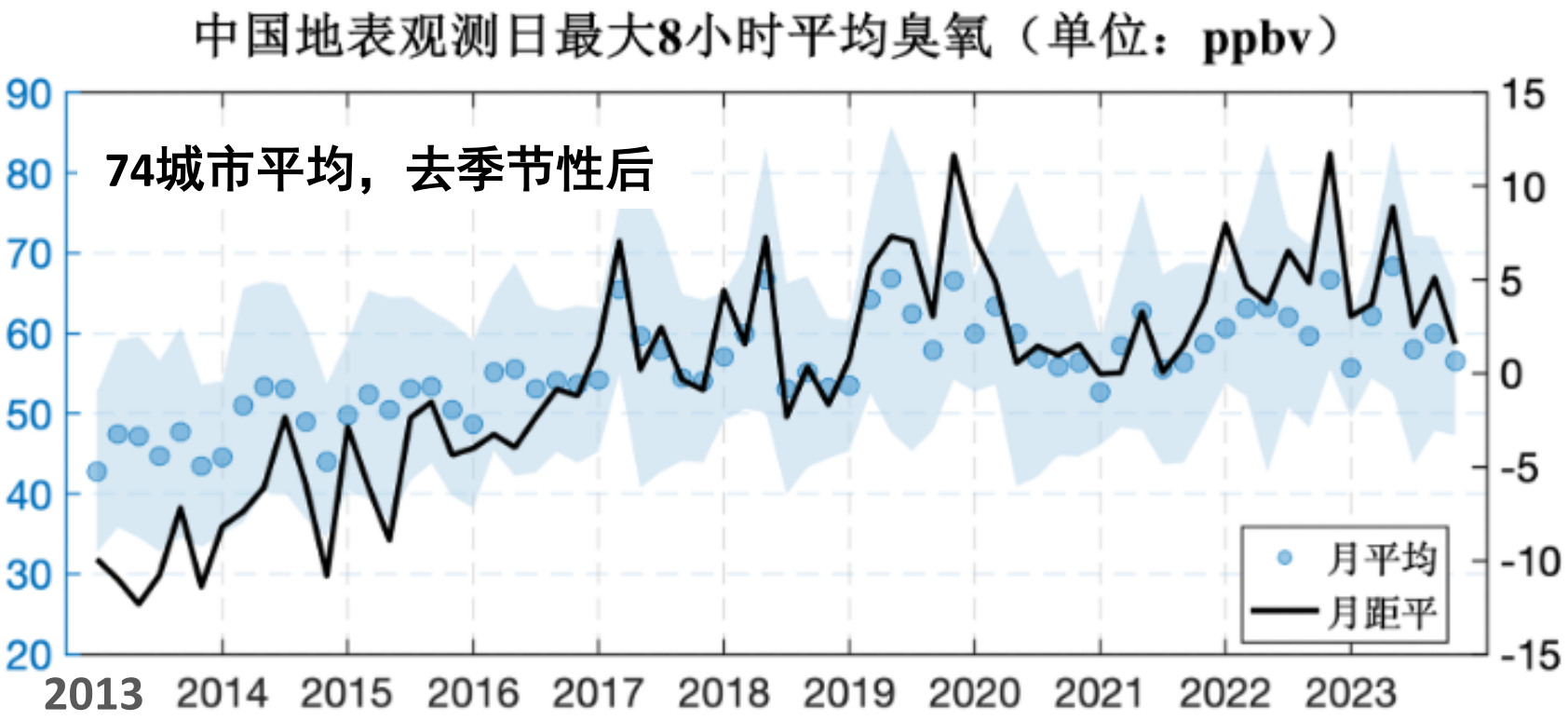
中国大气臭氧污染防治蓝皮书（2020）

China's Ozone Pollution Trend: 2015-2019



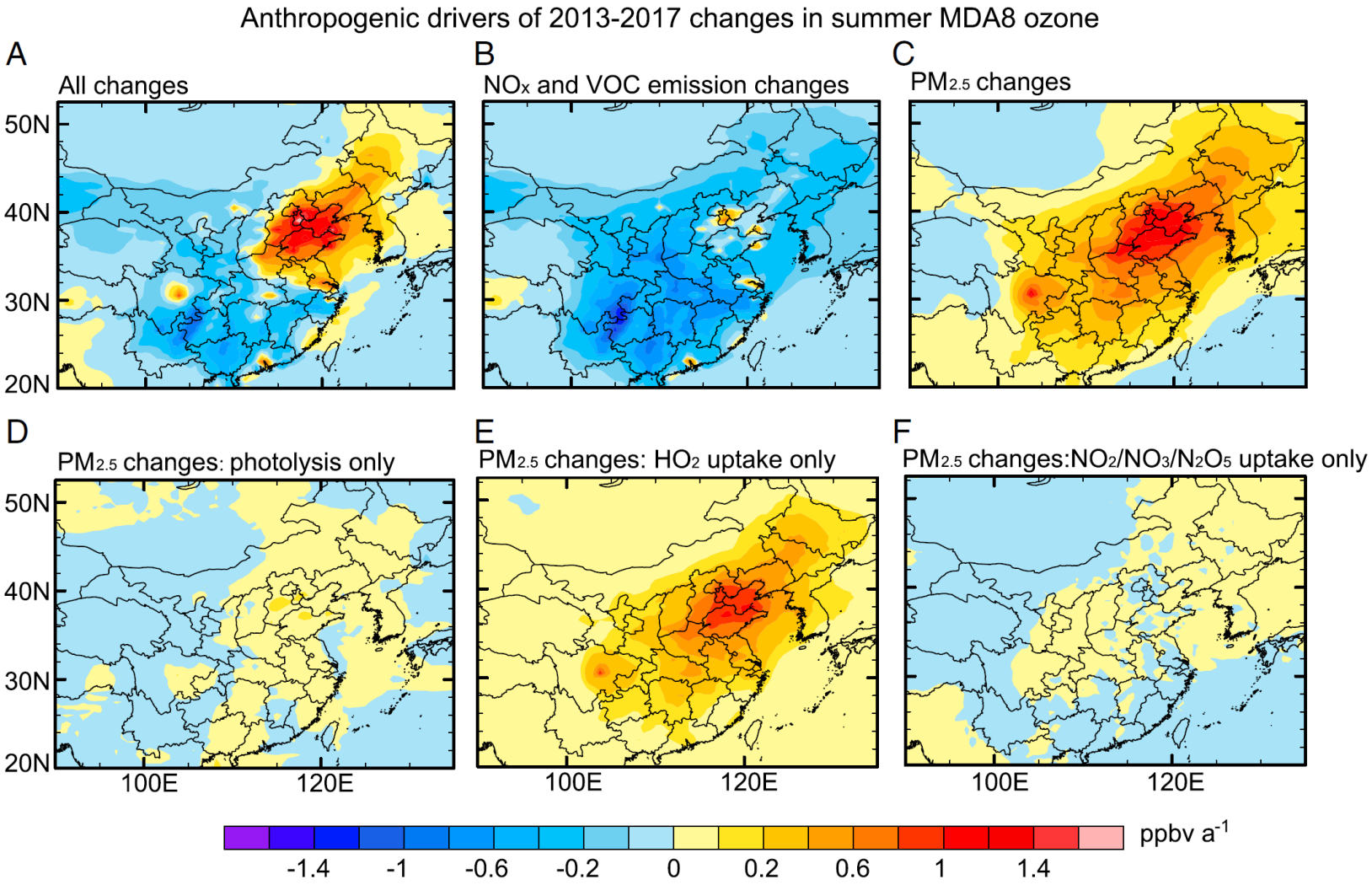
中国大气臭氧污染防治蓝皮书（2020）

China’s Ozone Pollution Trend: 2013-2023



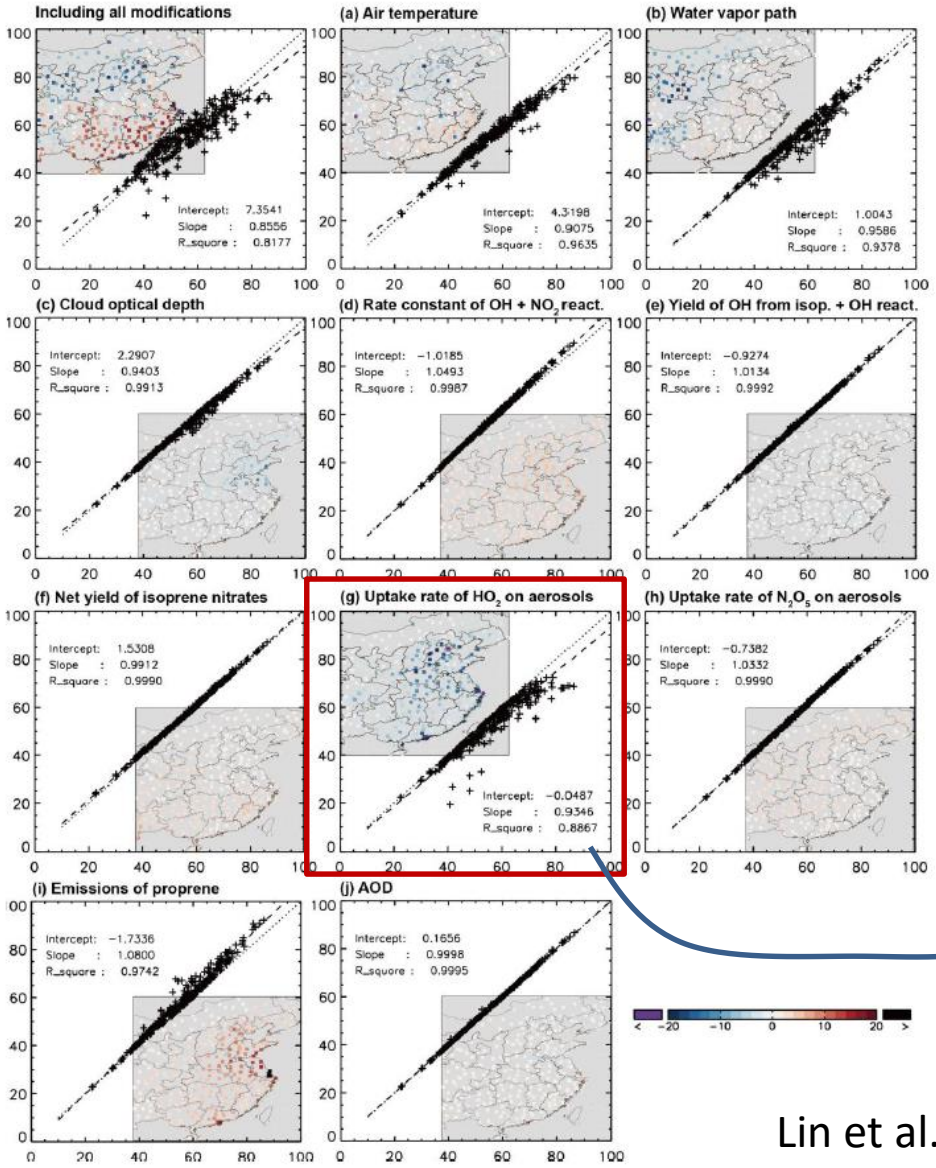
来源：叶兴沛

Controversy in Drivers of Ozone Trend over China



Li et al., 2019, PNAS

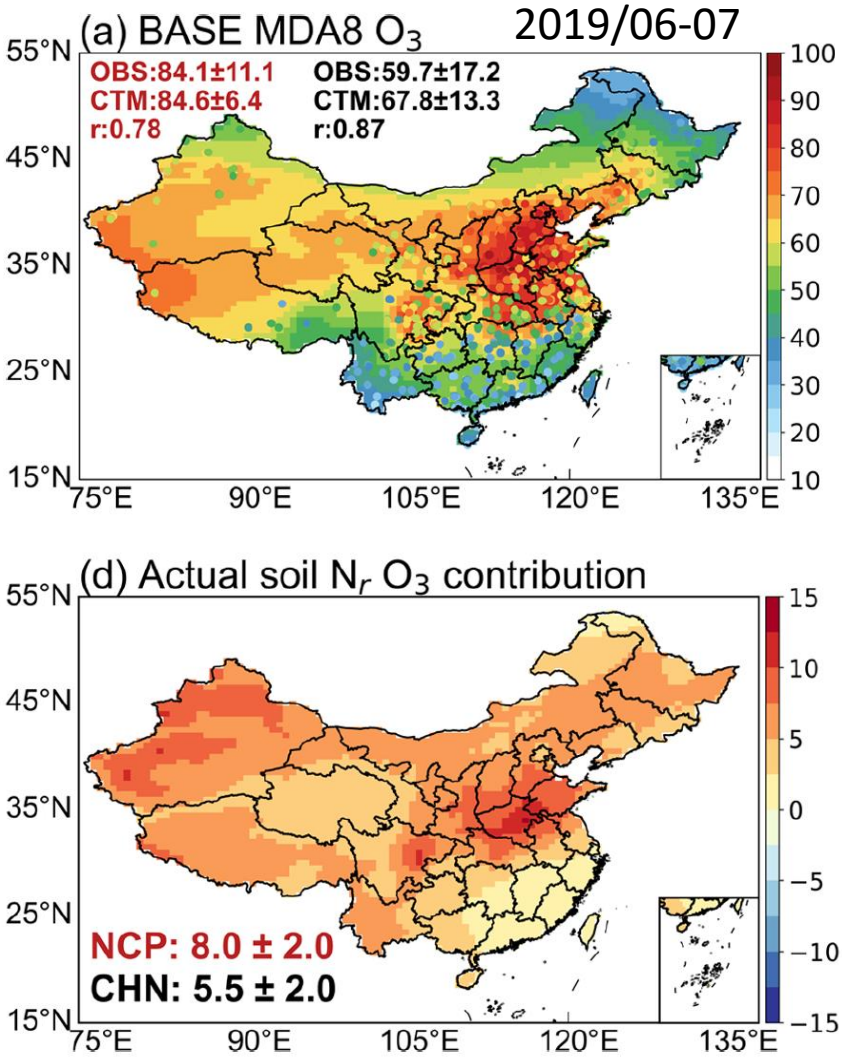
Controversy in Drivers of Ozone Trend over China

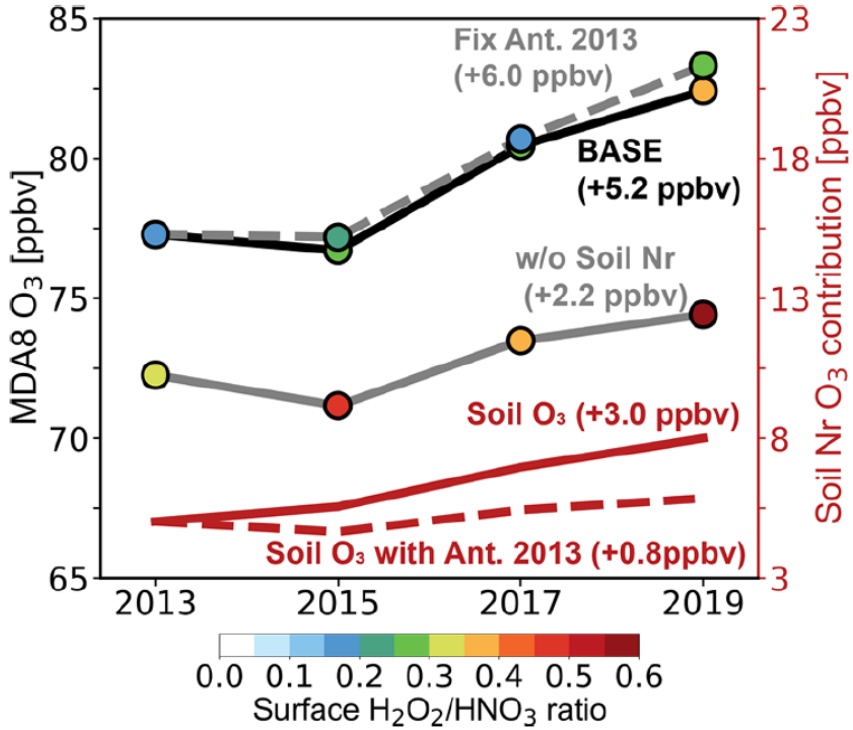


Uptake rate from 0.07 to 0.2

Lin et al., 2012, ACPD

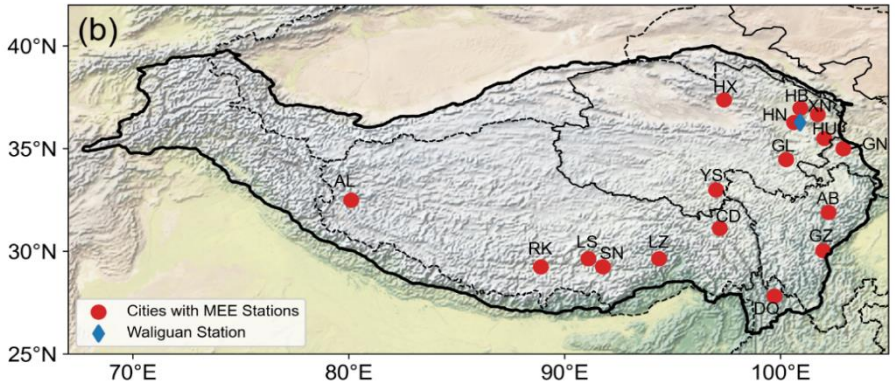
Drivers of Ozone Trend over China



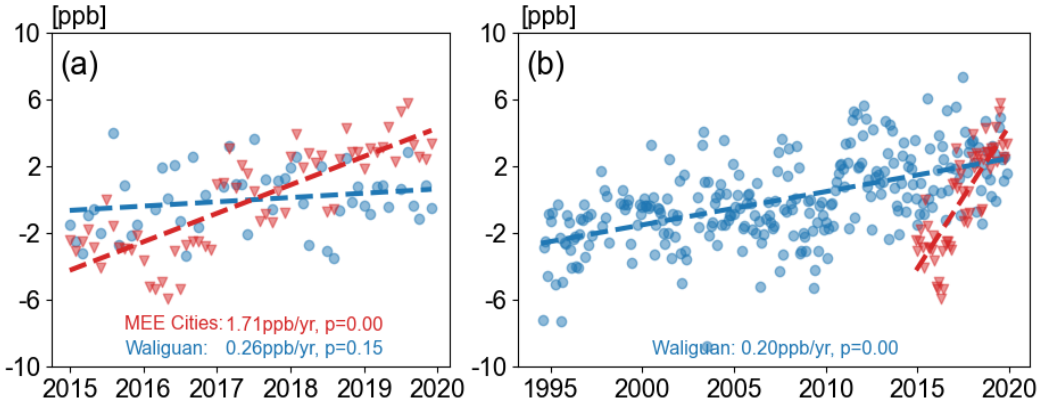


Tan et al., 2023, EST

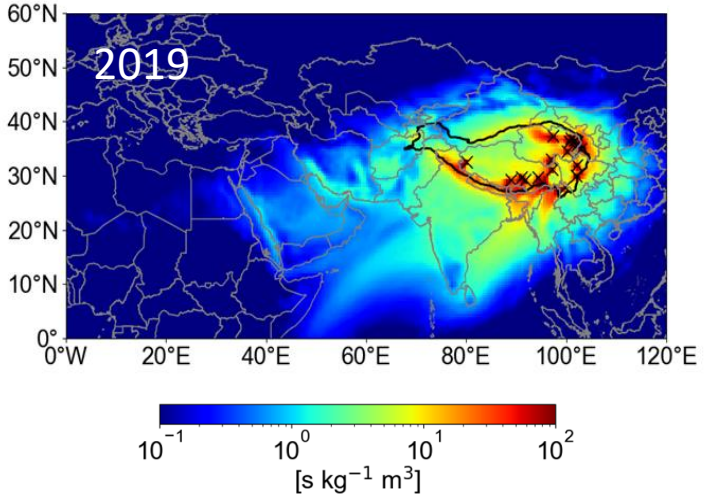
Rapid Ozone Growth over Tibet Plateau Caused by Local and Nonlocal Sources



Deseasonalized ozone growth

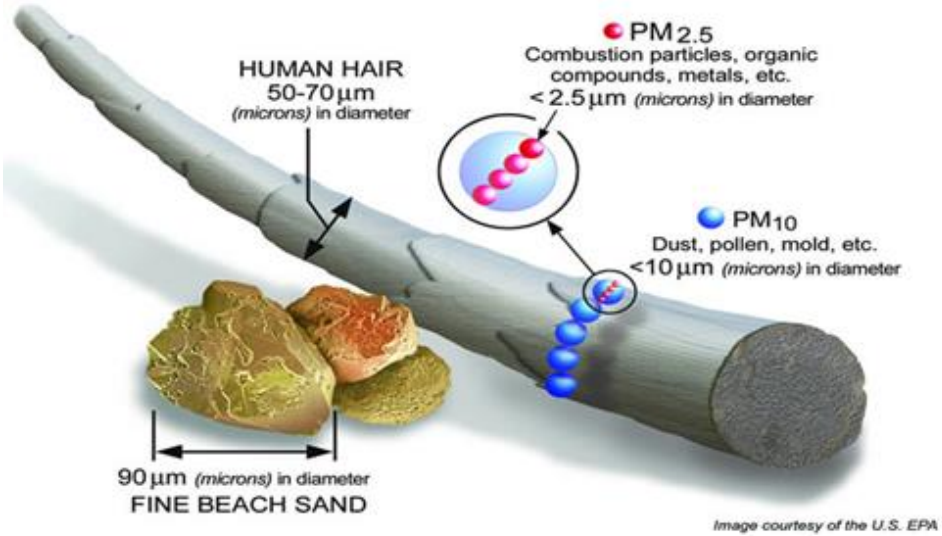


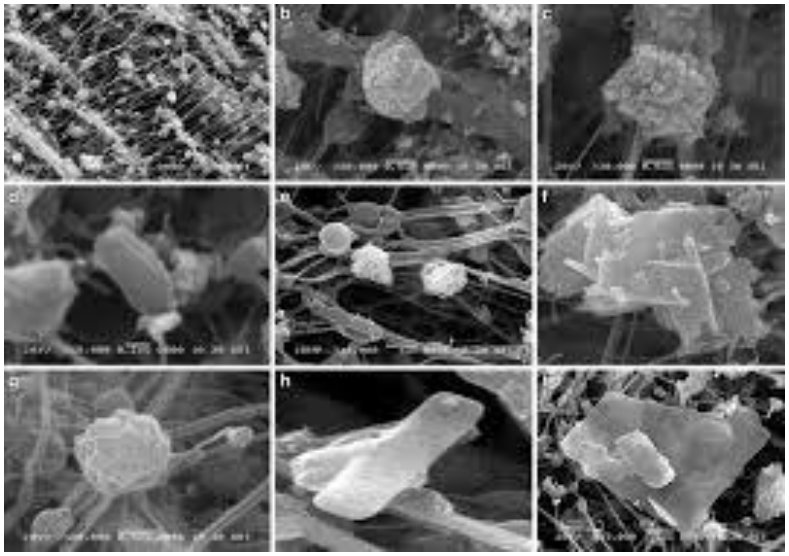
Quantity Emitted into Retroplume (QNR) for NOx

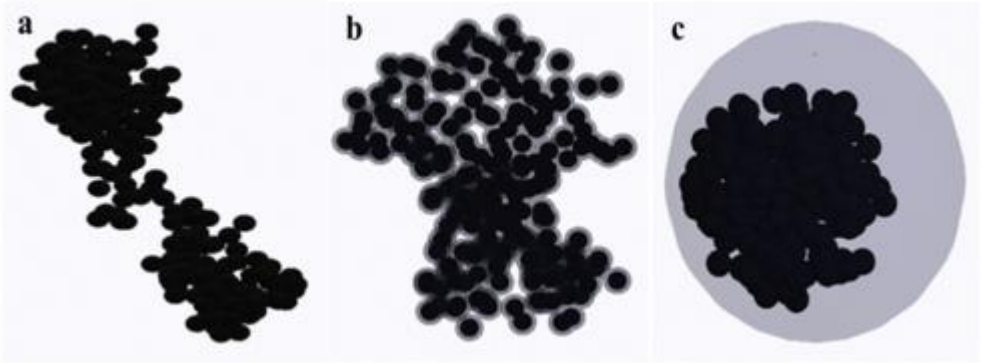


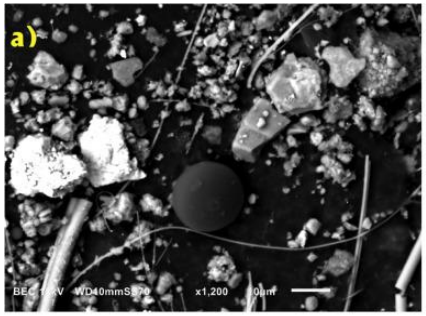
Xu et al., ACP, submitted

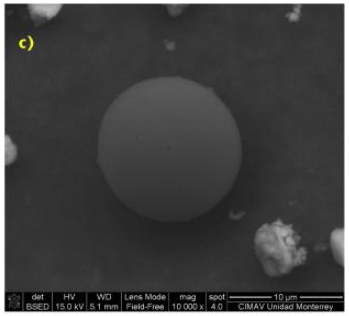
Morphology of Particulate Matter

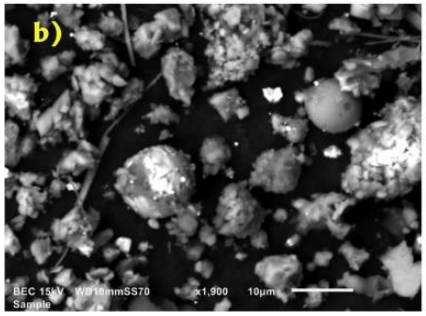


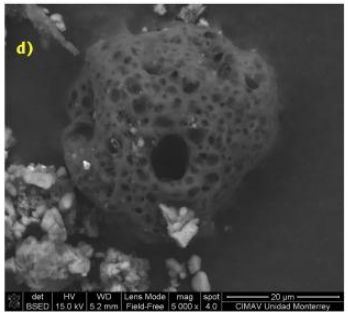




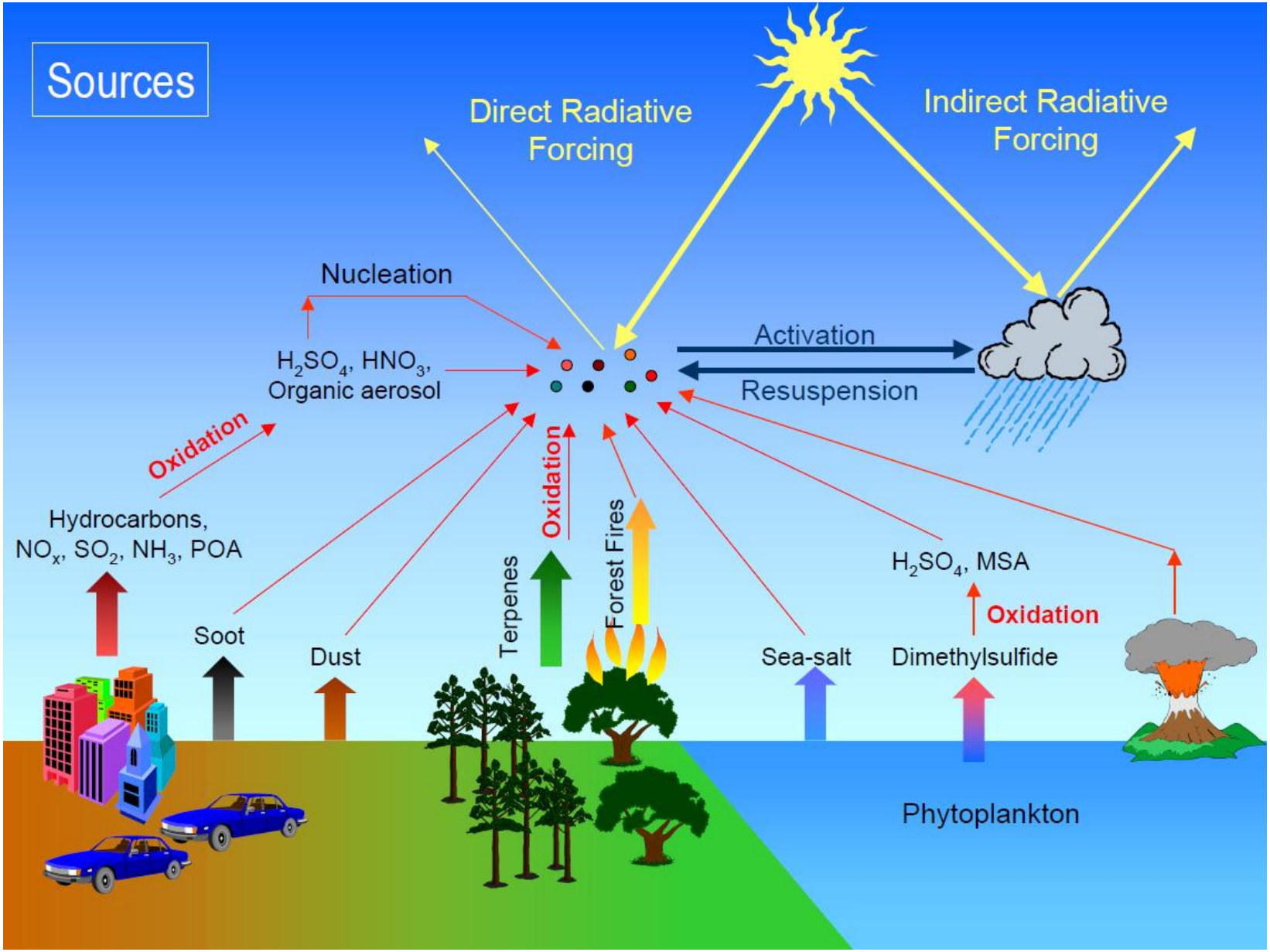








PM Sources, Sinks, and Transformation



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

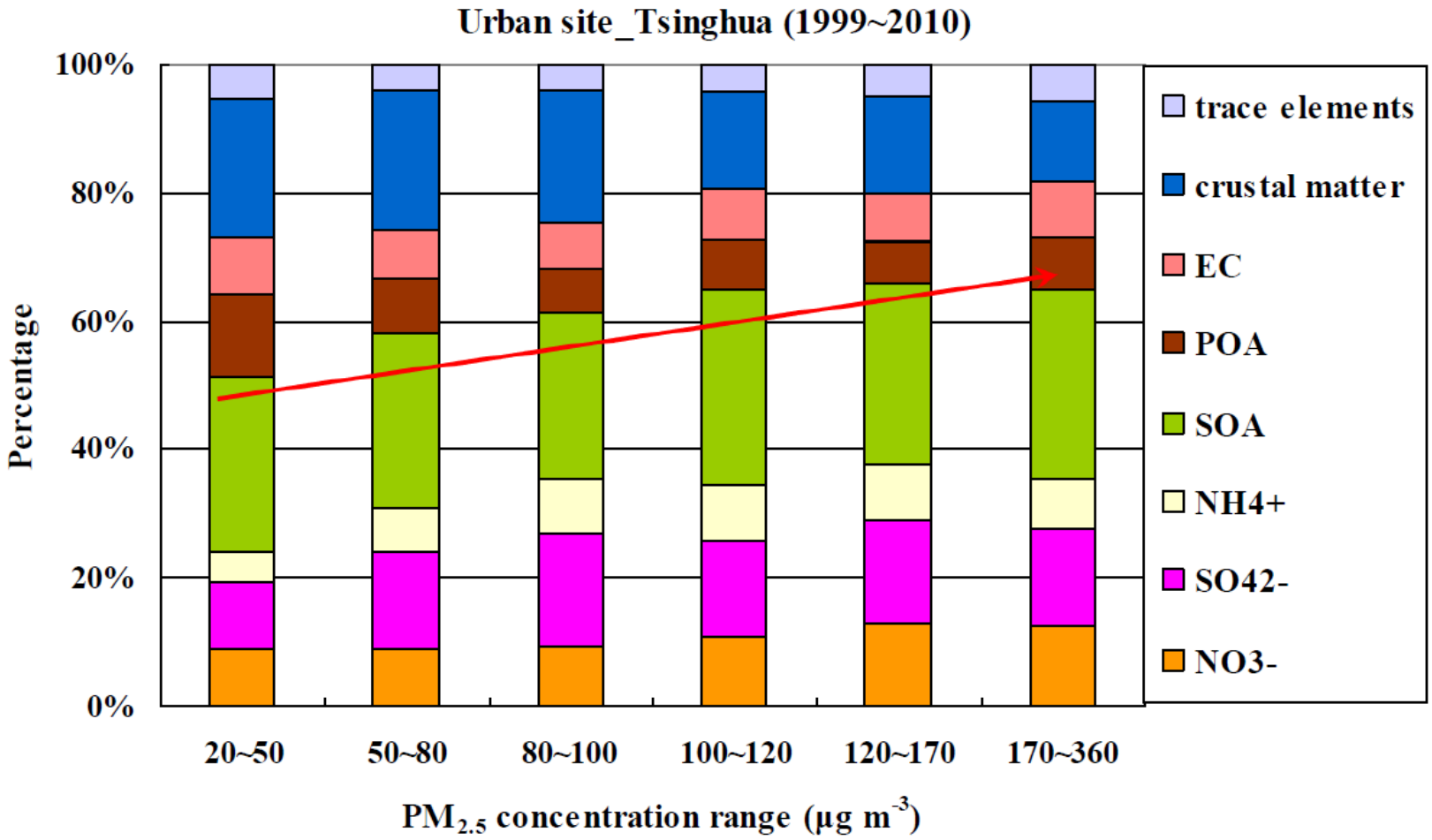
- Secondary aerosols: mostly anthropogenic; mostly small
  - Sulfate – anthropogenic; small
  - Nitrate – anthropogenic; typically small
  - Ammonium – anthropogenic; small
  - SOA – anthropogenic and natural; typically small; natural sources important mainly in summertime

Chemical Formation of Secondary Inorganic Aerosols

Type	Reaction #.	Reaction	Contributions to $PM_{2.5}$
original CMAQ			
Gas-phase chemistry (All species in gas phase)	R1	$SO_2 + OH + H_2O + O_2 \rightarrow H_2SO_4 + HO_2$	Sulfate
	R2	$NO_2 + OH \rightarrow HNO_3$	Nitrate
	R3	$N_2O_5 + H_2O \rightarrow 2HNO_3$	Nitrate
	R4	$NO_3 + HO_2 \rightarrow HNO_3 + O_2$	Nitrate
	R5	$NTR^a + OH \rightarrow HNO_3$	Nitrate
	R6	$NO_3 + VOCs^b \rightarrow HNO_3$	Nitrate
Aqueous-phase kinetic chemistry (All species in aqueous phase)	R7	$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O$	Sulfate
	R8	$HSO_3^- + MHP^c \rightarrow SO_4^{2-} + H^+$	Sulfate
	R9	$HSO_3^- + PAA^d \rightarrow SO_4^{2-} + H^+$	Sulfate
	R10	$SO_2 + O_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ + O_2$	Sulfate
	R11	$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2$	Sulfate
	R12	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	Sulfate
	R13	$SO_2 + H_2O + 0.5O_2 + Fe(III)/Mn(II) \rightarrow SO_4^{2-} + 2H^+$	Sulfate
Heterogeneous chemistry[e]	R14	$N_2O_5\,(g) + H_2O\,(aq) \rightarrow 2HNO_3\,(aq)$	Nitrate
	R15	$2NO_2\,(g) + H_2O\,(aq) \rightarrow HONO\,(aq) + HNO_3\,(aq)$	Nitrate
revised CMAQ			
Newly added heterogeneous chemistry	R16	$H_2O_2\,(g) + Aerosol \rightarrow Products$	Affect R7
	R17	$HNO_3\,(g) + Aerosol \rightarrow 0.5NO_3^- + 0.5NO_x\,(g)$	Renoxification
	R18	$HO_2\,(g) + Fe(II) \rightarrow Fe(III) + H_2O_2$	Affect R4 and R7
	R19	$N_2O_5\,(g) + Aerosol \rightarrow 2NO_3^-$	Nitrate
	R20	$NO_2\,(g) + Aerosol \rightarrow NO_3^-$	Nitrate
	R21	$NO_3\,(g) + Aerosol \rightarrow NO_3^-$	Nitrate
	R22	$O_3\,(g) + Aerosol \rightarrow Products$	Affect R10–R12
	R23	$OH\,(g) + Aerosol \rightarrow Products$	Affect R1–R2, R5
	R24	$SO_2\,(g) + Aerosol \rightarrow SO_4^{2-}$	Sulfate

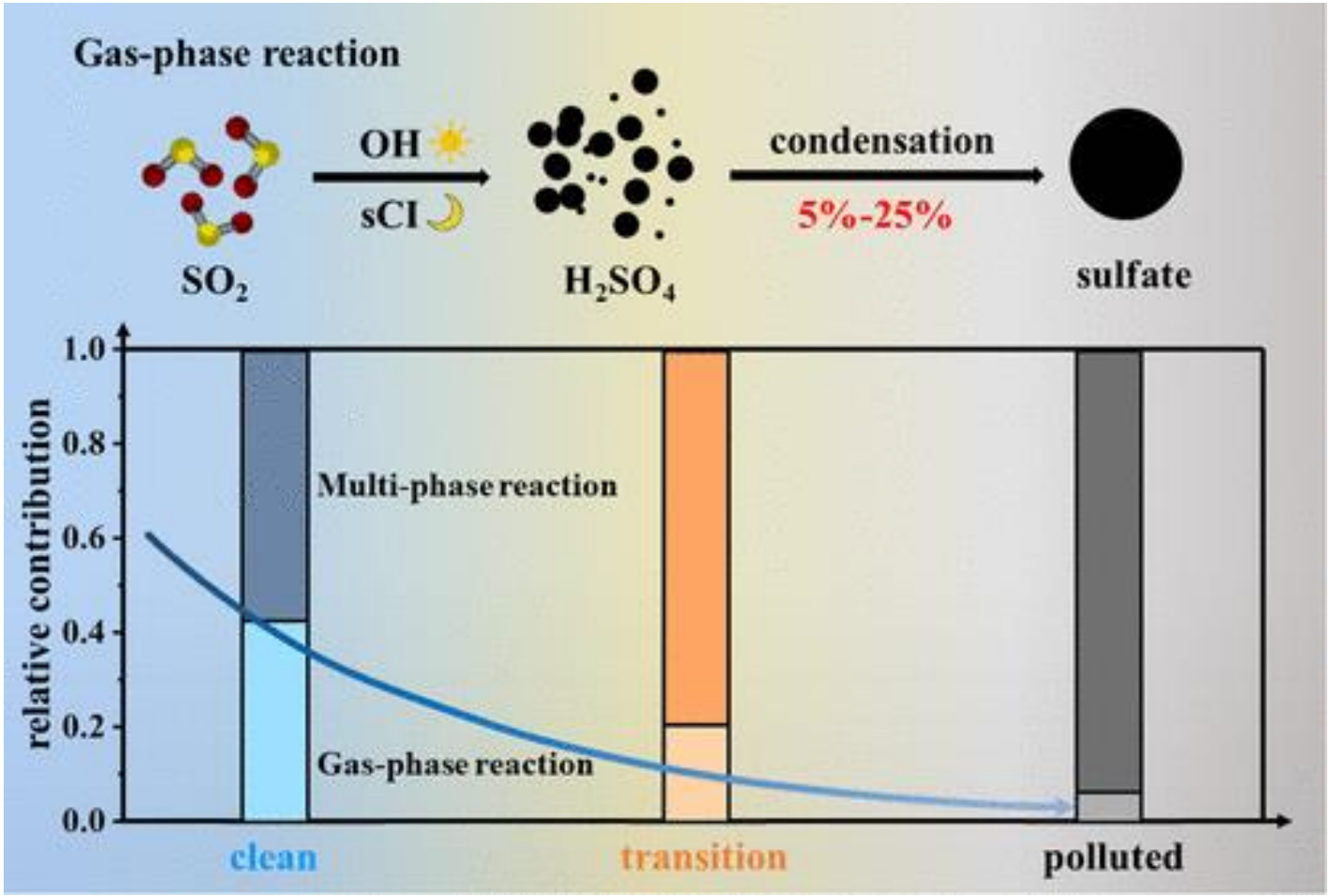
Zheng et al., 2015, ACP

Growing Fraction of Secondary $PM_{2.5}$ with Haze Severity



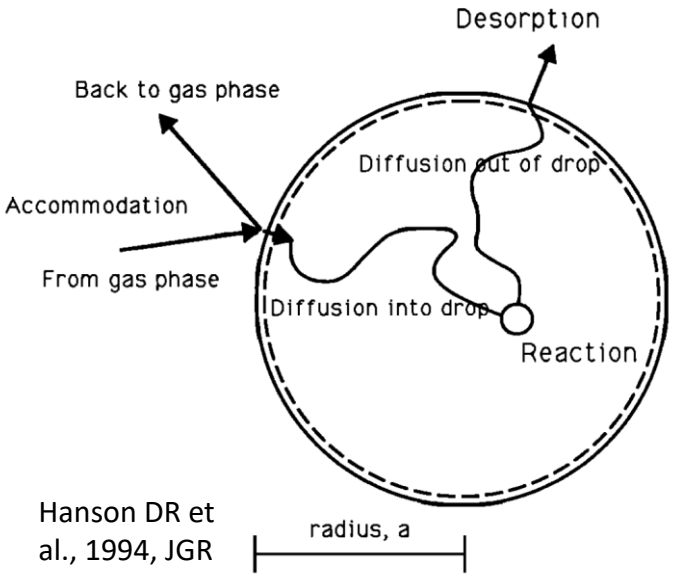
Kebin He

Increasing Importance of Heterogeneous Processes in Sulfate Formation at High PM Situations



Wang et al., ESTL, 2025

Heterogeneous Process



Hanson DR et al., 1994, JGR

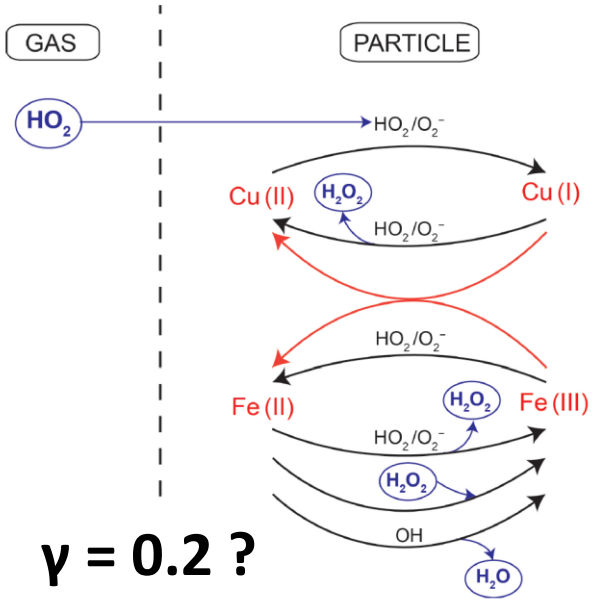
Gas ⟷ Particle Surface ⟷ Particle Bulk

(Effective) uptake coefficient, γ

- **Key processes:**
  - **HO_2 uptake**
  - **Sulfate formation**
  - **NO_2, N_2O_5, HNO_3, HONO**
  - **Carbon ageing**
  - **Halogen process**
- **Key questions:**
  - **pH in ambient aerosols**
  - **Amount & chemistry of dissolved TMI**
  - **Roles of organics**
  - **Suitability of current theory & model in polluted cases**

Heterogeneous Process: Roles of pH and TMI

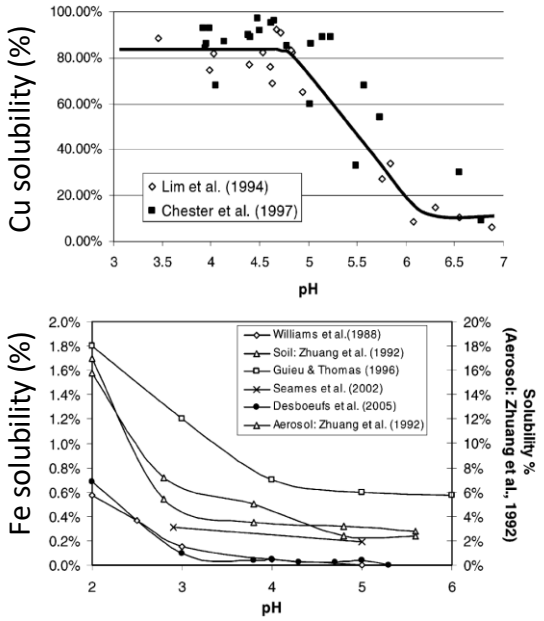
HO_2 Uptake



γ = 0.2 ?

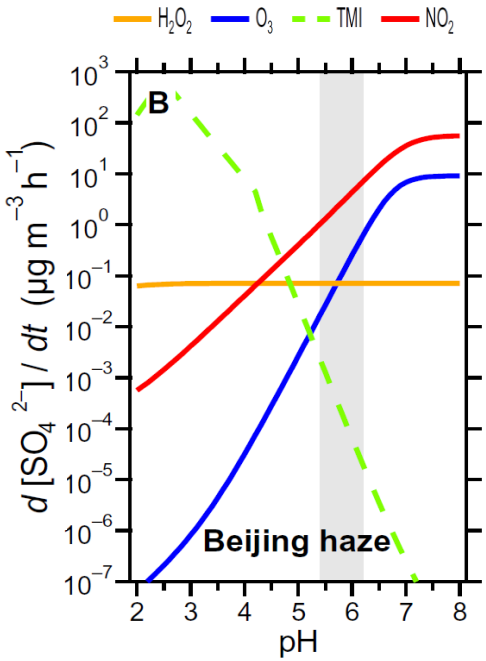
Mao JQ et al., 2013, ACP
Lin JT et al., 2012, ACP
Taketani F. et al., 2012, ACP

pH Dependence of TMI



Deguillaume L. et al., 2005, CR
Zhuang GS et al., 1992, Nature
Li WJ et al., 2017, SA

Sulfate Formation



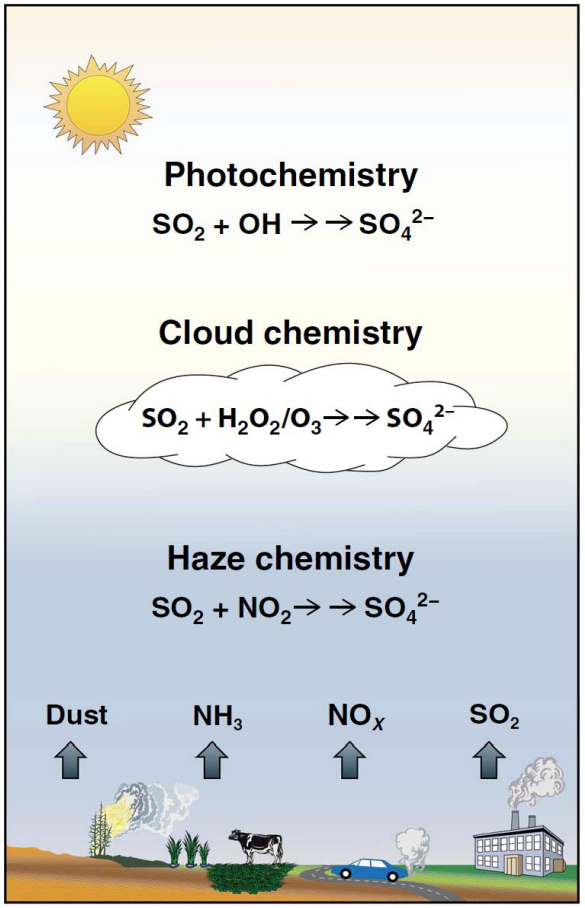
Cheng YF et al., 2016, SA
Wang GH et al., 2016, PNAS

- **Mass fraction of Cu in PM over E. China is 1.6-12 times that in the US, but the fraction of dissolved Cu depends on pH and is not clear.**
- **Roles of dissolved Fe (sole catalytic effect + coupled effect with Cu)?**
- **Roles of organics?**

NO_2-catalyzed Sulfate Formation at High pH

Aqueous phase:

$$2\,NO_2\,(aq) + HSO_3^-\,(aq) + H_2O\,(aq) \rightarrow 3\,H^+(aq) + 2\,NO_2^-\,(aq) + SO_4^{2-}(aq)$$



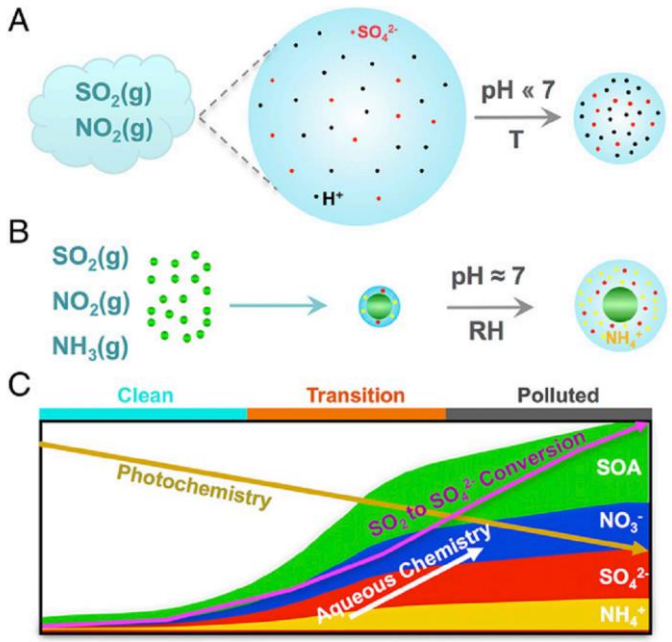
Cheng et al., 2017, Science Advance

Cloud/fog (large):

$$SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) + 2HONO(g).$$

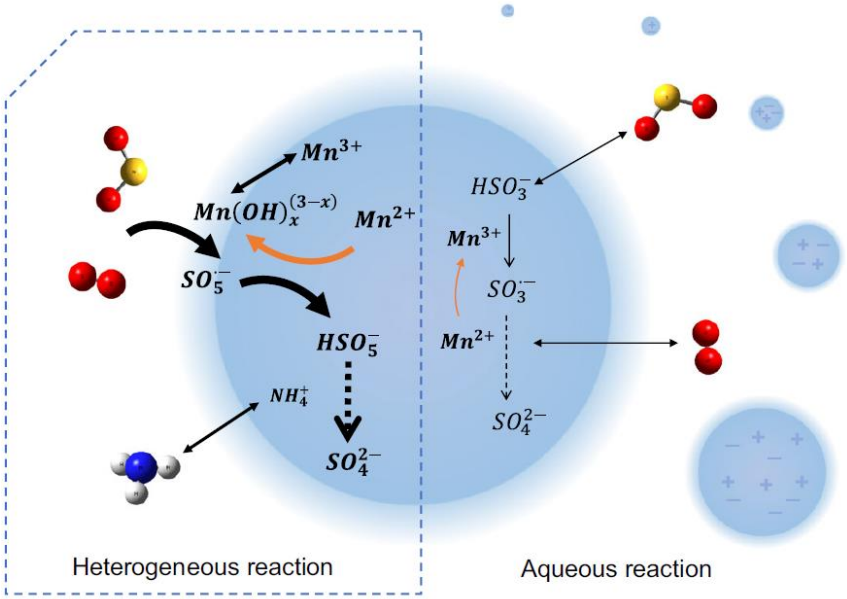
Aerosol (small, easily acidified):

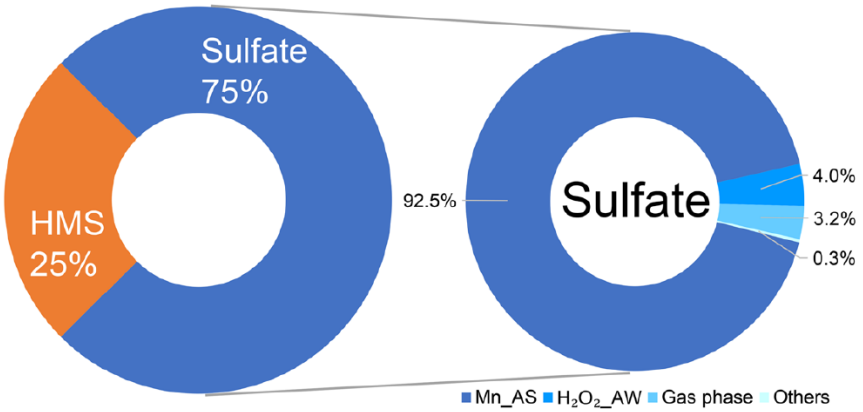
$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g).$$



Wang et al., 2016, PNAS

Mn-catalyzed Formation of Sulfate on Aerosol Surface





$$SO_2 + O_2 + Mn(OH)_x^{(3-x)} \rightarrow SO_5^{\cdot-} + Mn^{2+},\ x = 1, 2$$

$$SO_5^{\cdot-} + Mn^{2+} + H^+ \rightarrow Mn(OH)_x^{(3-x)} + HSO_5^-,$$

$$NH_3 + HSO_5^- + SO_2 + H_2O \rightarrow NH_4^+ + SO_4^{2-}.$$

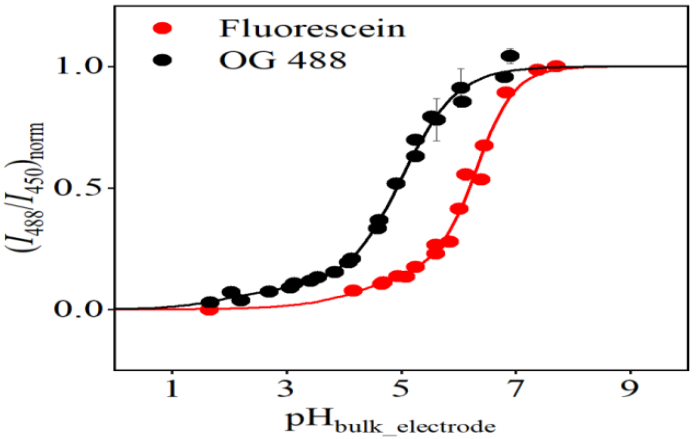
$$\frac{d[SO_4^{2-}]}{dt} = k \times f(H^+) \times f(T) \times f(I) \times [Mn^{2+}] \times [SO_2(g)] \times A$$

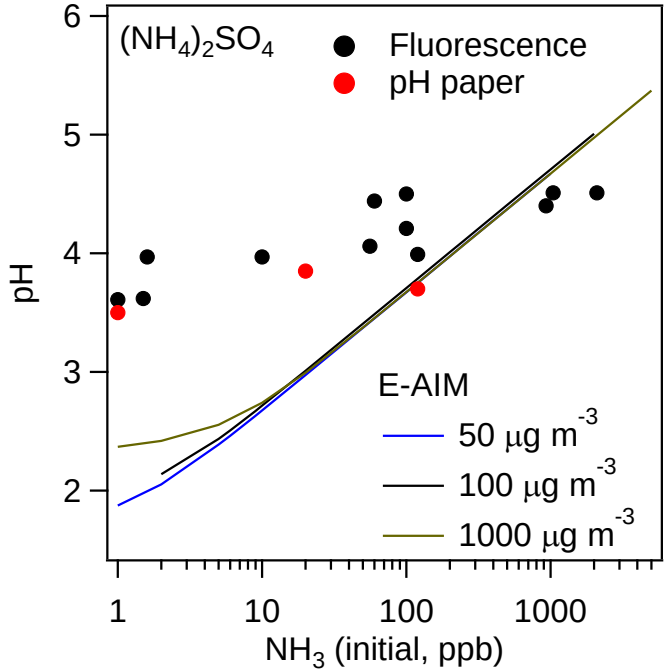
Wang et al., 2021, Nature Communications

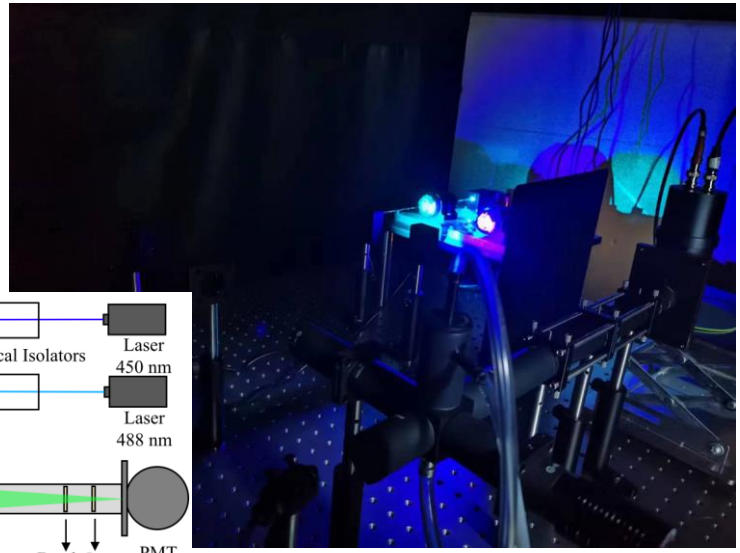
Conquering Challenge of Online Aerosol pH Measurement

Mikinori Kuwata @ PKU:

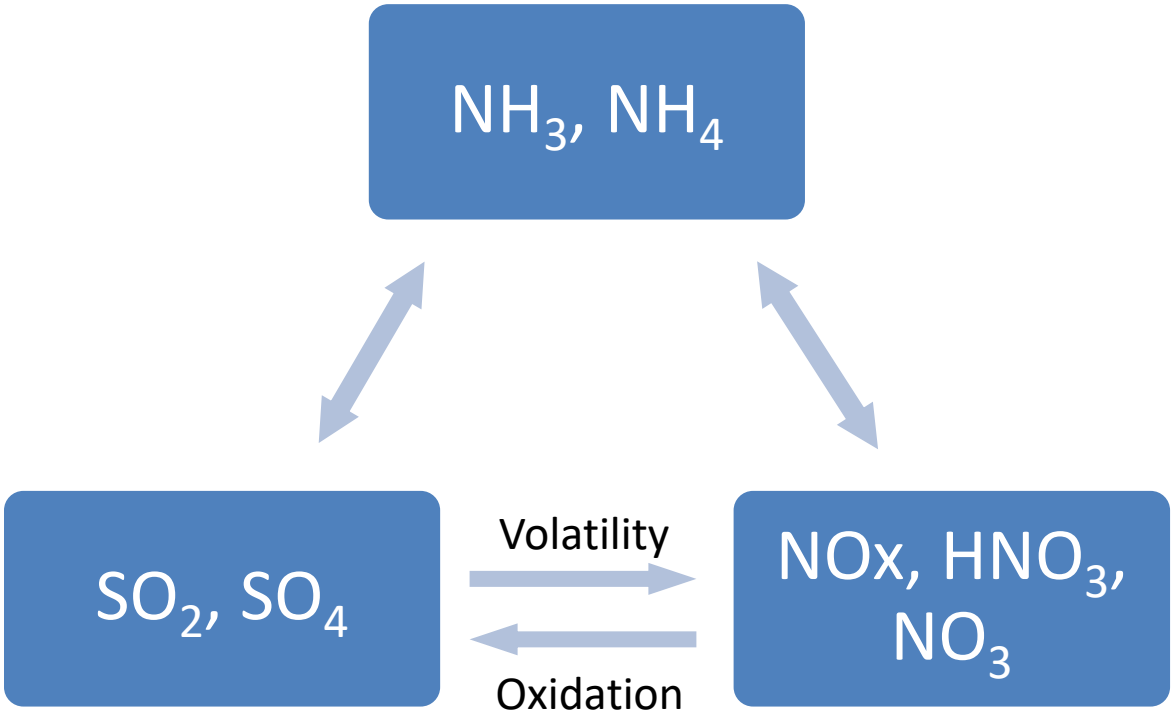
- **The only one instrument that is capable to measure pH of suspending sub-micrometer aerosol particles** (Li and Kuwata, 2023)
- **First demonstration of the limitation of thermodynamic models for estimating pH**



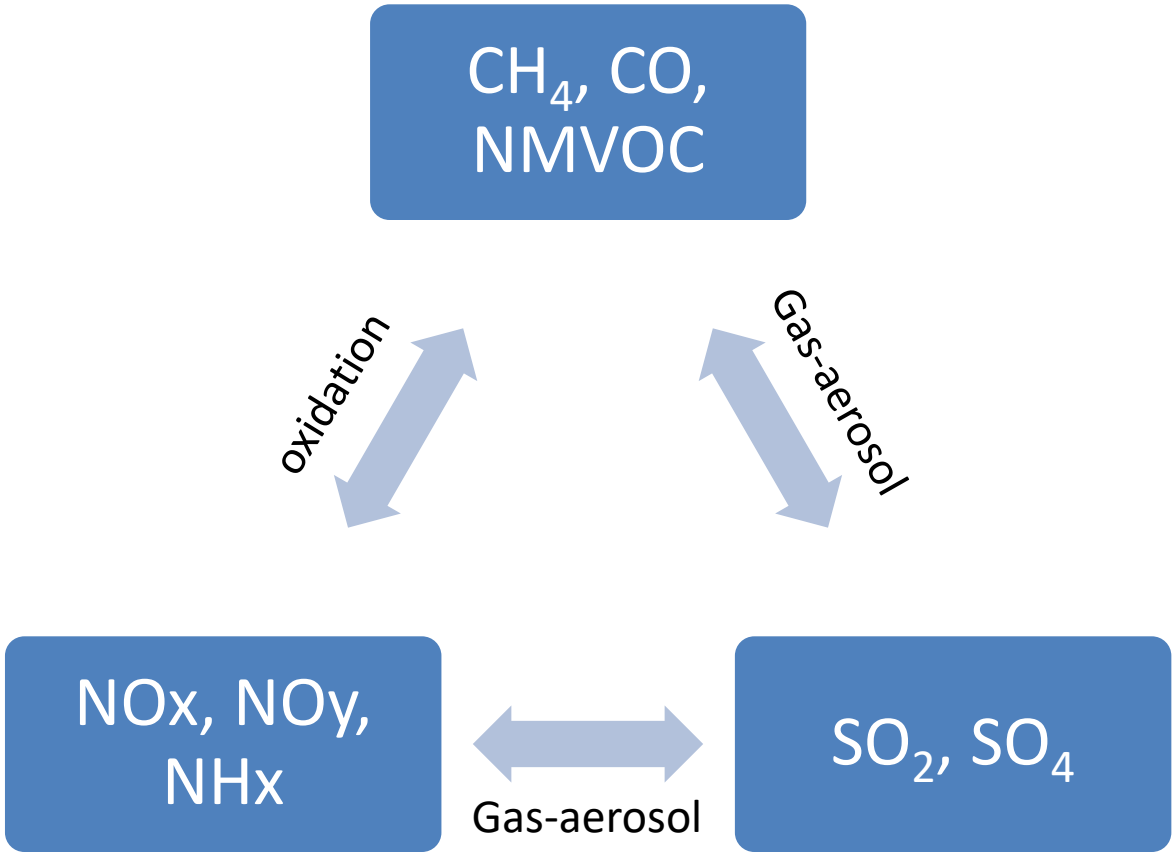




Sulfate-Nitrate-Ammonium Interactions

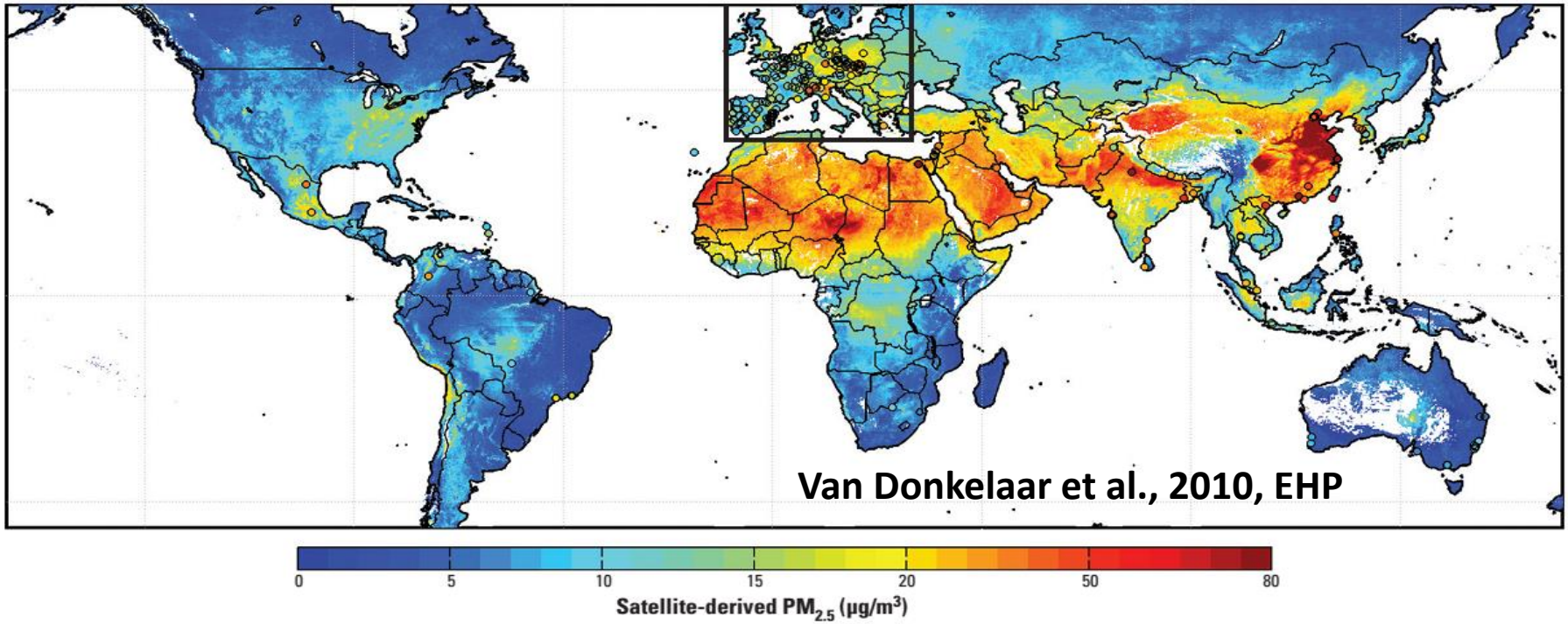


Carbon-Nitrogen-Sulfur Interactions



China Has World's Most Severe PM Pollution

Surface $PM_{2.5}$ concentration derived from satellite



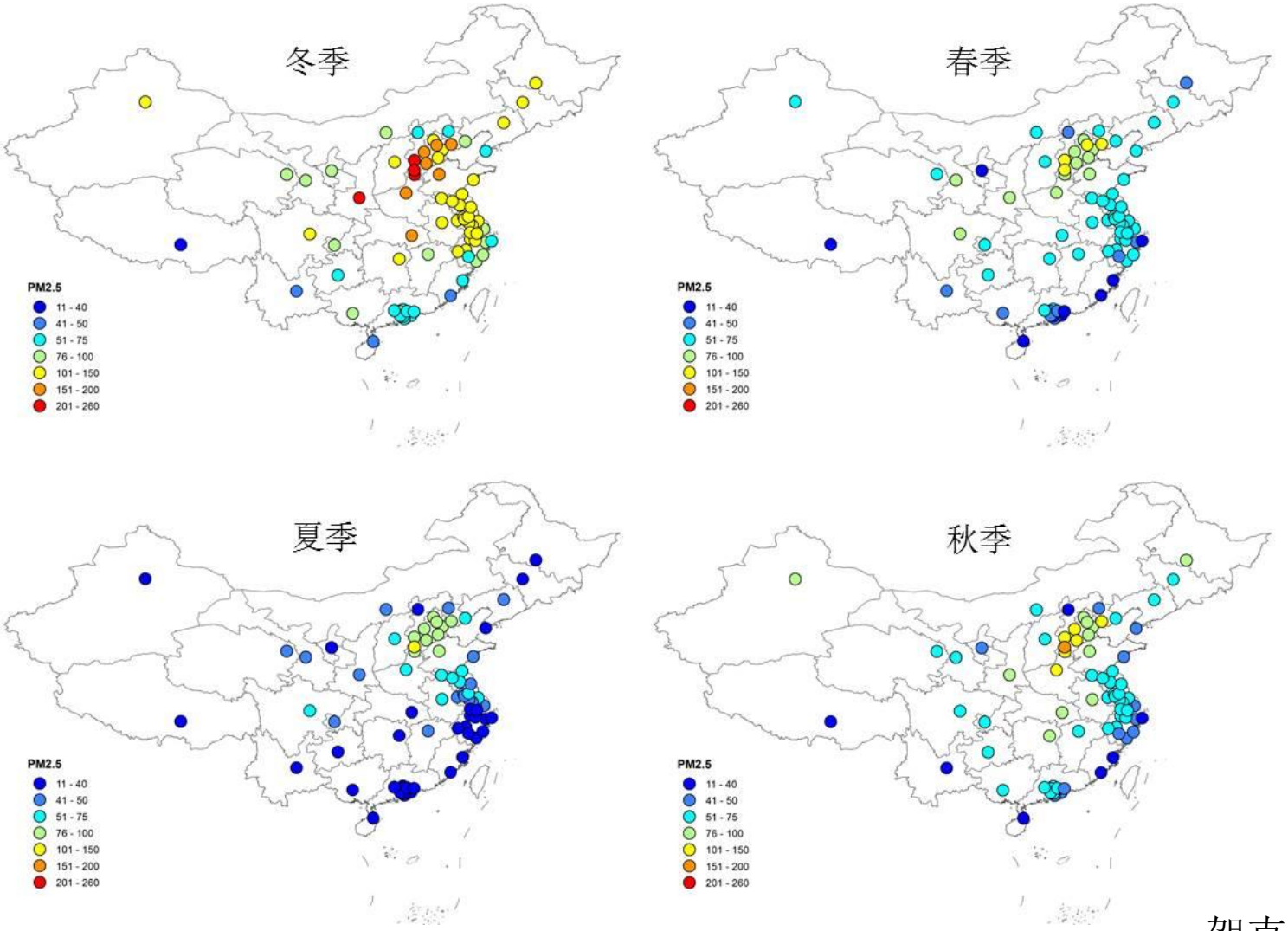
23,000,000 Chinese
live in areas with > 100 µg/m³

v.s.

Beijing in 2013:
90 µg/m³

v.s. **WHO Guideline: 10 µg/m³, WHO IT1: 35 µg/m³**

Seasonal Variation of $PM_{2.5}$ in China

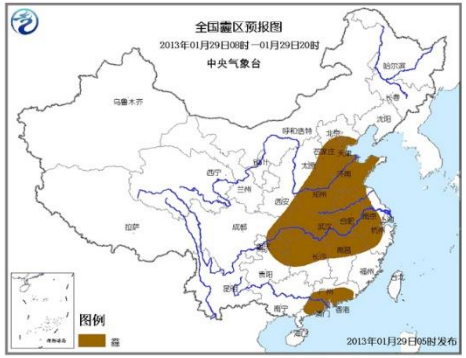


贺克斌，2014

Severe Haze in 2013



Jan 14-15, 2013



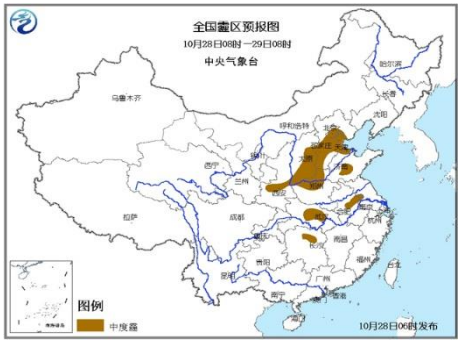
Jan 29, 2013



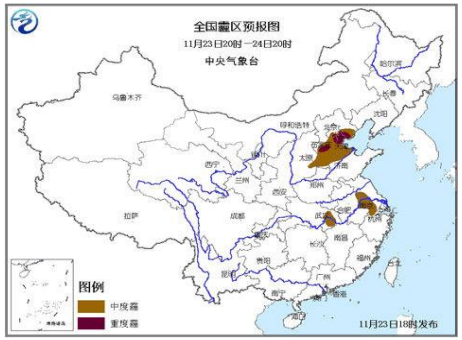
Feb 24-25, 2013



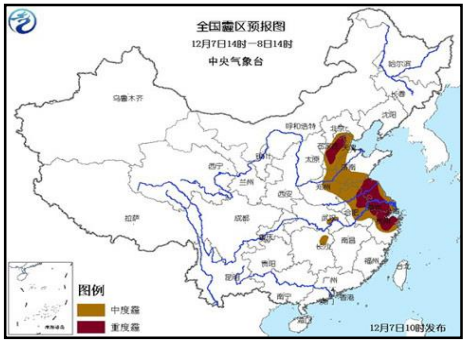
Oct 06-07, 2013



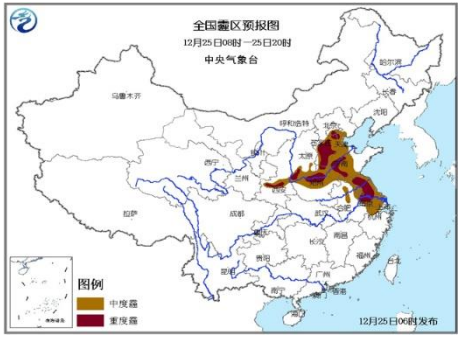
Oct 28-29, 2013



Nov 23-24, 2013



Dec 07-08, 2013



Dec 25, 2013

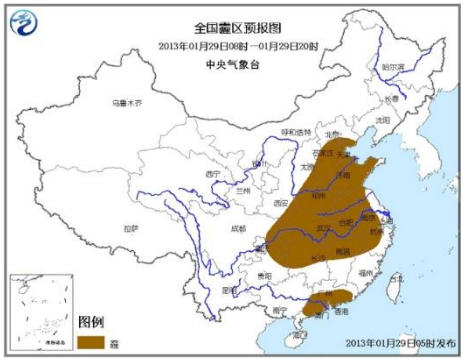
贺克斌，2014

Severe Haze in January 2013

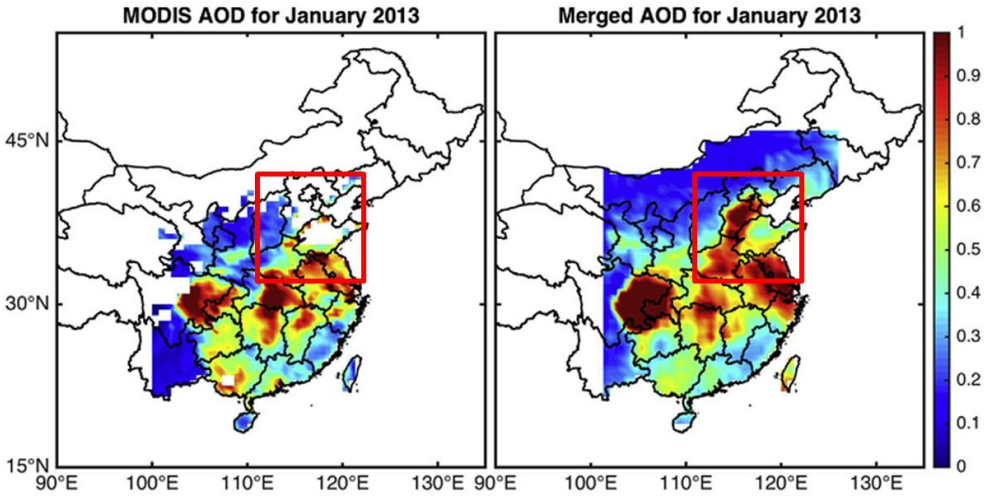
Jan 14-15, 2013



Jan 29, 2013

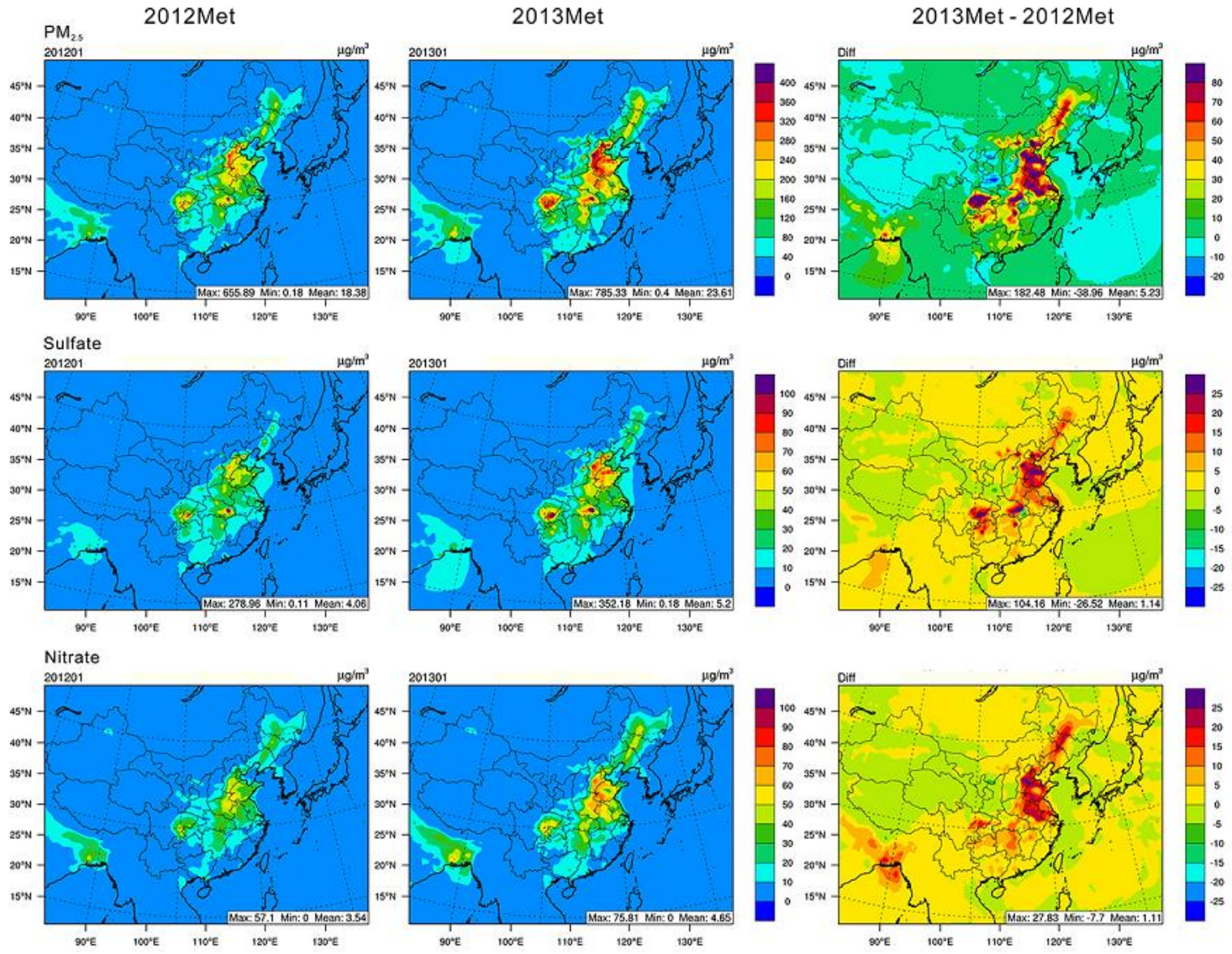


贺克斌，2014



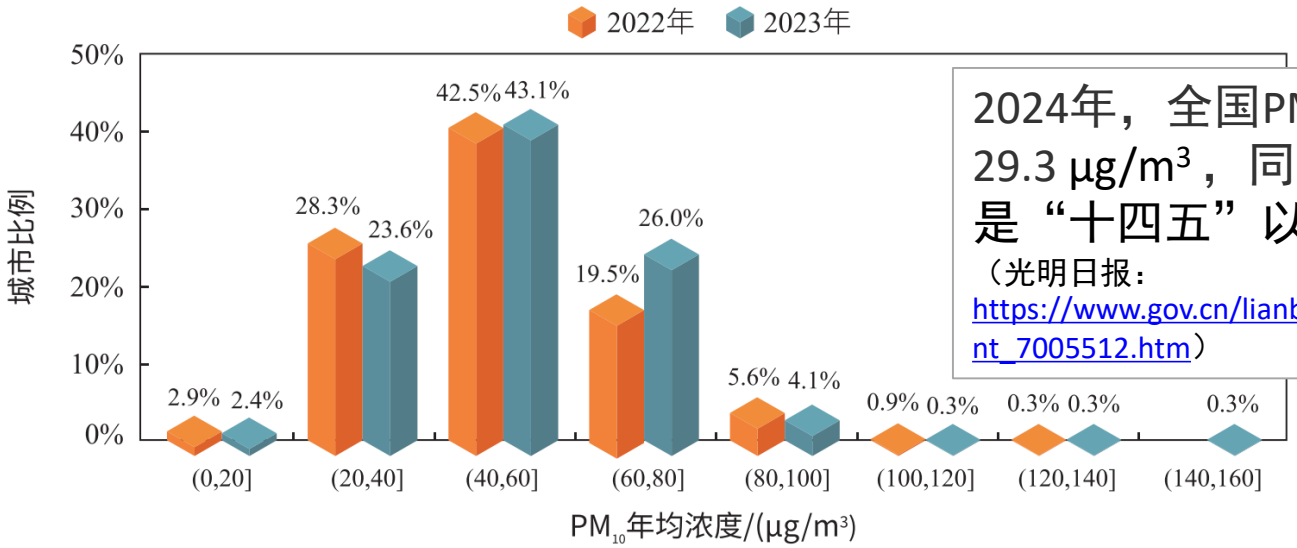
Lin and Li, AE, 2016

Contribution of Meteorology to Jan 2013 Haze



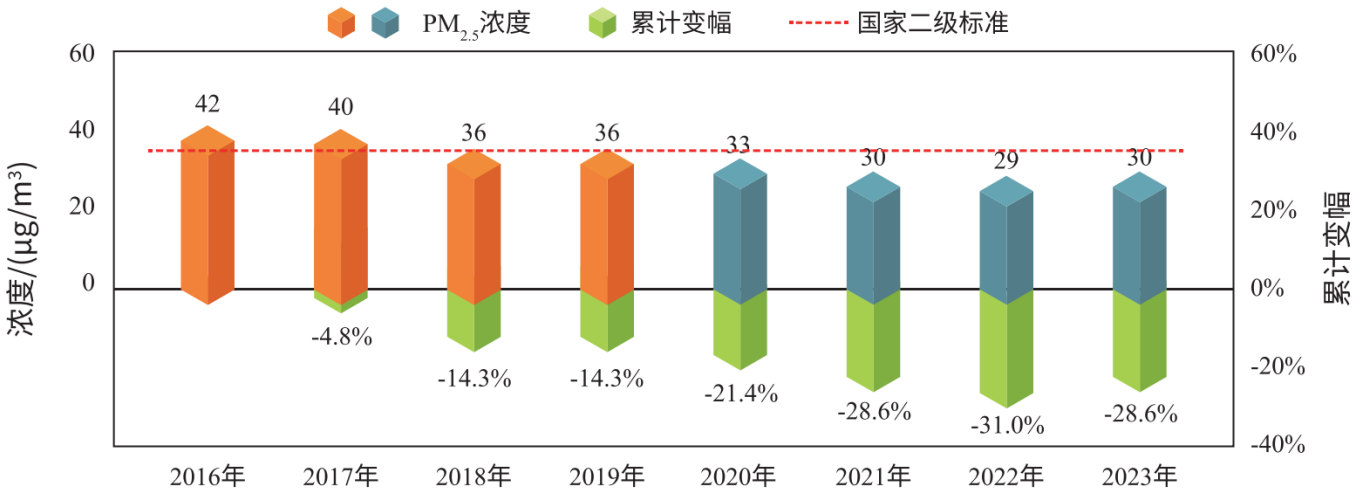
Zheng et al., 2015, ACP

$PM_{2.5}$ Pollution Changes in China



2024年，全国$PM_{2.5}$平均浓度为29.3 μg/m³，同比下降2.7%，是“十四五”以来次好年

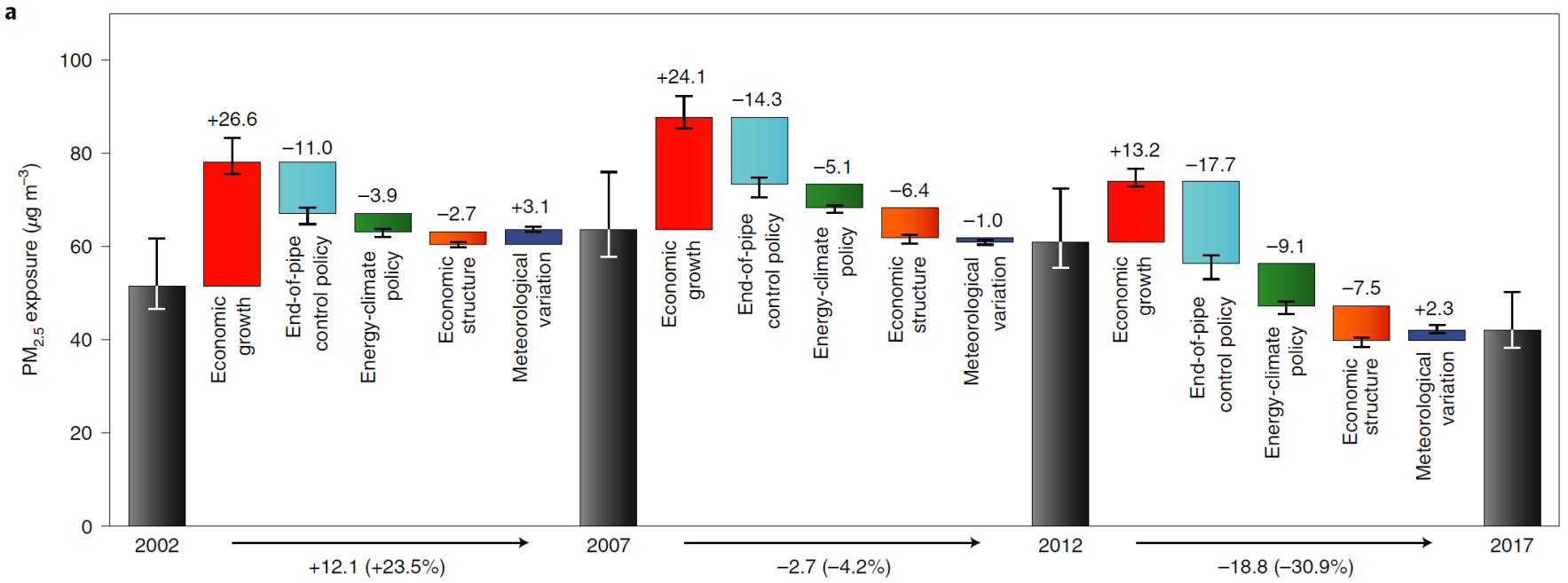
（光明日报：https://www.gov.cn/lianbo/bumen/202502/content_7005512.htm）



中国生态环境公报2023

Drivers of $PM_{2.5}$ Pollution Trends over China

Population-weighted $PM_{2.5}$ pollution: 2002–2017



Geng et al., 2021, Nature Geoscience

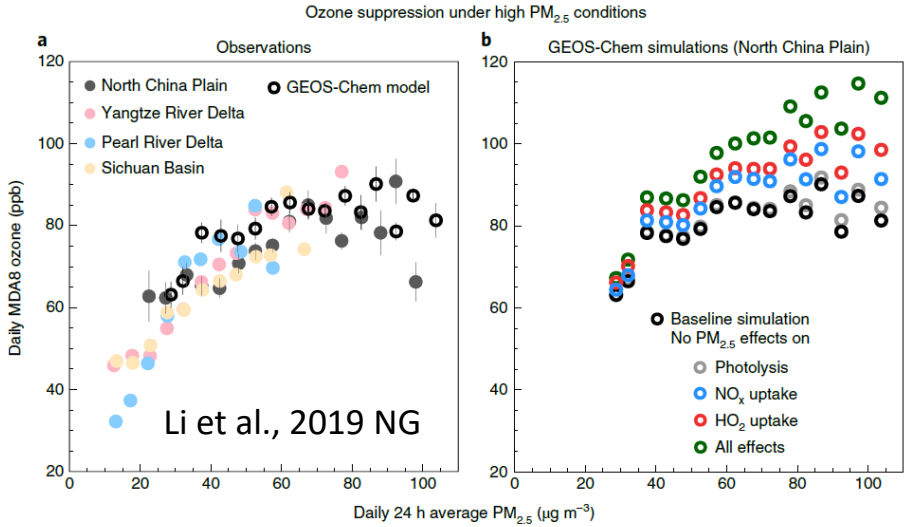
Interactions of Ozone and PM

Effects of ozone on PM:

- ✓ **Oxidation (O_3, OH, H_2O_2) to form secondary PM**
- ✓ **Meteorology (small effects)**
- ✓ **Biogenic emissions**

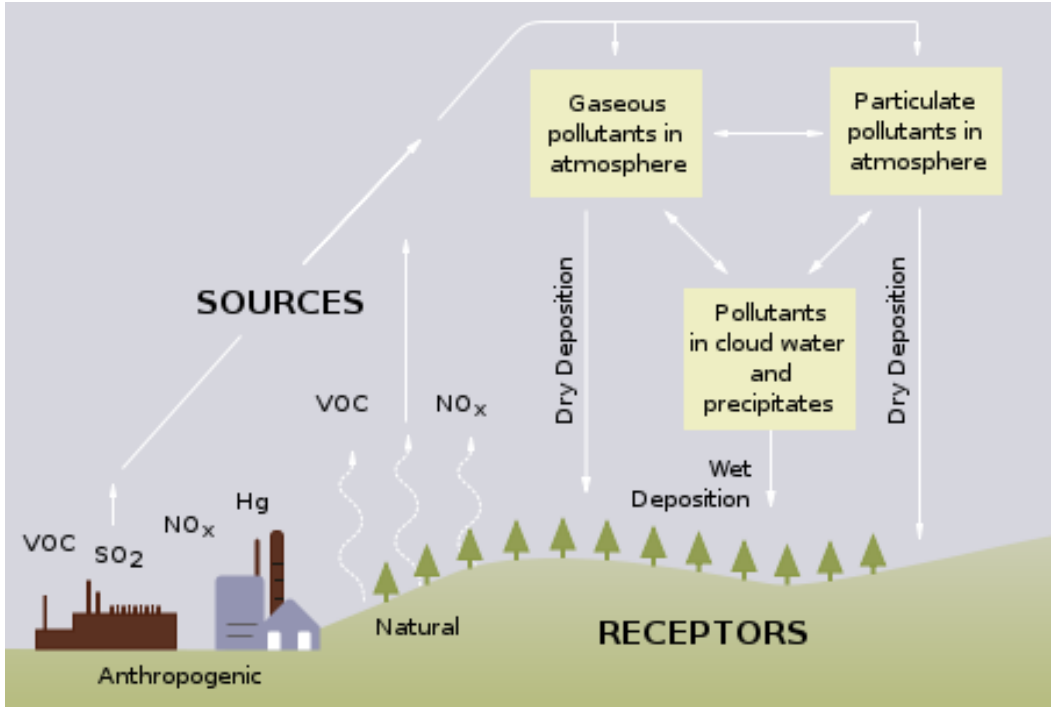
Effects of PM on ozone:

- ✓ **Heterogeneous processes of oxidants (e.g., HO_2)**
- ✓ **Radiation (actinic flux)**
- ✓ **Meteorology**
- ✓ **Biogenic emissions**



γ_HO_2 = 0.2; γ_NO_2 = 1e-5; γ_NO_3 = 1e-3

Acid Deposition



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

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

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

Hetero: $NO_2 + SO_2 + H_2O(s) \rightarrow SO_4^{-2}$?

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

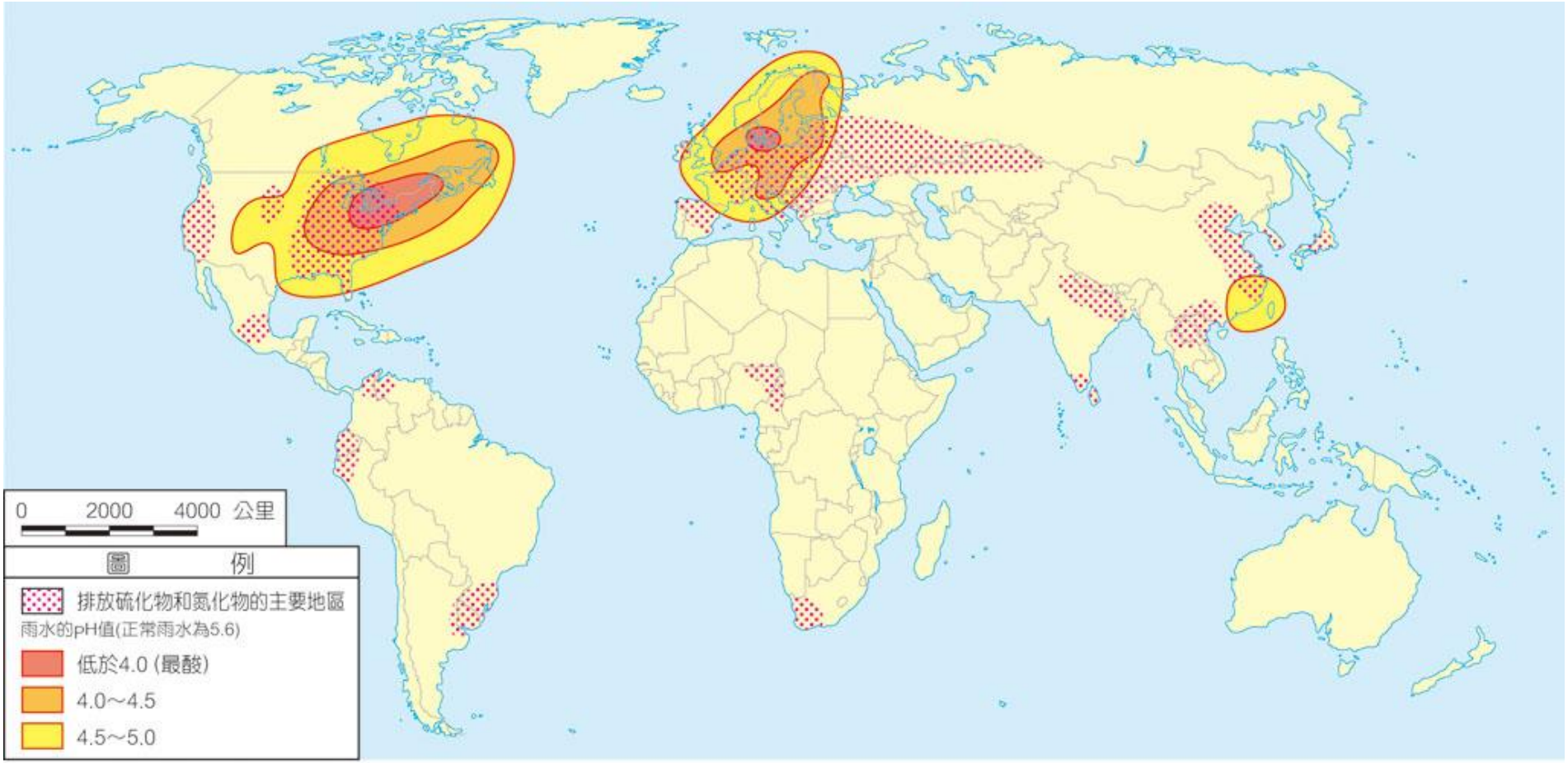
Hetero: $NO_2 + H_2O(s) \rightarrow NO_3^-$?

Hetero: $N_2O_5 + H_2O(s) \rightarrow 2HNO_3$

VOC + OH (NO_x, O_3, H_2O_2) $\rightarrow \ldots \rightarrow$ organic acids

Acids are balanced by mineral or ammonium ions

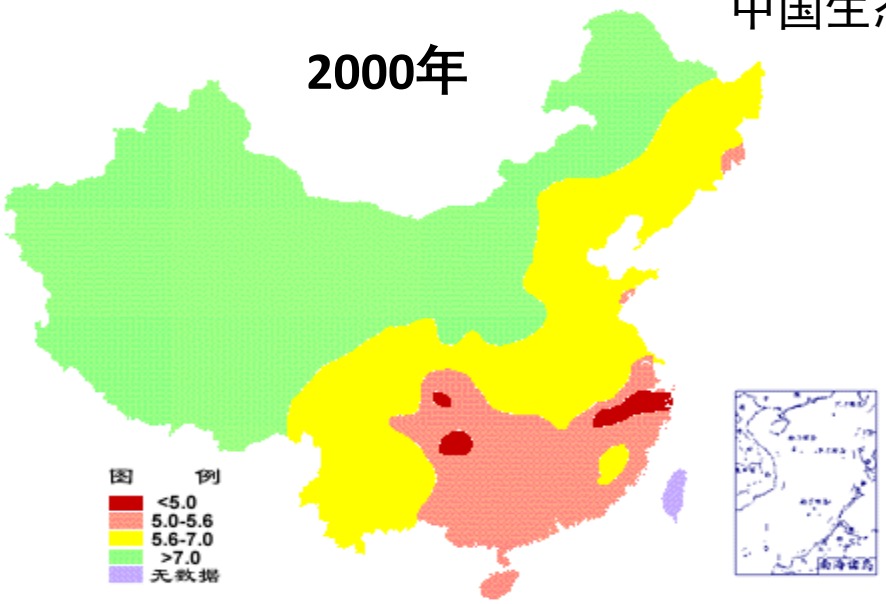
Acid Deposition



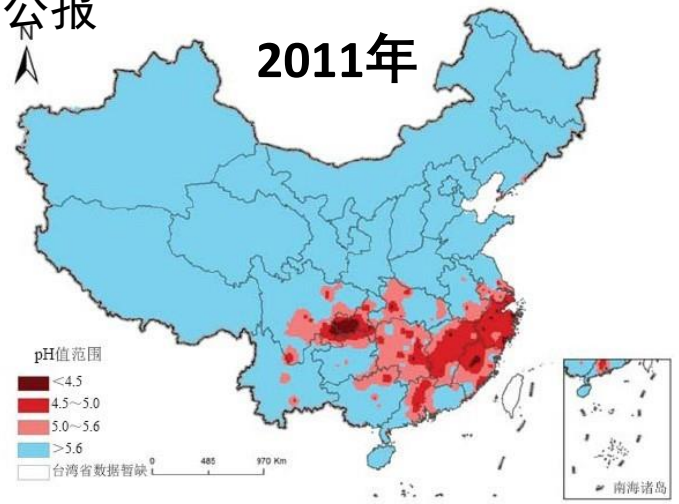
中国降水pH值分布

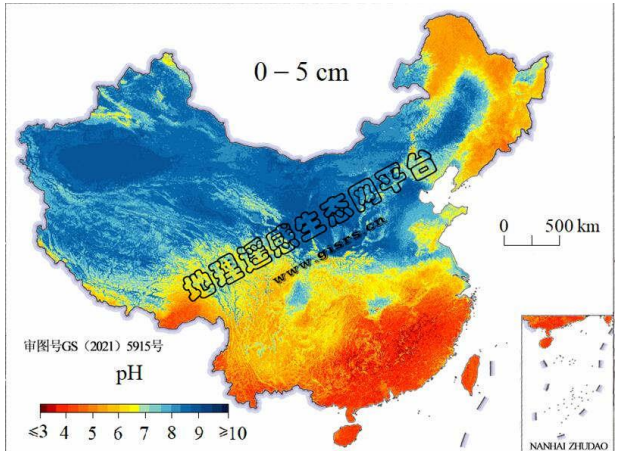
中国生态环境状况公报

2000年



2011年





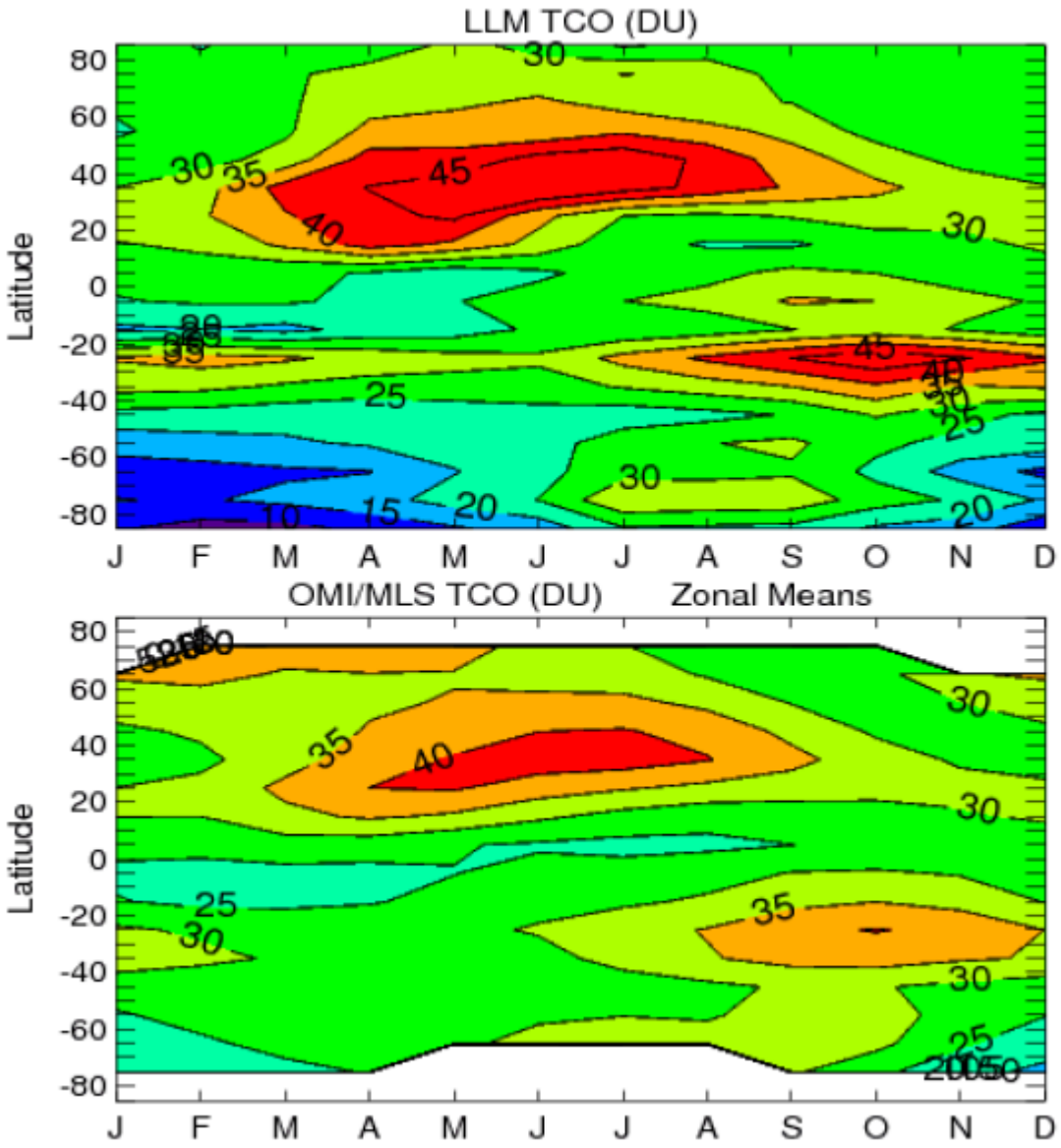
2023年



Quiz

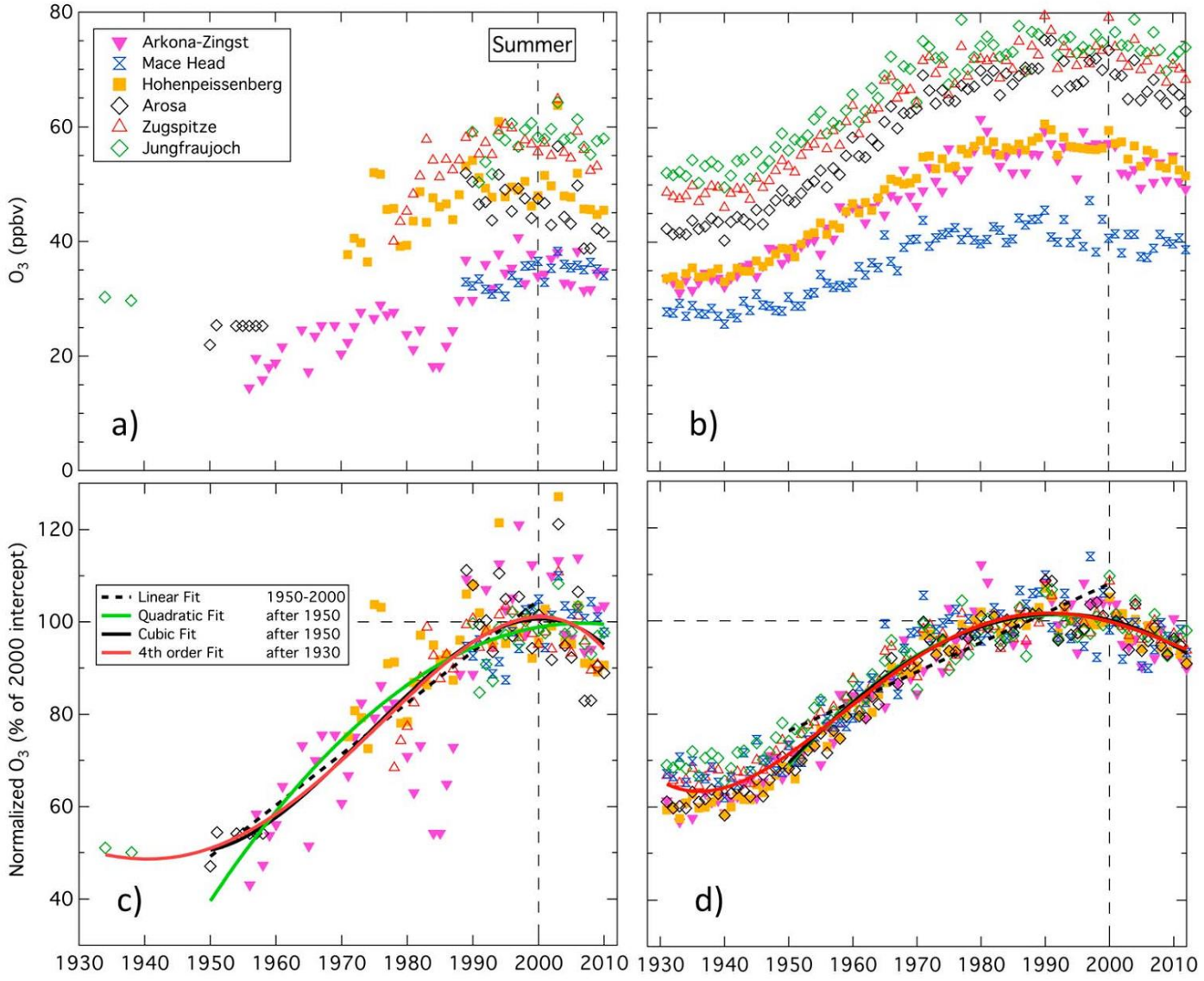
1. Based on the collision theory, why does the reaction rate constant of bimolecular reactions tend to increase with T?
2. Can we consider NO_2 and ozone to be in the same chemical family (i.e., Ox)?
3. Potential human influences on recent tropospheric OH trends
4. How would NOx emissions affect the lifetime of OH?
5. Impacts of NOx on ozone at different cases: troposphere, boundary layer, urban, rural
6. 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?
7. How would changes in NOx affect the formation of nitrate and sulfate?
8. Why did China's $PM_{2.5}$, but not ozone, pollution decline with emission control over the past decade?
9. How can ozone and PM pollution affect each other?

Meridional – Seasonal Cross Section



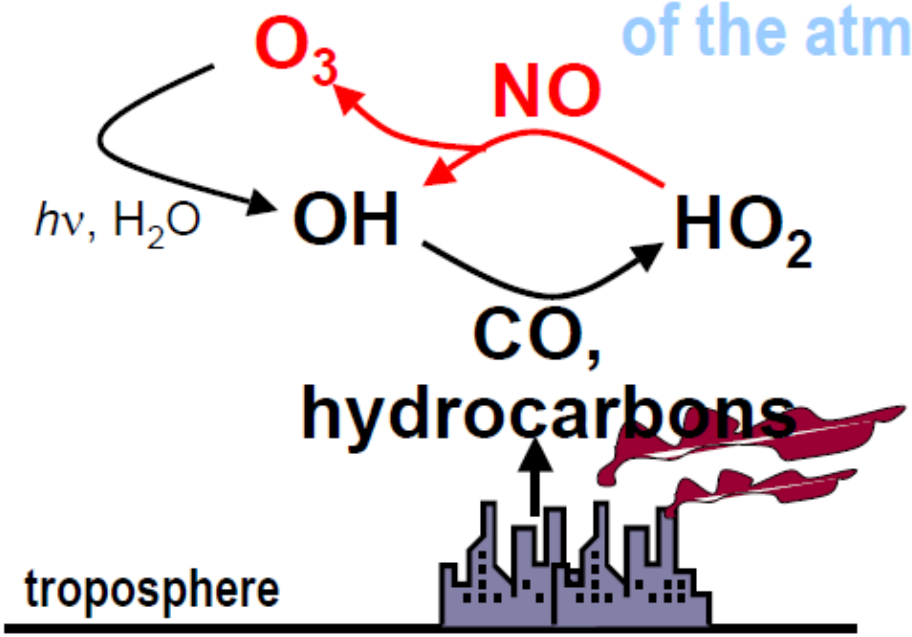
Ziemke et al., 2011

Long-term Ozone Trends at Background Sites



Parrish et al., 2014, JGR

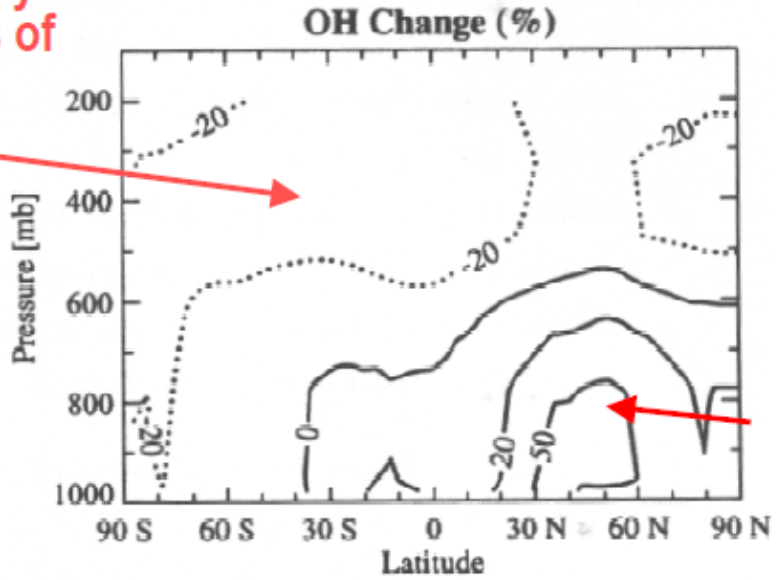
Have human activities changed the oxidizing capacity of the atmosphere?



→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

Meridional Distribution of Tropospheric Ozone

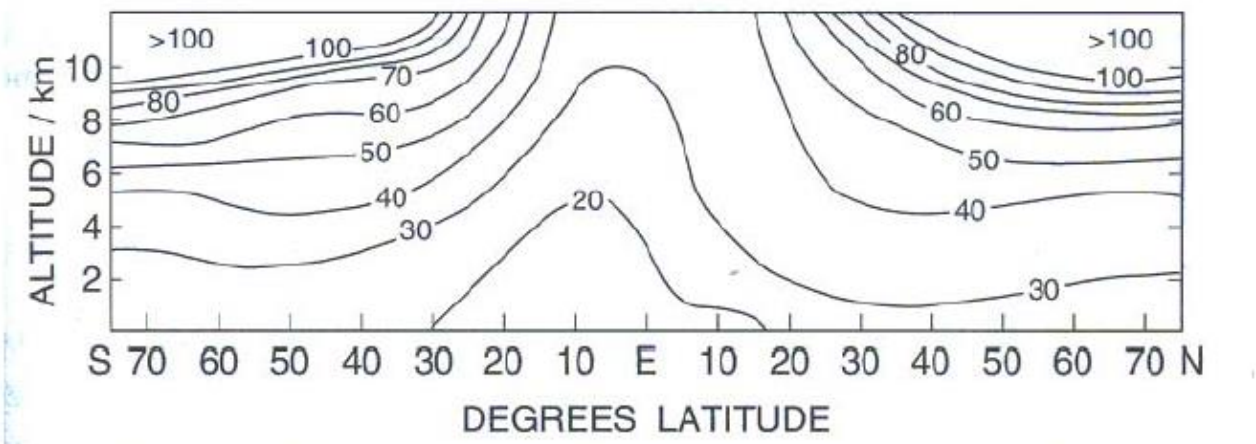
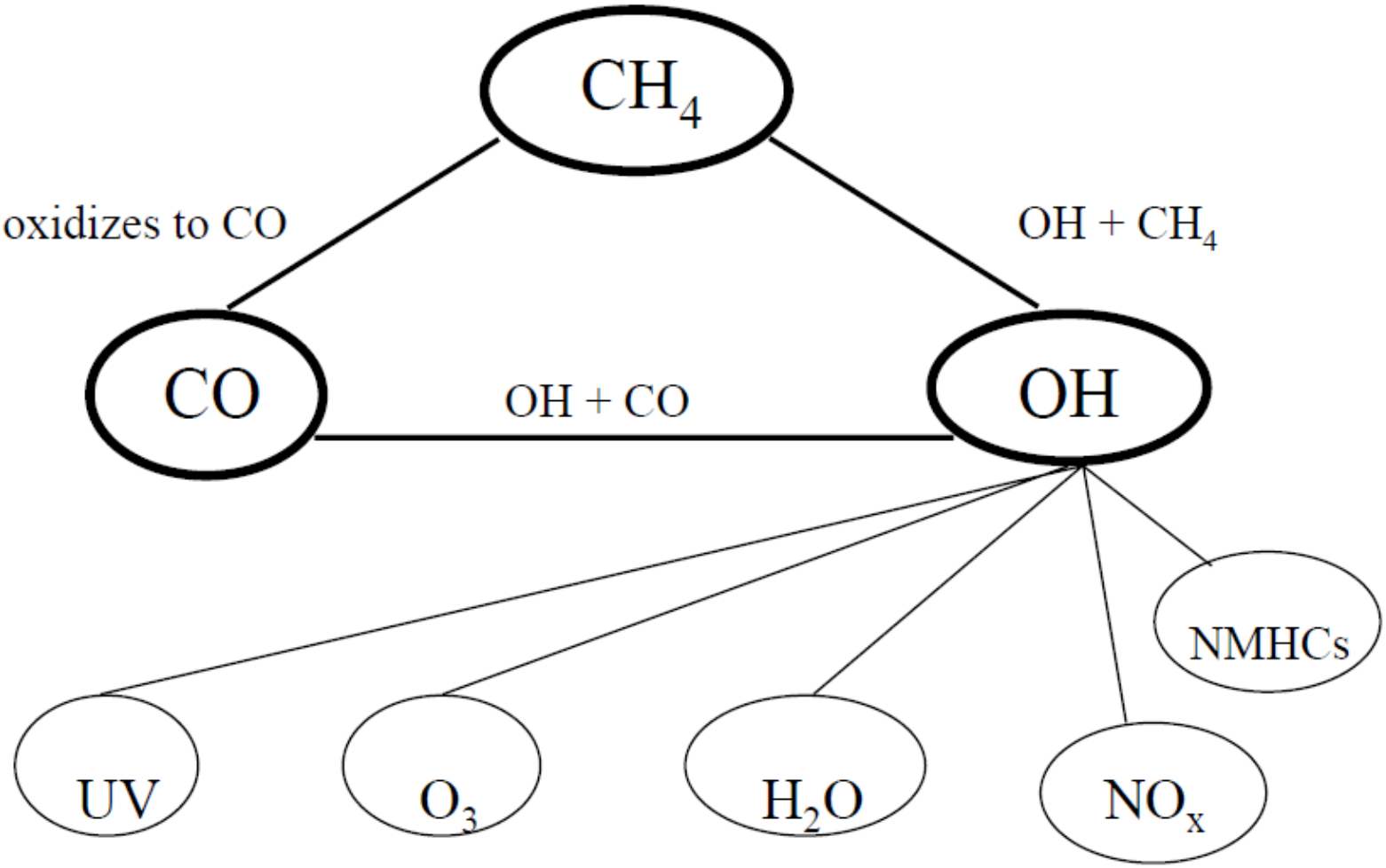


FIGURE 5.6 Seasonally averaged meridional distribution of ozone according to the analysis of Fishman and Crutzen (1978a, b). Contours indicate equal mixing ratios (unit: nmol mol^{-1}).

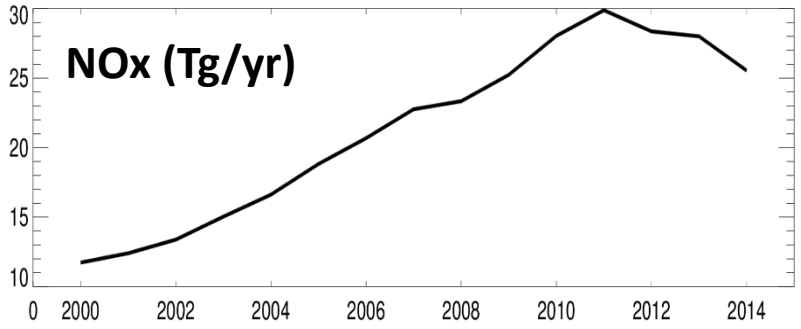
- An excess of ozone in the Northern Hemisphere at altitudes below about 5 km
- Northern Hemisphere contains 40% more zone on average than the Southern Hemisphere
- The ozone concentrations in the Tropics are lower than at mid-latitudes

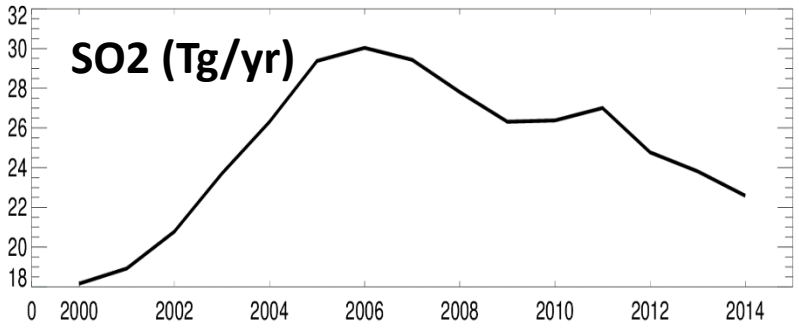
Fishman and Crutzen, 1978

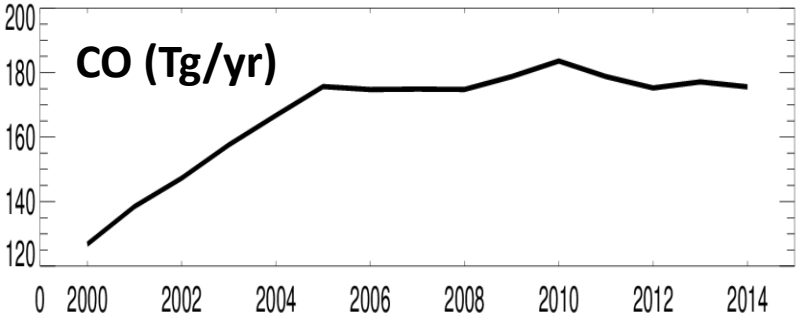
Simplified $CO/CH_4/OH$ Chemistry

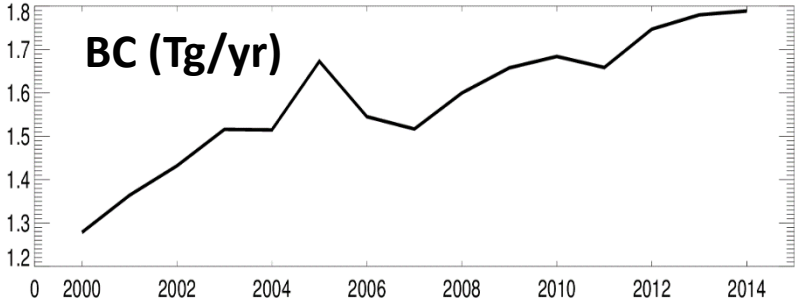


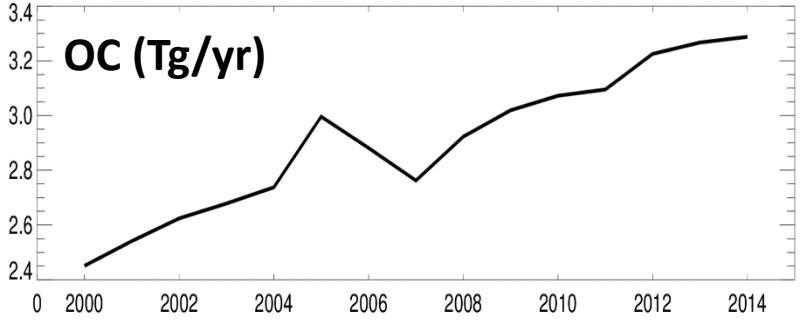
Anthropogenic Emissions in China: 2000-2014











Source: Yu Zhao

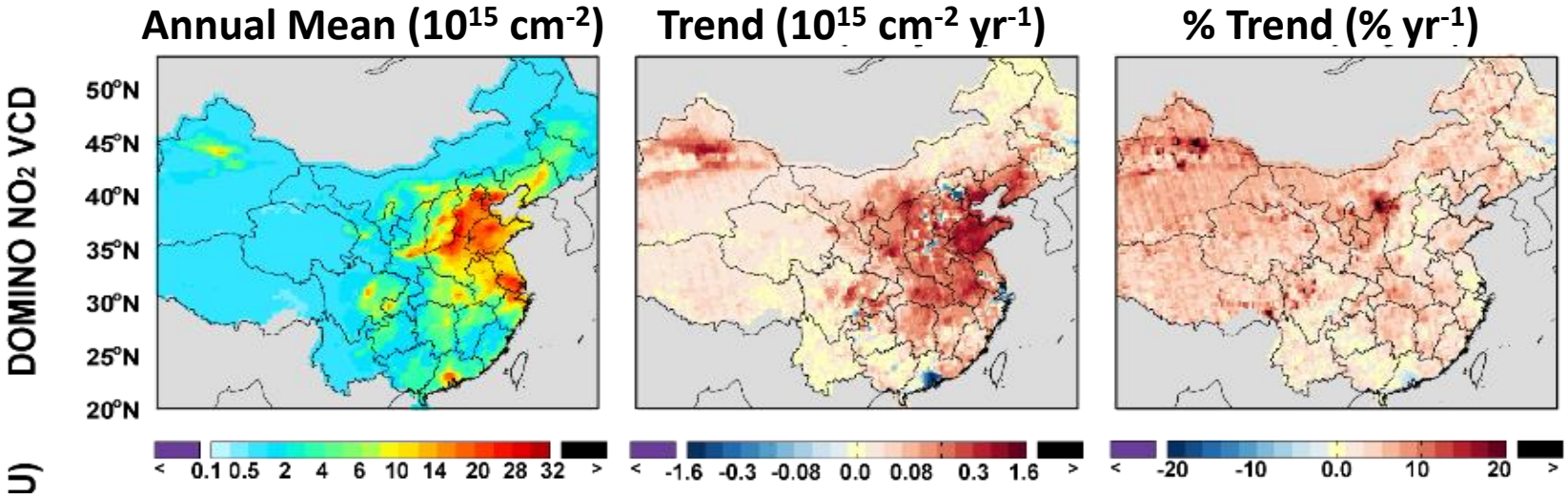
Increases of NO_2 VCD: West versus East China

OMI NO_2 Trends over 2005 – 2013

Cui et al., 2016, ACP

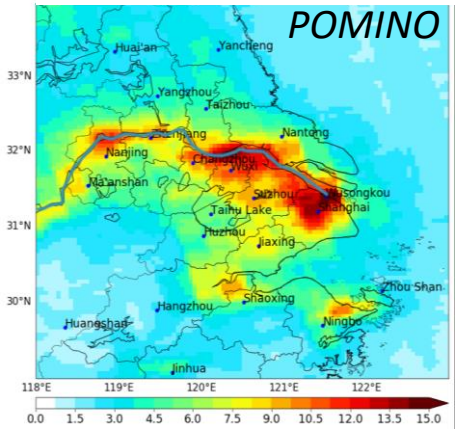
	Region	Average NO_2 in 2005[a] 10^{15} molecules cm^{-2}	NO_2 trend[b] (% yr^{-1})	NO_x emission reduction plan of 2015 (%)[c]
Northwest	Gansu	0.9 (0.4, I)	7.5 ± 1.2	3.1
	Inner Mongolia	1.1 (0.4, I)	10.2 ± 1.3	5.8
	Ningxia	1.4 (0.4, I)	12.3 ± 1.7	4.9
	Qinghai	1.0 (0.5, II)	11.2 ± 1.2	−15.3
	Shaanxi	2.3 (0.5, II)	10.5 ± 1.0	9.9
	Xinjiang	1.0 (0.5, II)	15.1 ± 2.0	0
Southwest	Chongqing	2.2 (0.5, III)	7.8 ± 0.9	6.9
	Guangxi	1.2 (0.5, III)	4.0 ± 0.5	8.8
	Guizhou	1.3 (0.5, III)	6.9 ± 1.0	9.8
	Sichuan	1.7 (0.5, III)	6.1 ± 0.7	6.9
	Yunnan	0.7 (0.5, III)	4.2 ± 0.3	5.8
Region	West	1.3 (0.5, II)	8.6 ± 0.9	5.7
	Northwest	1.2 (0.5, II)	11.3 ± 1.0	4.5
	Southwest	1.4 (0.5, III)	5.9 ± 0.6	7.6
	BTH	9.2 (0.7, IV)	5.3 ± 0.8	13.9
	YRD	7.2 (1.2, V)	4.1 ± 0.6	17.7
	PRD	8.0 (1.2, VI)	-3.3 ± 0.3	16.9

Yan et al., 2017



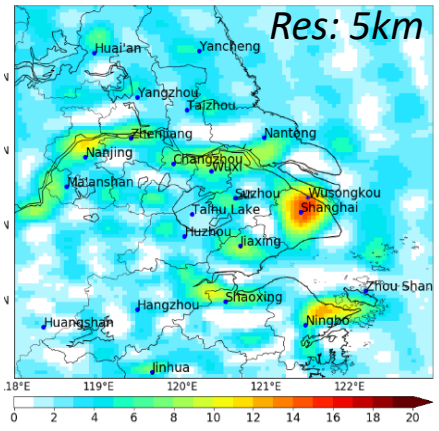
Satellite+Model Derived High-res (5 km) Emissions Reveal Biases in Bottom-up Inventories

OMI NO_2 VCDs



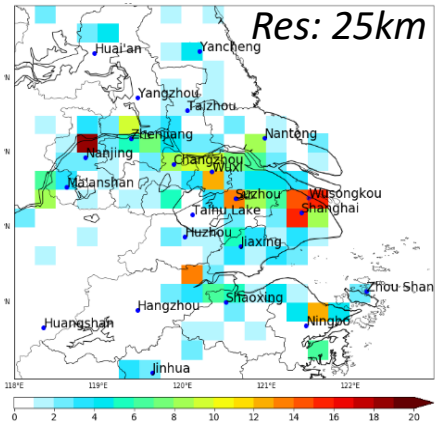
10^{15} molec. cm^{-2}

OMI + PHLET emis

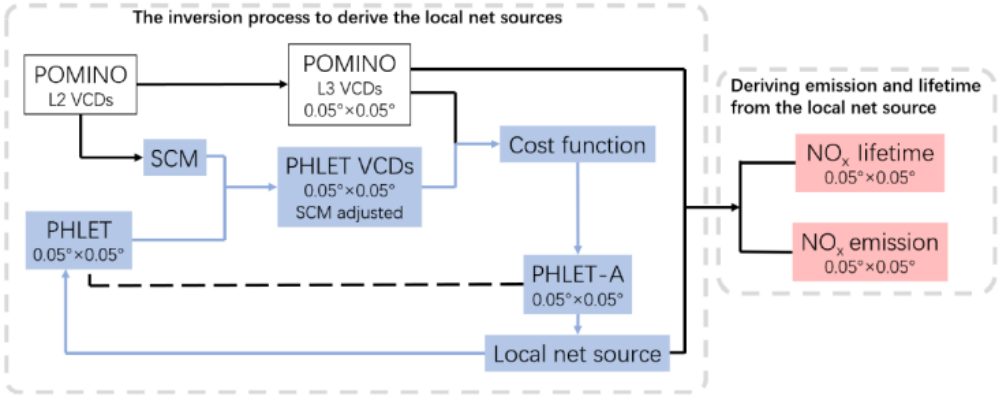


kg km^{-2} h^{-1}

MEIC emissions



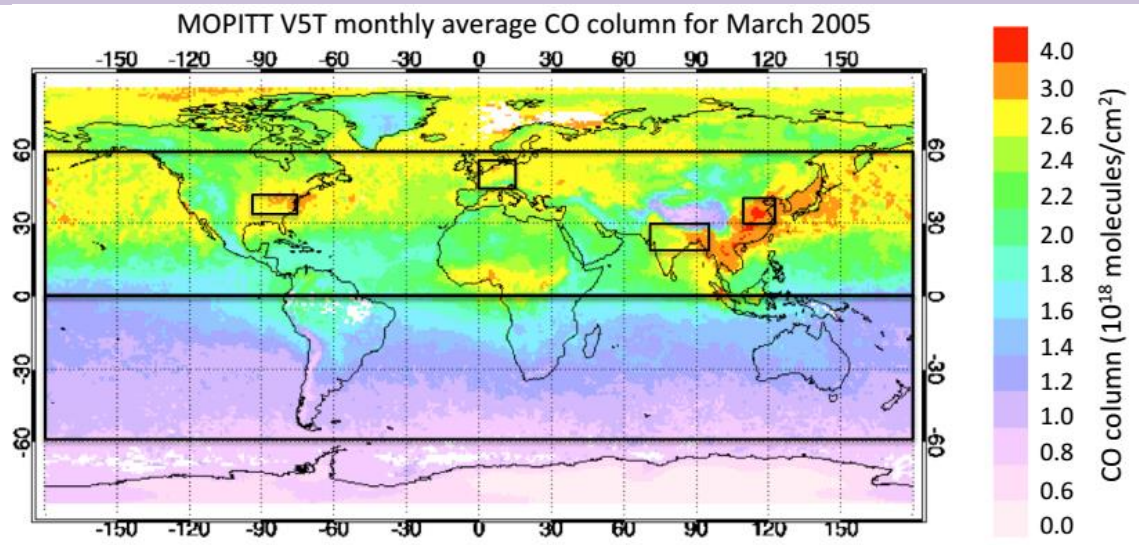
kg km^{-2} h^{-1}



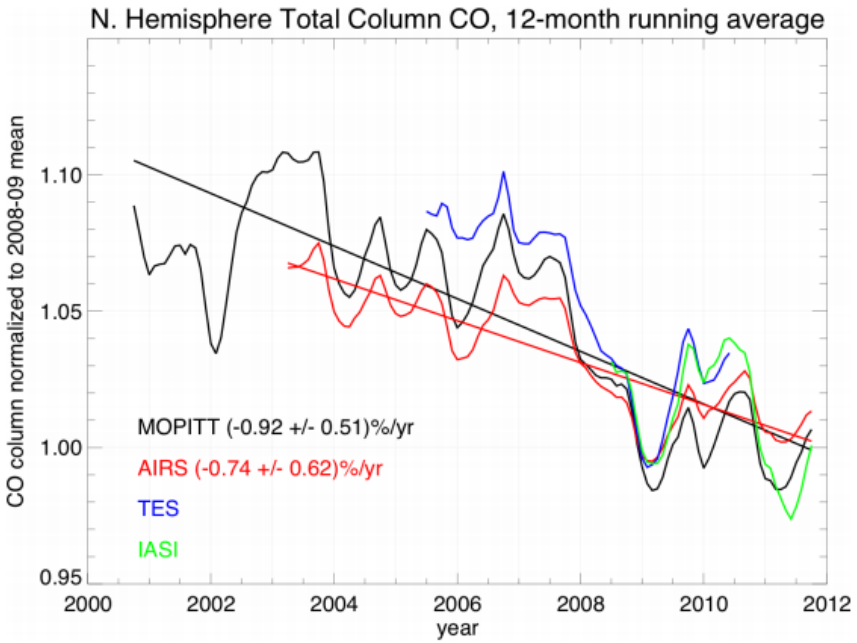
- Inversion model built from scratch
- Transport and nonlinear chemistry accounted for in emission estimate

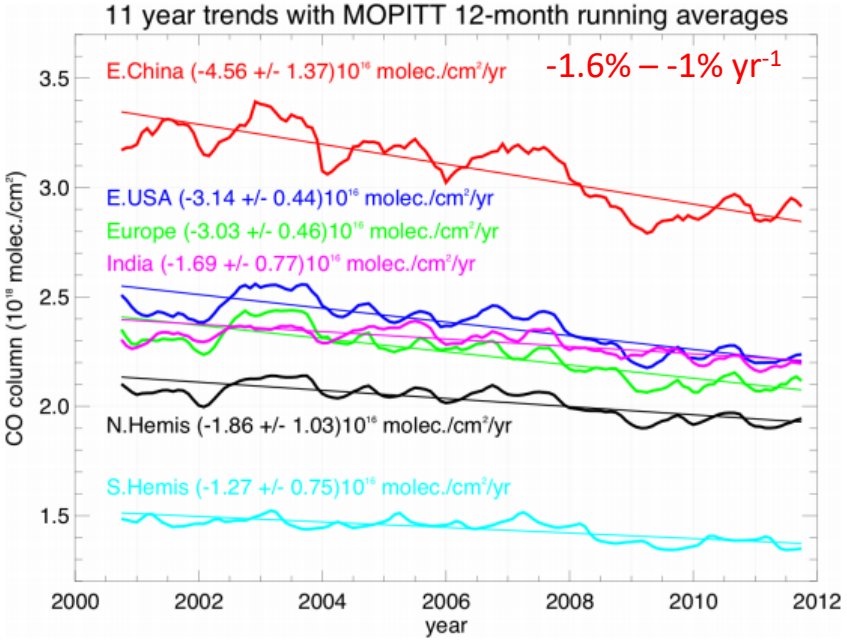
Kong et al., 2019, ACP

Changes in Tropospheric CO: 2000-2012

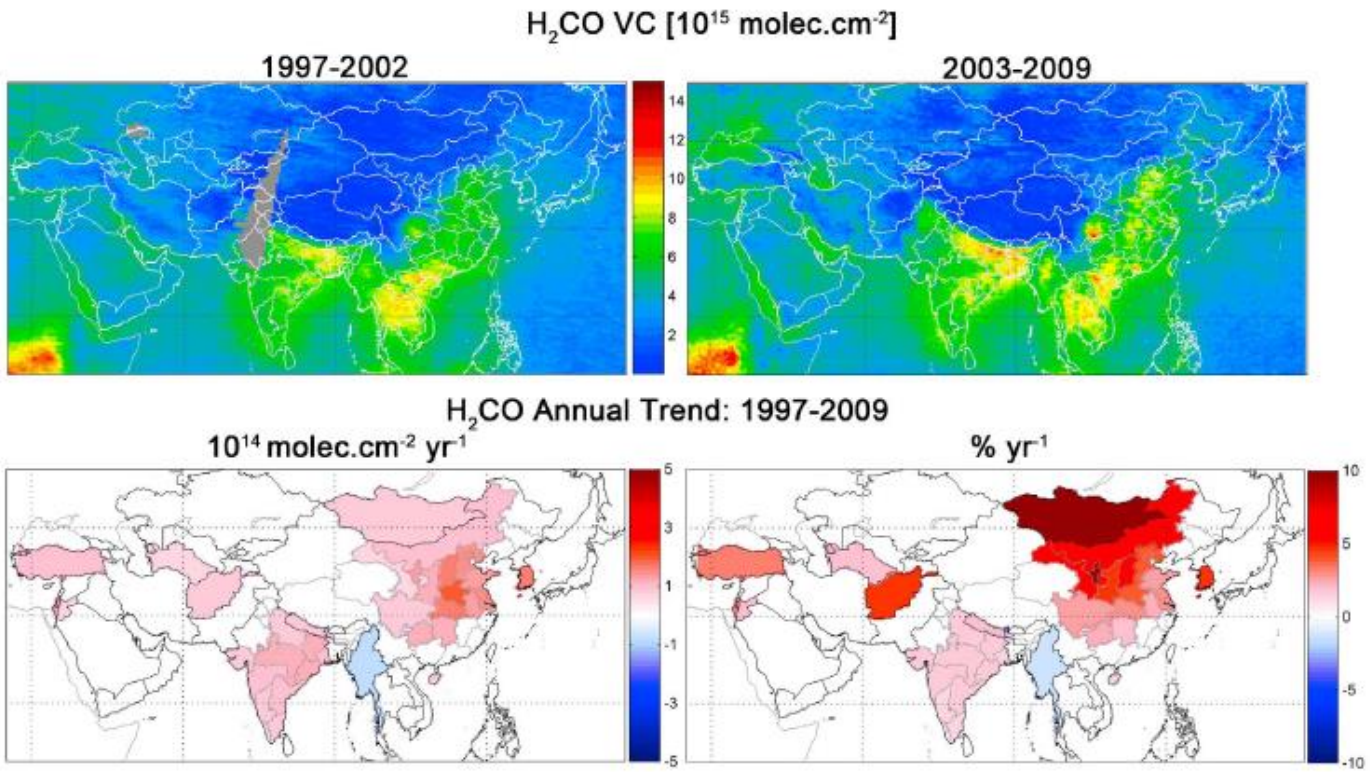


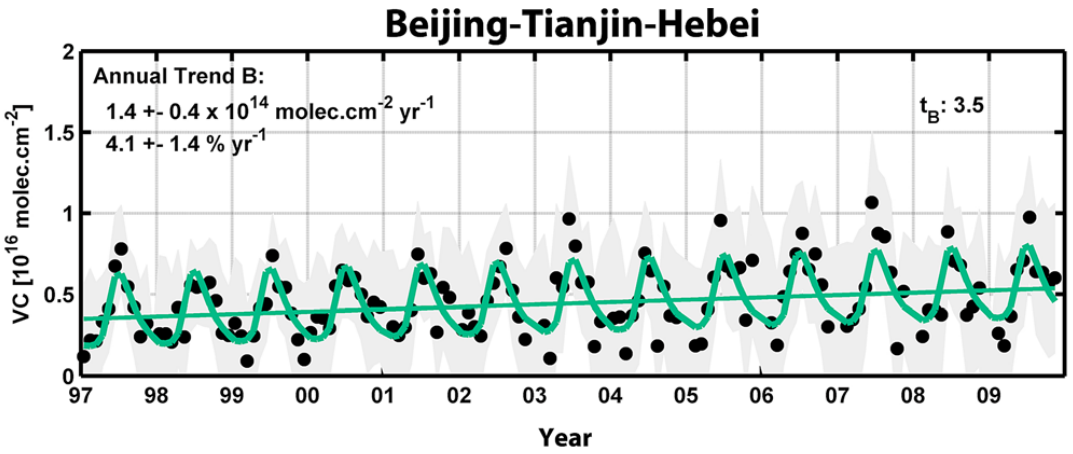
Worden et al., 2013, ACP





Trends of VCDs of HCHO in Asia: 1997 – 2009

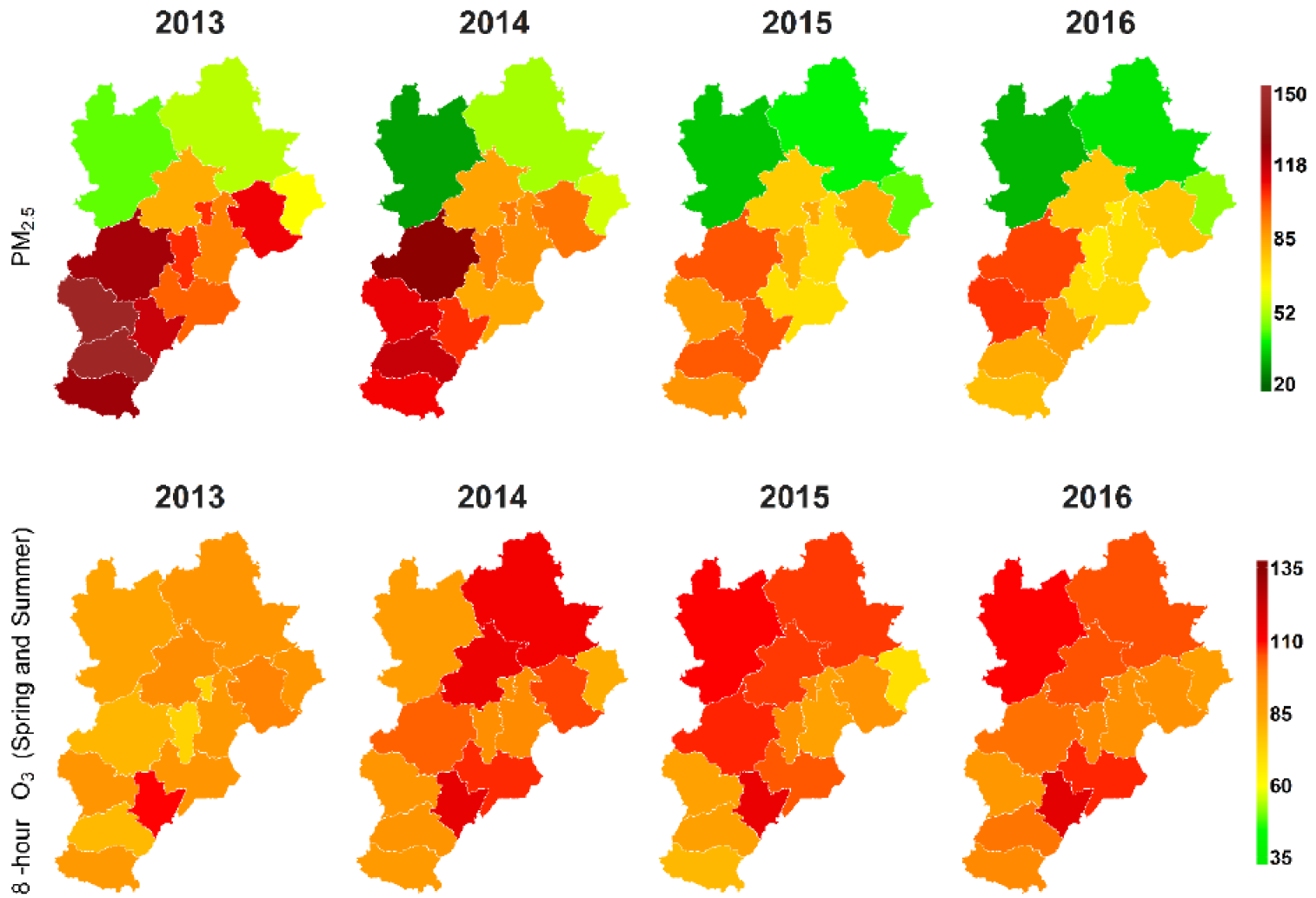




De Smedt et al., 2010

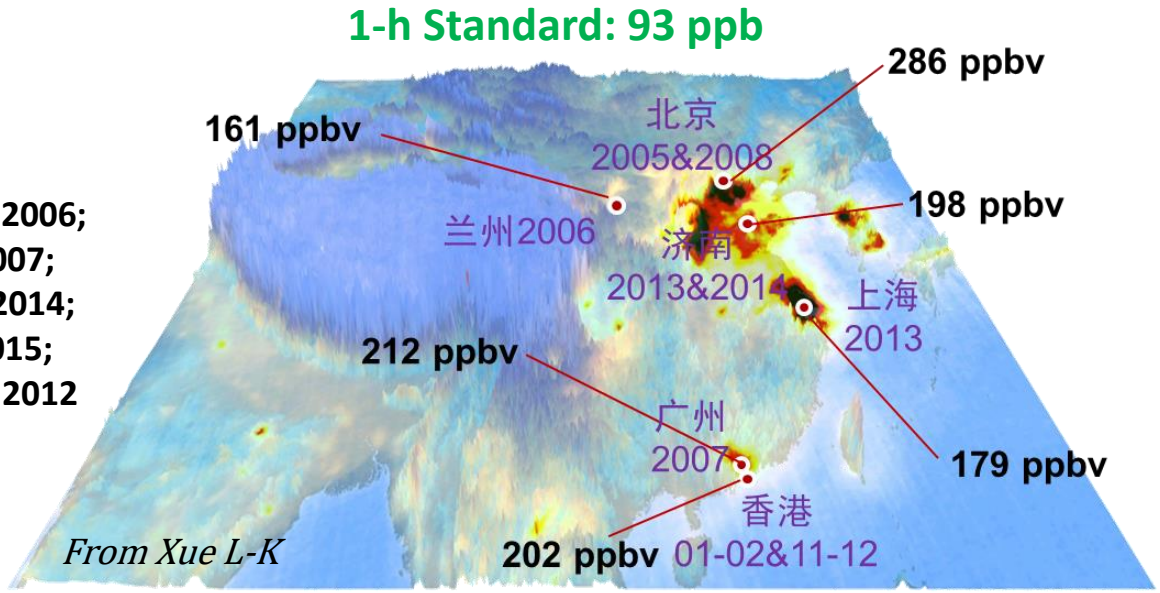
Changes in O_3 and $PM_{2.5}$ Pollution over BTH

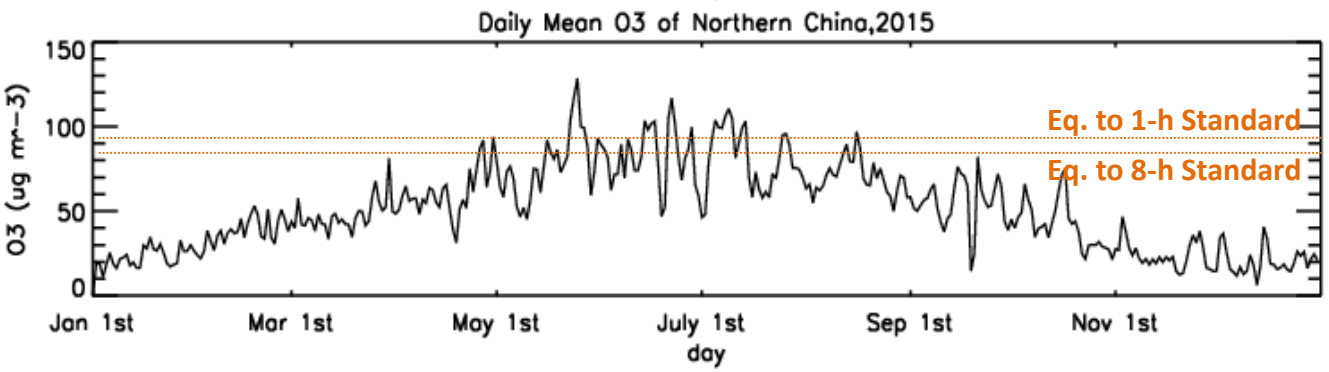
After statistical adjustment for meteorological changes



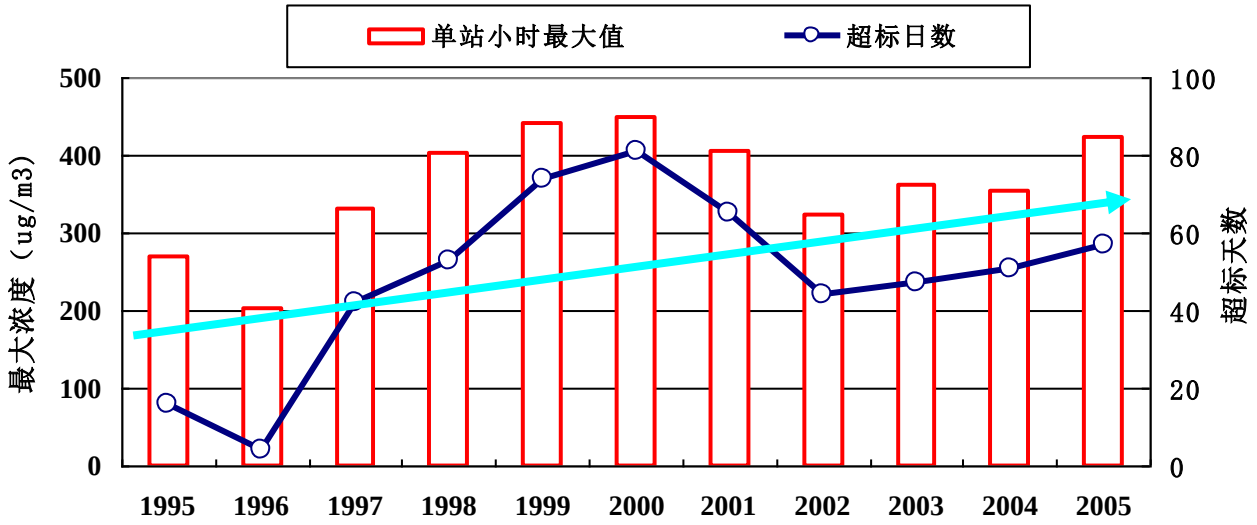
China Is Facing Increasingly Severe Ozone Pollution

Wang et al., GRL 2006;
Zhang et al., 2007;
Xue et al., ACP, 2014;
Shi et al. AR 2015;
Zhang et al. JGR 2012



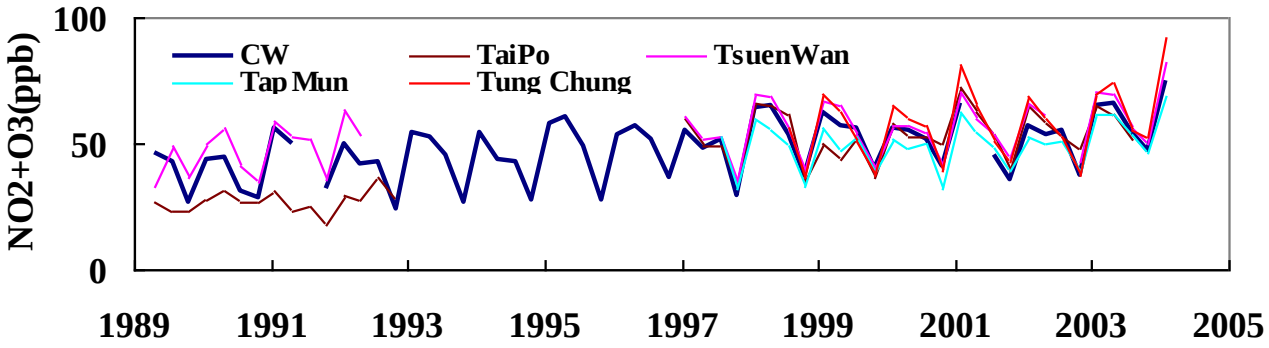


Trends of O_3 in Beijing and PRD



Beijing,

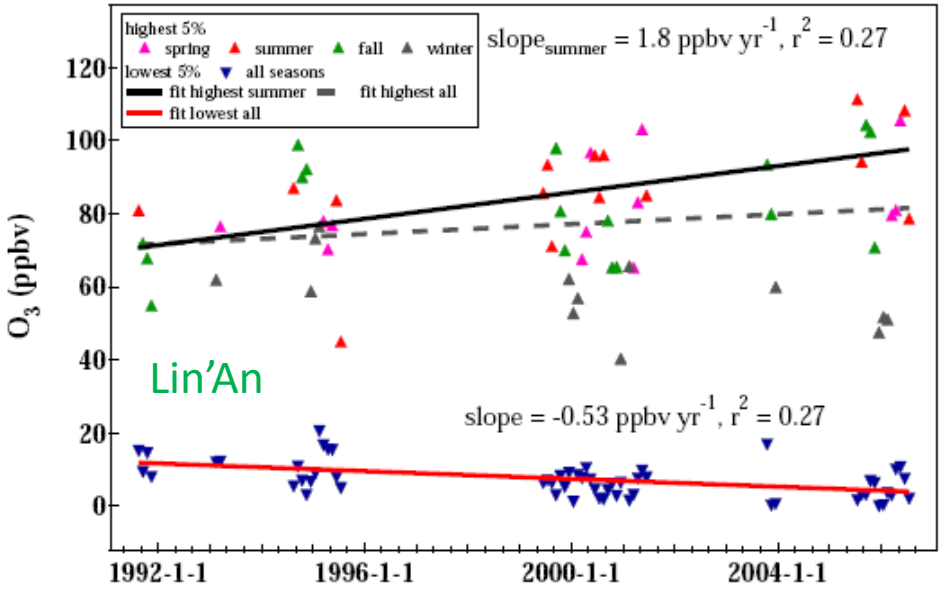
Max O_3 and days over STD



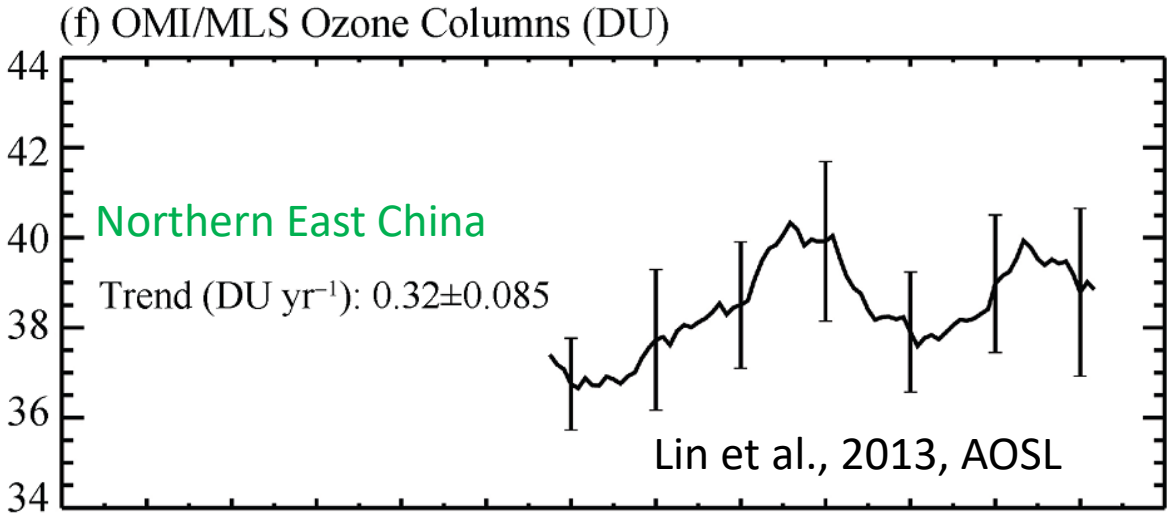
Hong Kong: Daytime O_3 concentration

O_3: 1ppb/yr

Background O_3 Concentrations are Increasing

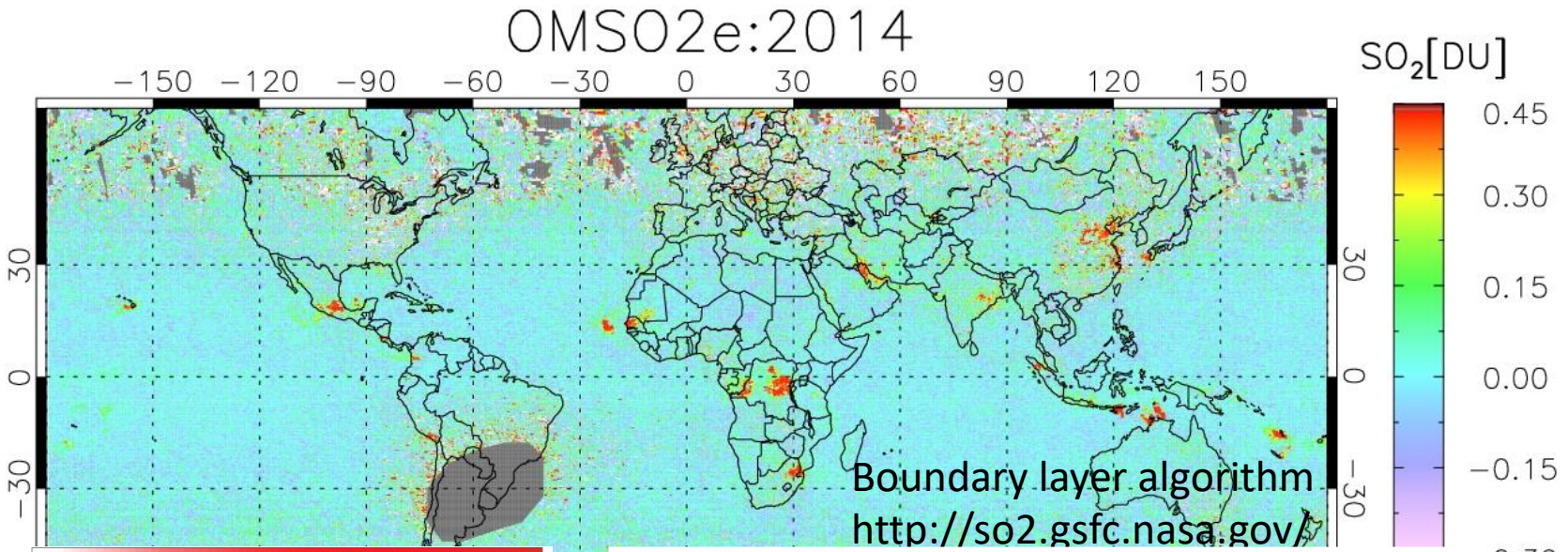


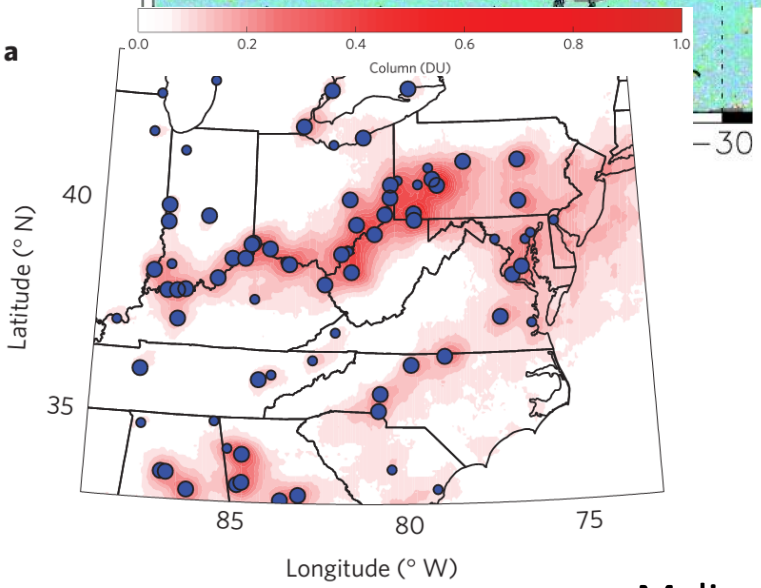
Xu et al., 2008, ACP

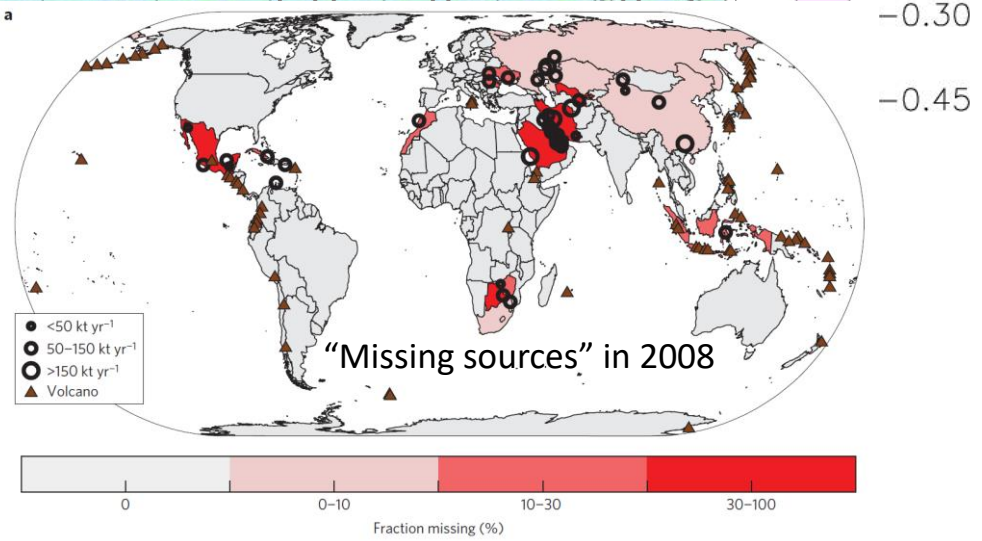


Lin et al., 2013, AOSL

OMI-retrieved VCDs of Tropospheric SO_2







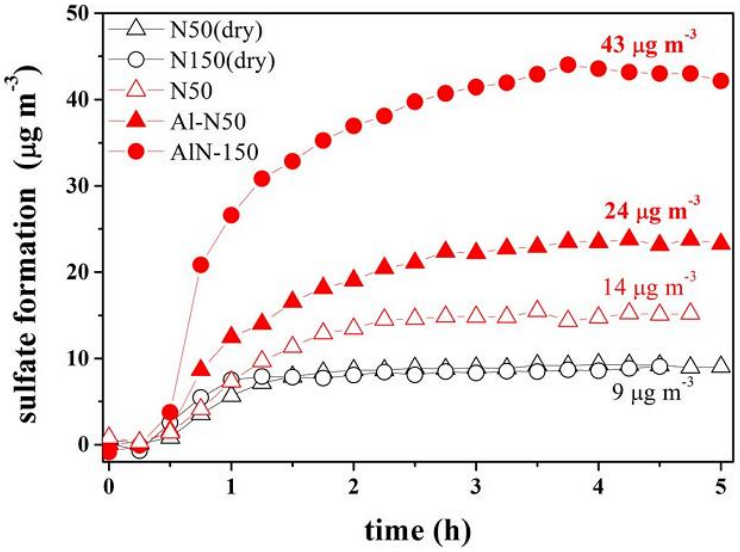
Mclinden et al., 2016 Nature Geoscience

NO_x-catalyzed Sulfate Formation

NO_x-catalyzed sulfate formation on mineral dust surface:

$$SO_2 + 2NO_2 + M \rightarrow M - SO_4 + 2NO$$

$$2NO + O_2 + M \rightarrow 2NO_2$$



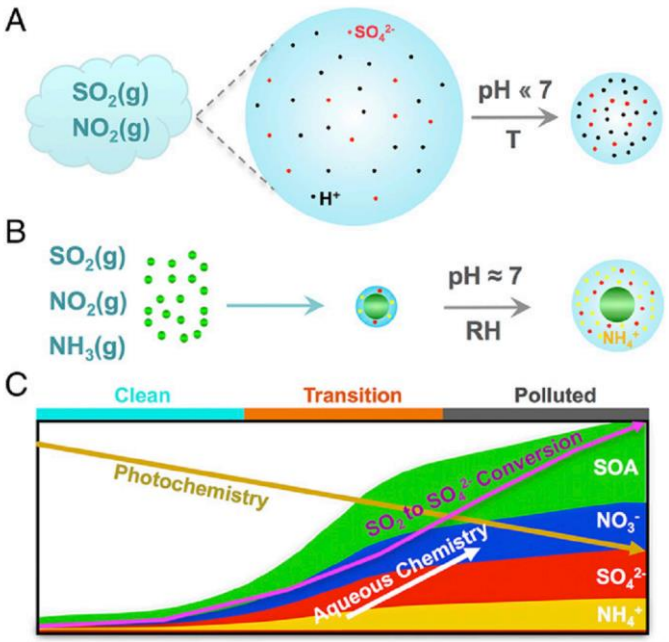
He et al., 2014, SR

Cloud/fog (large):

$$SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) + 2HONO(g).$$

PM (small, easily acidified):

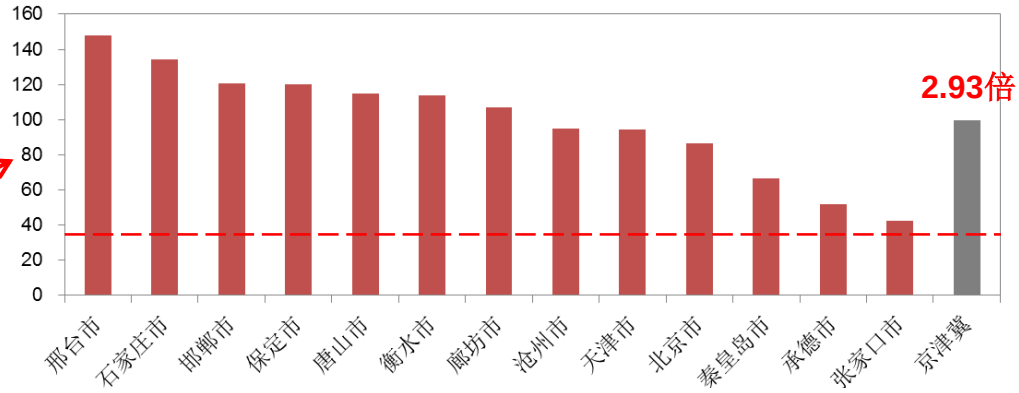
$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g).$$



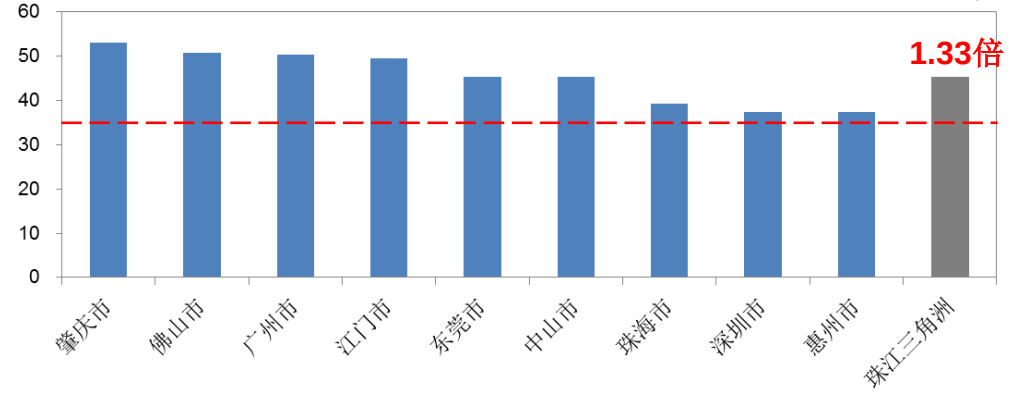
Wang et al., 2016, PNAS

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



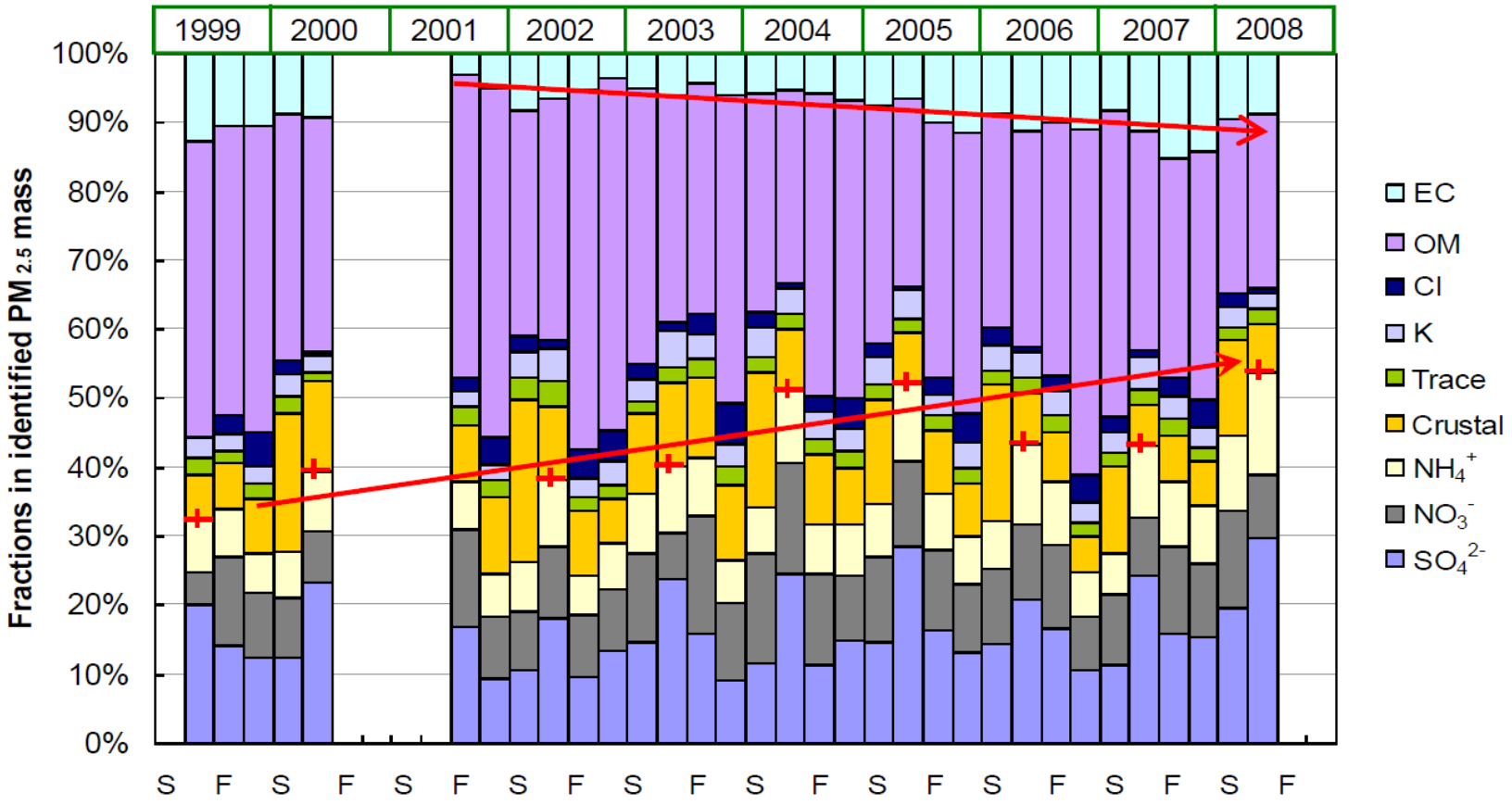






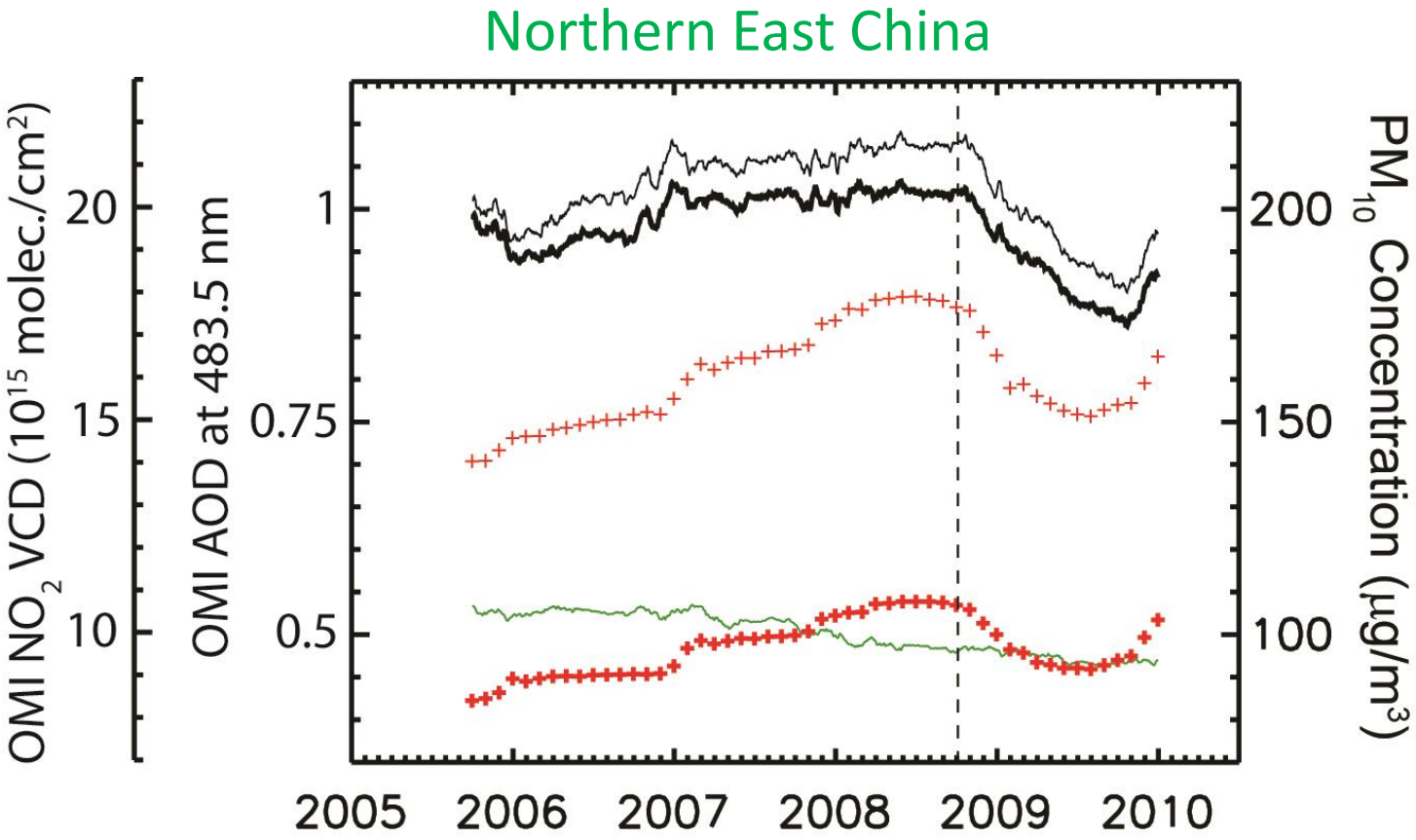
贺克斌，2014

Growing Fraction of Secondary $PM_{2.5}$ with Time at Beijing



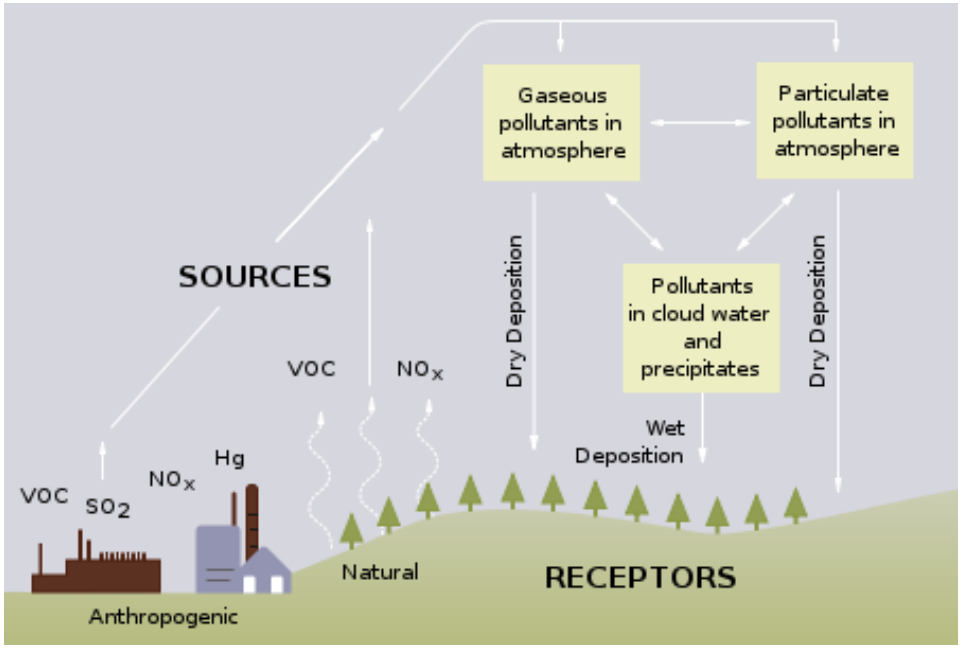
Kebin He

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



Lin et al., 2010

Acid Deposition



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

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

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

Hetero: $NO_2 + SO_2 + H_2O(s) \rightarrow SO_4^{-2}$?

Hetero: $TMI + SO_2 + H_2O(s) \rightarrow SO_4^{-2}$?

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

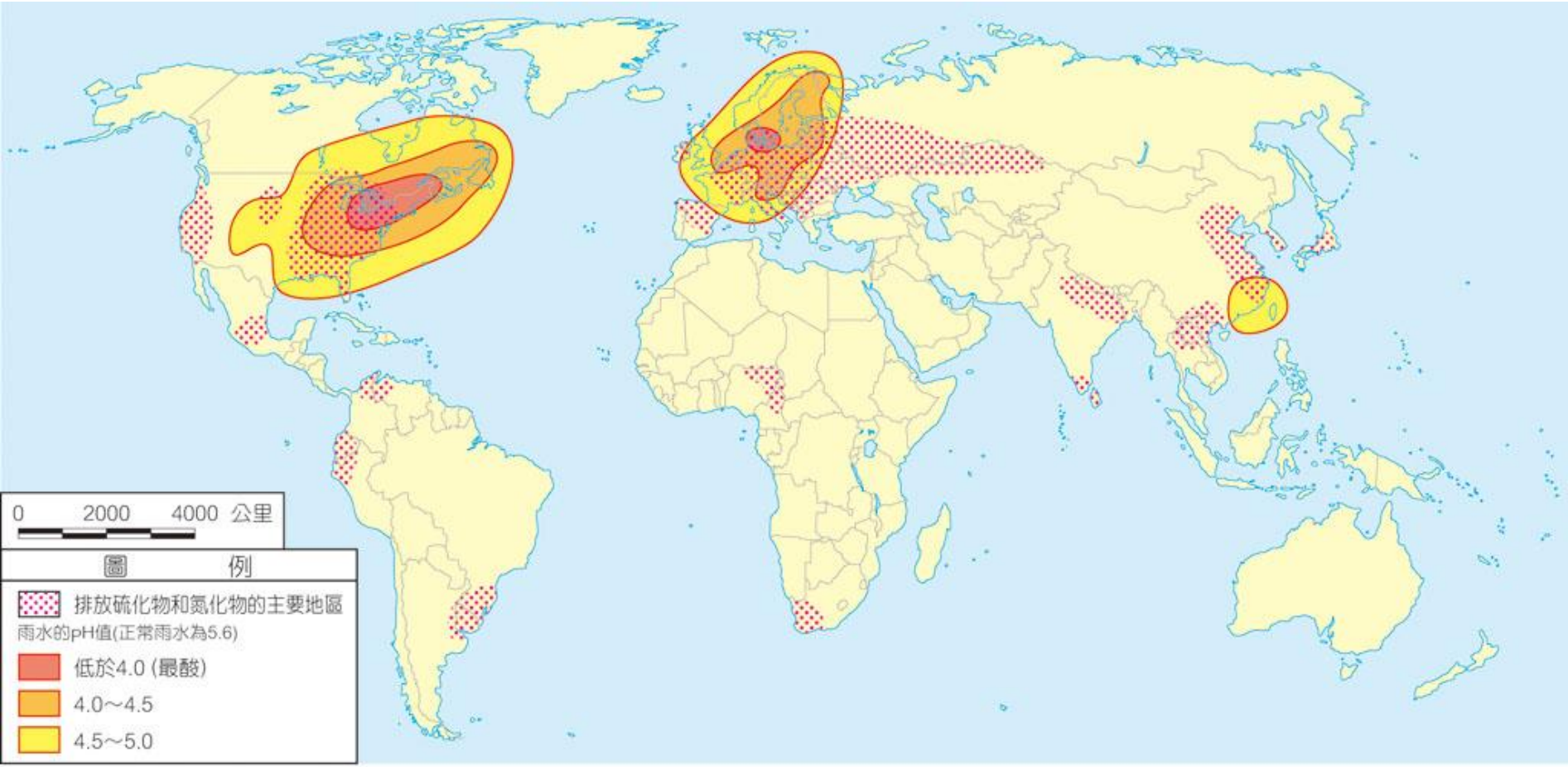
Hetero: $NO_2 + H_2O(s) \rightarrow NO_3^-$?

Hetero: $N_2O_5 + H_2O(s) \rightarrow 2HNO_3$

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

Acids are balanced by mineral or ammonium ions

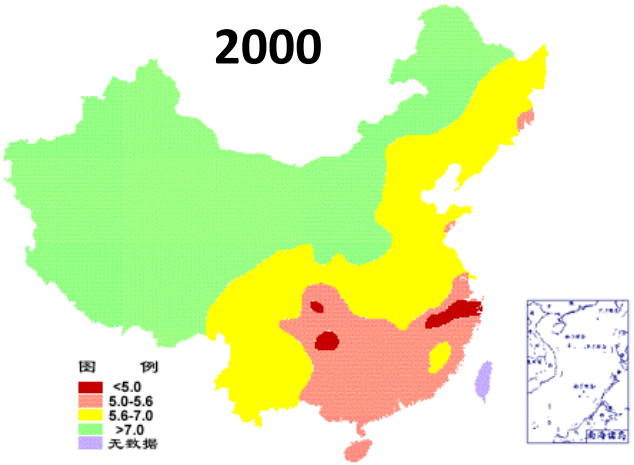
Acid Deposition

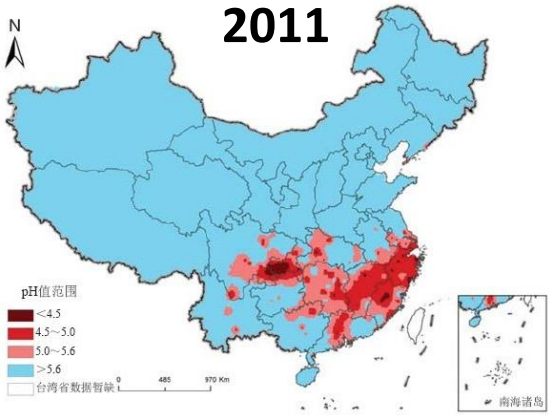


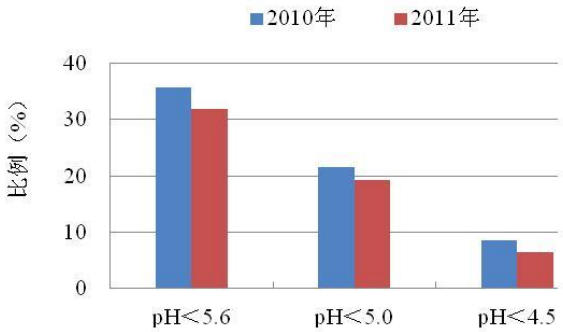
Acid Rain in China

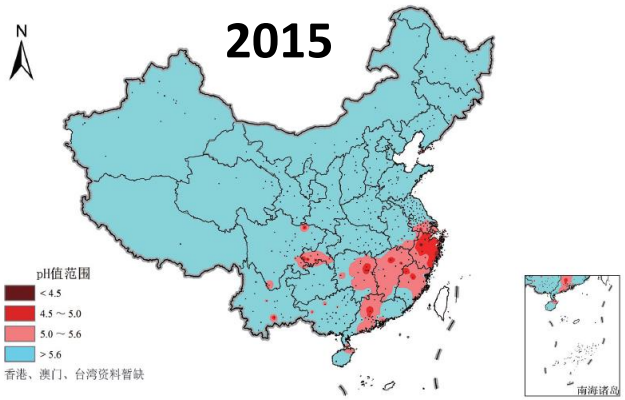
2011: 12.9% of China's land is affected by acid rain

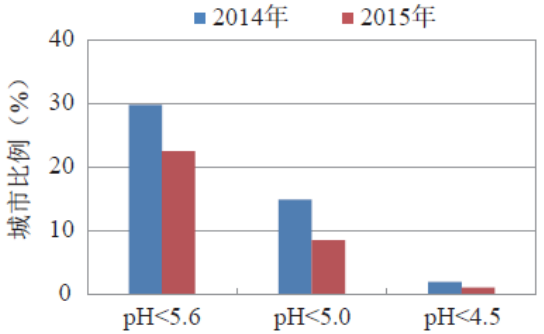
2015: 7.6% of China's land is affected by acid rain







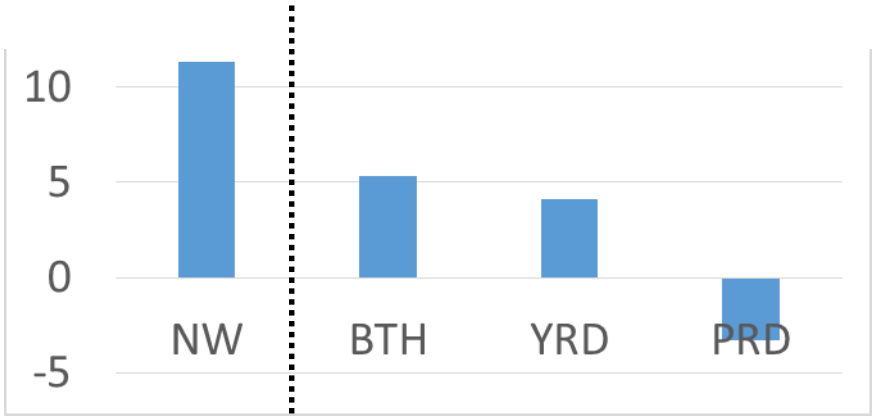




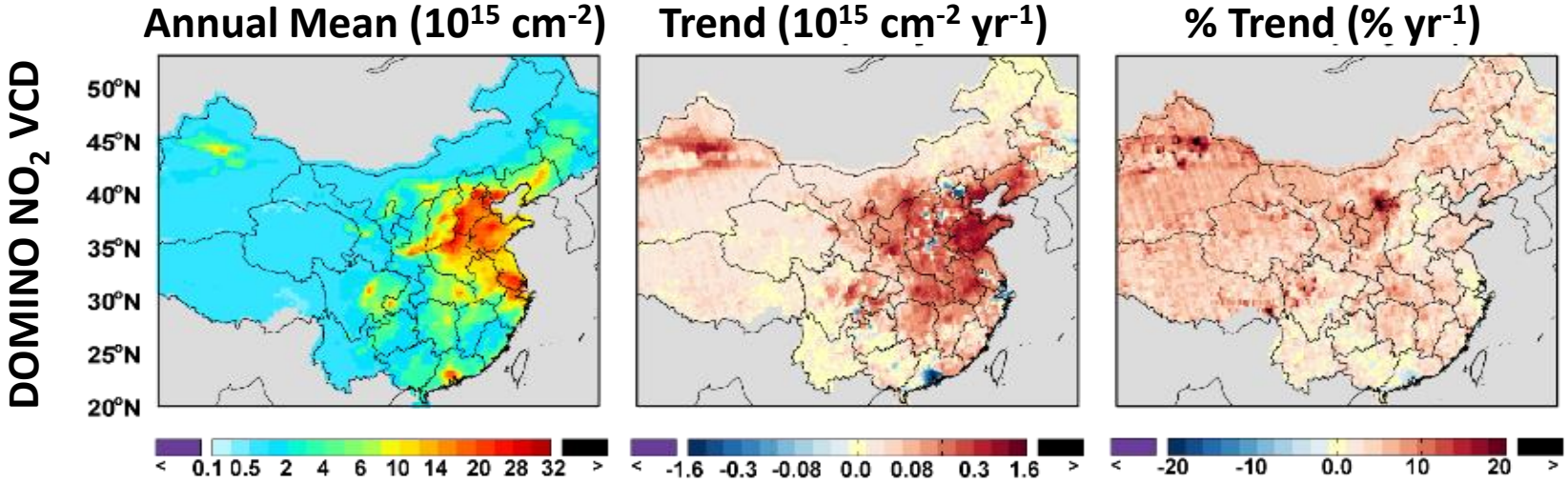
中国环境状况公报

Growth of NO_2 VCDs over 2005–2013: West vs. East China

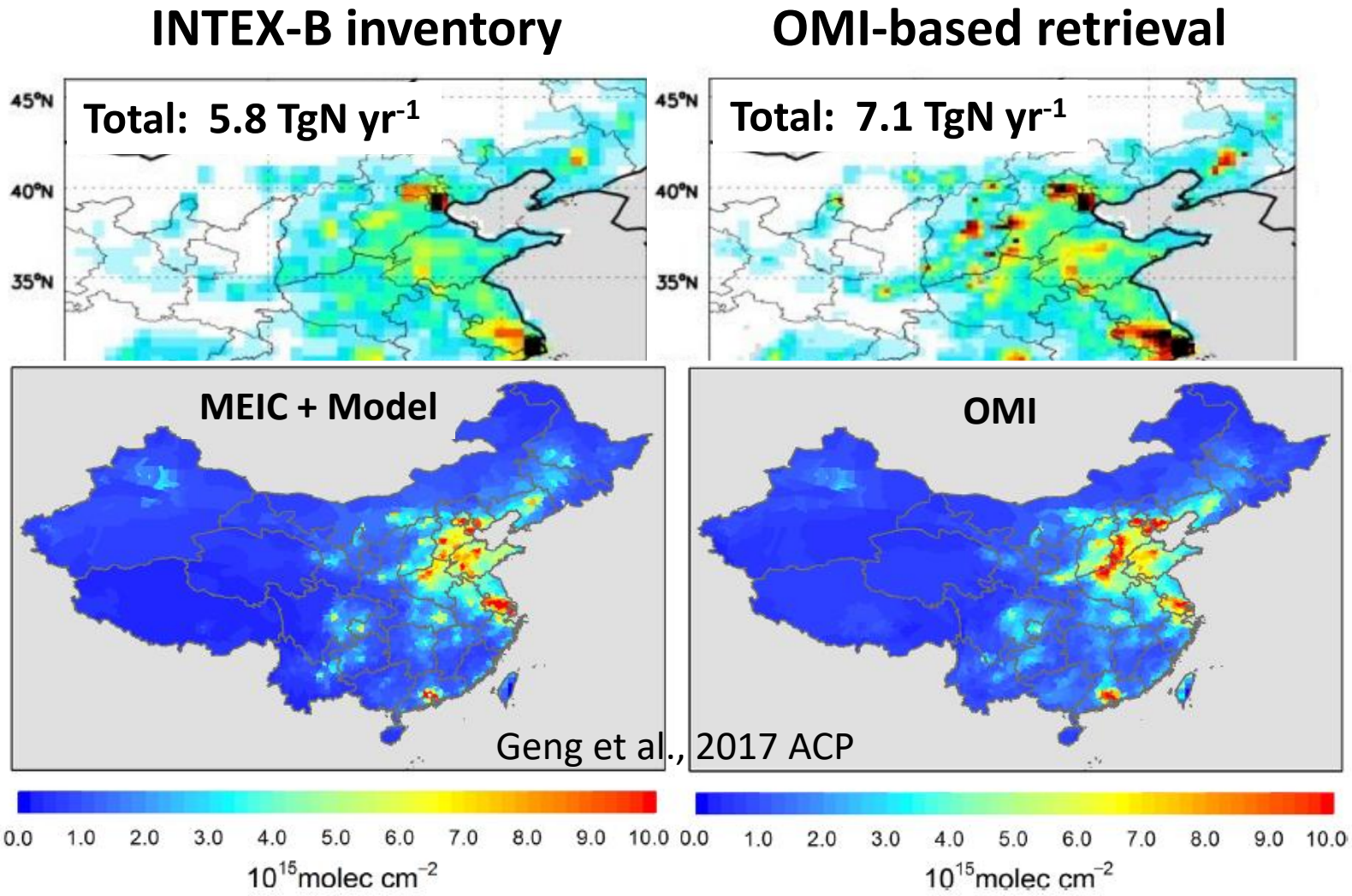
Cui et al., 2016 ACP



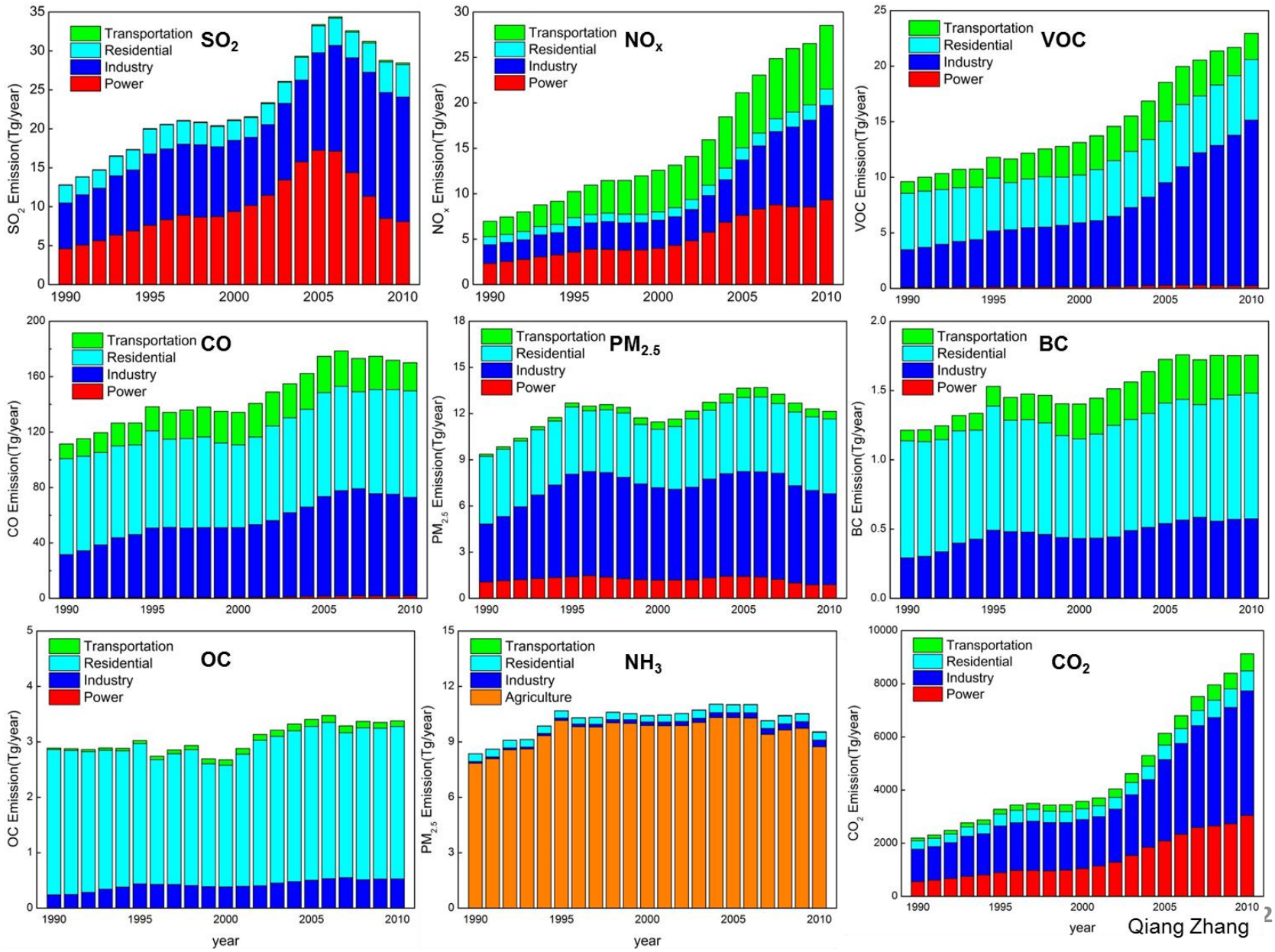
Yan et al., in prep



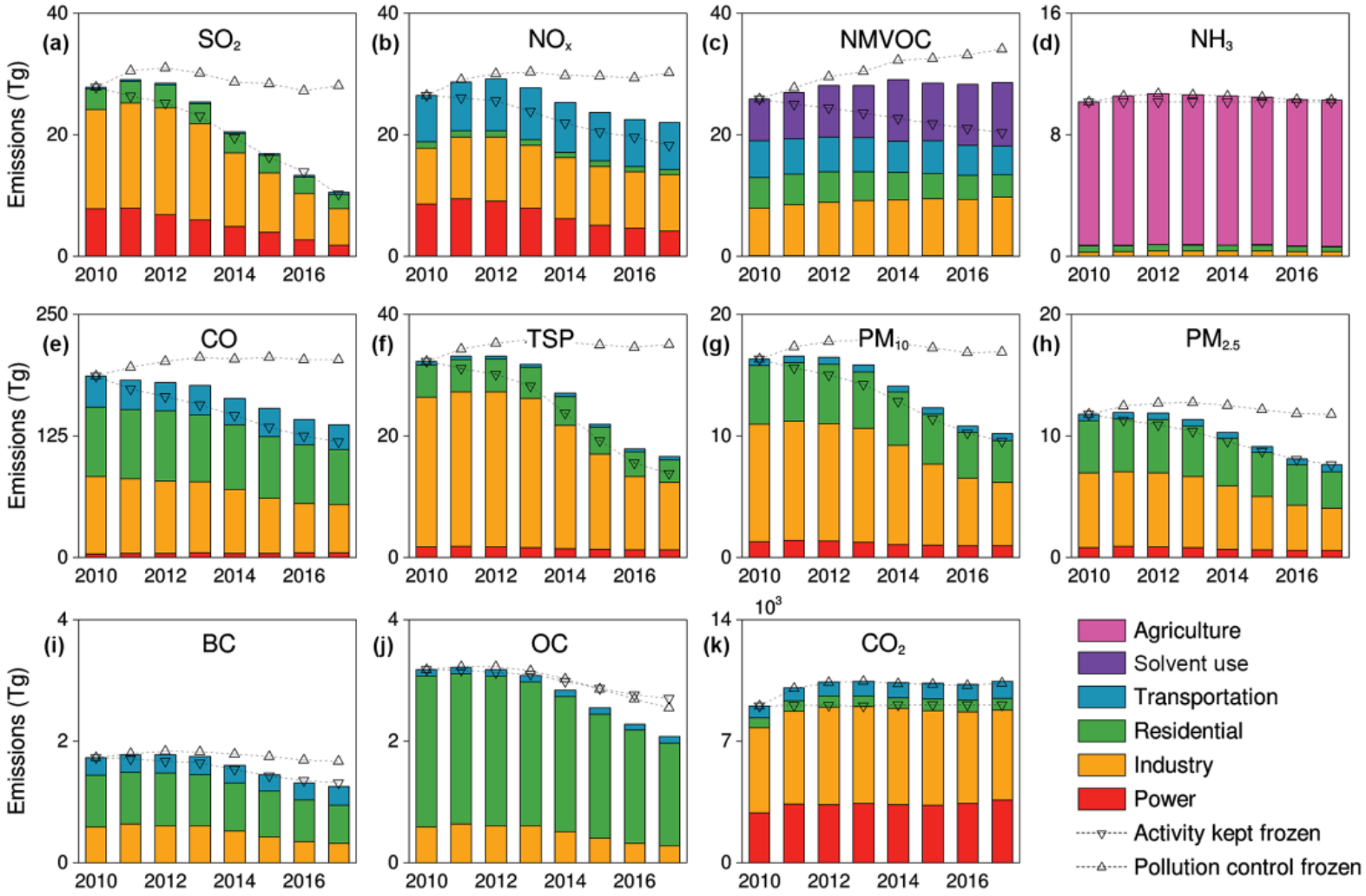
Satellite+Model Derived High-res (25 km) Emissions Reveal Urban Biases in Bottom-up Inventories



Anthropogenic Emissions in China: 1990-2010

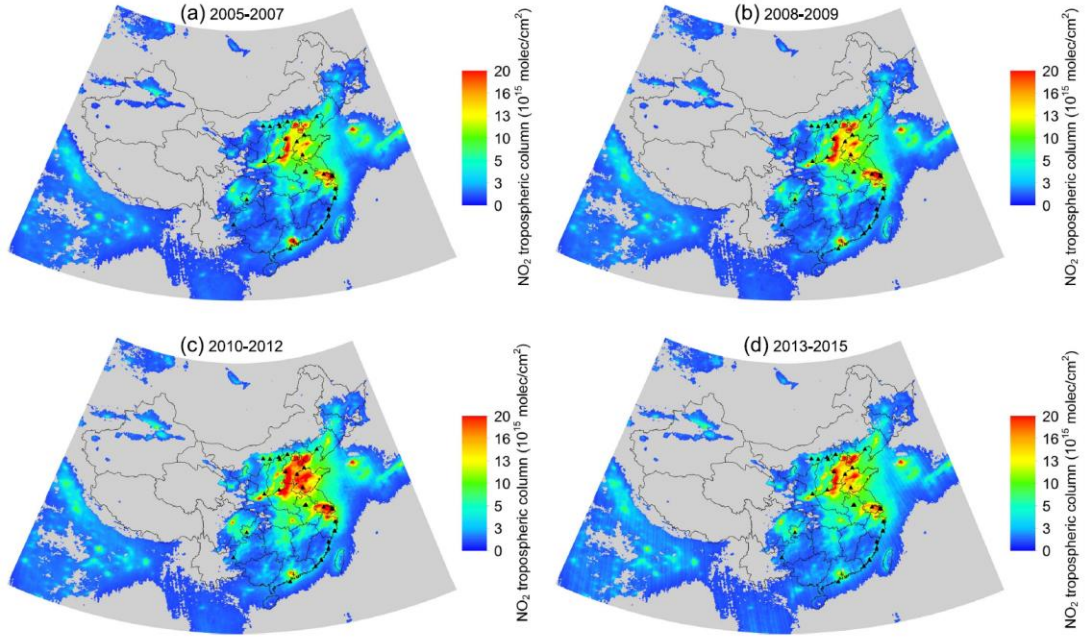


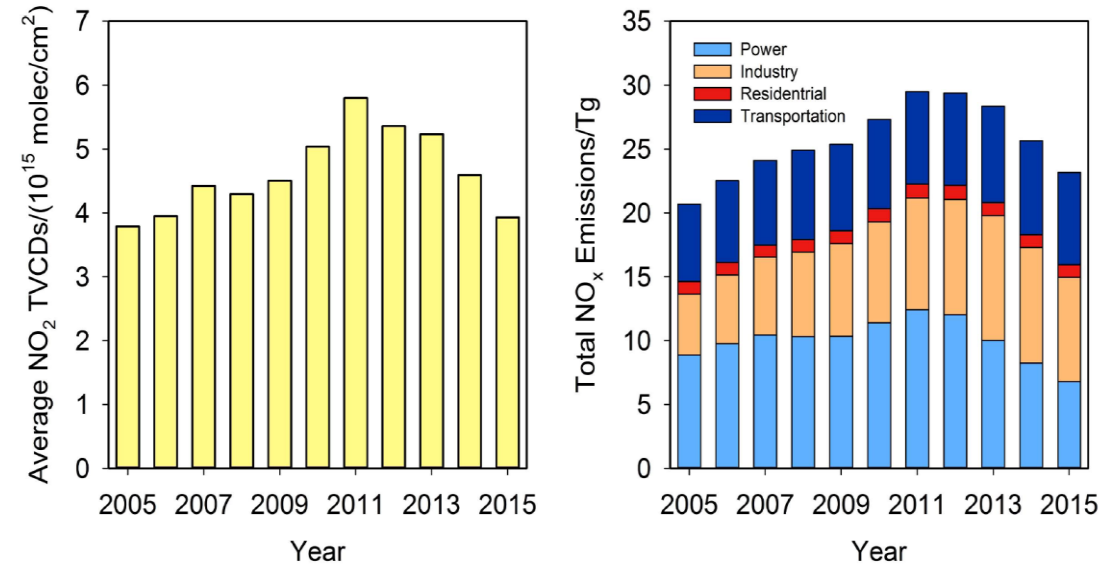
Anthropogenic Emissions in China: 2010-2017

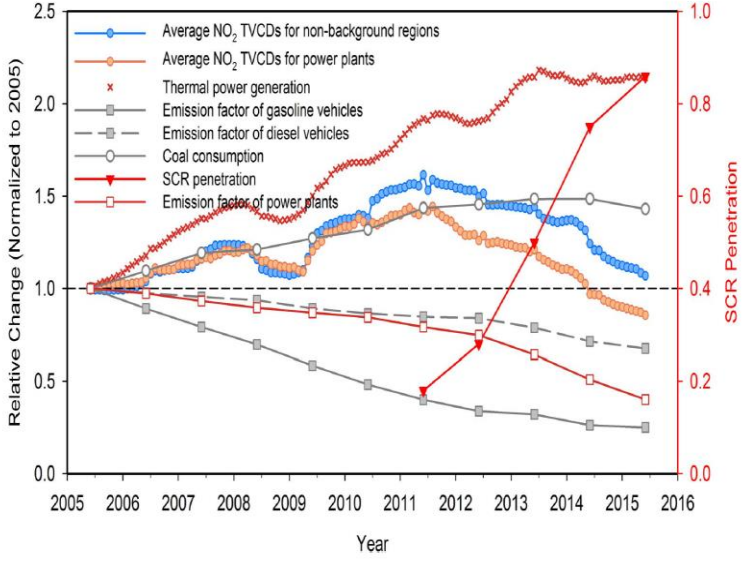


Zheng et al., ACP, 2018

Recent Reductions in NO_2 VCD over China



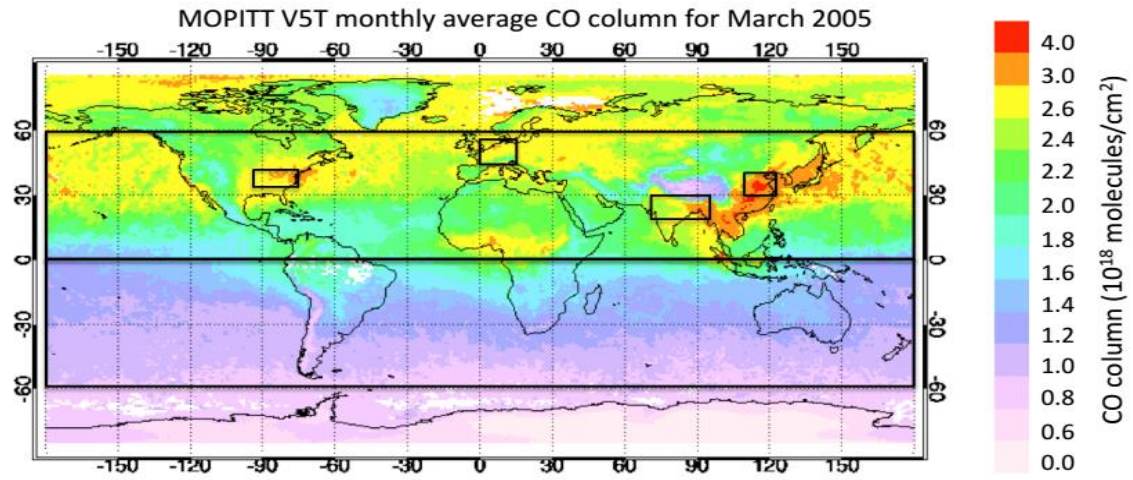


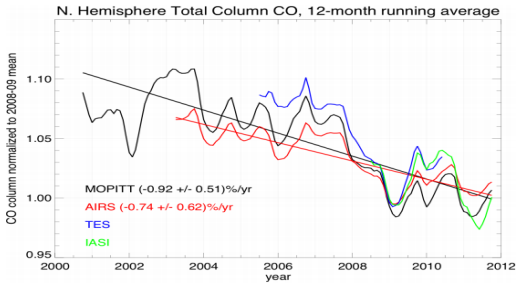


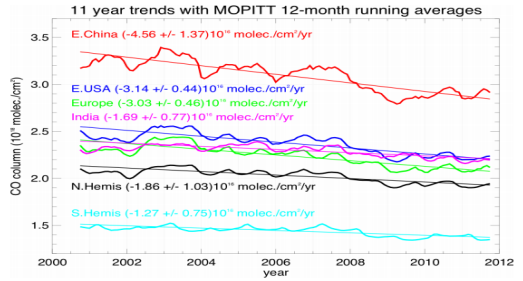
Liu et al., 2016, ERL

Changes in Tropospheric CO: 2000-2016

CO column based on multiple products (Worden et al., 2013 ACP)



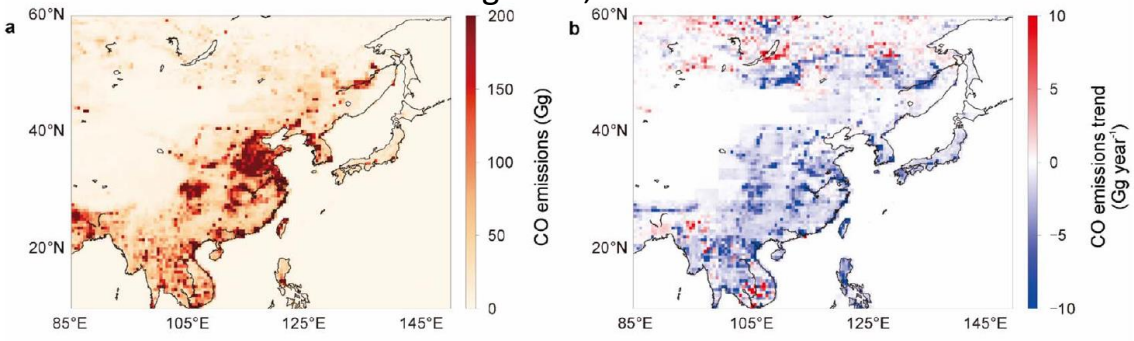




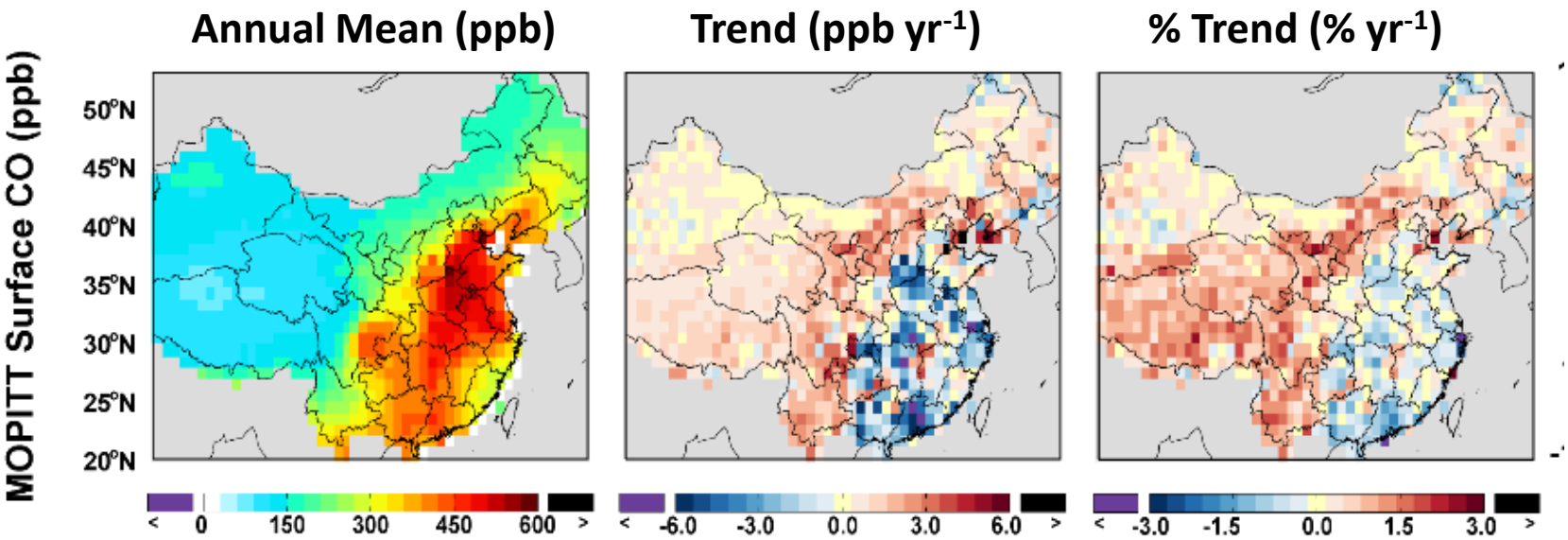
E. China: -1.6% – -1% yr^{-1}

CO emissions over 2005-2016 based on MOPITT v7

Zheng et al., 2018 ERL

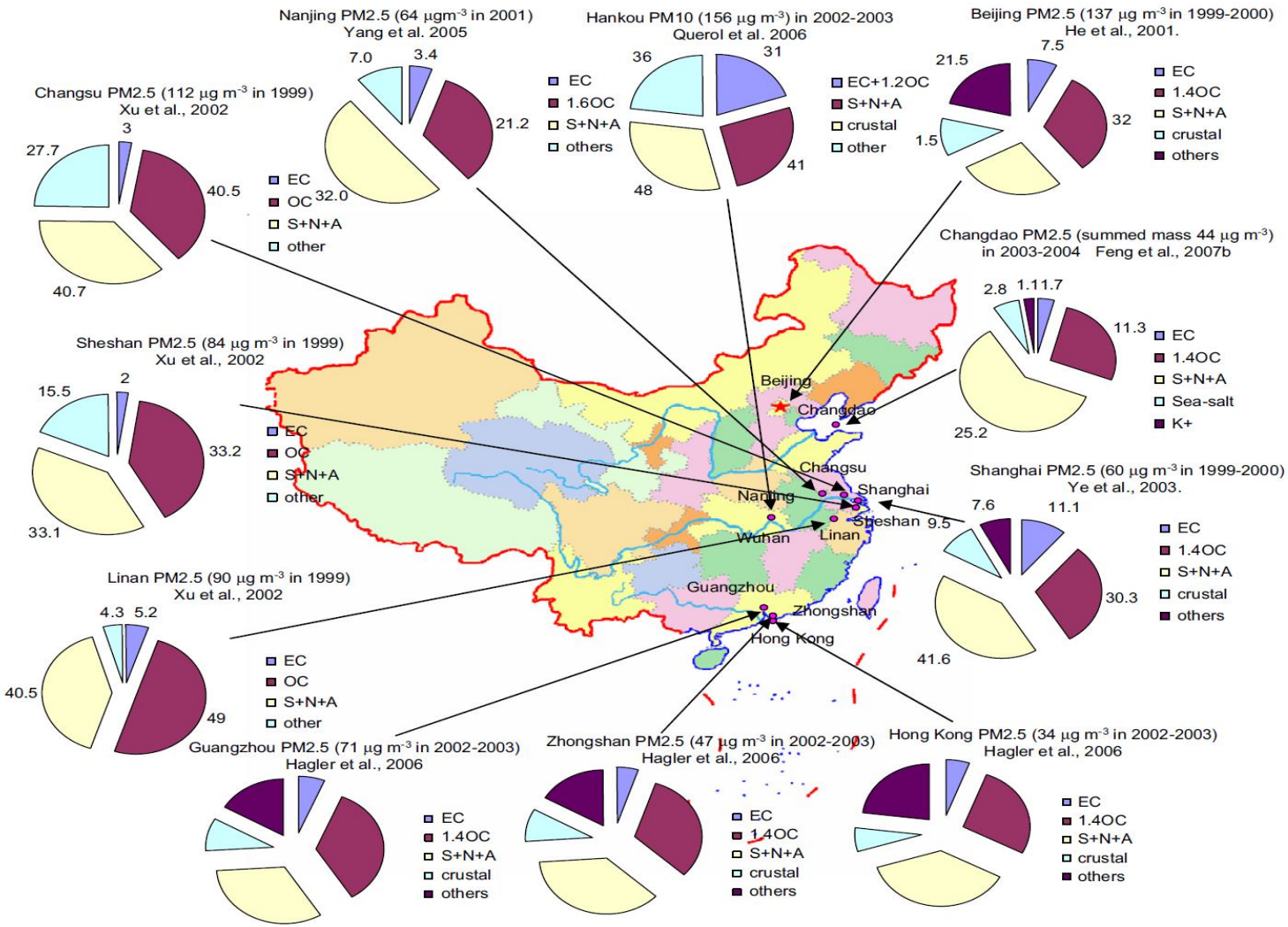


Changes in CO at 700 hPa: 2004-2012



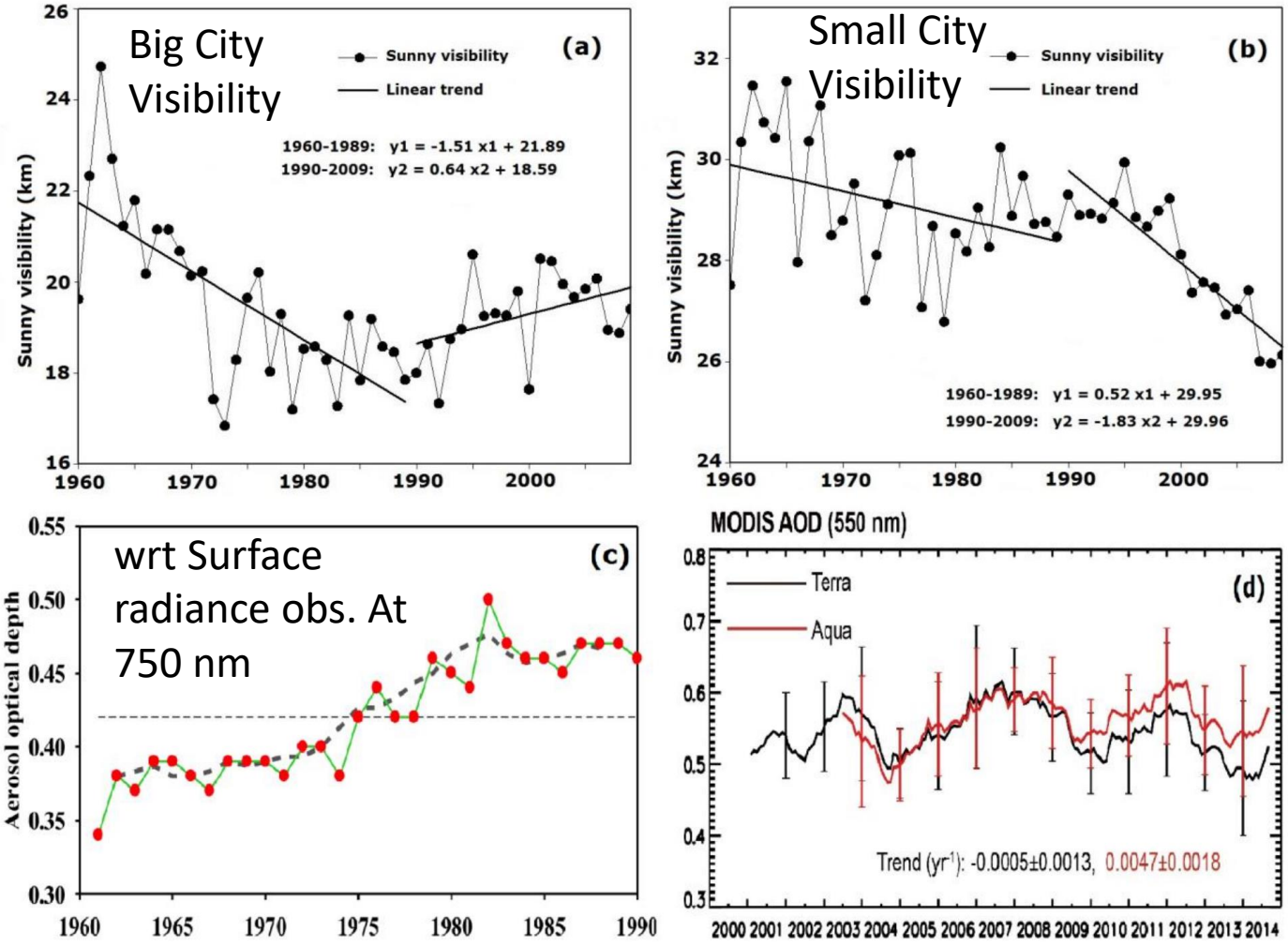
Yan et al., 2017

Speciated PM Measurements in China



Fang et al., 2009

Trends of Visibility and AOD over China: 1960 – 2014



Lin et al., 2013, AOSL; Li et al., 2016, RoG