CHAPTER 5

TROPOSPHERIC CHEMISTRY
&
AIR POLLUTION

北京大學
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

Basic Concepts of Chemistry

- **Photolysis: A + hv → B + C**

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

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

- **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_f *** [A] * [B] +** k_b *** [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:

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

$$k_o(T) = k_o^{300}\left(\frac{T}{300}\right)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \qquad k_\infty(T) = k_\infty^{300}\left(\frac{T}{300}\right)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Basic Chemistry

- $NO + O_3 \rightarrow NO_2$ (R1)
- $NO_2 + h\nu \rightarrow NO + O$ (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

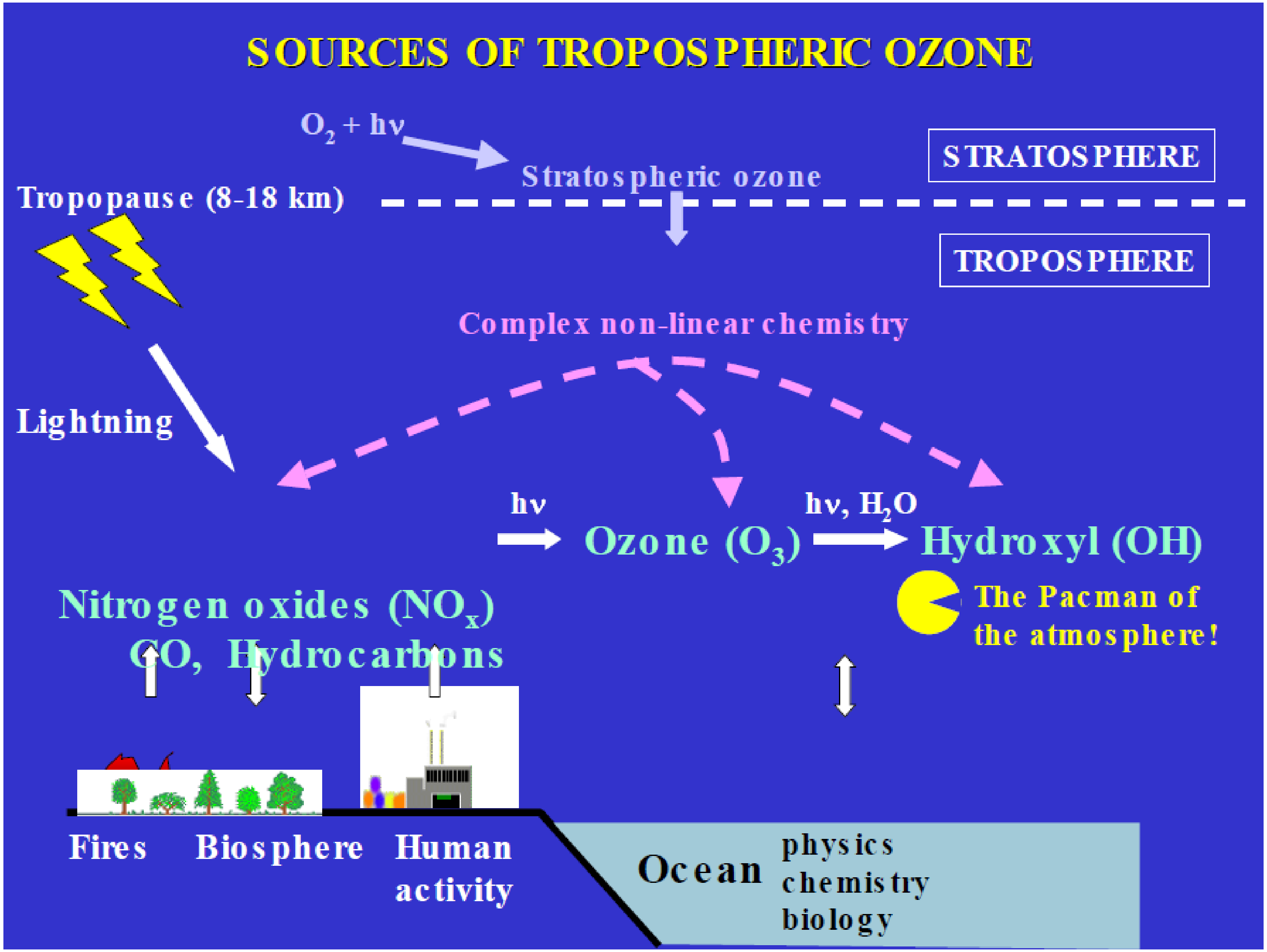
*** This is one of the most important relations regulating concentrations of NO, NO_2 and O_3 in the troposphere.

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.

Sources of Tropospheric Ozone



Photochemistry for Tropospheric Ozone

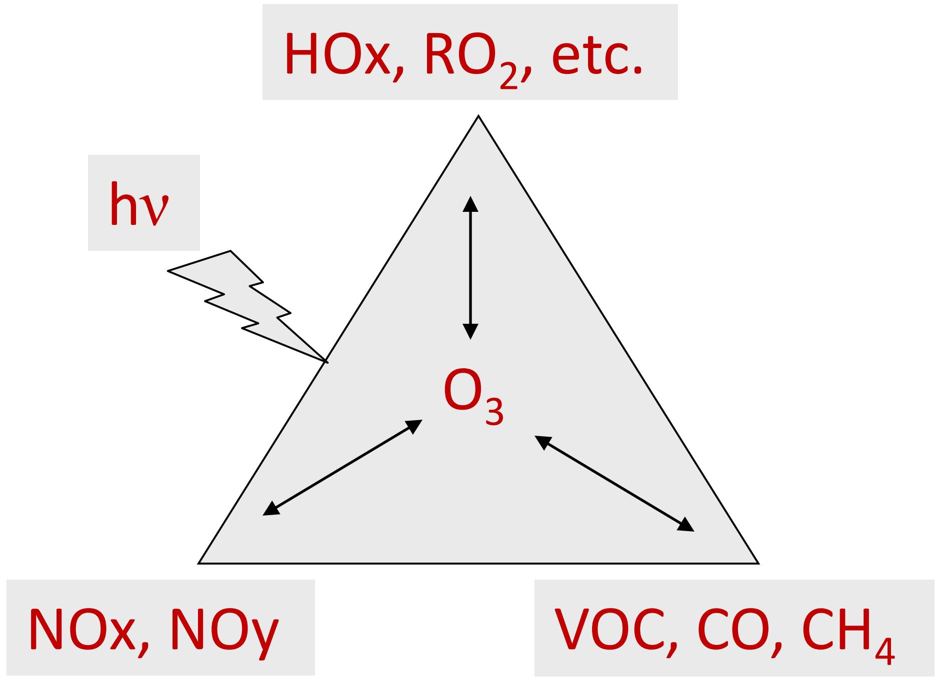
Production

- Initiation
  - $CO + OH (+ O_2) \rightarrow CO_2 + HO_2$
  - $RH + OH (+ O_2) \rightarrow RO_2 + H_2O$ (RH: VOC)
- Propagation
  - $NO + RO_2 (+ O_2) \rightarrow \text{Carbonyl} + NO_2 + HO_2$
  - $NO + HO_2 \rightarrow OH + NO_2$
  - $NO_2 + h\nu \rightarrow NO + O(^3p)$ ($\lambda < 420$ nm)
  - $O(^3p) + O_2 + M \rightarrow O_3 + M$
- Termination
  - $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
  - $HO_2 + RO_2 \rightarrow ROOH + O_2$
  - $OH + NO_2 + M \rightarrow HNO_3 + M$

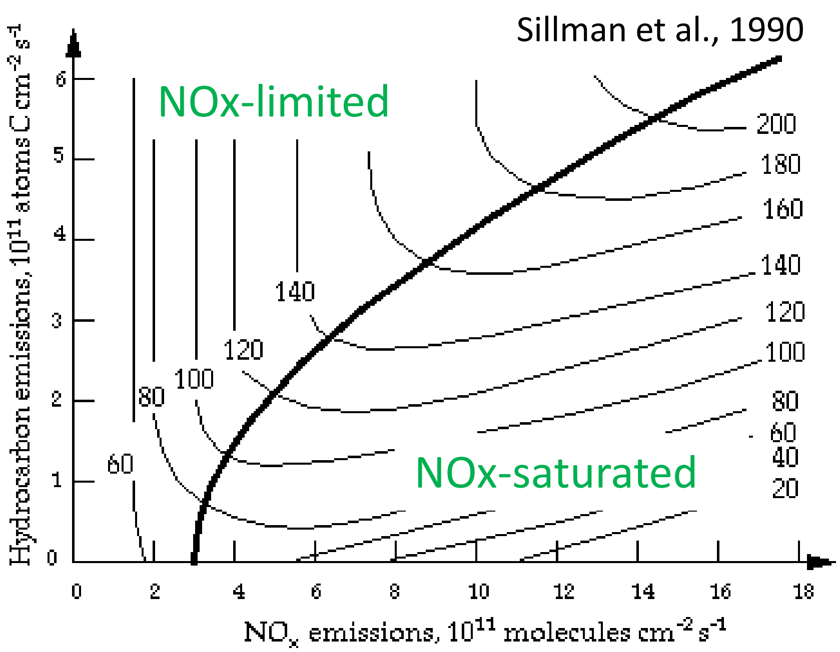
Destruction

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



Ozone mixing ratio as a function of NOx and NMVOC emissions



More Chemistry

Gaseous chemistry (important if weak hv):

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

Heterogeneous chemistry:

- $N_2O_5 + H_2O(s) \rightarrow 2HNO_3$
- $NO_2 + H_2O(s) \rightarrow$ HONO (important source of 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.)

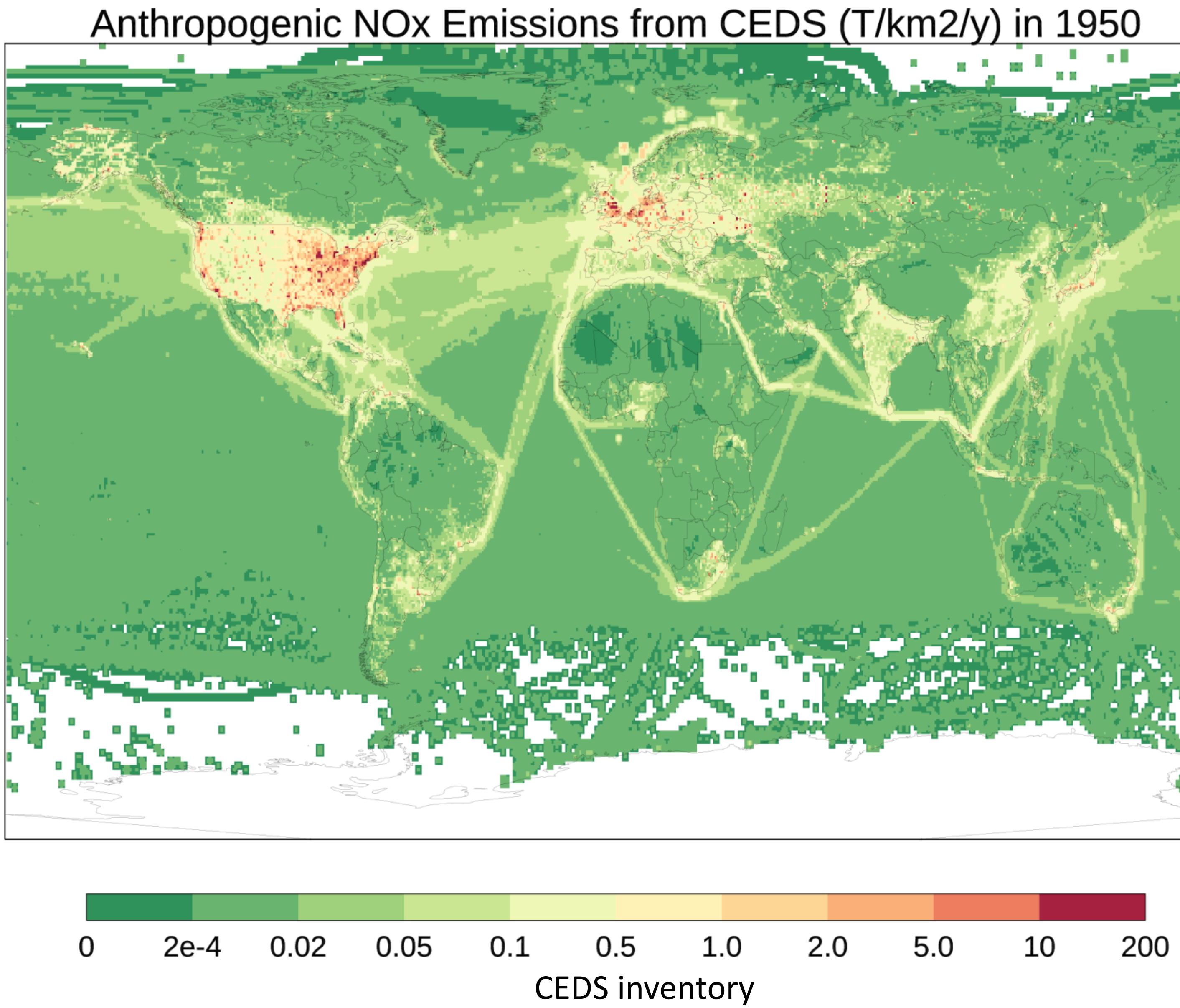
NOx Emissions by Source

NOx Budget

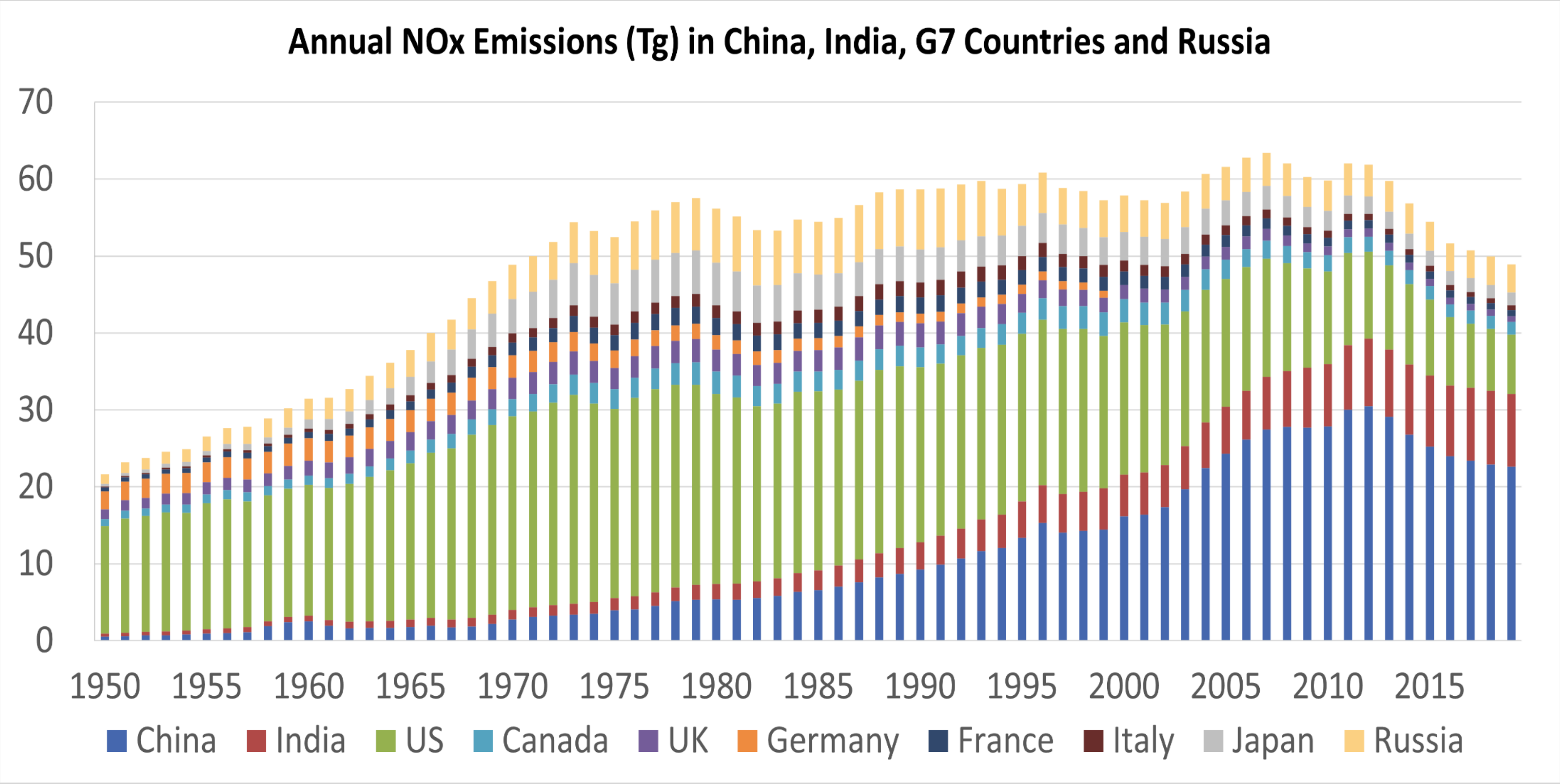
Table 4.8: Estimates of the global tropospheric NO_x budget (in TgN/yr) from different sources compared with the values adopted for this report.

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**

Anthropogenic NOx Emissions: 1950-2014

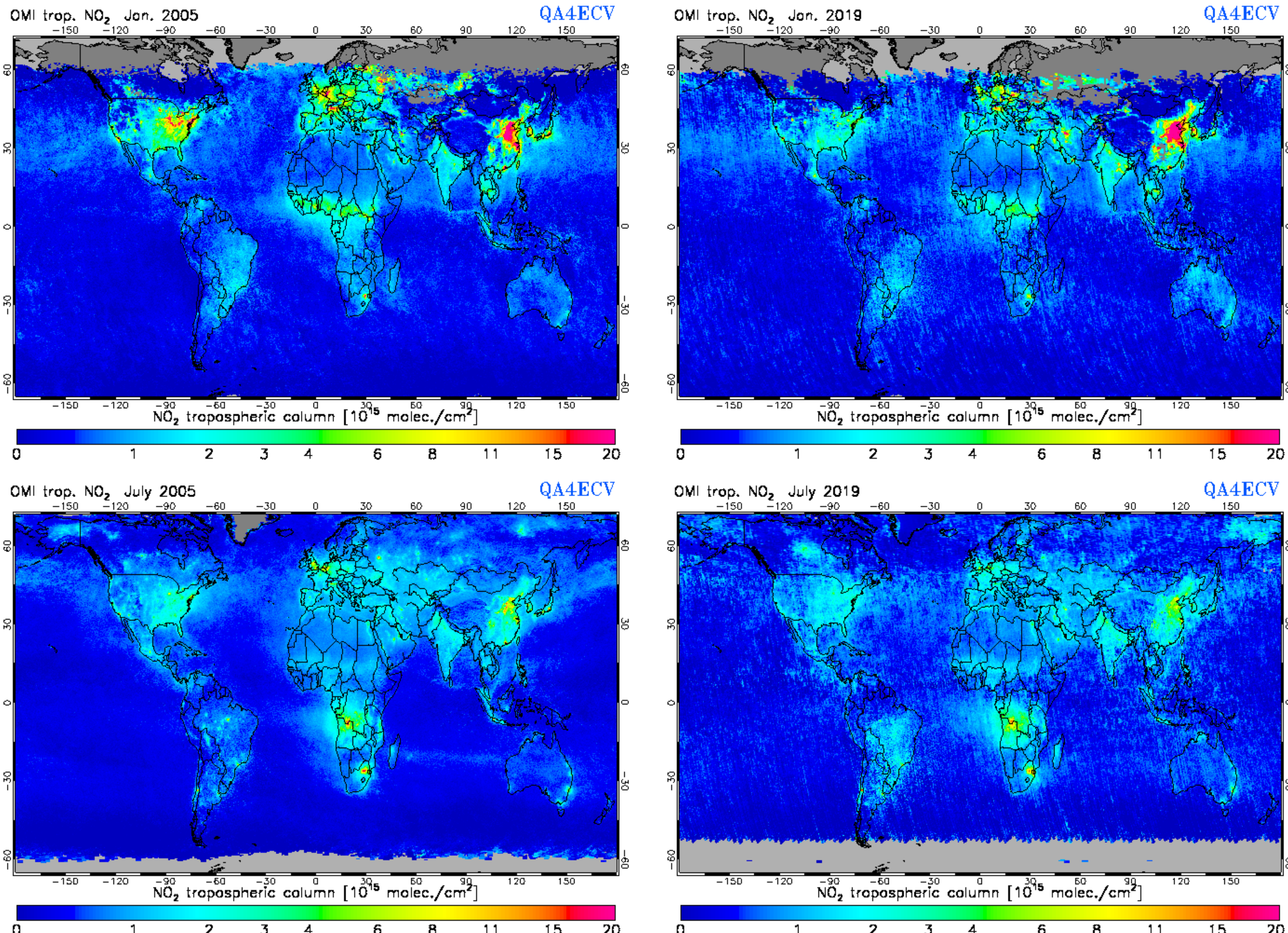


Anthropogenic Emissions of NOx: 1950-2019



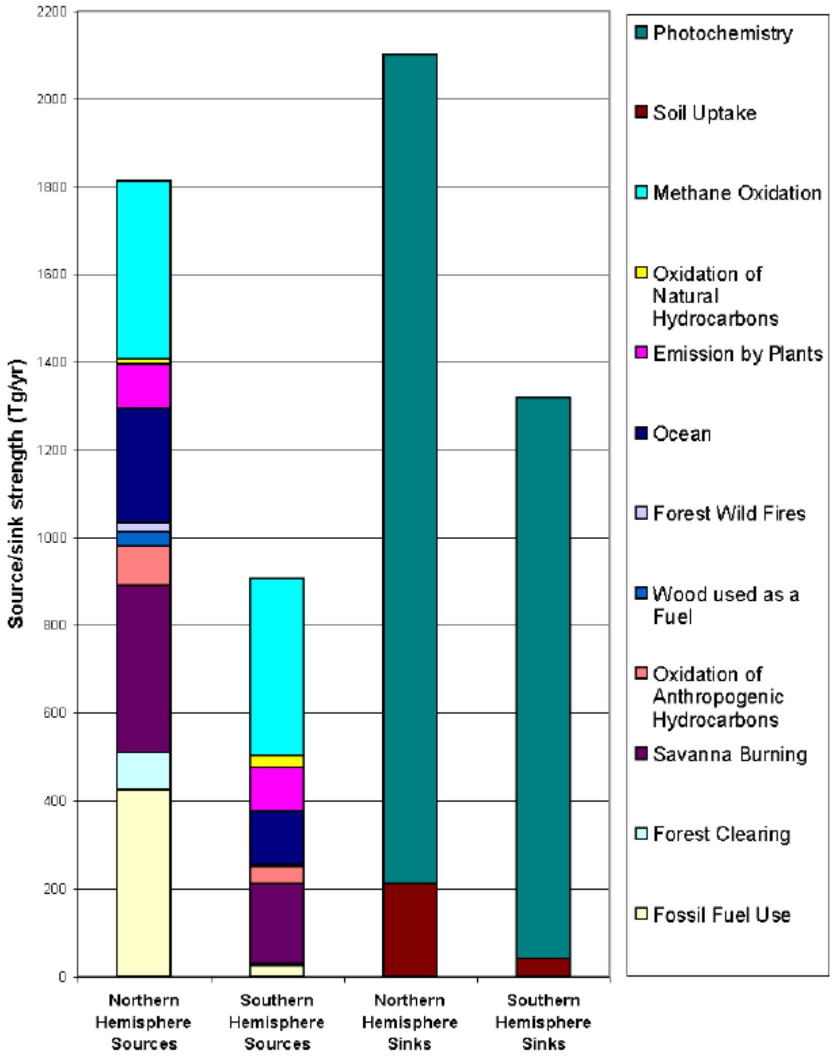
CEDS v2 inventory

Tropospheric NO_2 Column: 2005-2019



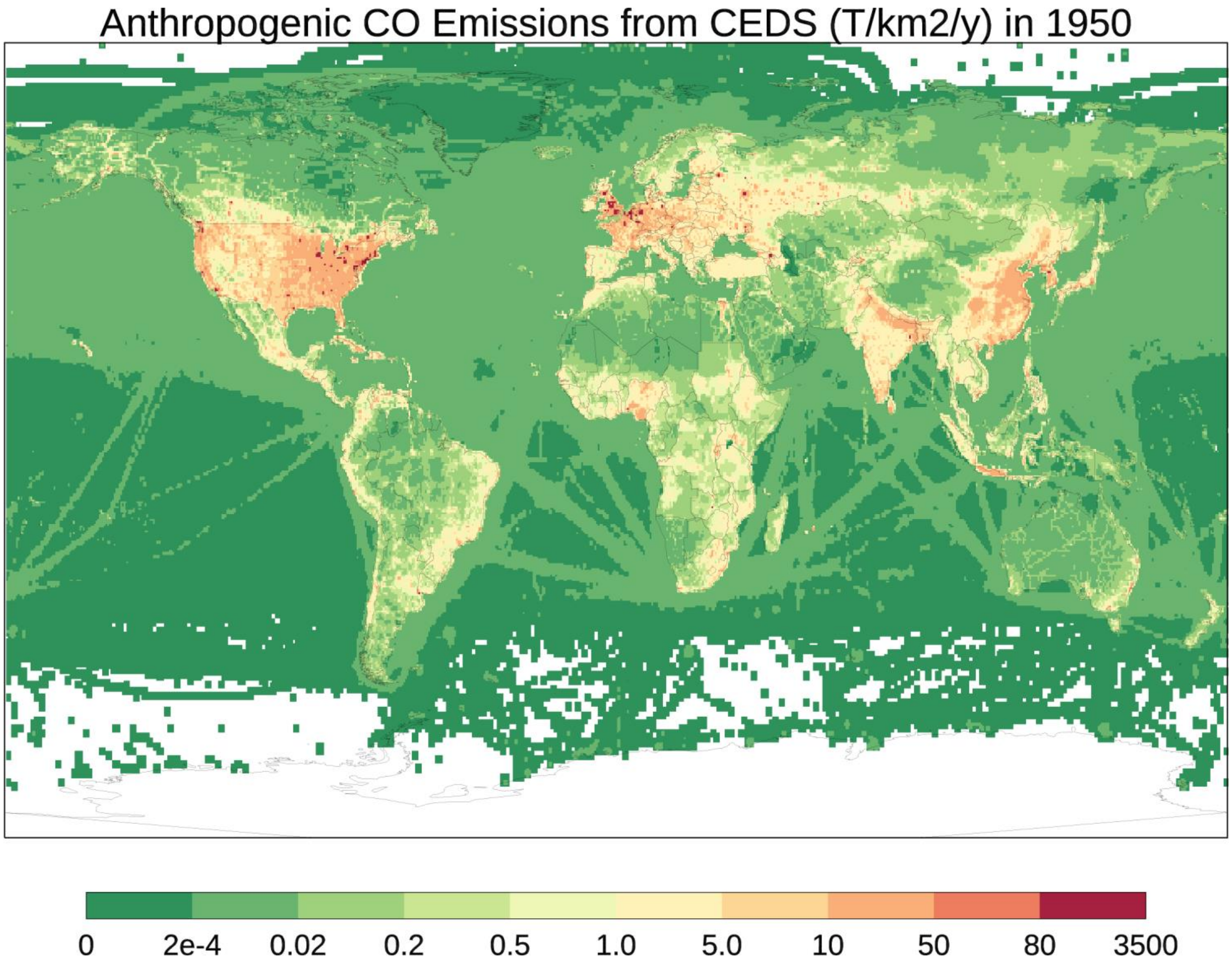
www.temis.nl

Sources of Sinks of CO



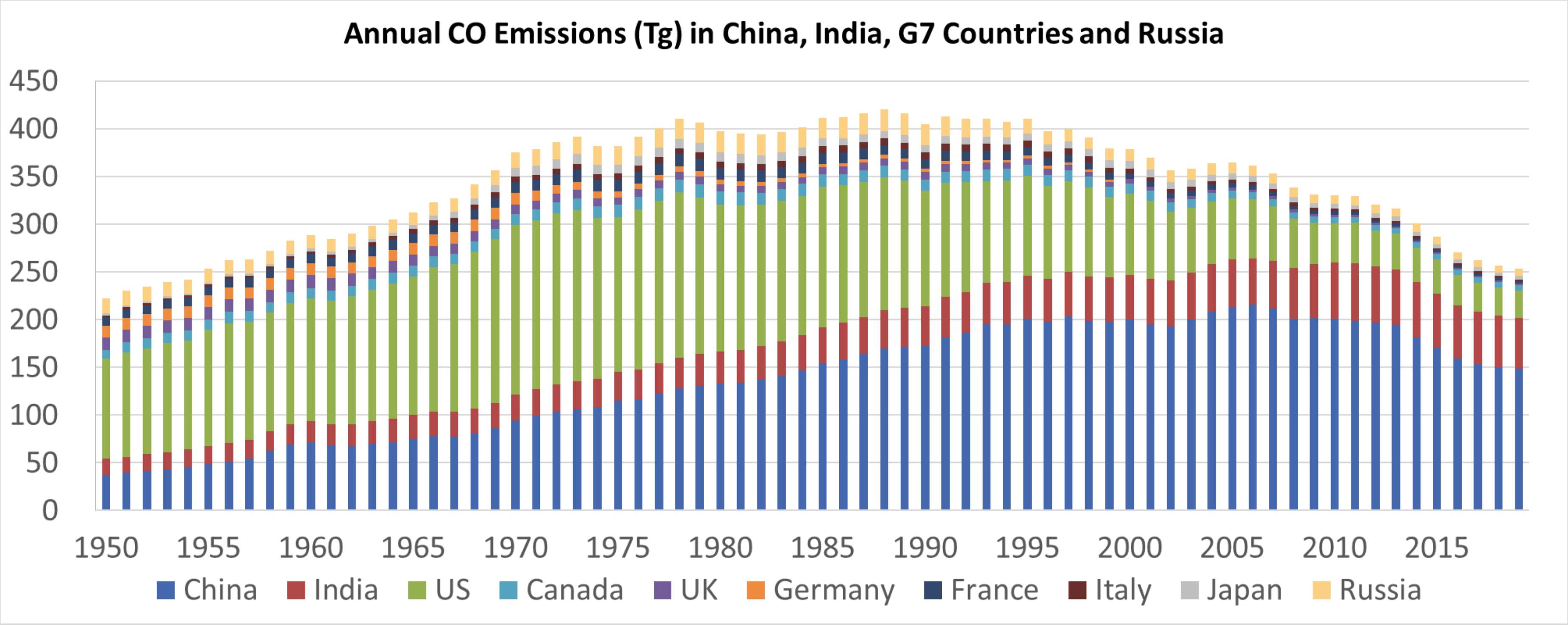
Logan et al. (1981)

Anthropogenic Emissions of CO: 1950-2014



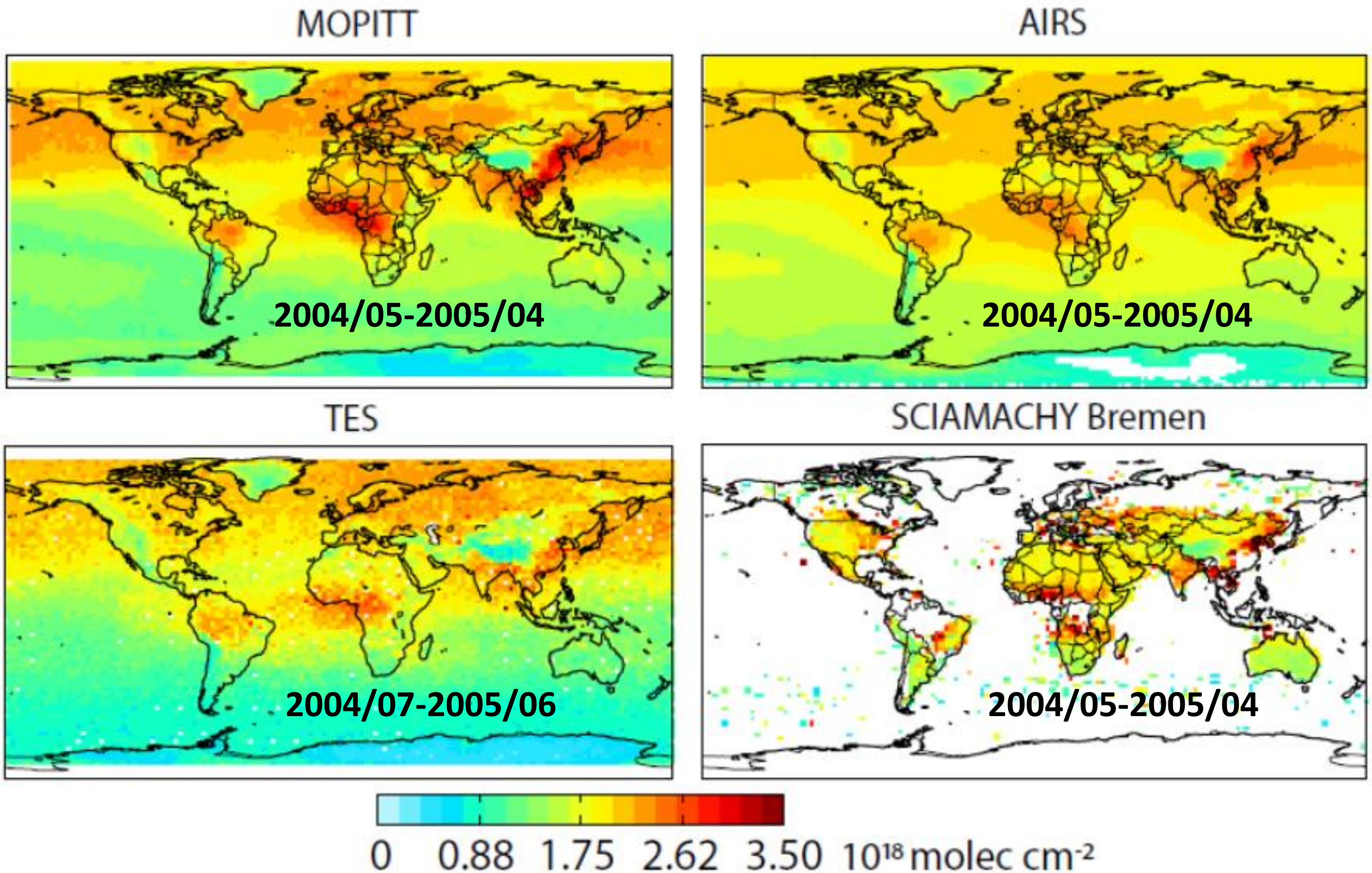
CEDS inventory

Anthropogenic Emissions of CO: 1950-2019



CEDS v2 inventory

Satellite Measurements of CO



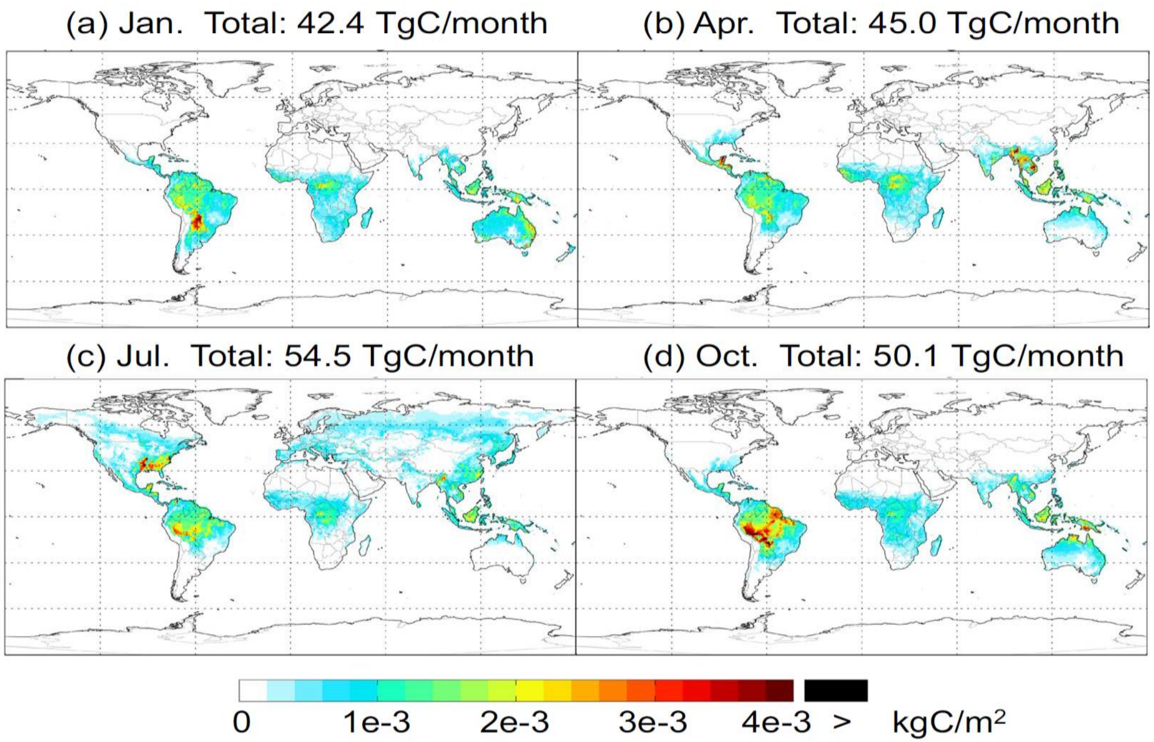
Kopacz et al., 2010, ACP

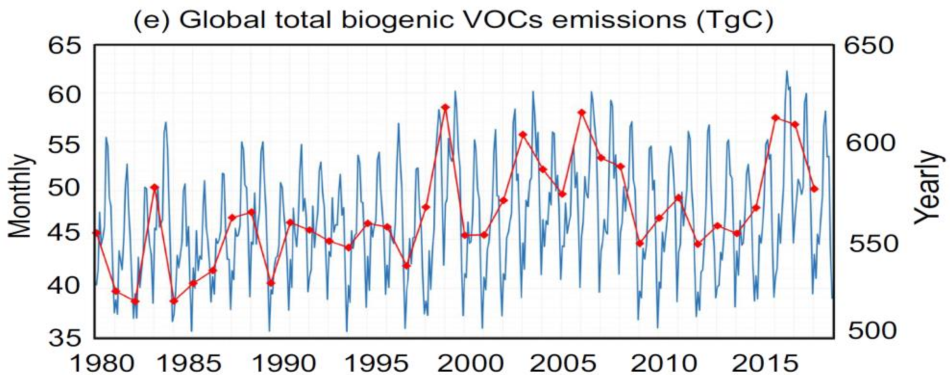
Sources of Non-Methane Volatile Organic Compounds

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)*	200-600*TgC/yr*
	单萜烯	monoterpenes	125 TgC/yr
		other VOC	520 TgC/yr
	Oceanic emissions		6-36 TgC/yr

Brasseur et al., 1998; Weng HJ et al., SD, 2020

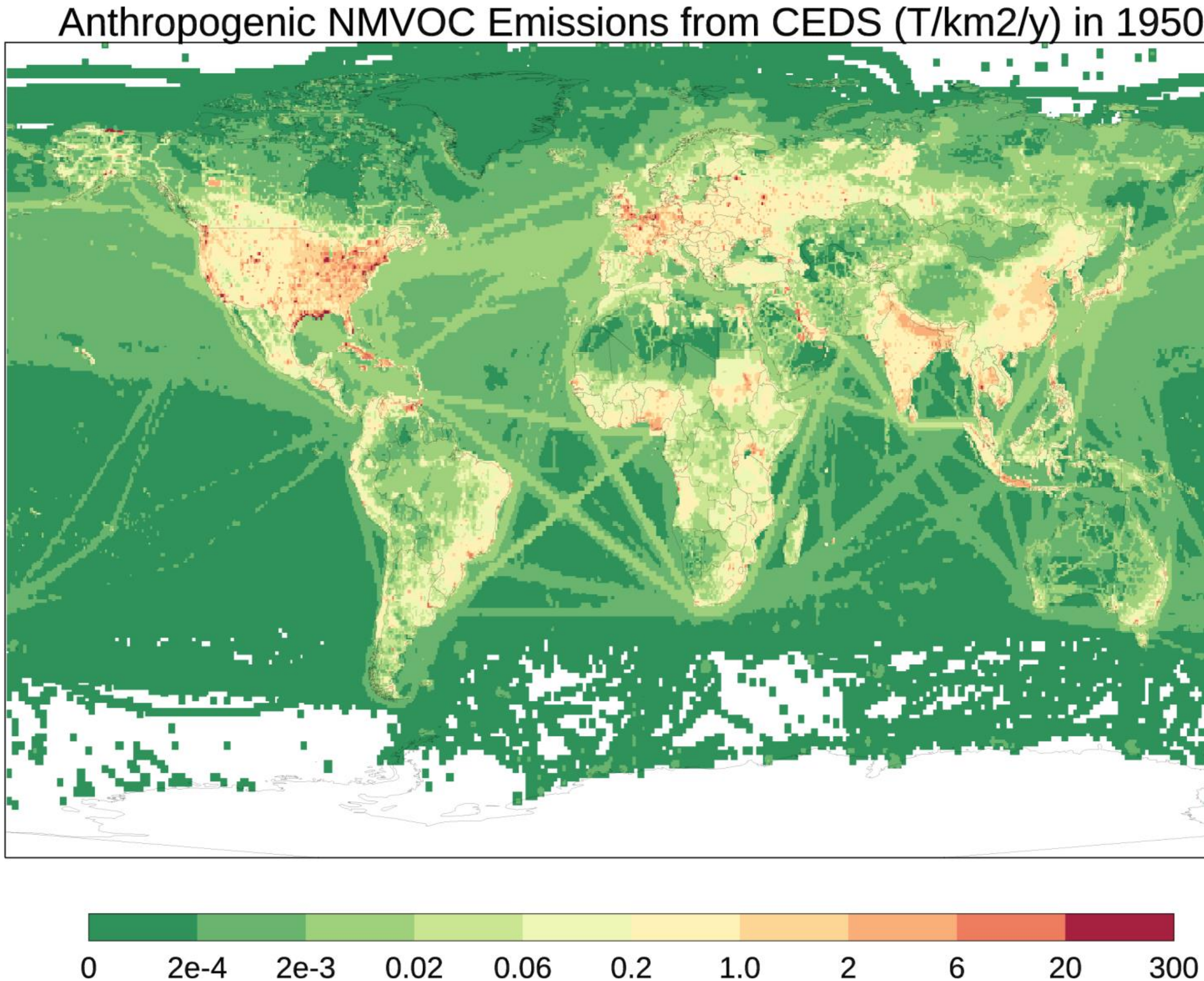
Biogenic NMVOC Emissions: 1980–2017





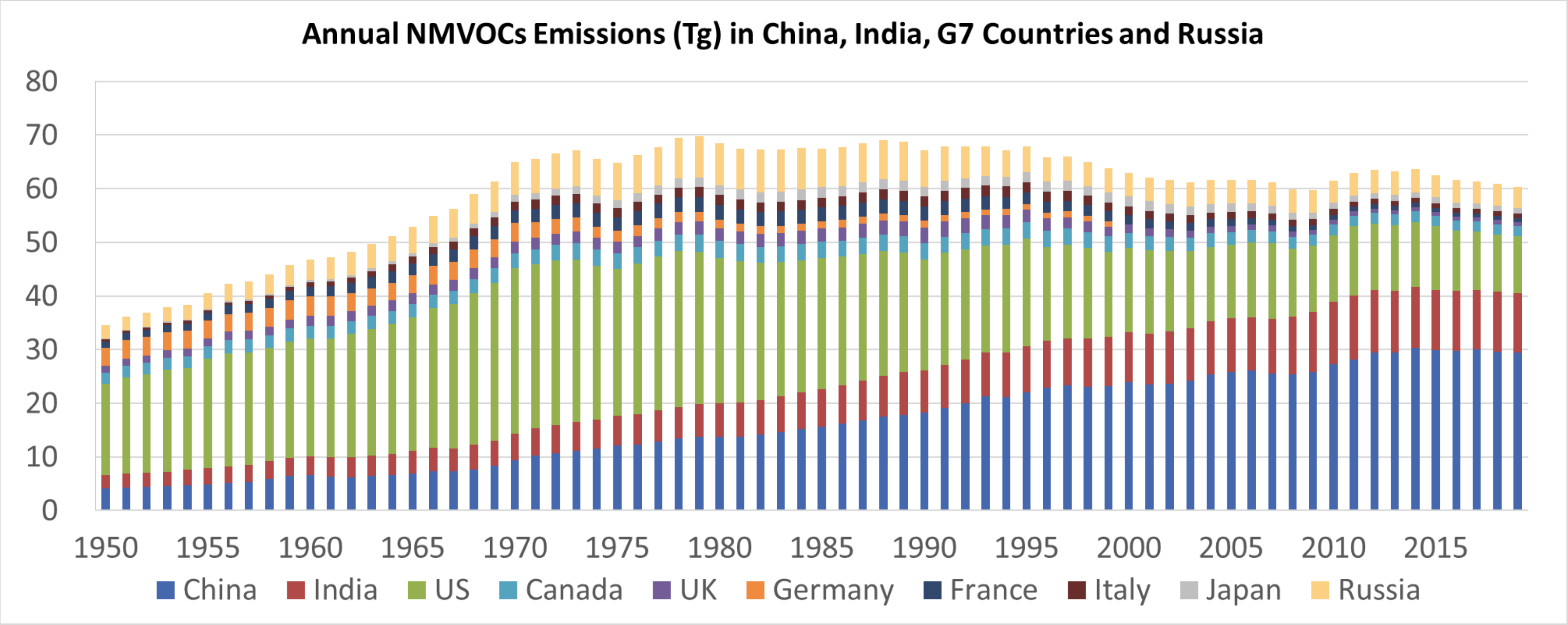
Weng HJ et al., SD, 2020

Anthropogenic NMVOC Emissions: 1950-2014



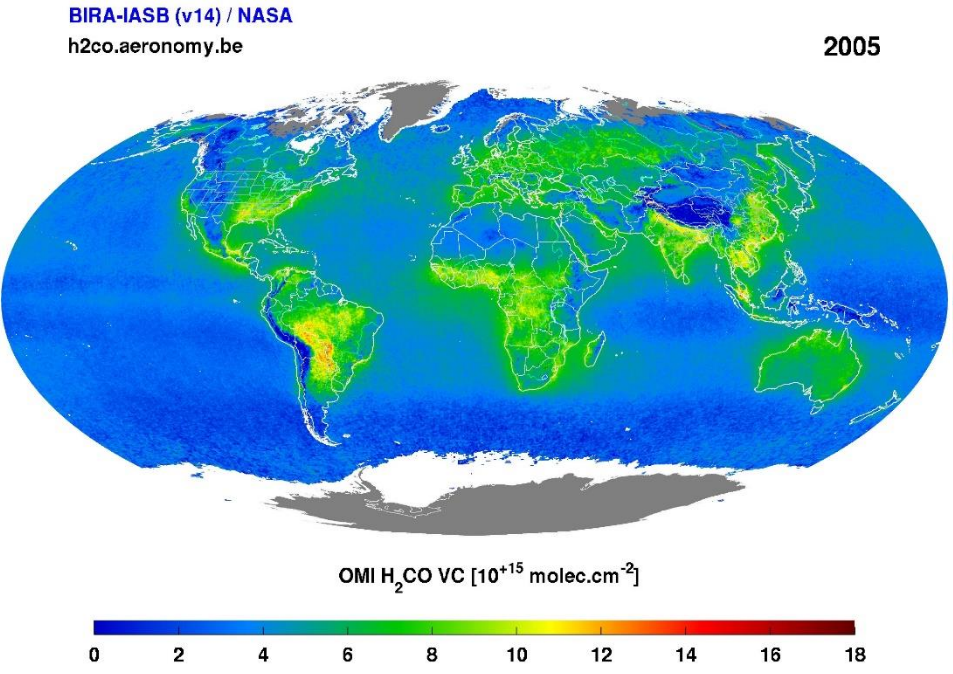
CEDS inventory

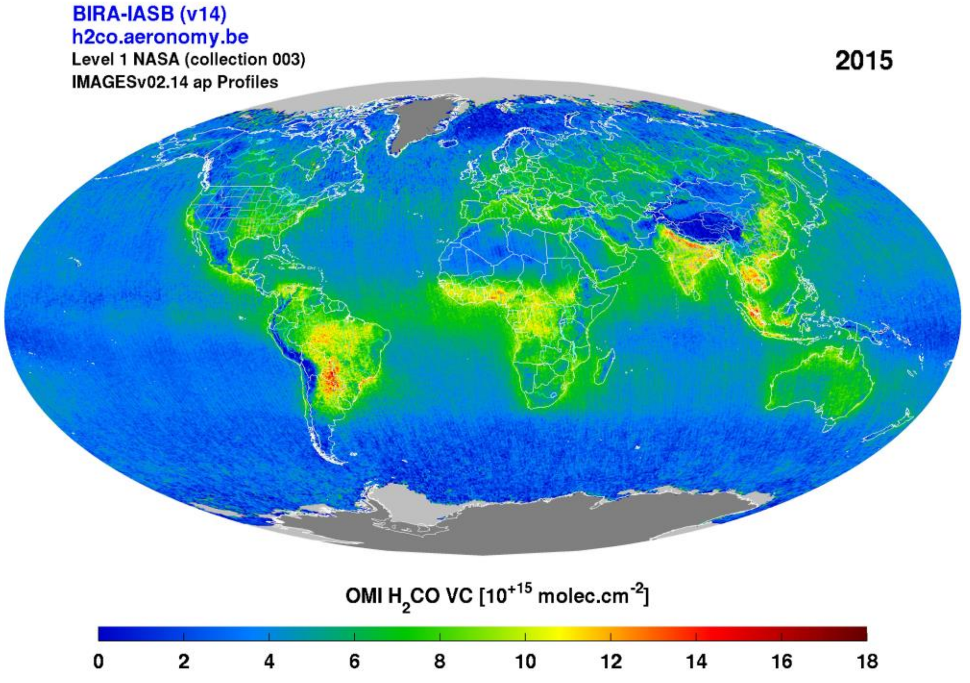
Anthropogenic Emissions of NMVOC: 1950-2019



CEDS v2 inventory

Tropospheric HCHO Column: 2005-2015





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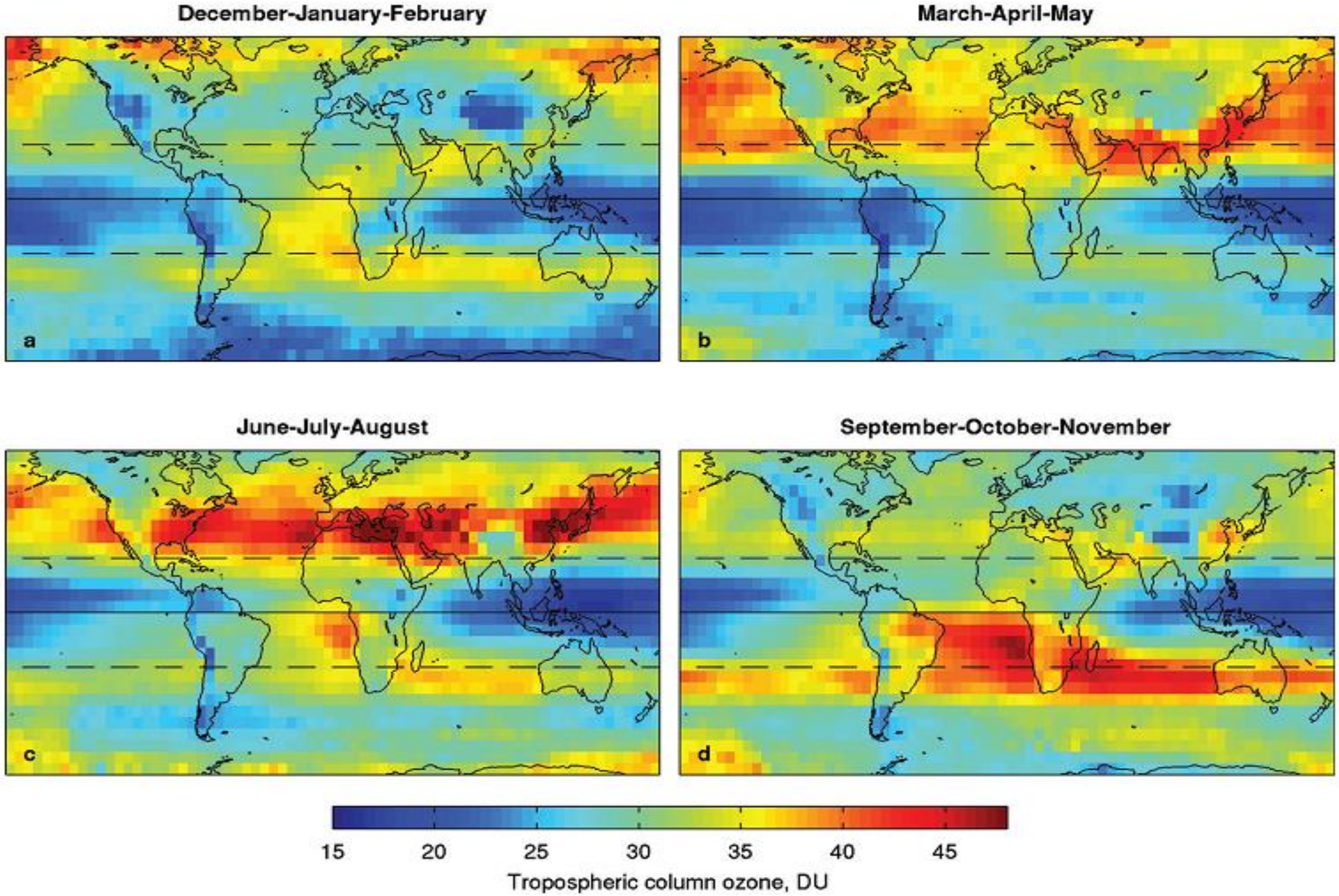
Tropospheric Ozone Column Seen From Space

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



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

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 %

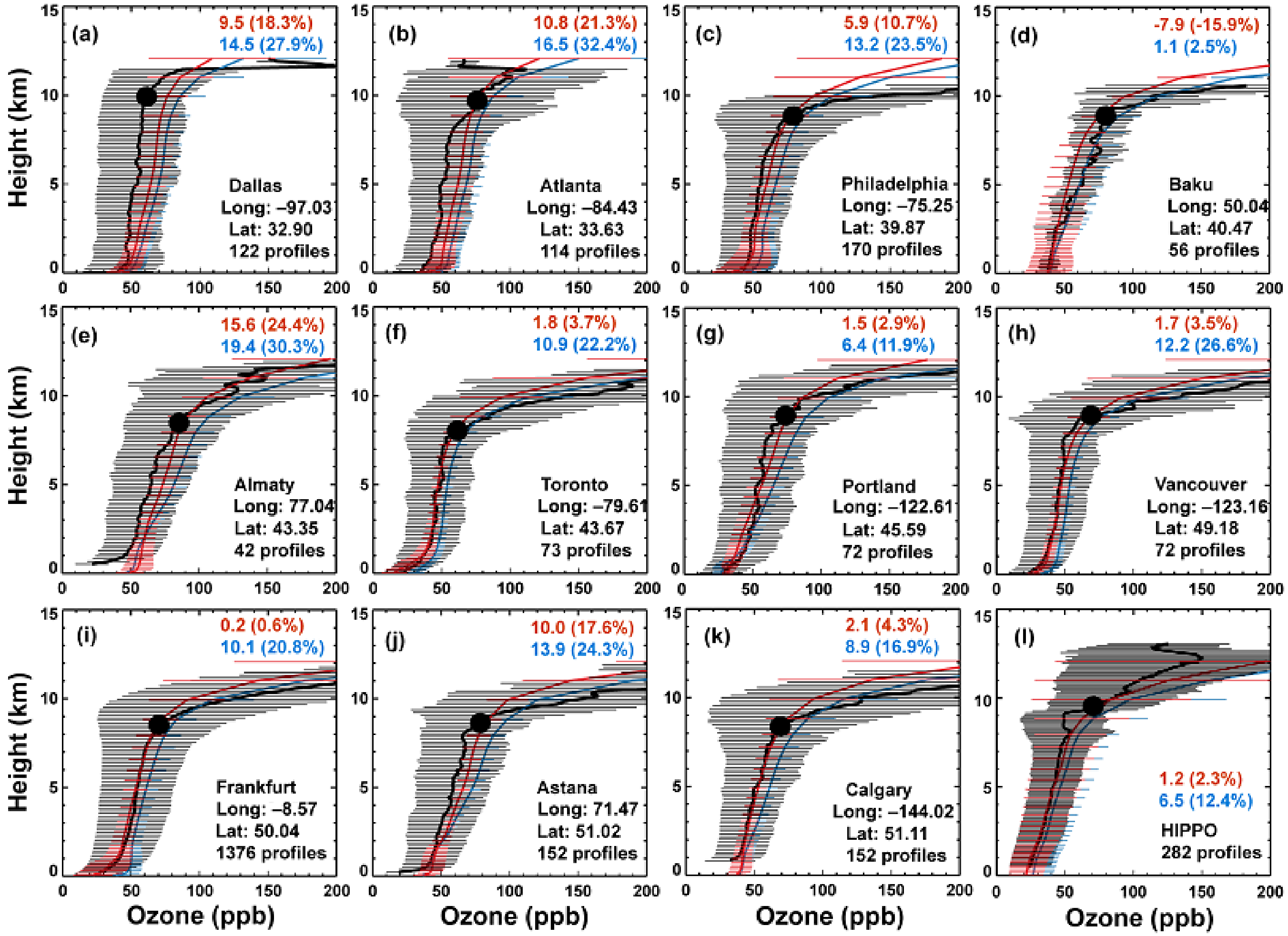
$O_x = O_3 + O + NO_2 + 2NO_3 + 3N_2O_5 + PANs + HNO_3 + HNO_4$ (Wu et al., 2007)

Yan et al., 2016

Vertical Profile of O_3 in the Troposphere

Comparisons with MOZIAC and HIPPO profiles

Obs
Two-way
Global

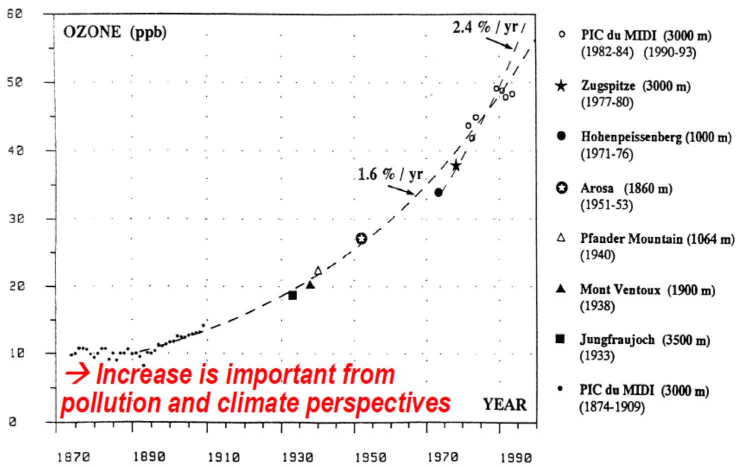


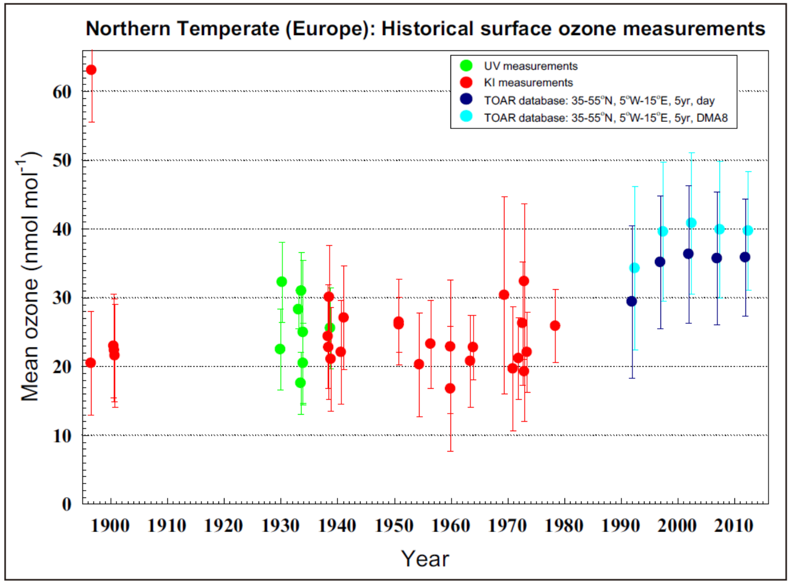
Yan Y.-Y. et al., ACP, 2014, 2016

Long-term Trends of Near-Surface Ozone

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

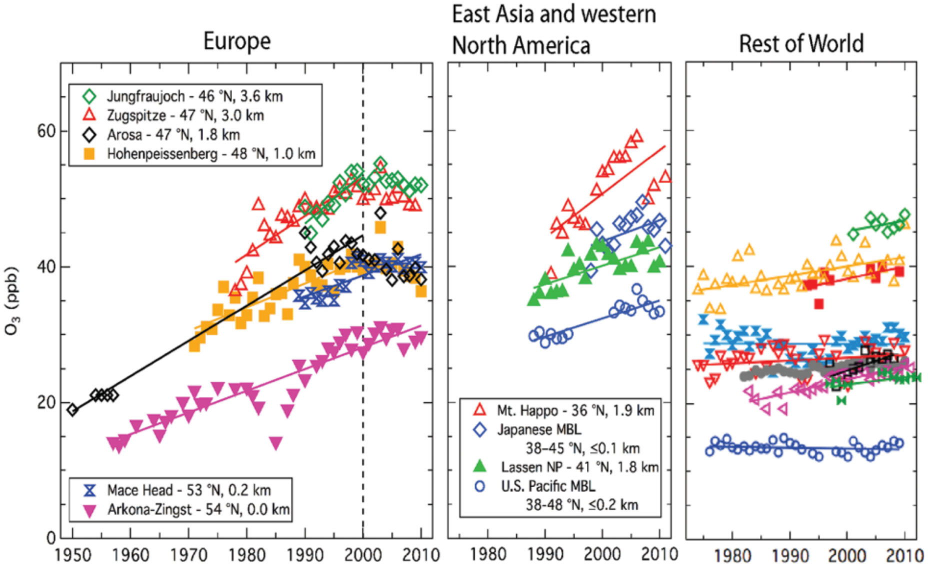
Ozone trend from European mountain observations, 1870-1990 [Marenco et al.,1994]





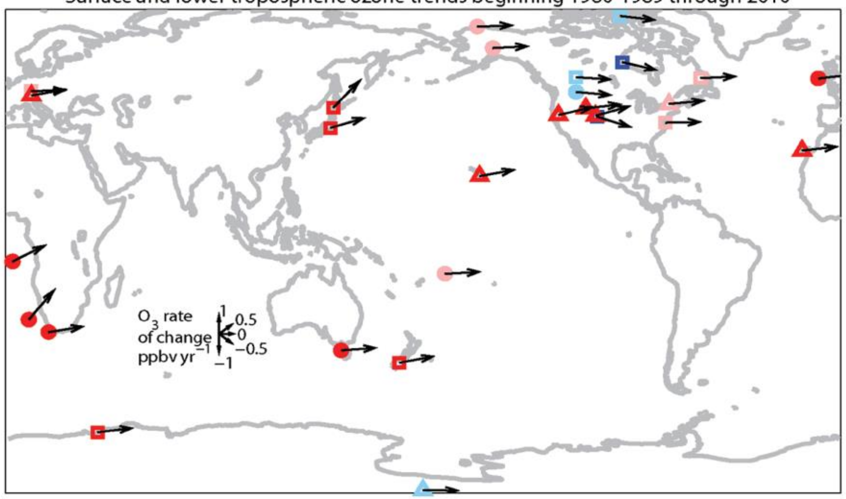
Tarasick et al., 2019 Elementa

Long-term Trends of Near-Surface Ozone

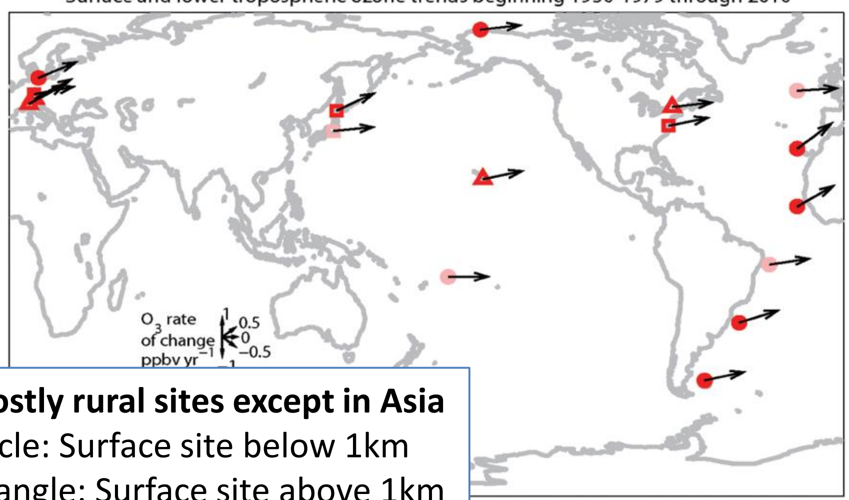


Trends in annual average ozone (mostly rural sites except in Asia)

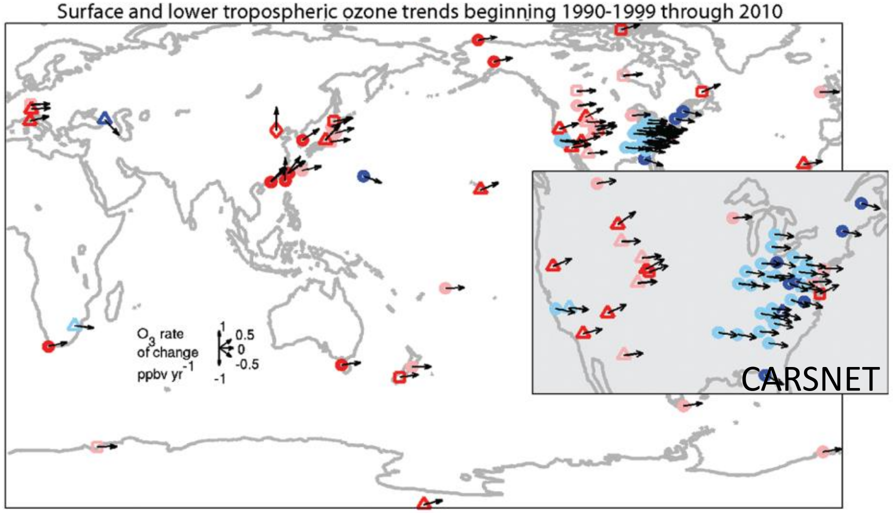
Surface and lower tropospheric ozone trends beginning 1980-1989 through 2010



Surface and lower tropospheric ozone trends beginning 1950-1979 through 2010



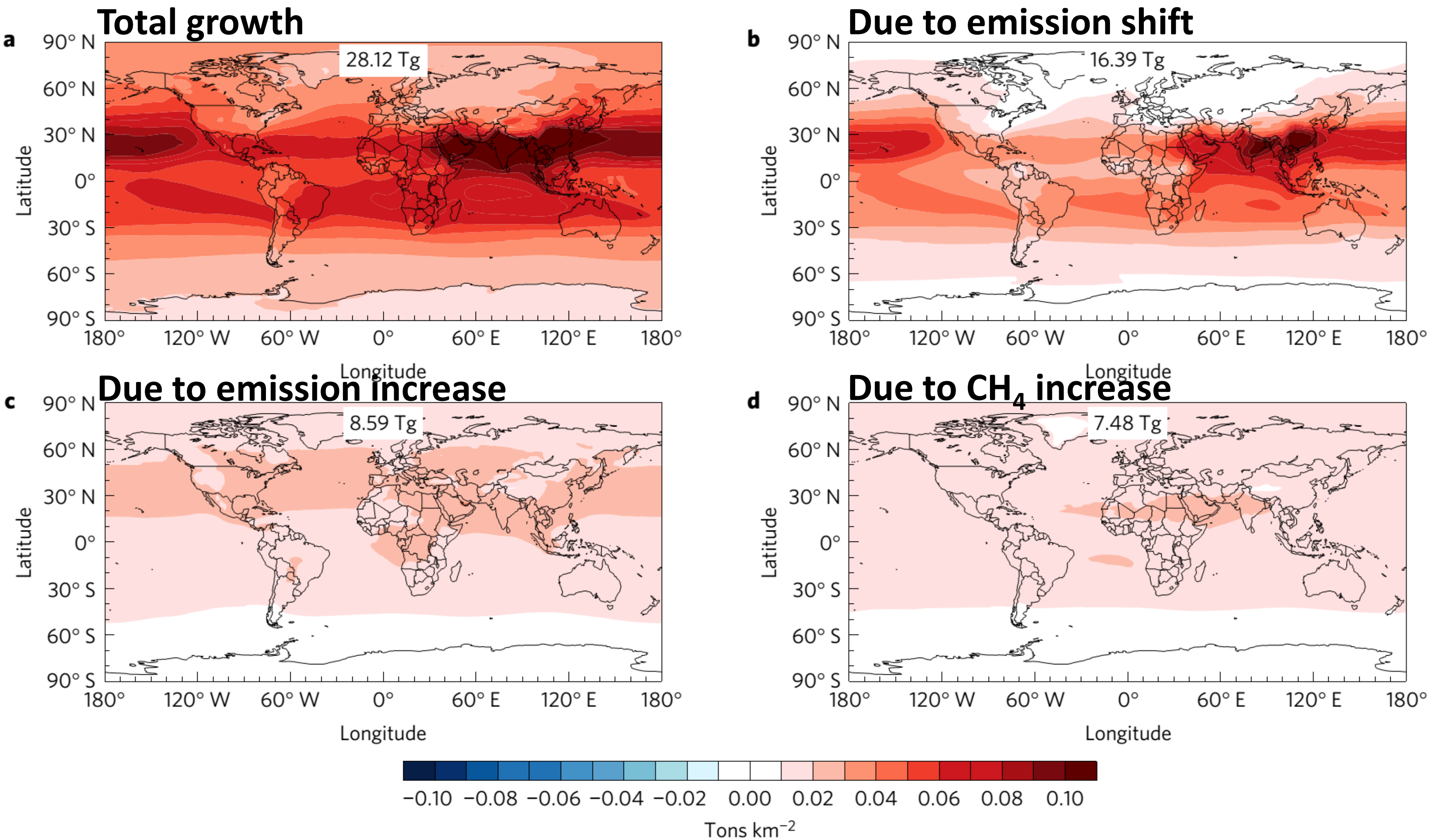
Surface and lower tropospheric ozone trends beginning 1990-1999 through 2010



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

Factoring Affecting O_3 Growth between 1980 and 2010

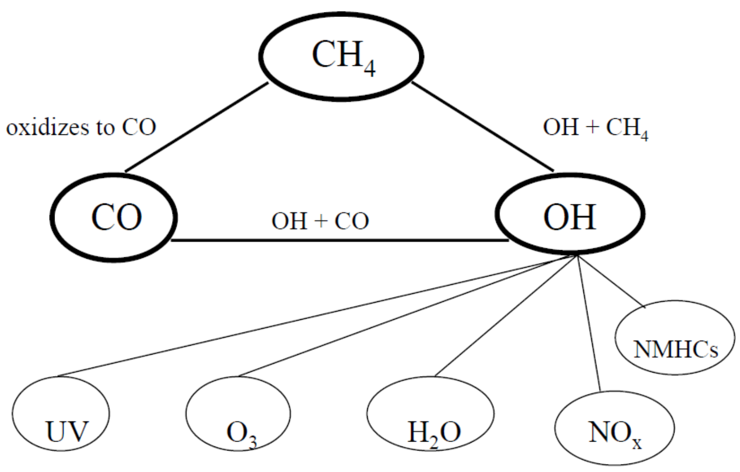


Zhang et al., 2016, Nature Geoscience

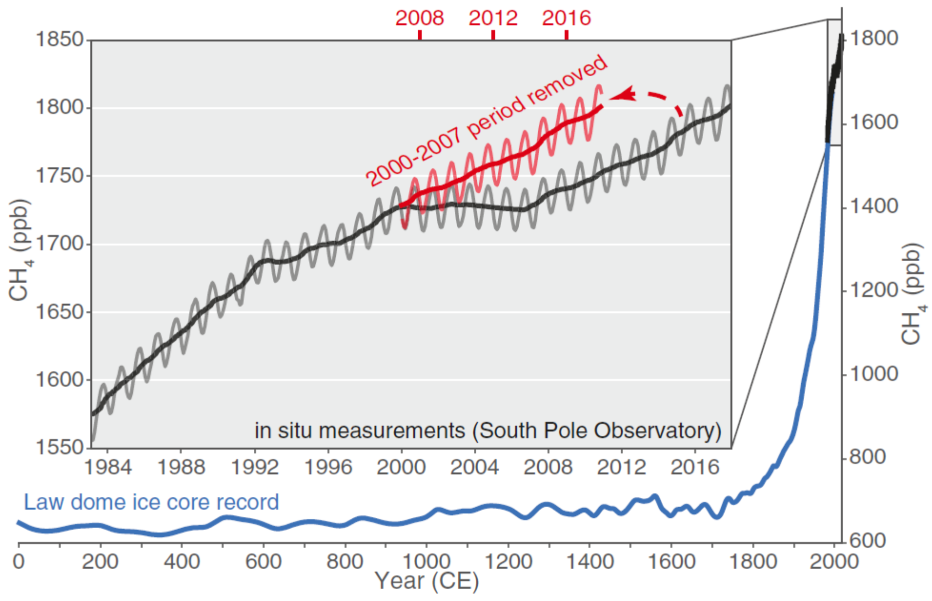
Atmospheric OH

- 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

Simplified CH_4/OH/CO Chemistry



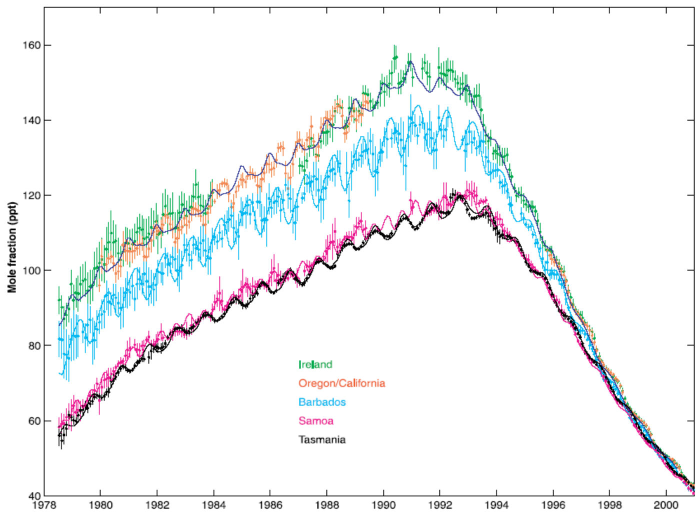
Changes in CH_4

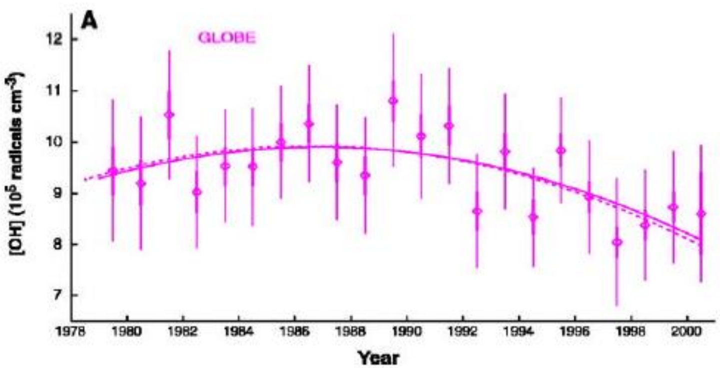


Turner et al., 2019, PNAS

Atmospheric OH Variations

CH_3CCl_3甲基氯仿



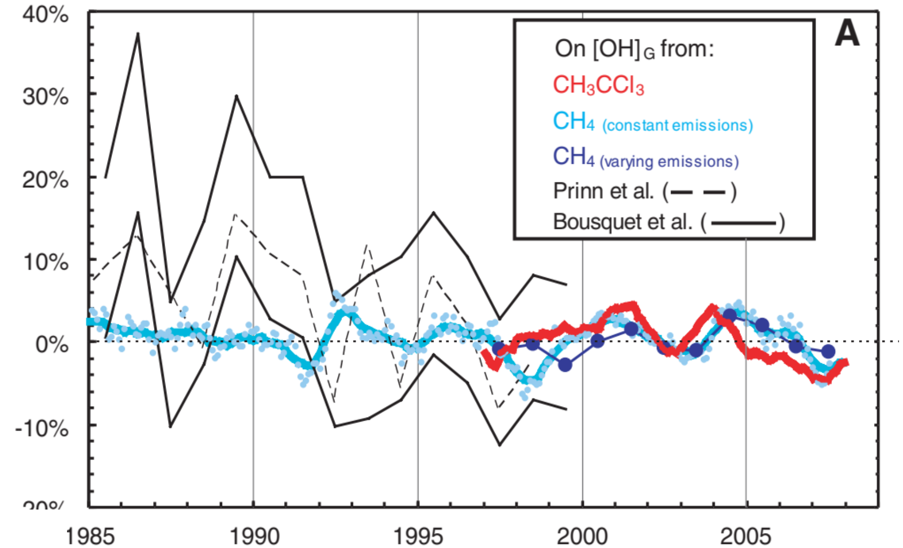


Prinn et al., 2001

Emis — Obs. change

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

Loss rate — Global mass

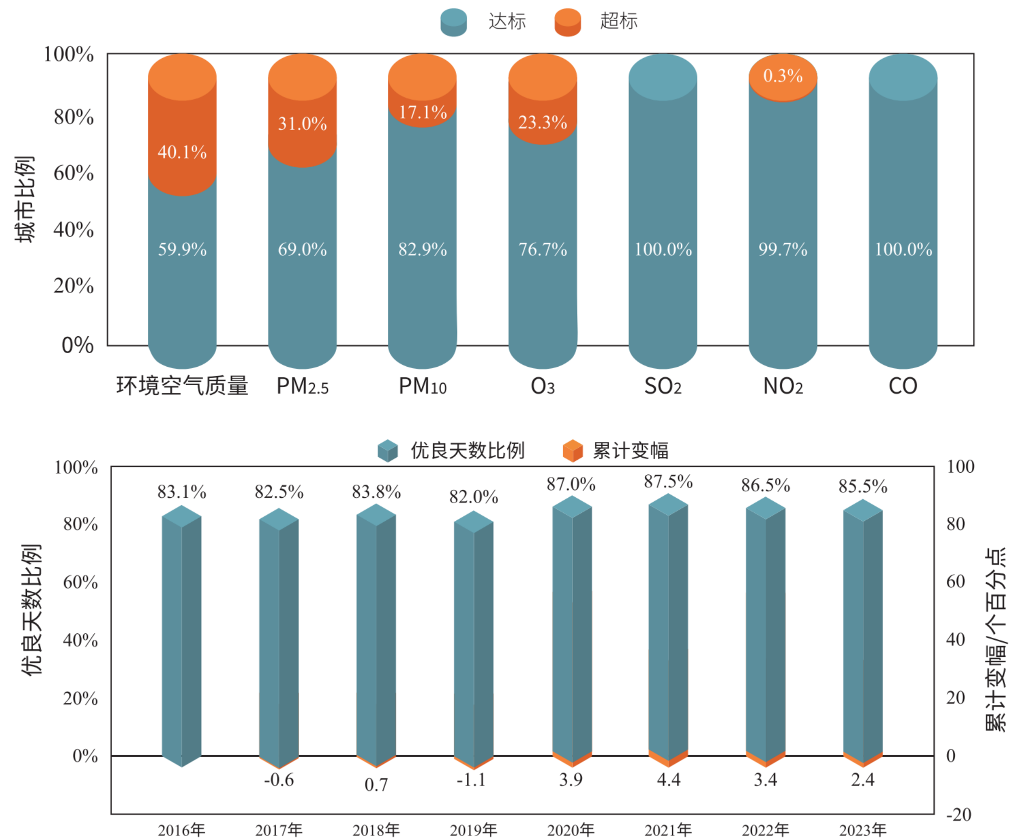


Montzka et al., Science, 2011

Near-Surface Air Pollution

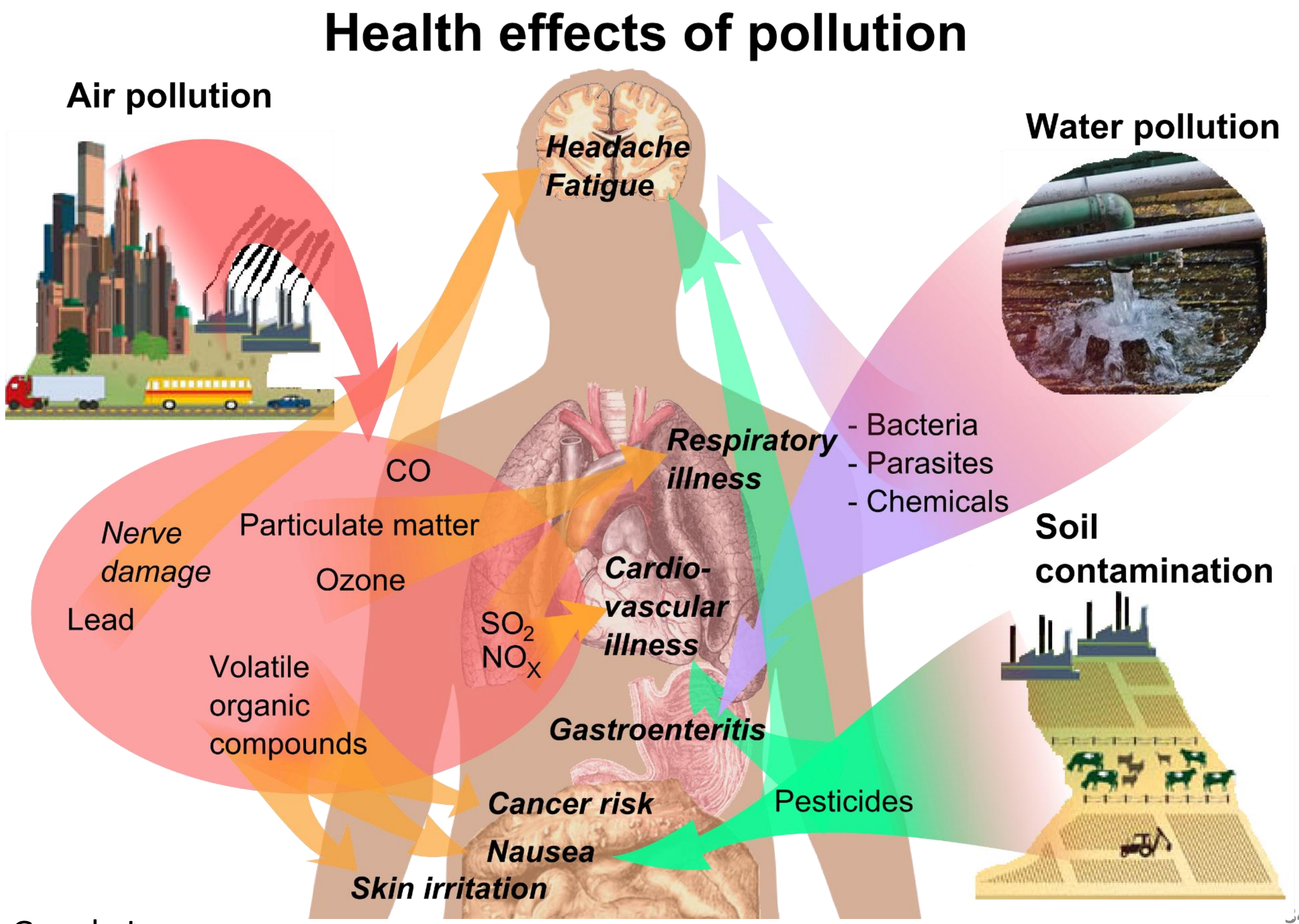
- **Outdoor Air Pollution**
  - ✓ **Ozone**
  - ✓ **$PM_{2.5}$**
  - ✓ **Acid deposition**
- **Consequences**
  - ✓ **Health impacts**
  - ✓ **Agriculture**
  - ✓ **Ecosystems**

Chinese Air Quality Status



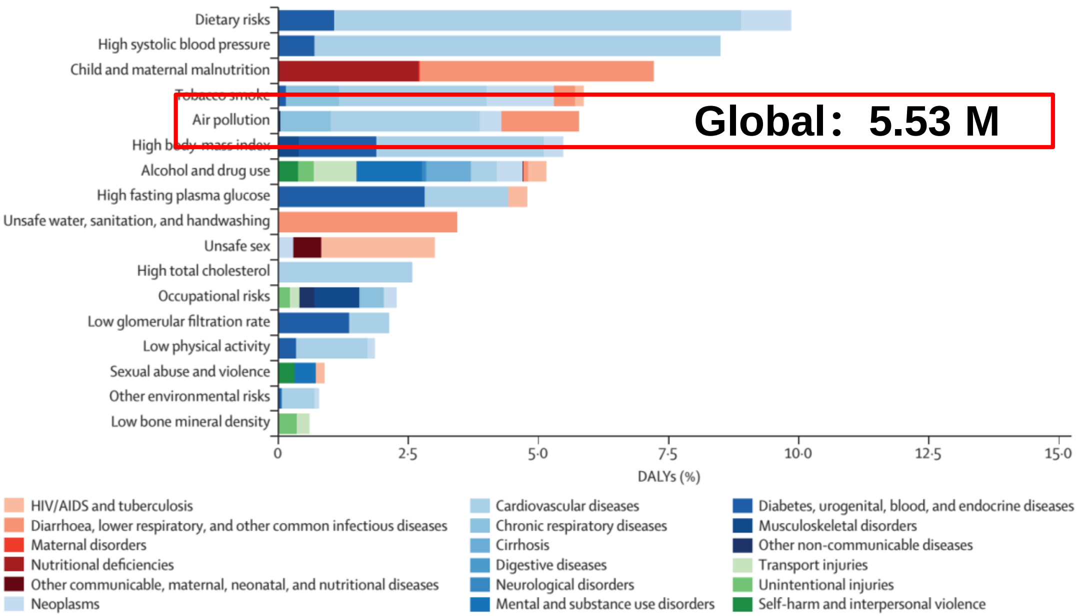
中国生态环境公报2023

How Pollution Affects the Human Body ?

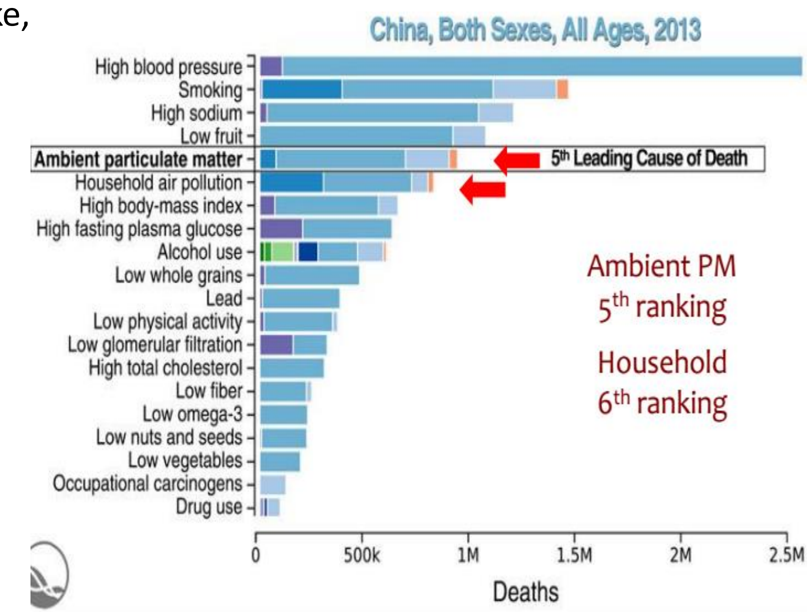


Google Image

Air Pollution Is The Leading Environmental Risk Factor of Global Burden of Disease



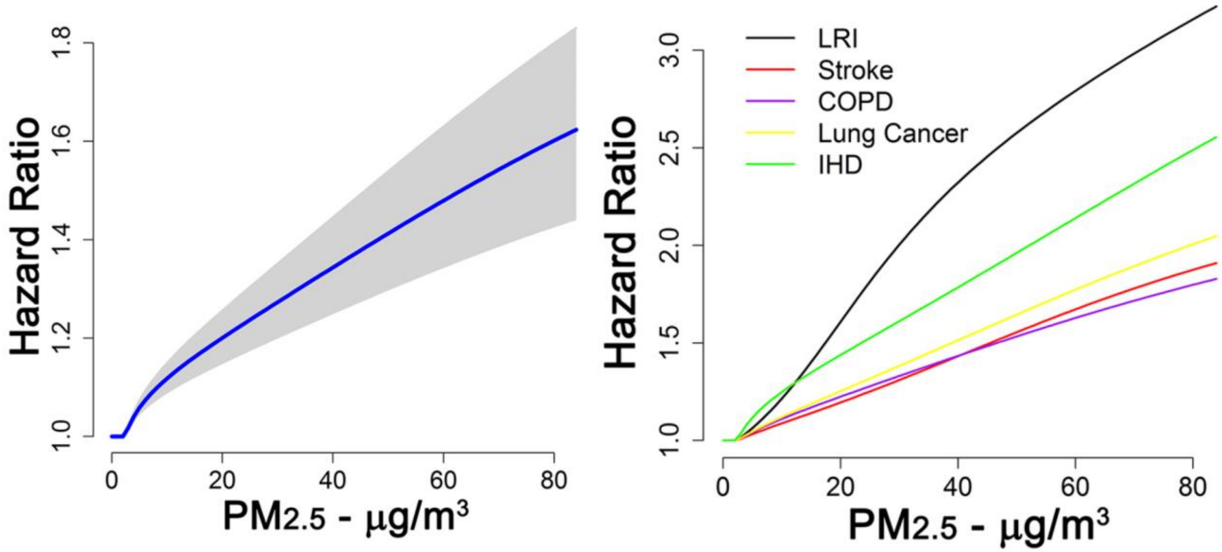
Four main PM-related diseases: Ischemic heart disease (IHD), Stroke, Lung cancer, Chronic obstructive pulmonary disease (COPD)



Forouzanfa et al., 2016, Lancet (GBD 2013)

Health Impacts of Air Pollution

Burnett et al., 2018 PNAS

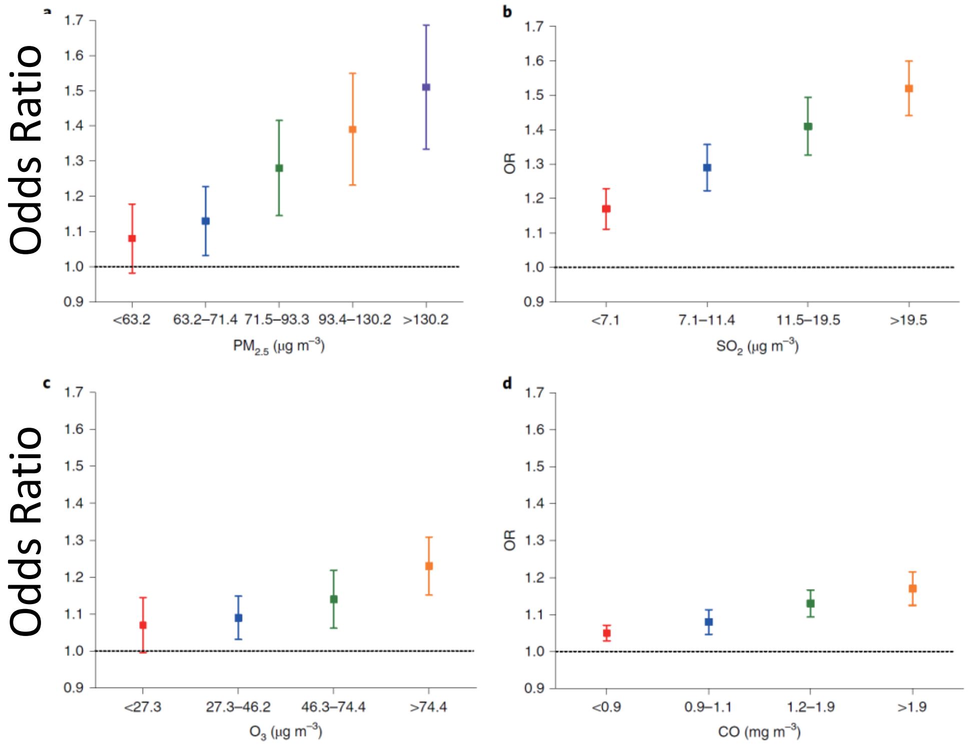


Di et al., 2017 NEJM

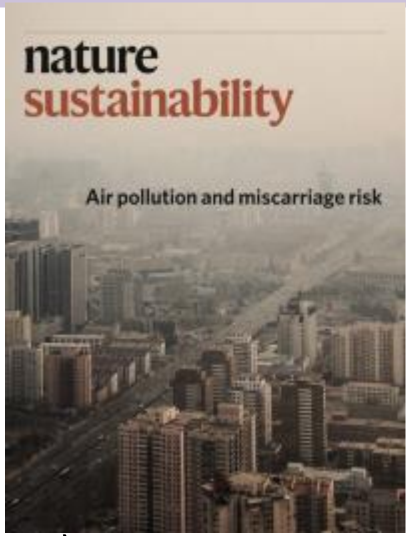
Table 2. Risk of Death Associated with an Increase of 10 μg per Cubic Meter in $PM_{2.5}$ or an Increase of 10 ppb in Ozone Concentration.*

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)

Linking Maternal Air Pollution Exposure to MAFT



Zhang LQ et al., 2019, Nature Sustainability



Method:

- 250,000 clinical data (Liu WW)
- MEE air pollution data (Lin JT)
- Meteorological data (Lin JT)
- Logistic regression (Zhang LQ)
- Restricted cubic spline regression (Zhang LQ)

- Logistic regression 逻辑回归

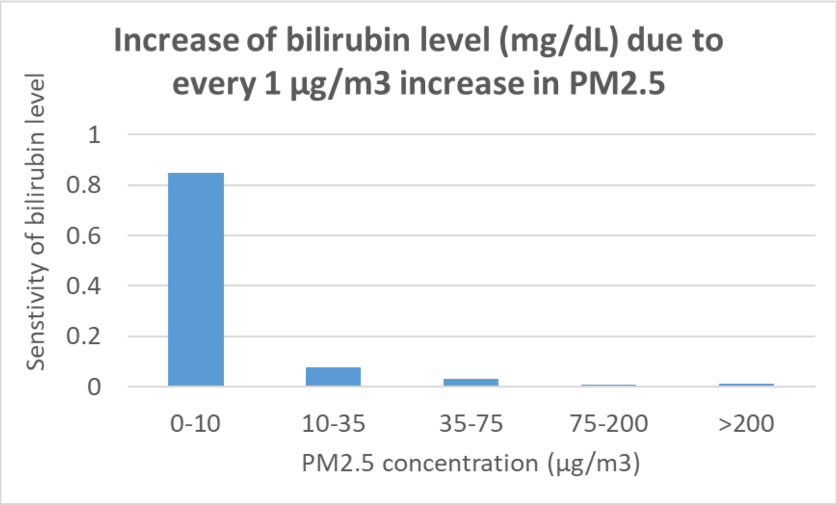
$$\ln\left(\frac{P}{1-P}\right) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_6 X_6 + \beta_7 X_7 + \gamma(\text{lat}) + \delta(\text{long})$$

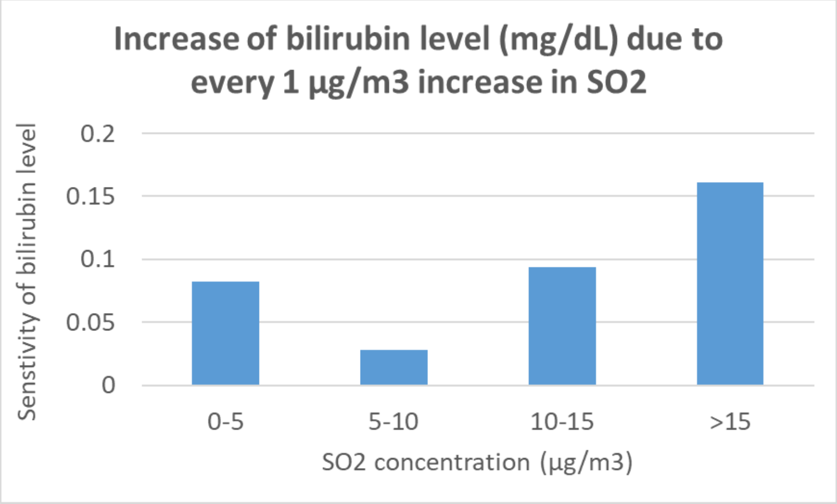
- Restricted cubic spline regression

$$\text{RCS}(x, k) = \sum_{i=1}^{k-1} \beta_i S_i(X) \qquad \text{OR}_i = \exp(\beta_i)$$

MAFT = Missed abortion in the first trimester 稽留流产

Linking Air Pollution Exposure to Neonatal Jaundice





Zhang LQ et al., 2019,

Nature Communications

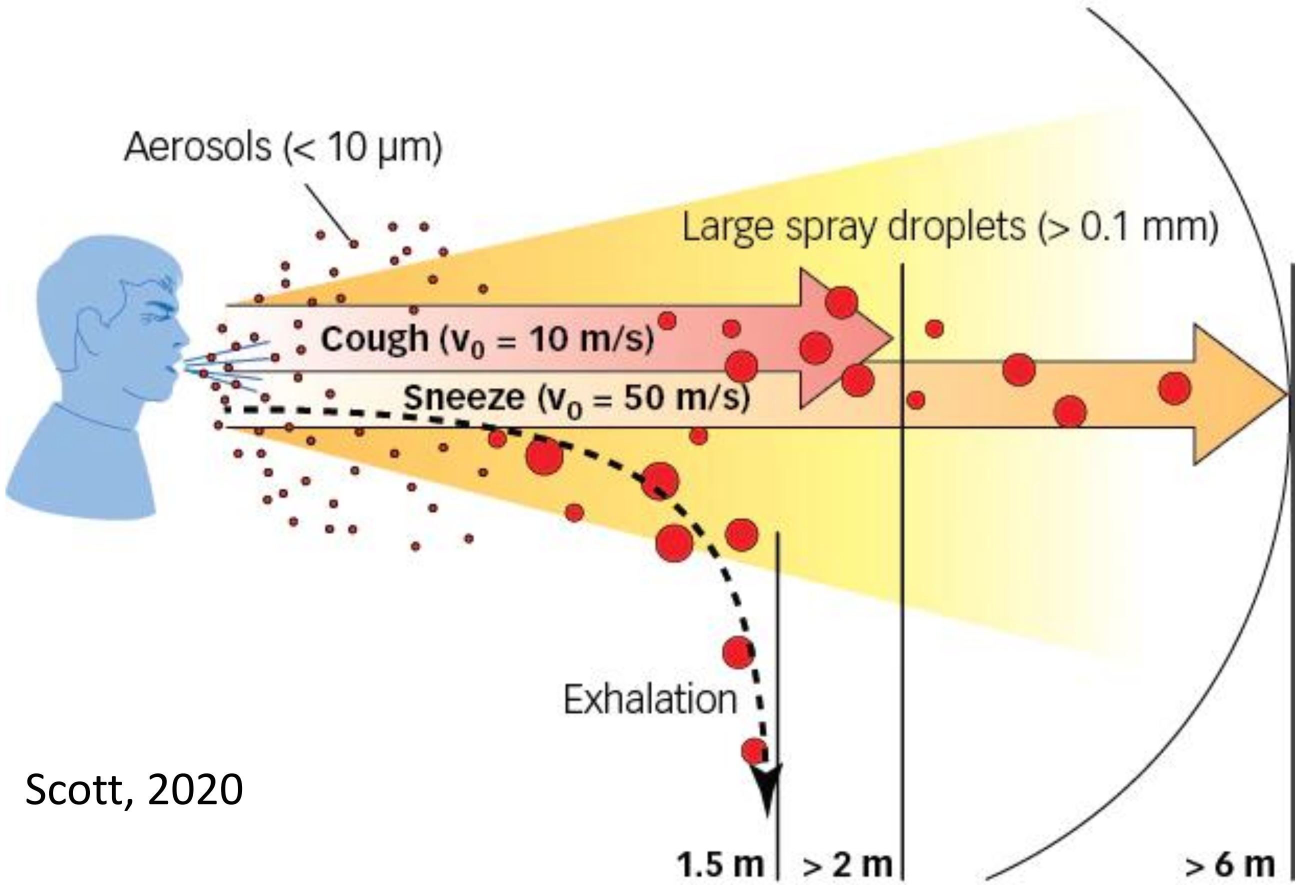
Method:

- 25,000 clinical data (Liu WW)
- MEE air pollution data (Lin JT)
- Meteorological data (Lin JT)
- General additive model (Zhang LQ)

$$g(u) = \beta_0 + s(\mathrm{PM}_{2.5}, \mathrm{df}_1) + s(\mathrm{SO}_2, \mathrm{df}_2) + s(\mathrm{CO}, \mathrm{df}_3) + \lambda_1(\mathrm{rh}) + \lambda_2(\mathrm{tem}) + \lambda_3(\mathrm{ph}) + \lambda_4(\mathrm{gd}) + \lambda_5(\mathrm{fd}) + \lambda_6(\mathrm{pr}) + \lambda_7(\mathrm{ms}) + \lambda_8(\mathrm{uc}) + \lambda_9(\mathrm{ip}) + \lambda_{10}(\mathrm{hy}) + \lambda_{11}(\mathrm{an})$$

Likely Transmission of COVID-19 through PM

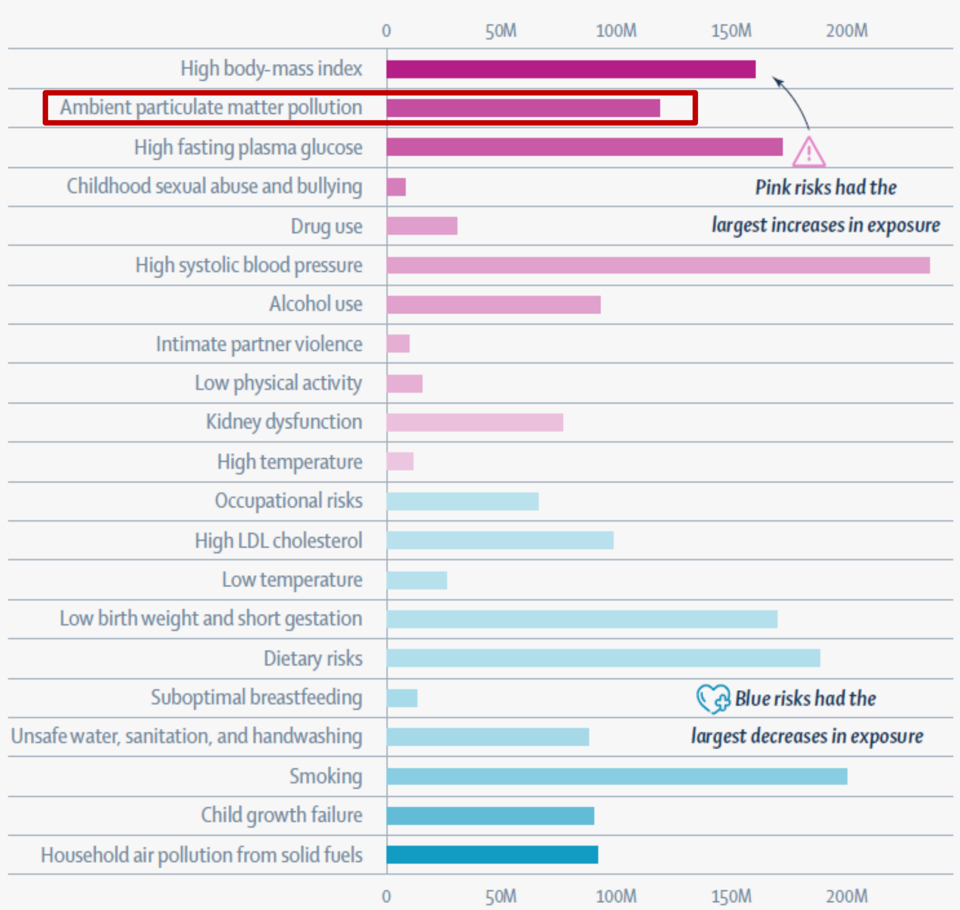
Figure 3: How COVID-19 is transmitted through aerosol particles



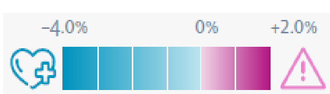
Scott, 2020

Health Impacts of Air Pollution

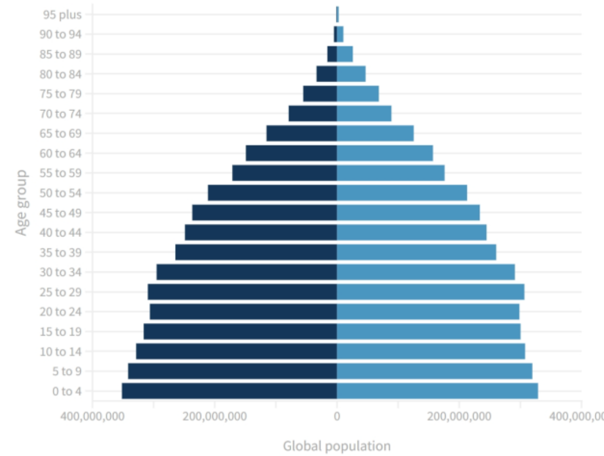
Years of healthy life lost (DALYs) in 2019



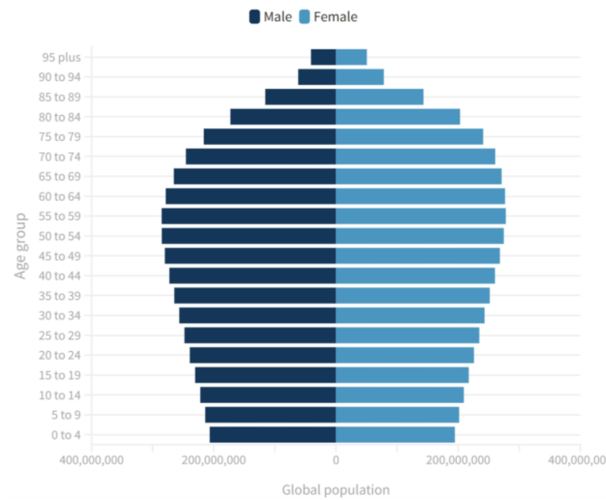
% change from 2010



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

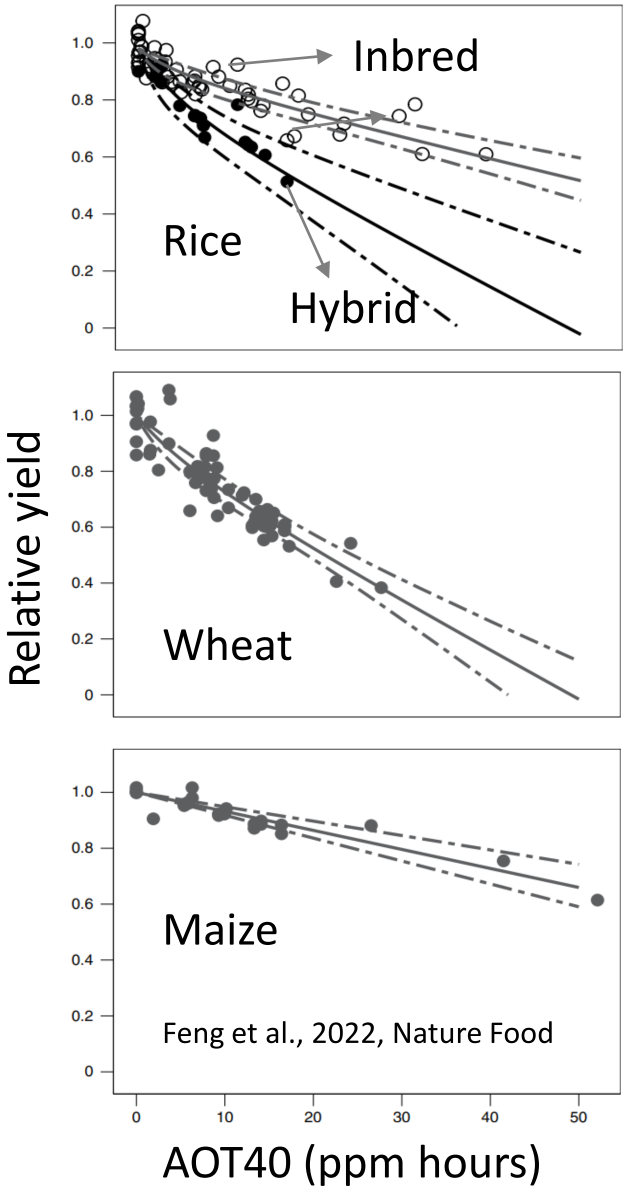


Population in 2017



Population in 2100

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 :

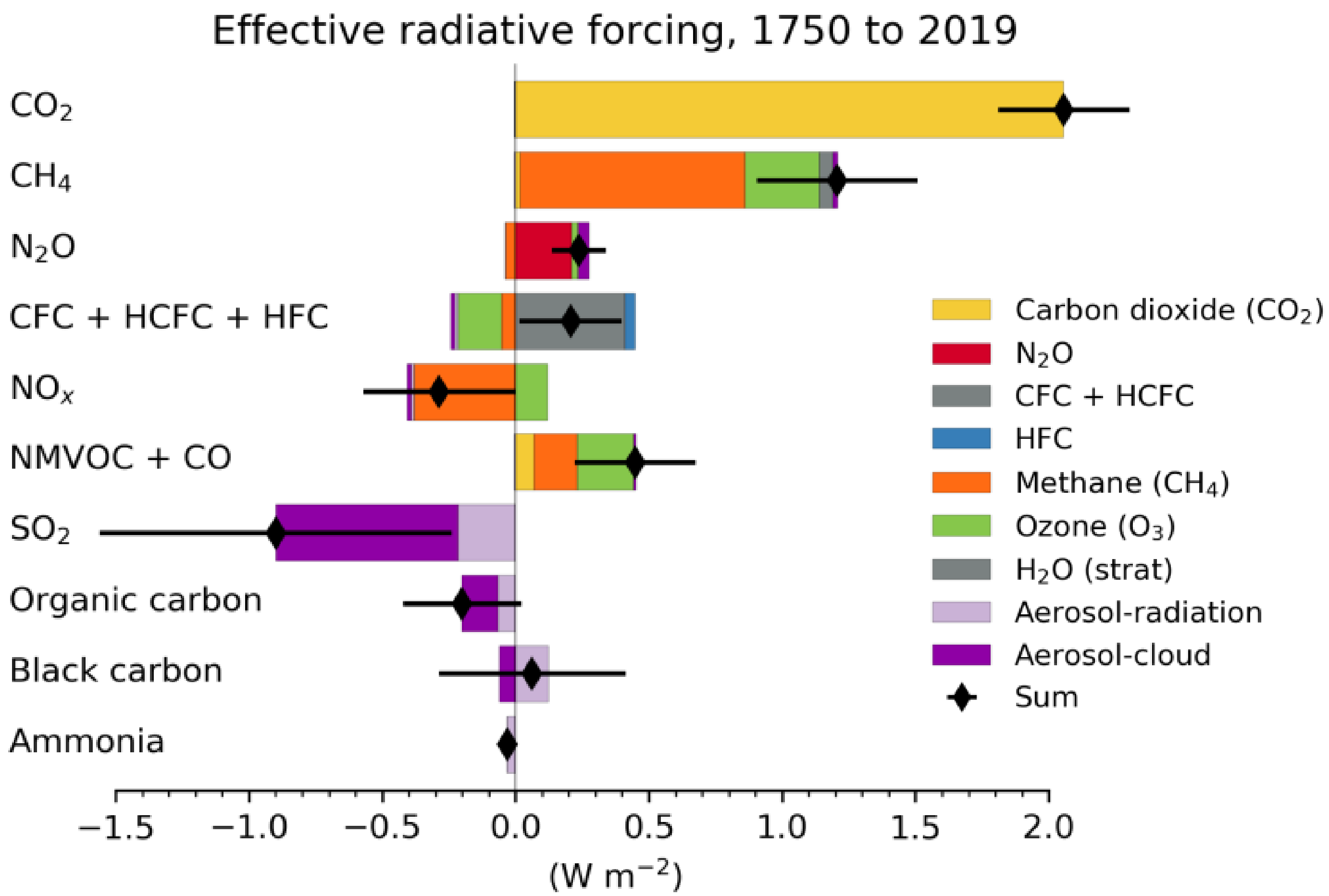
$$AOT40 = \sum_{i=1}^{n} \left([O_3]_i - 0.04 \right), \ for\ o_3 \geq 0.04ppm$$

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

Acid Rain As a Major Environmental Problem

Effects of Acid Rain

Air Pollutants As Short-Lived Climate Forcers



IPCC, 2021

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

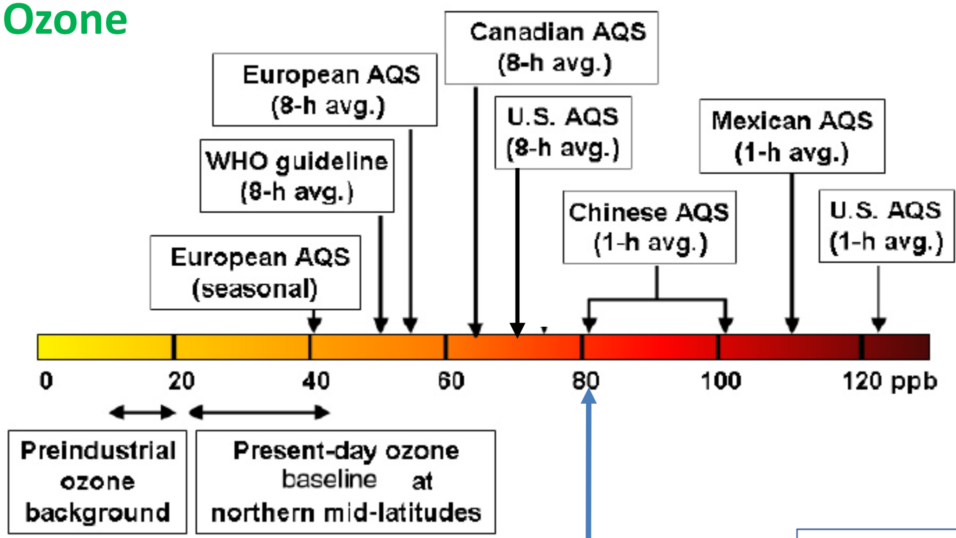
[a] 99th百分位 (i.e. 每年3–4 天超标)

[b] 年最大6个月MDA8滑动平均值，其中MDA8为日最大8小时浓度滑动均值。

数据来源：WHO, 2021
表格来源：https://cese.pku.edu.cn/kycg/131451.htm

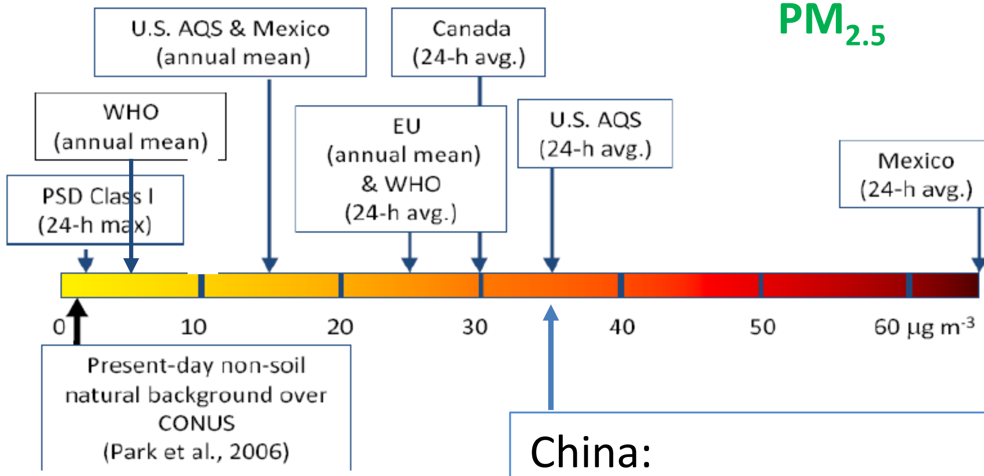
Ambient Air Quality Standards

Ozone



China:
81.5 ppb (160 μg m^{-3})
for MDA8 O_3

$PM_{2.5}$



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/（μg/m³）	二氧化硫（SO_2）1 小时平均/（μg/m³）[1]	二氧化氮（NO_2）24 小时平均/（μg/m³）	二氧化氮（NO_2）1 小时平均/（μg/m³）[1]	颗粒物（粒径小于等于 10μm）24 小时平均/（μg/m³）	一氧化碳（CO）24 小时平均/（mg/m³）	一氧化碳（CO）1 小时平均/（mg/m³）[1]	臭氧（O_3）1 小时平均/（μg/m³）	臭氧（O_3）8 小时滑动平均/（μg/m³）	颗粒物（粒径小于等于 2.5μm）24 小时平均/（μg/m³）
	0	0	0	0	0	0	0	0	0	0	0
优	50	50	150	40	100	50	2	5	160	100	35
良	100	150	500	80	200	150	4	10	200	160	75
轻度	150	475	650	180	700	250	14	35	300	215	115
中度	200	800	800	280	1 200	350	24	60	400	265	150
重度	300	1 600	[2]	565	2 340	420	36	90	800	800	250
严重	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

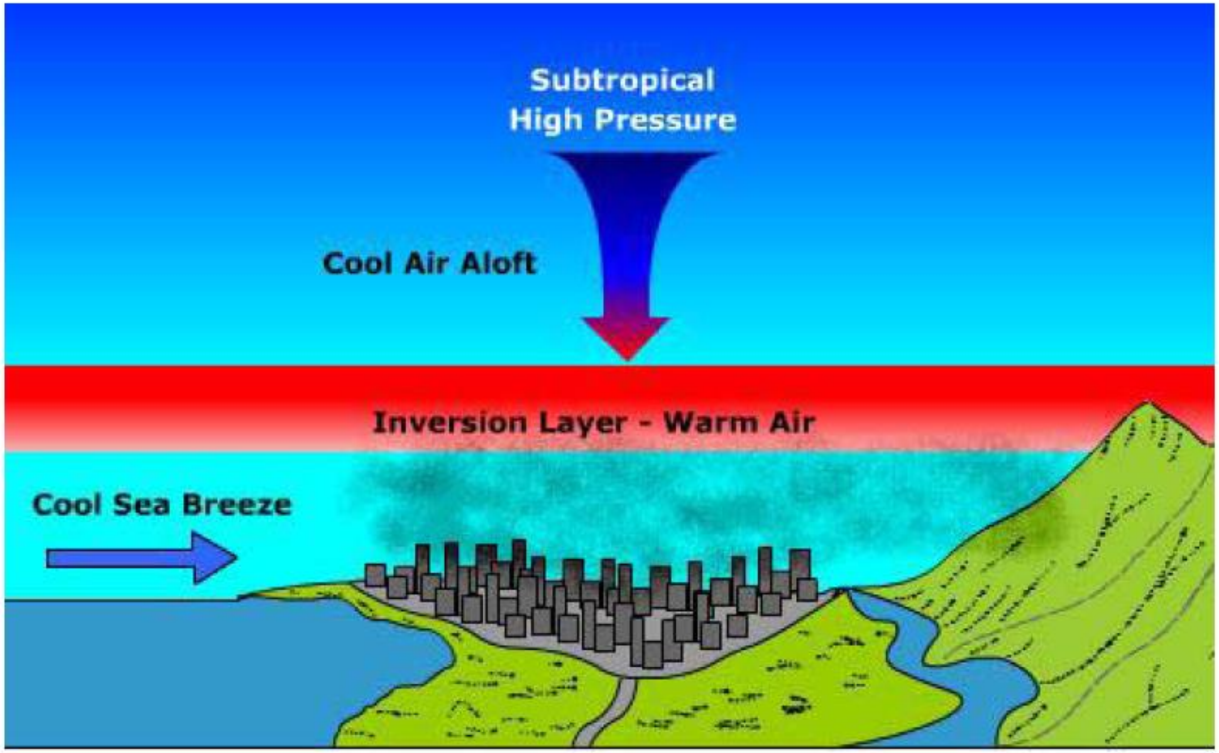
2018年9月1日前：参比状态为1atm、273K（气体和颗粒物）

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

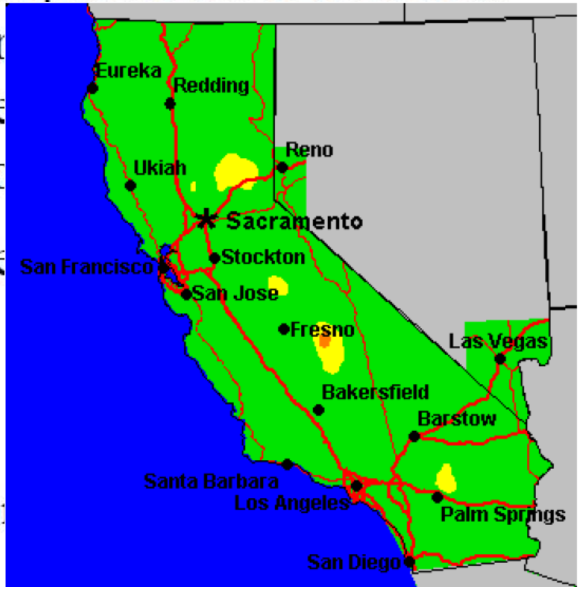
Photochemical Smog

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

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
alo



- 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 for Tropospheric Ozone

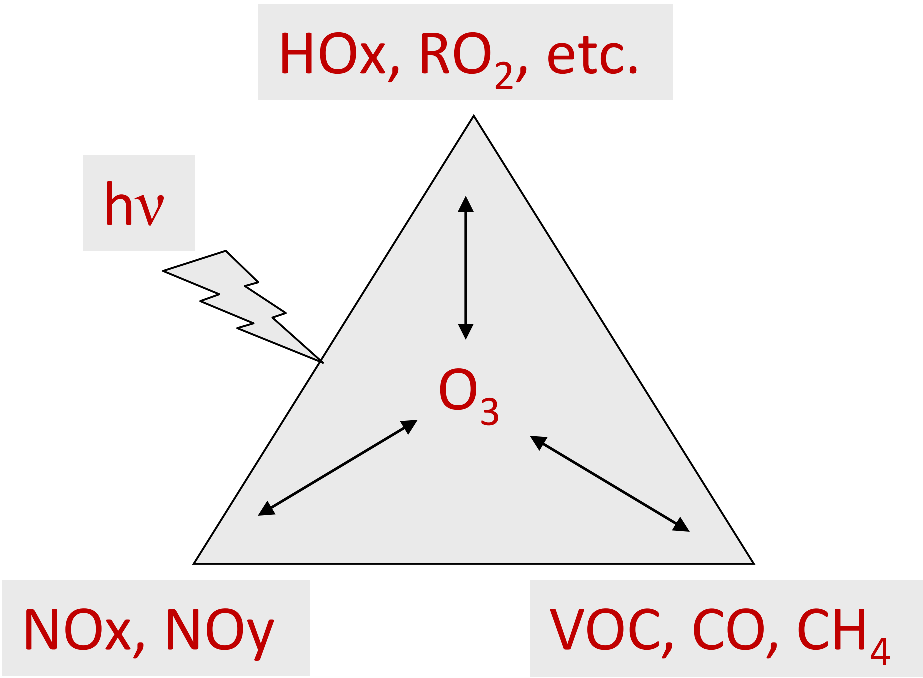
Production

- **Initiation**
  - $CO + OH\ (+ O_2) \rightarrow CO_2 + HO_2$
  - $RH + OH\ (+ O_2) \rightarrow RO_2 + H_2O$ (RH: VOC)
- **Propagation**
  - $NO + RO_2\ (+ O_2) \rightarrow \text{Carbonyl} + NO_2 + HO_2$
  - $NO + HO_2 \rightarrow OH + NO_2$
  - $NO_2 + h\nu \rightarrow NO + O(^3p)$ ($\lambda < 420$ nm)
  - $O(^3p) + O_2 + M \rightarrow O_3 + M$
- **Termination**
  - $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
  - $HO_2 + RO_2 \rightarrow ROOH + O_2$
  - $OH + NO_2 + M \rightarrow HNO_3 + M$

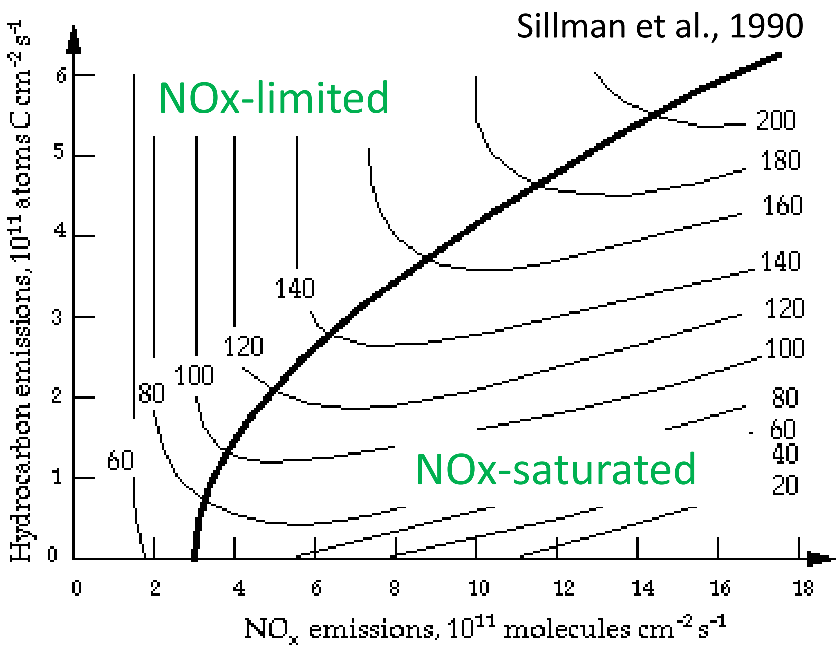
Destruction

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



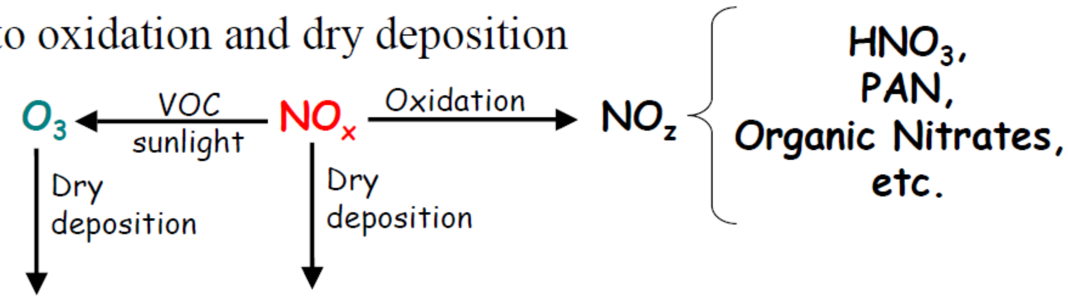
Ozone mixing ratio as a function of NOx and NMVOC emissions



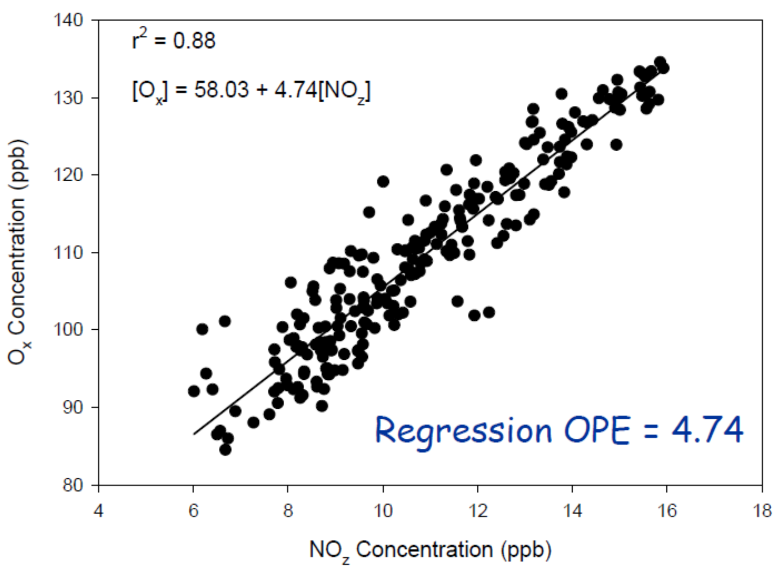
Ozone Production Efficiency (OPE)

General definition (Sillman, 2000, JGR)

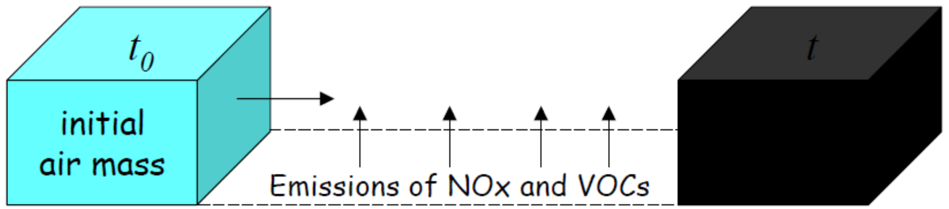
Number of O_3 molecules produced by a molecule of NO_x before it is lost from the $NO_x - O_3$ cycle due to oxidation and dry deposition



Regression OPE



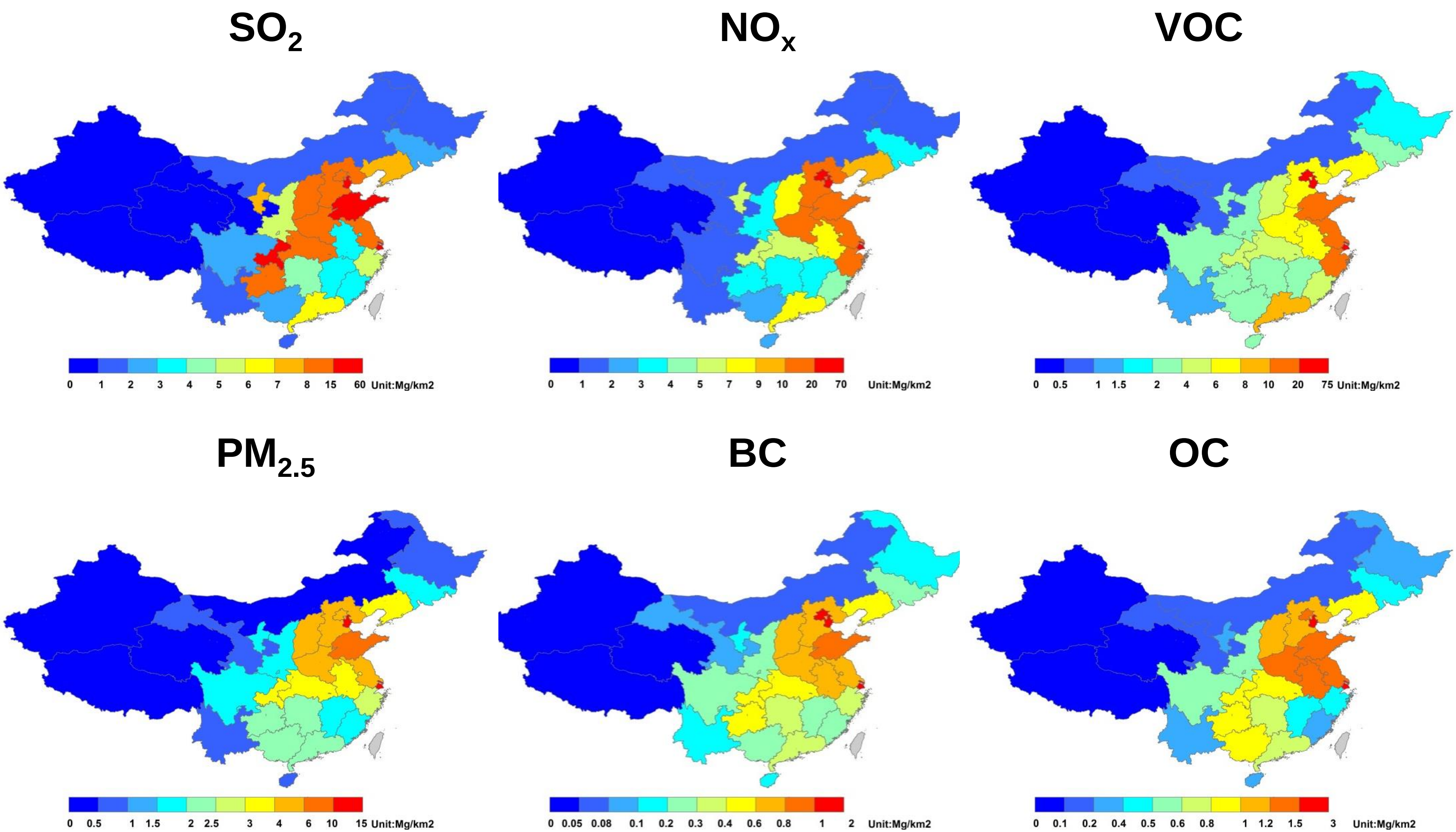
Lagrangian OPE



Lagrangian OPE

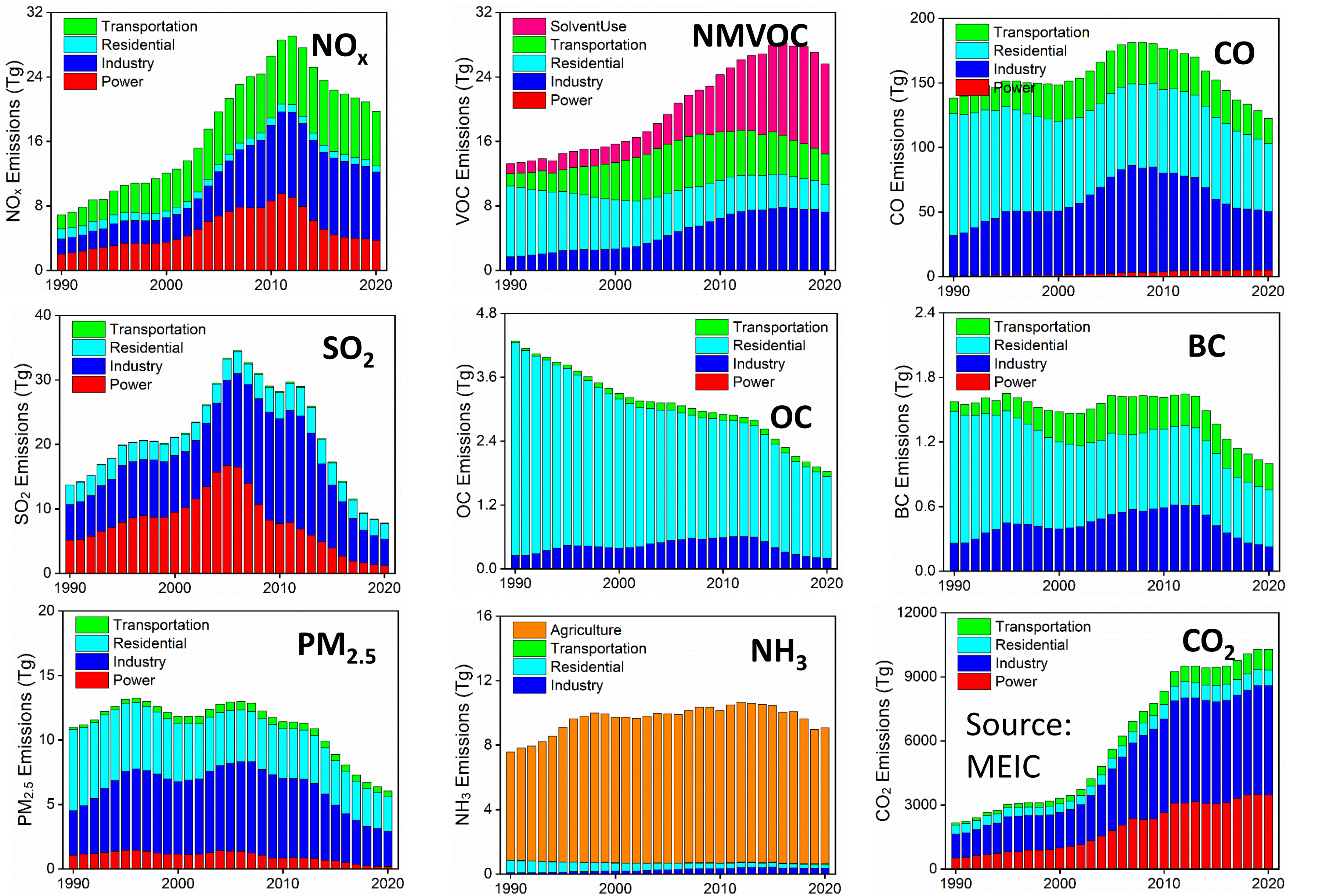
$$\text{Lagrangian OPE}(t) = \frac{\Delta[O_3(t)]_{prod}}{\Delta[NO_x(t)]_{dest}}$$

Anthropogenic Emissions in China

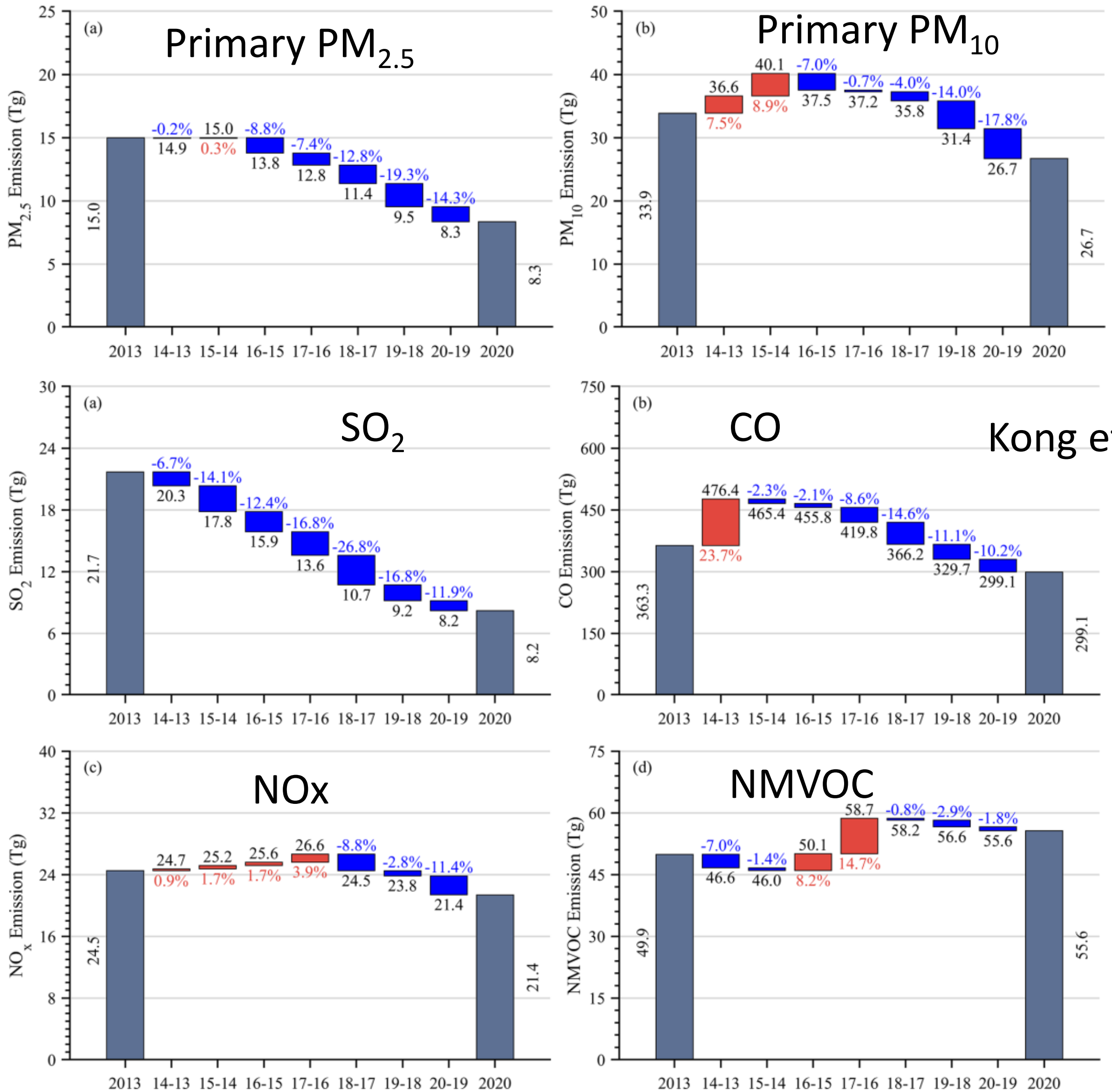


贺克斌，2014

Anthropogenic Emissions in China: 1990-2020



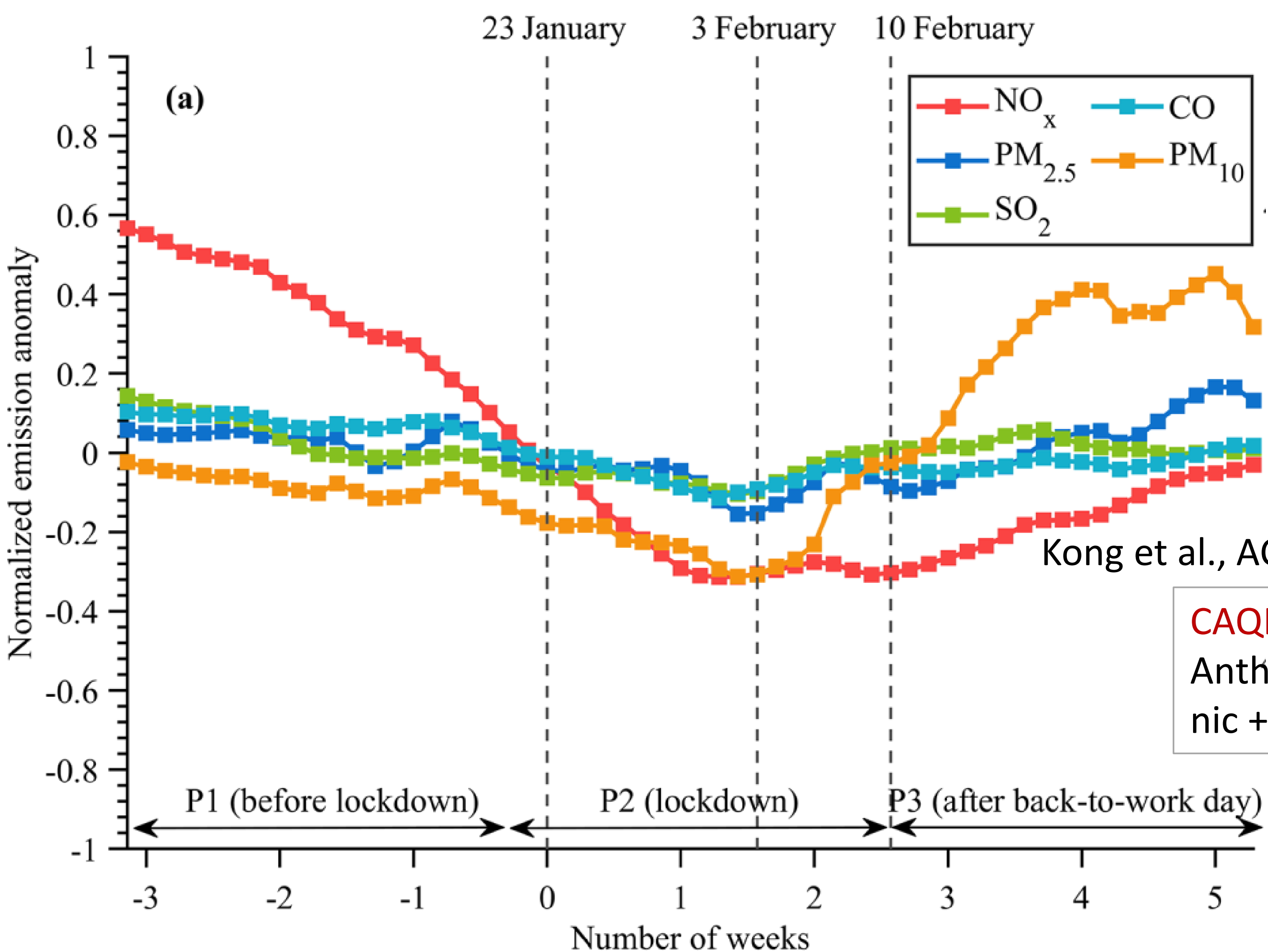
Chinese Emission Trends over 2013–2020 Constrained from Surface Concentration Measurements



Kong et al., ESSD, 2024

CAQIEI data: Anthropogenic + natural

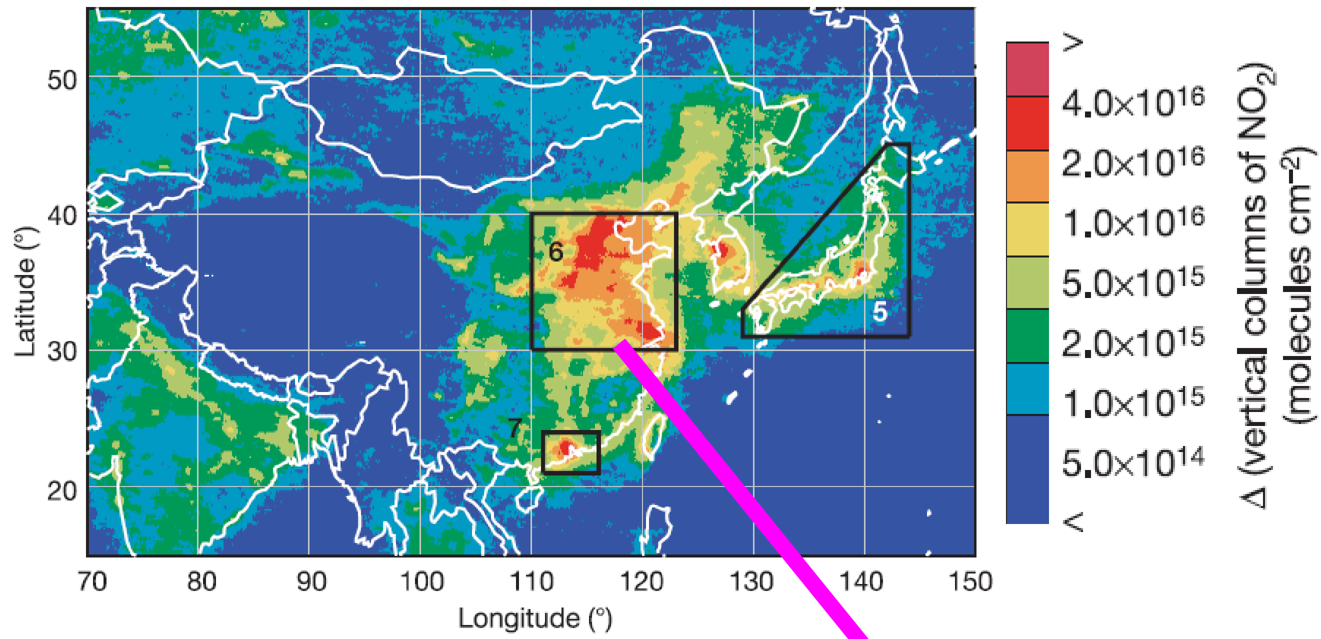
Impacts of COVID-19 on Chinese Emissions Constrained from Surface Concentration Measurements



Kong et al., ACP, 2023

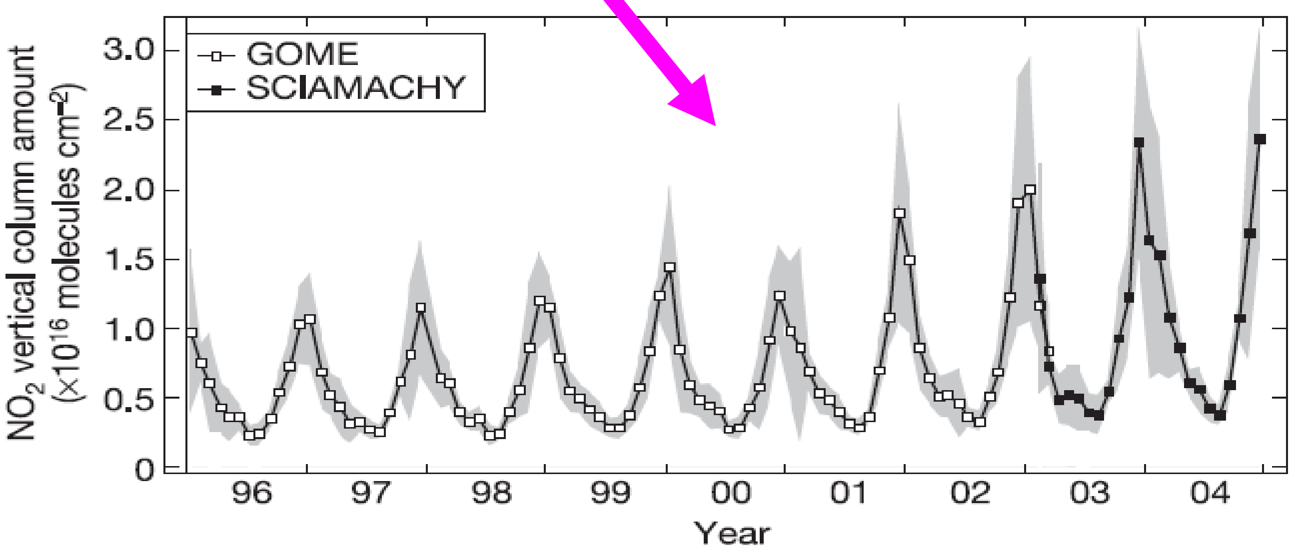
CAQIEI data: Anthropogenic + natural

Increases of NO_2 VCD Observed from Space

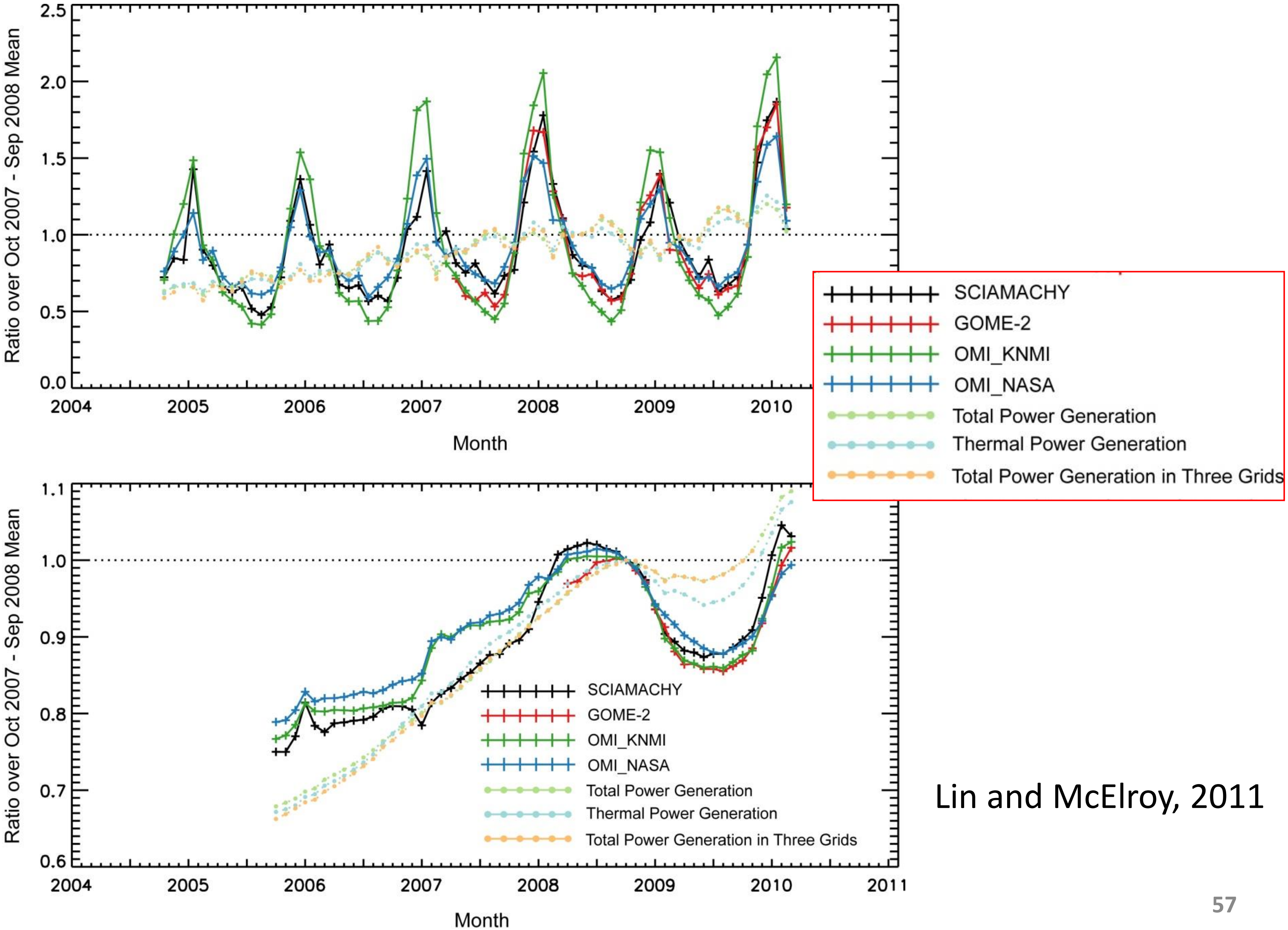


Tropospheric NO_2 vertical columns (2003,12~2004,11)

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

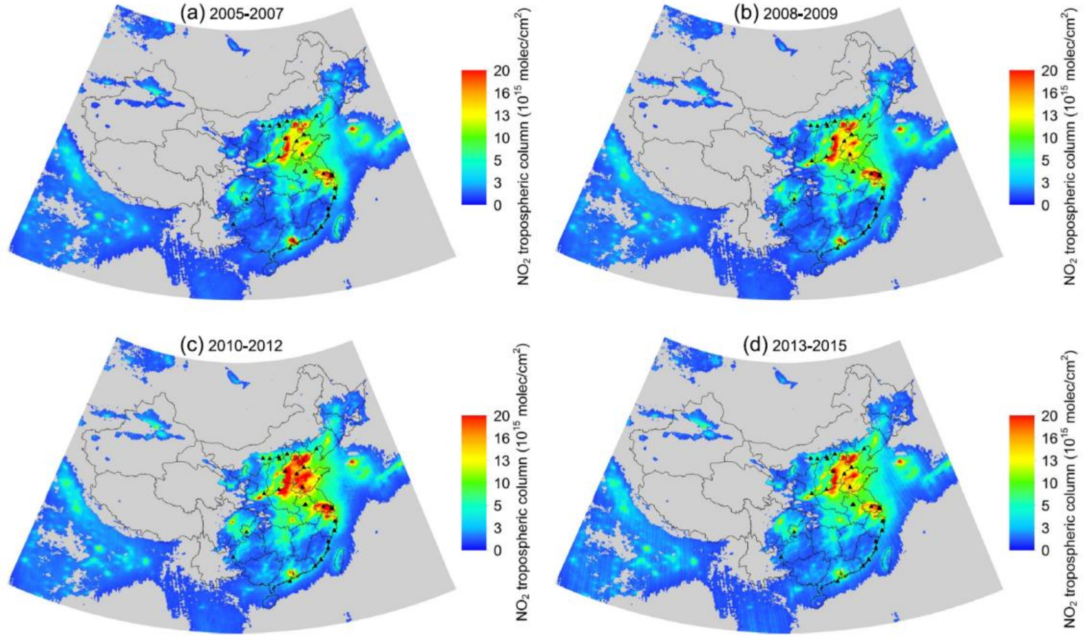


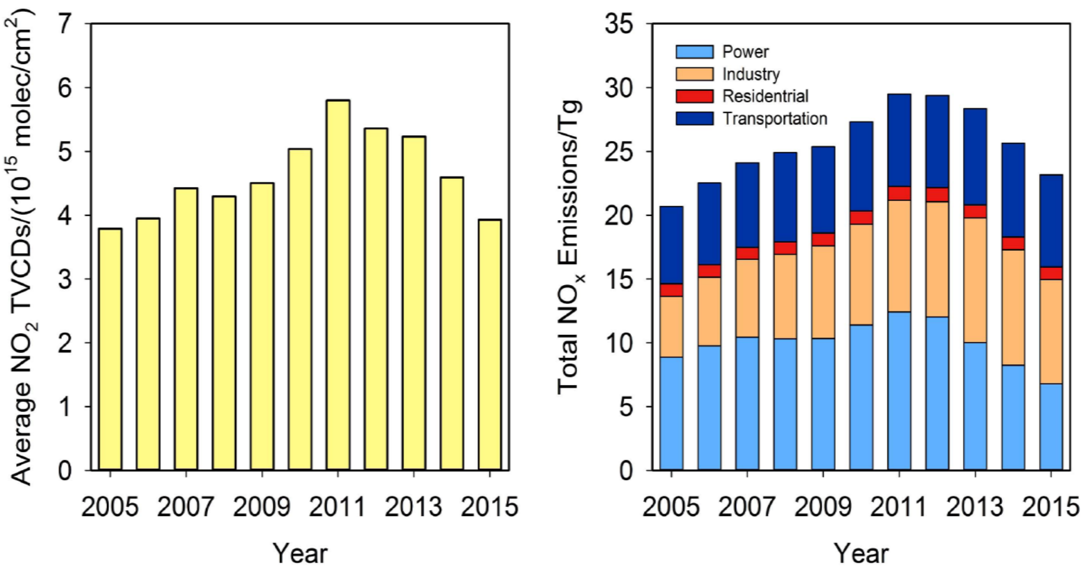
Increases of NO_2 VCD Observed from Space

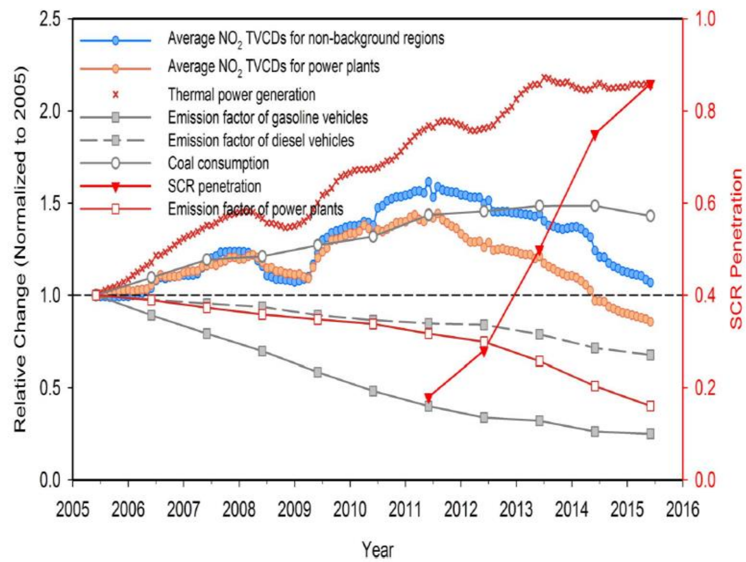


Lin and McElroy, 2011

Recent Reductions in NO_2 VCD over China





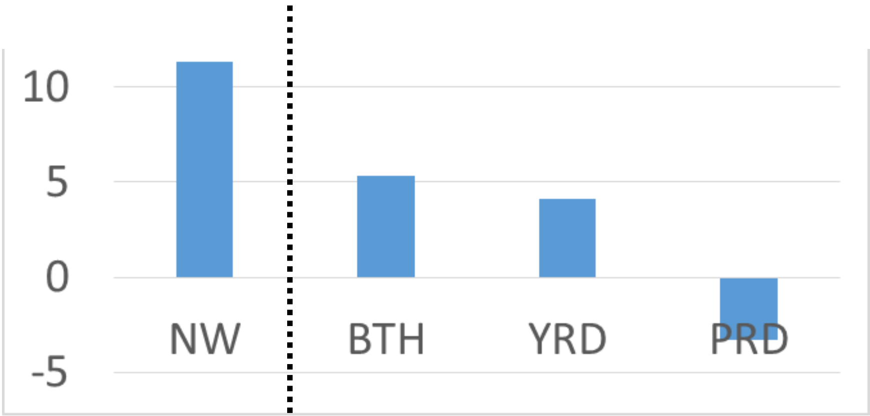


Liu et al., 2016, ERL

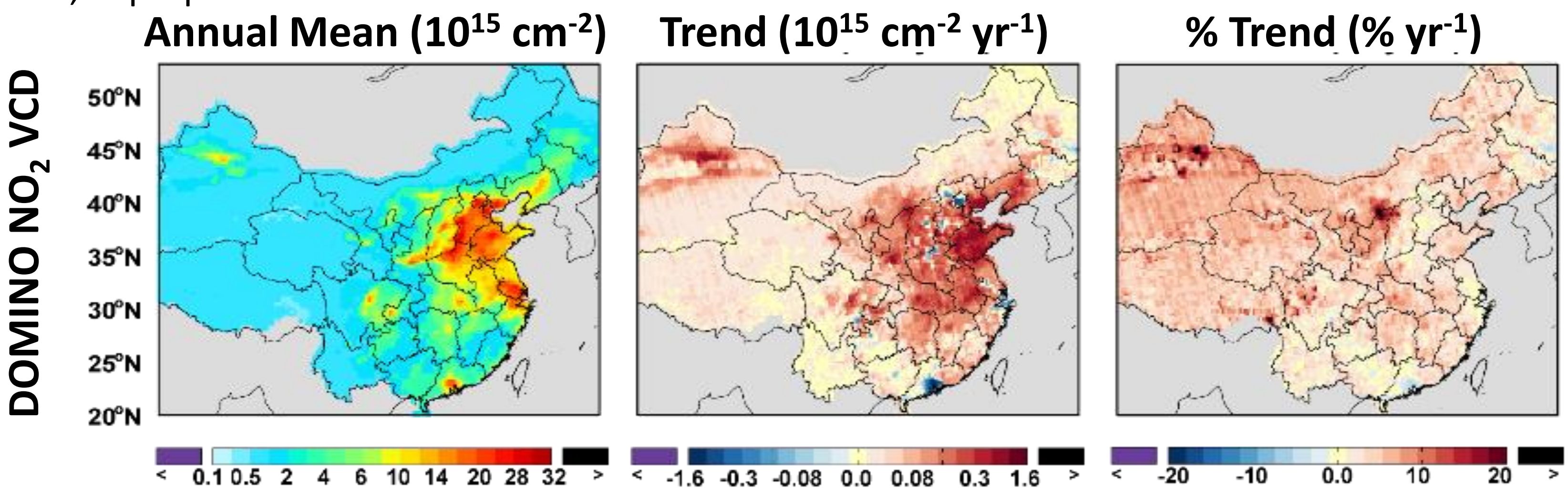
Growth of NO_2 VCDs over 2005–2013: West vs. East China

Cui et al., 2016 ACP

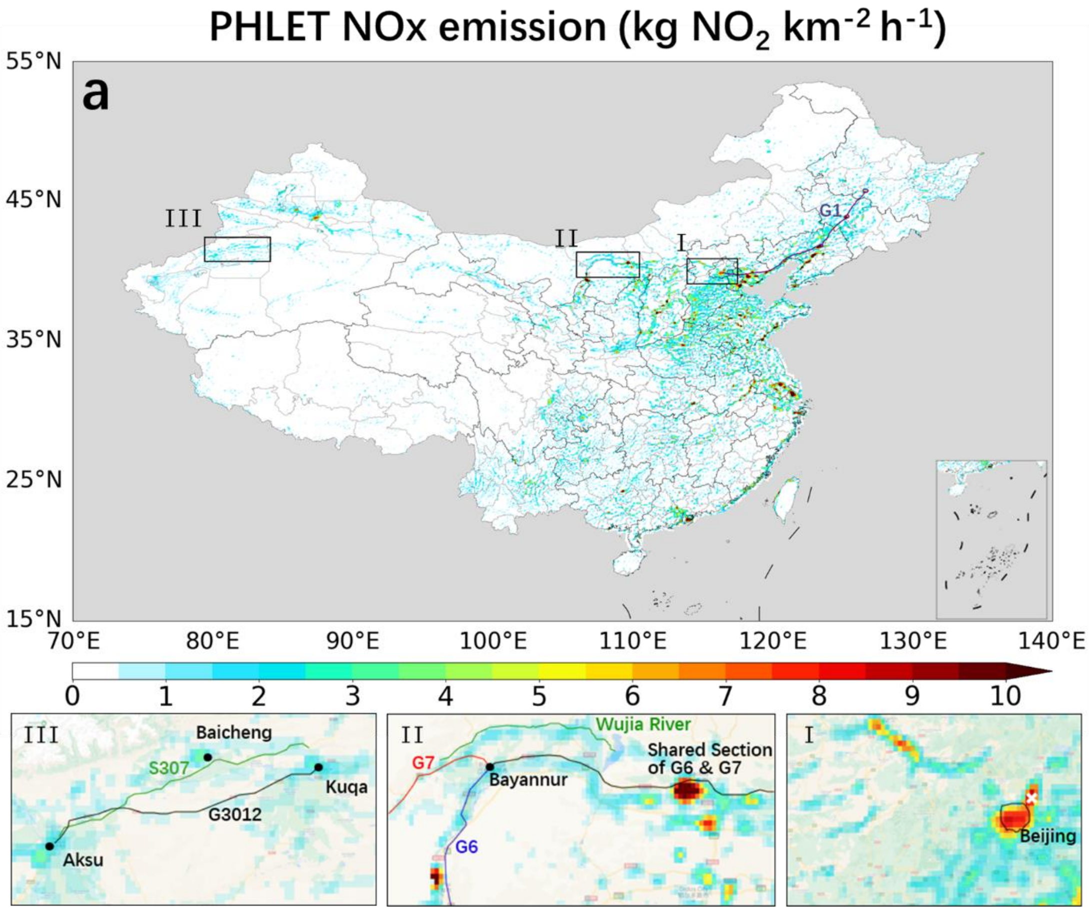
Growth Rate (%/yr) over 2005–2013

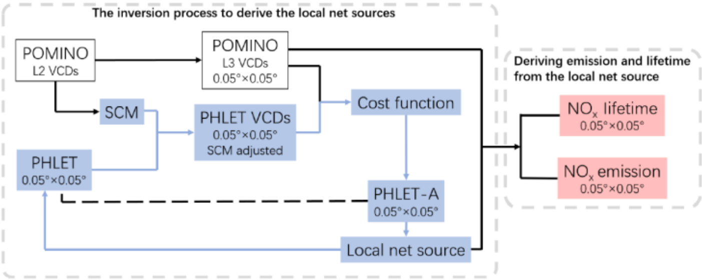


Yan et al., in prep



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

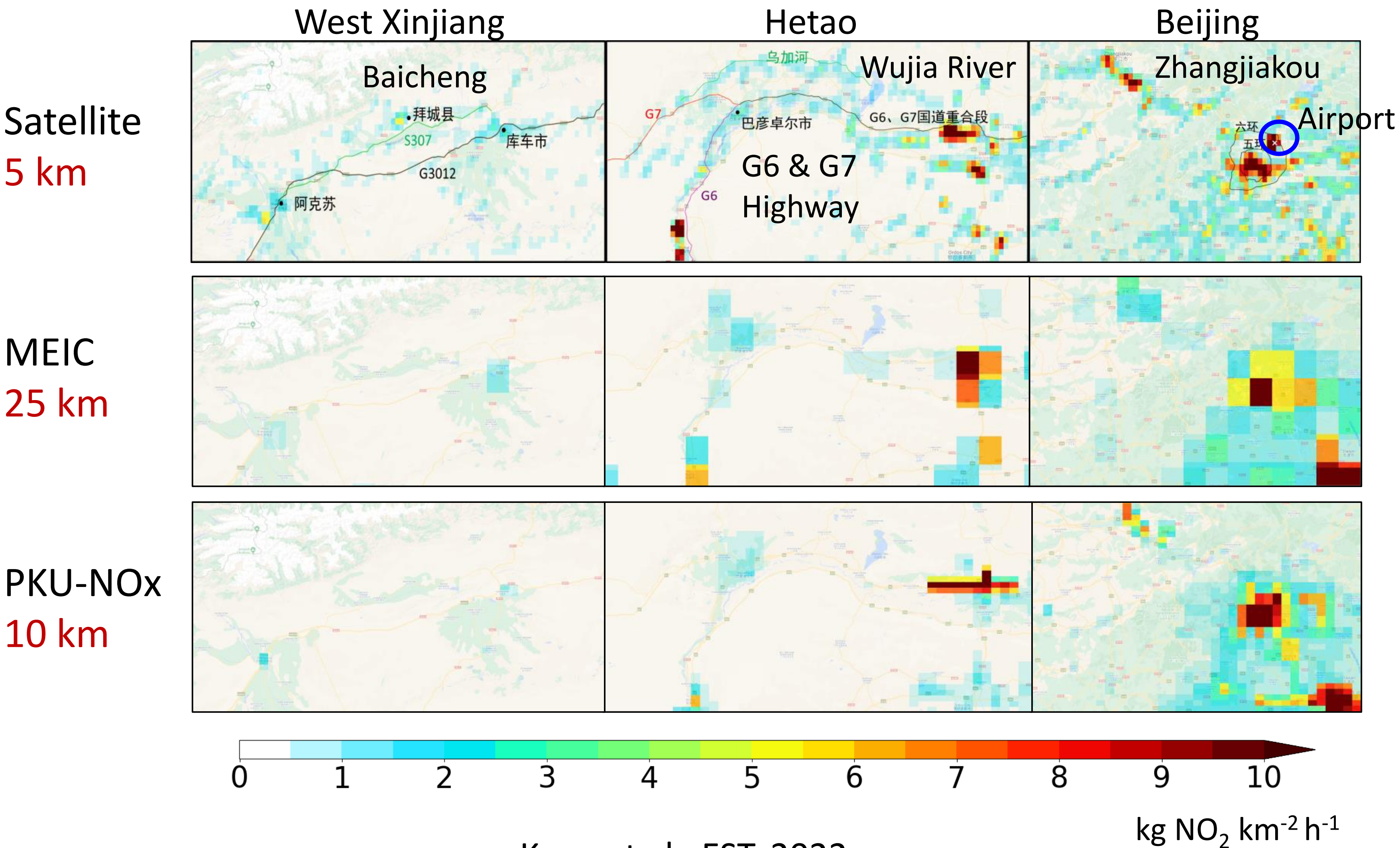




- Inversion model built from scratch
- Transport and nonlinear chemistry accounted for in emission estimate

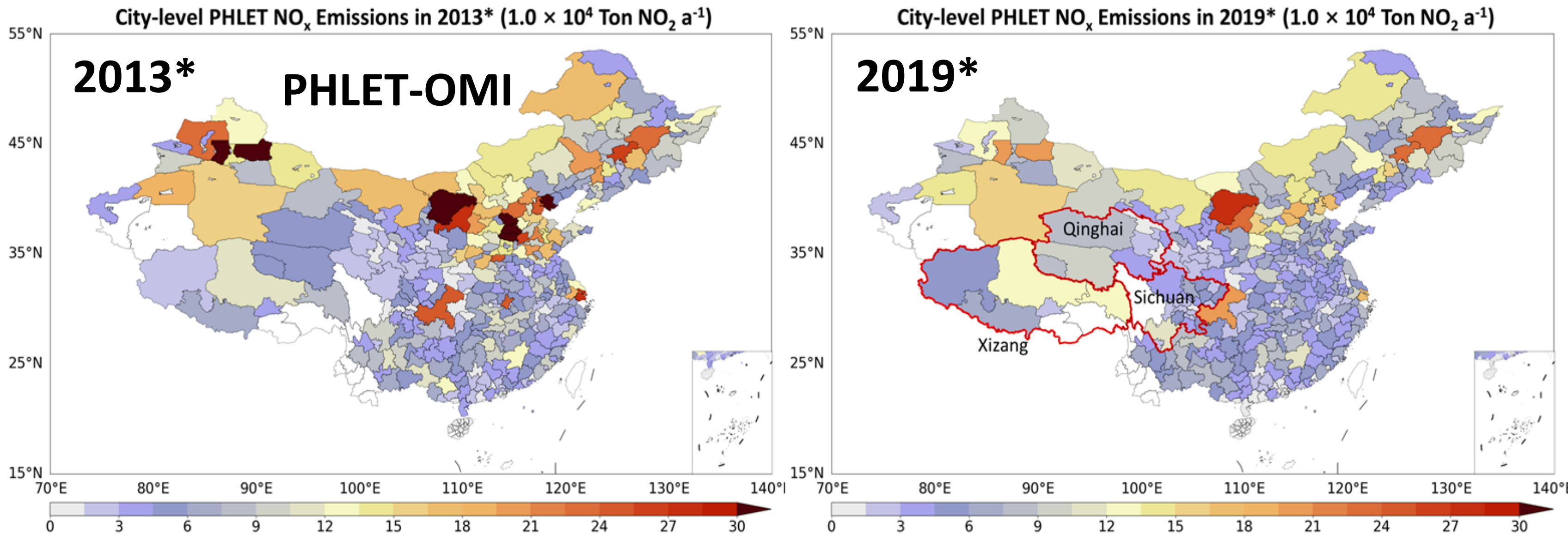
Kong et al., 2019, ACP; Kong et al., 2022, EST

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

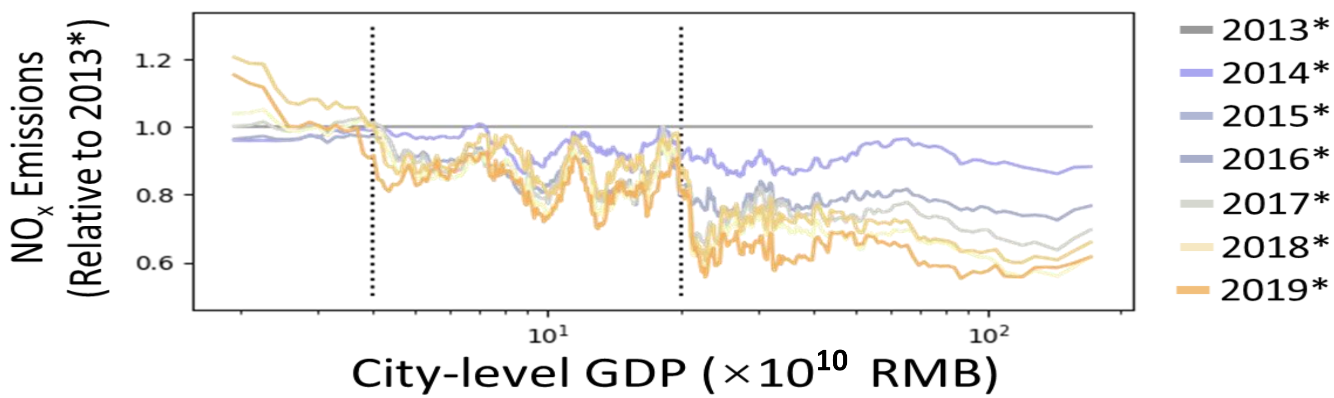


Kong et al., EST, 2022

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



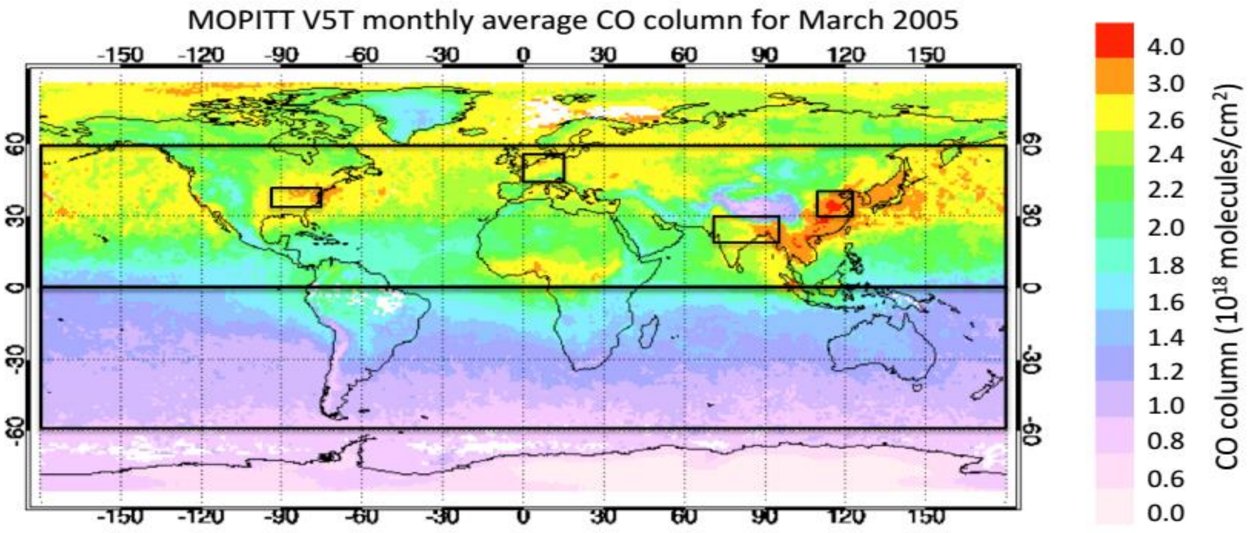
Emission change versus Economic volume

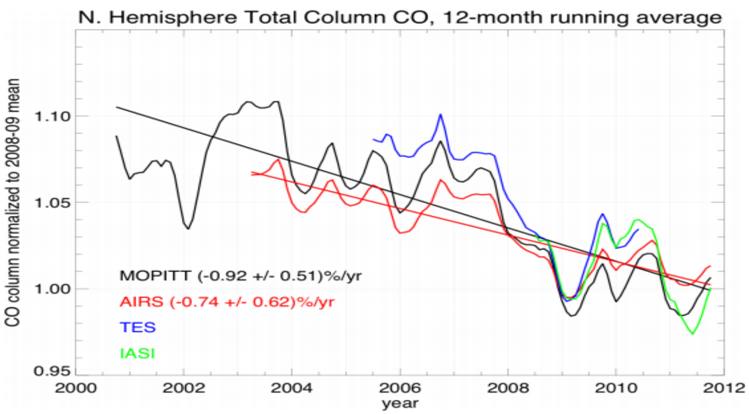


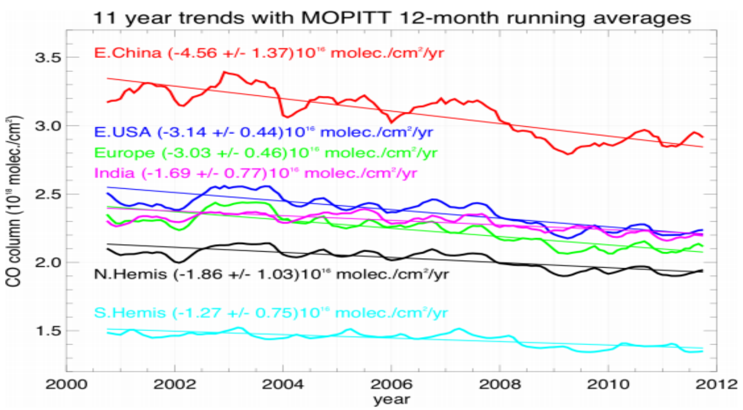
Kong et al., in prep

Changes in Tropospheric CO Column

CO tropospheric column density (Worden et al., 2013 ACP)



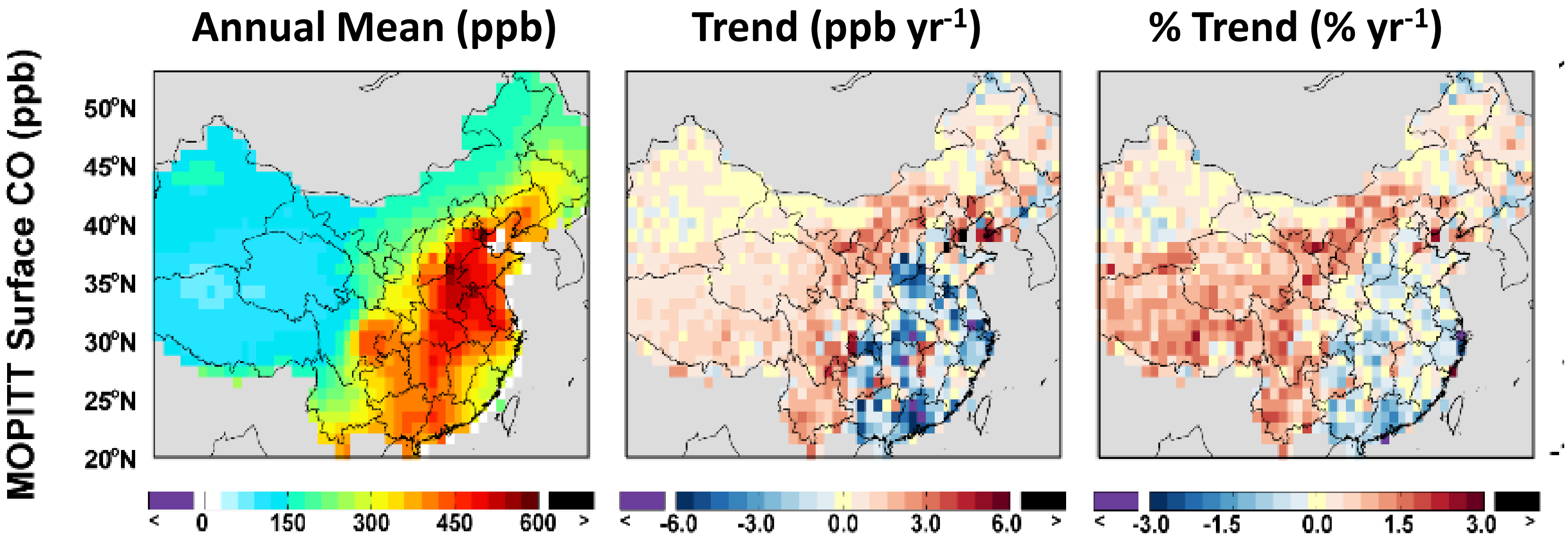




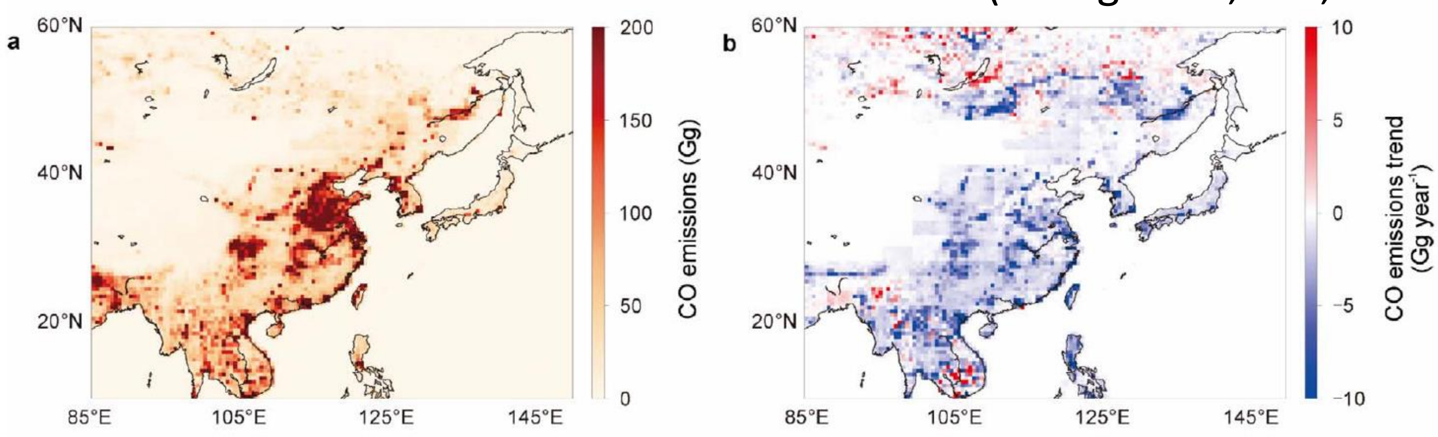
E. China: -1.6% – -1% yr^{-1}

Changes in CO over East Asia

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

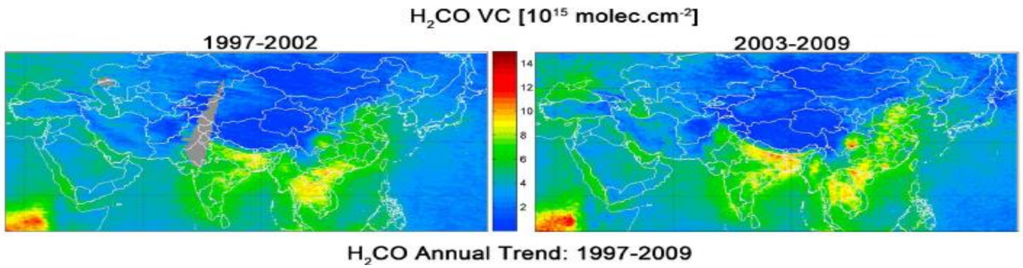


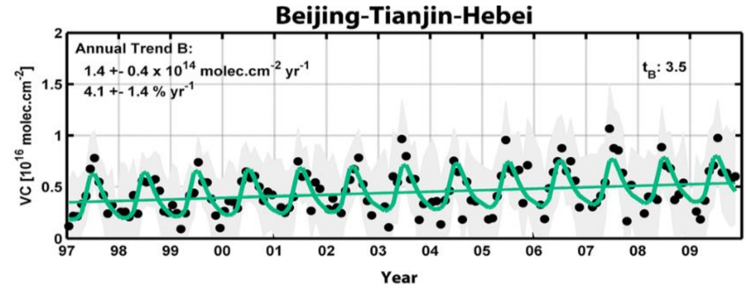
CO emissions over 2005-2016 based on MOPITT v7 (Zheng et al., ERL, 2018)



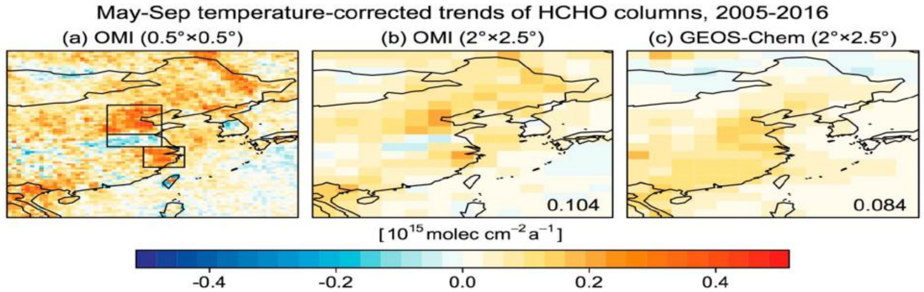
Trends of VCDs of HCHO in Asia: 1997–2009

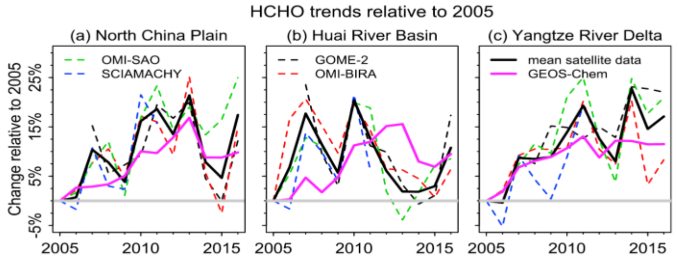
OMI VCD by BIRA (De Smedt et al., 2010 ACP)



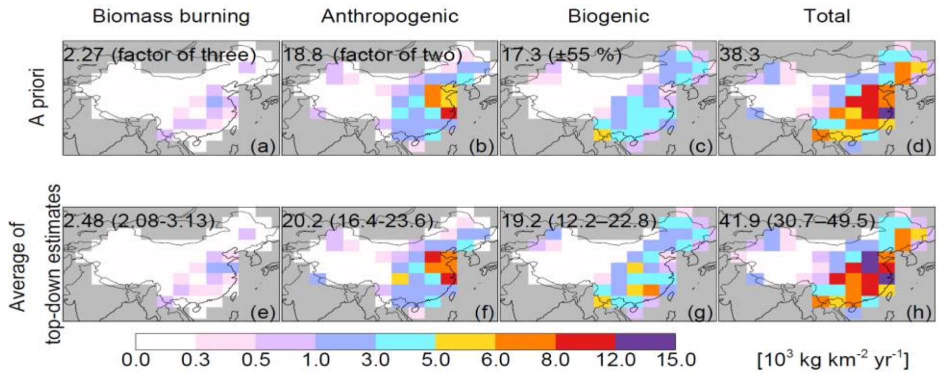


Multiple VCD products (Shen et al., 2019 GRL)



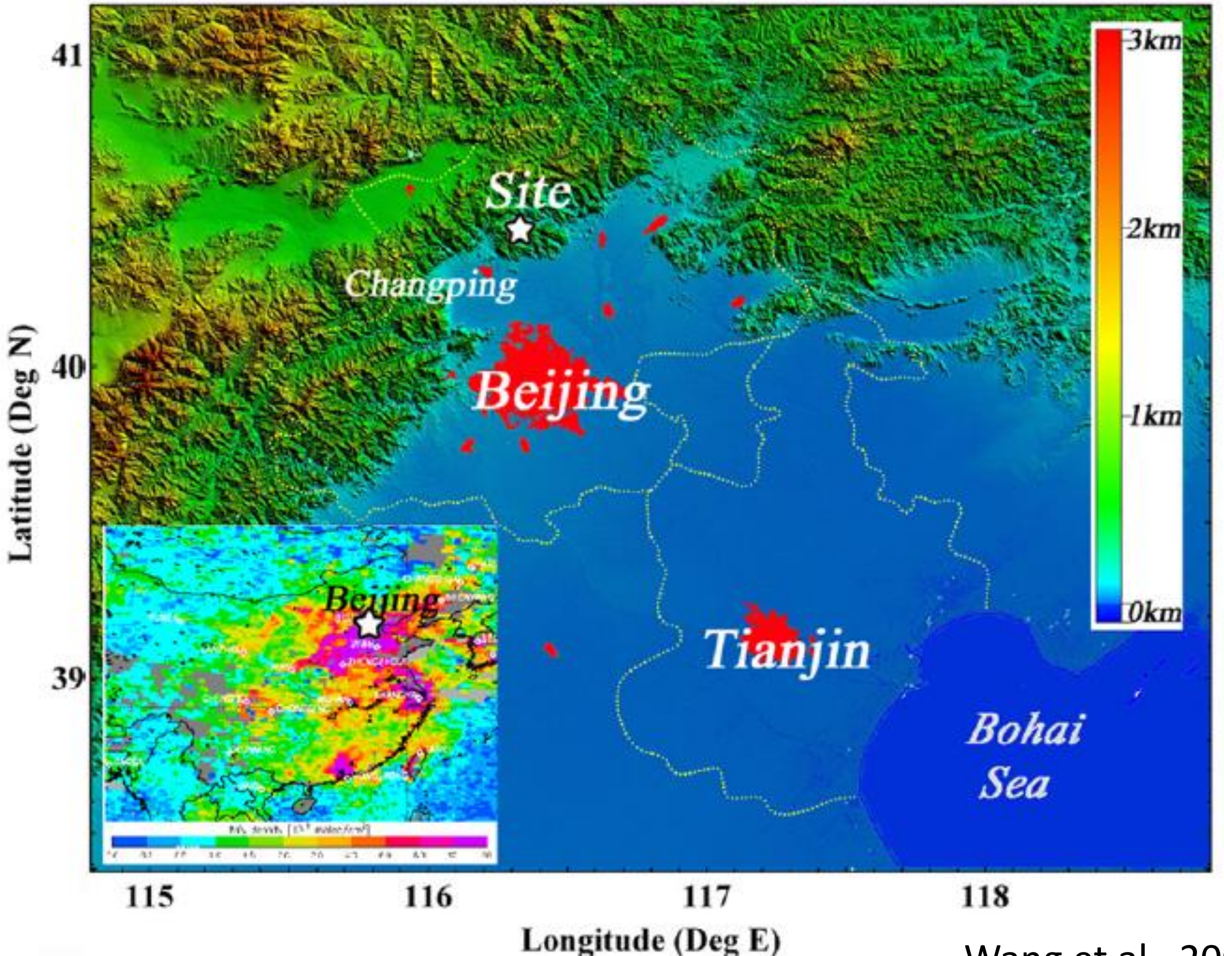


Emission constraint for 2007 based on OMI & GOME-2A HCHO and CHOCHO data (Cao et al., 2018 ACP)



Ozone Air Pollution over Beijing

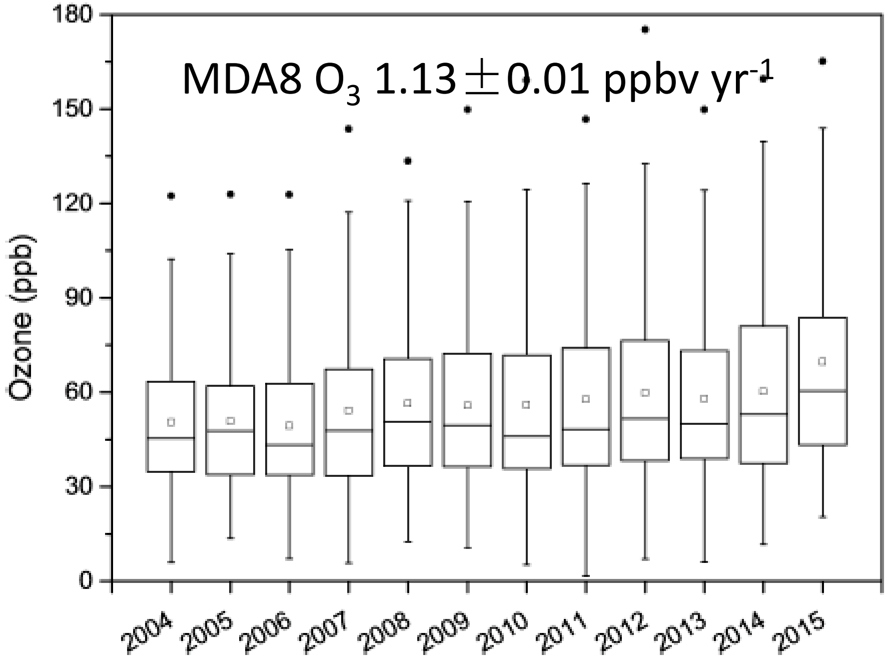
- Lots of emissions of NOx and VOC
- High temperature, little cloud
- Weak southerly



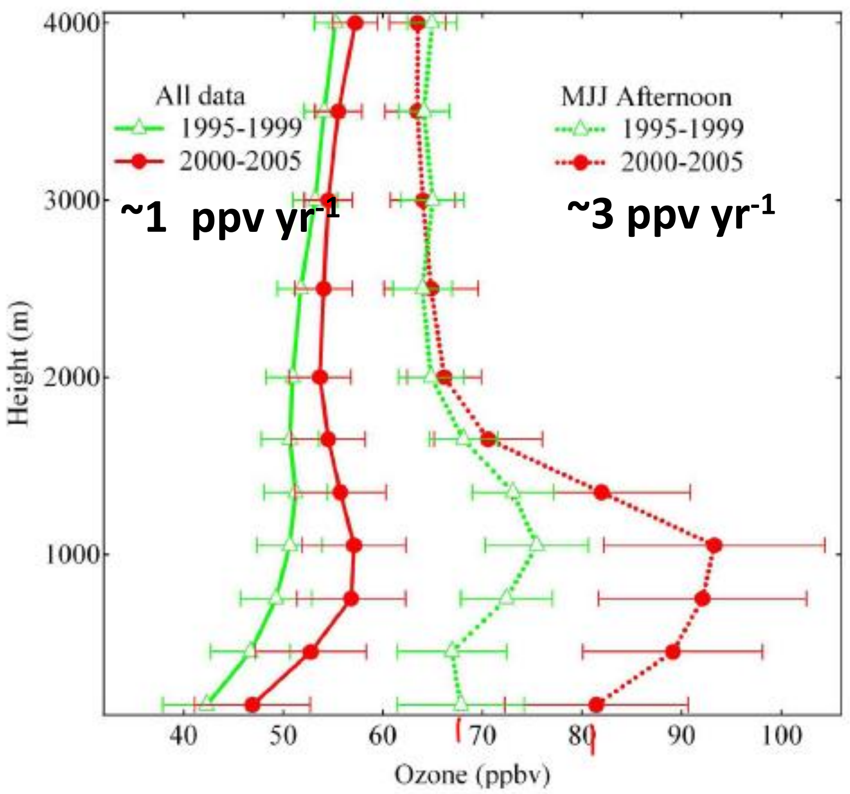
Wang et al., 2006

Growing Ozone Pollution over Beijing

Shangdianzi, regional background



Beijing airport, MOZAIC

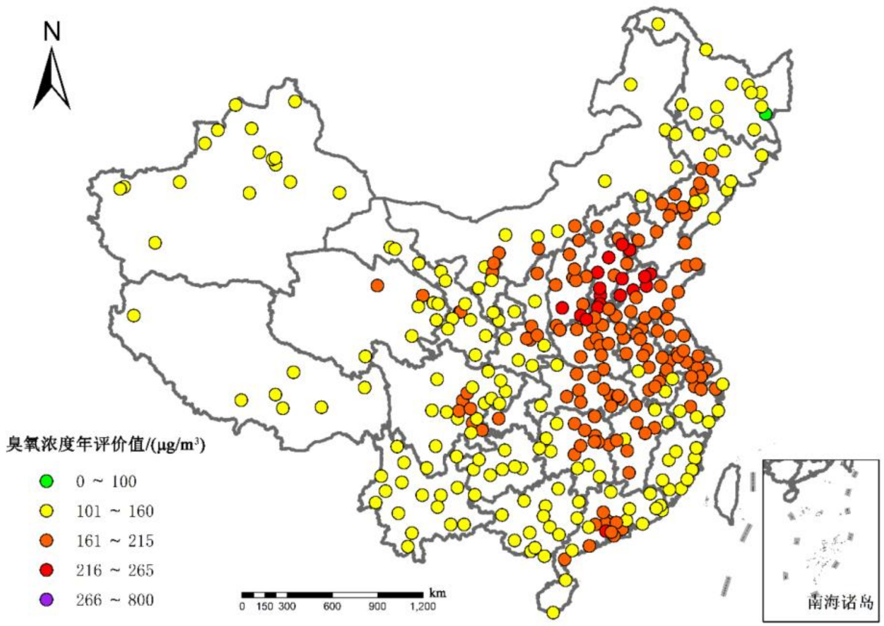


Emission changes in VOCs dominated

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

Severe Ozone Pollution over China

2019年，337个城市
臭氧MDA8h 90%分位值



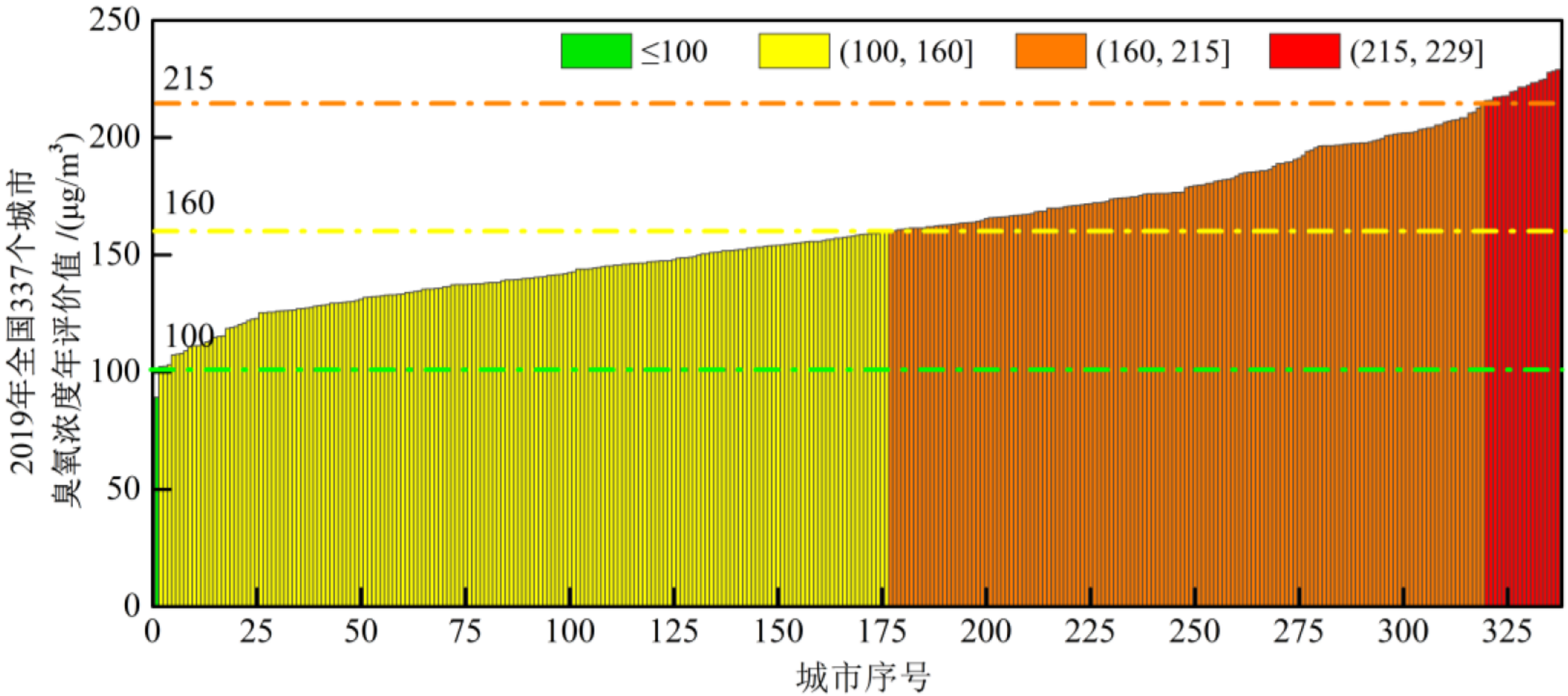
2023年，339个城市
臭氧MDA8h 90%分位值

中国大气臭氧污染防治蓝皮书（2020）

中国生态环境公报2023

Severe Ozone Pollution over China

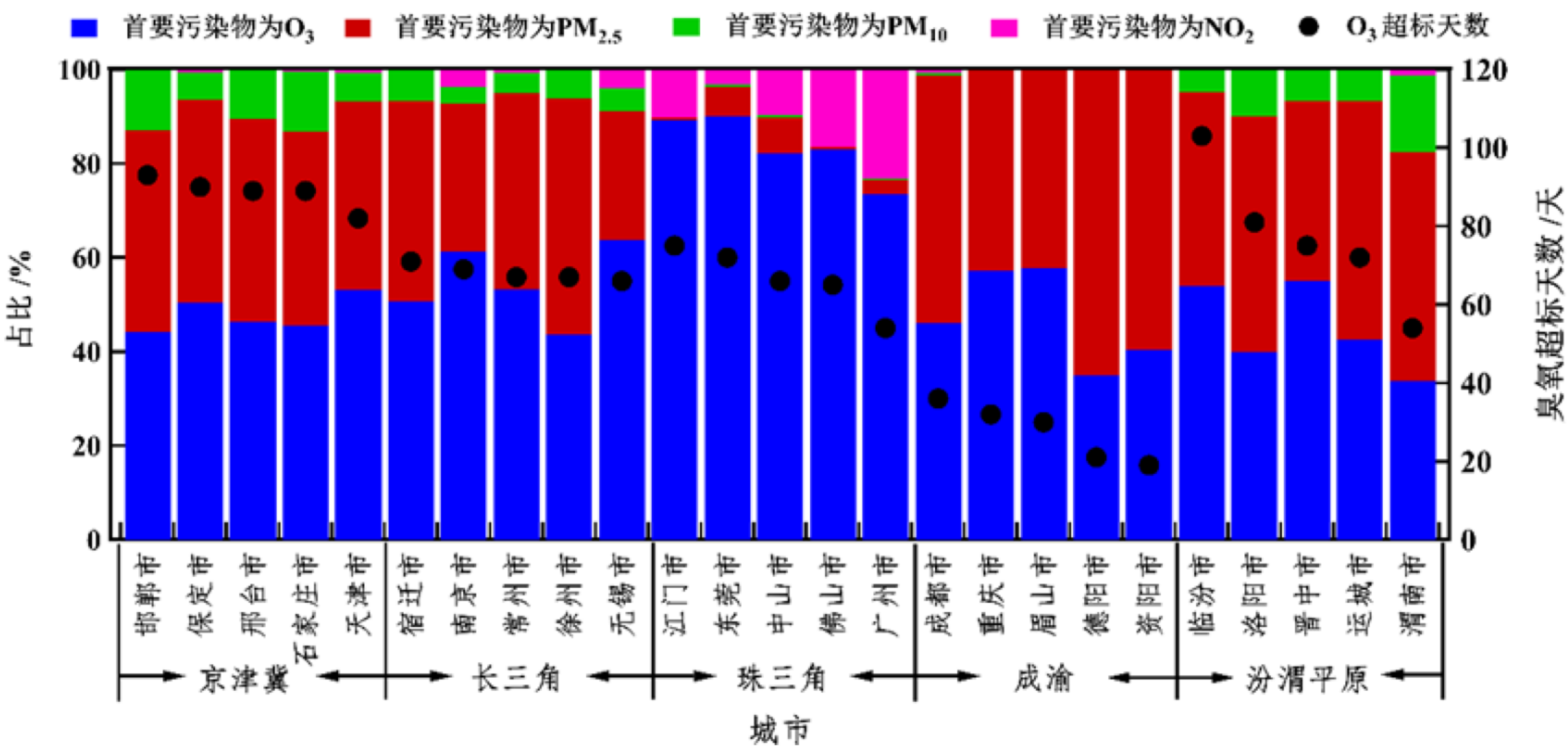
2019年，337个城市，臭氧MDA8h 90%分位值



中国大气臭氧污染防治蓝皮书（2020）

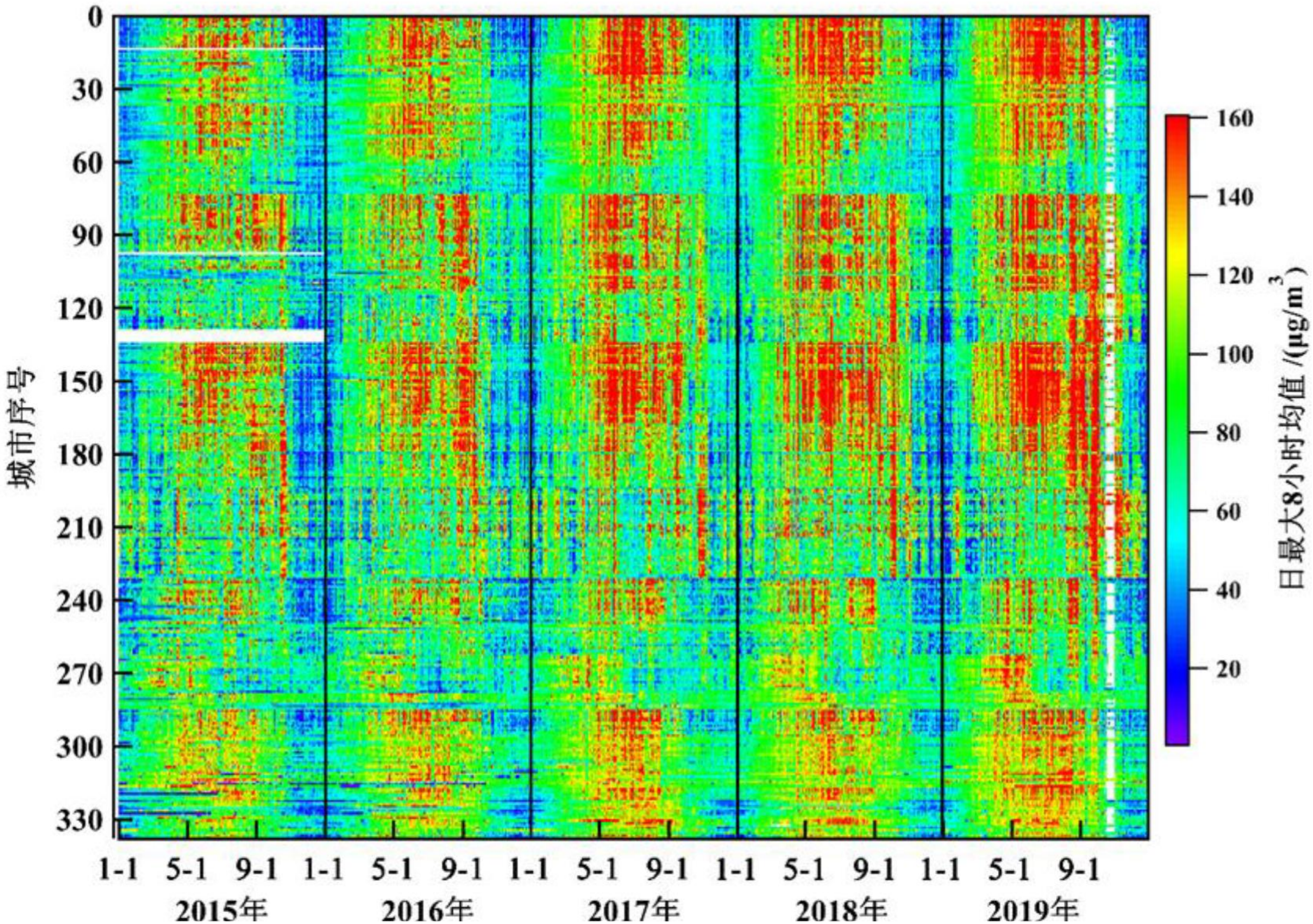
Severe Ozone Pollution over China

2019年，337个城市，首要污染物



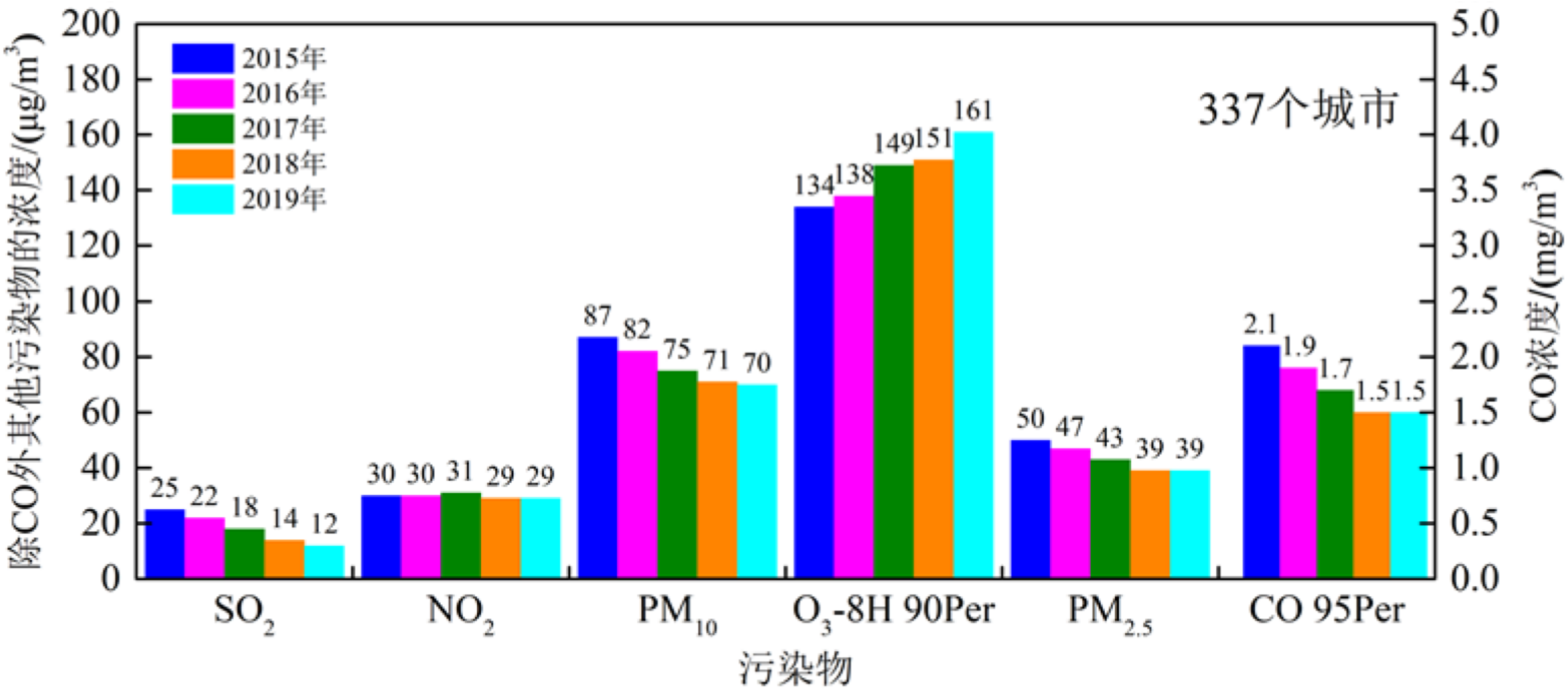
中国大气臭氧污染防治蓝皮书（2020）

Severe Ozone Pollution over China



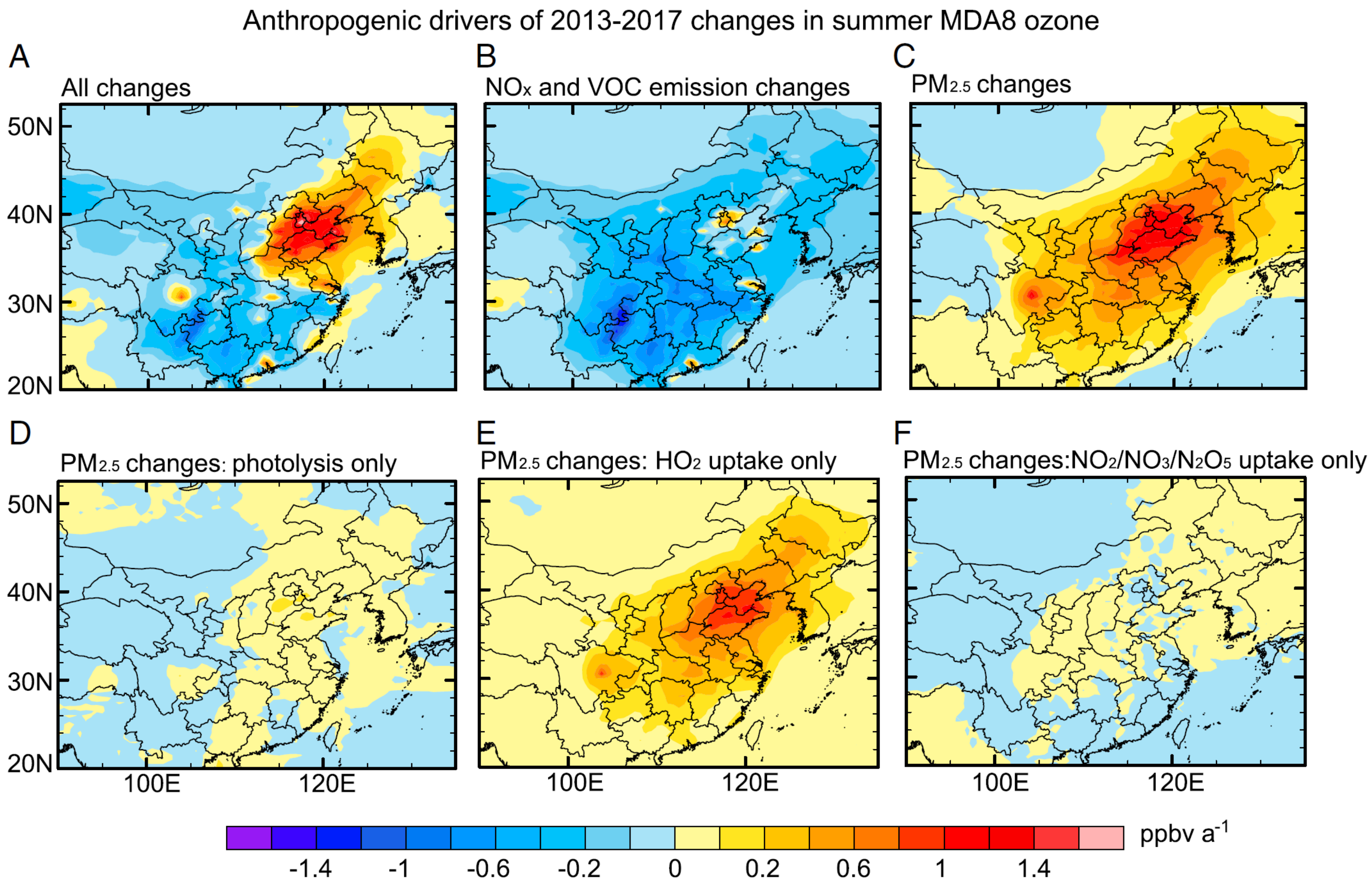
中国大气臭氧污染防治蓝皮书（2020）

Severe Ozone Pollution over China



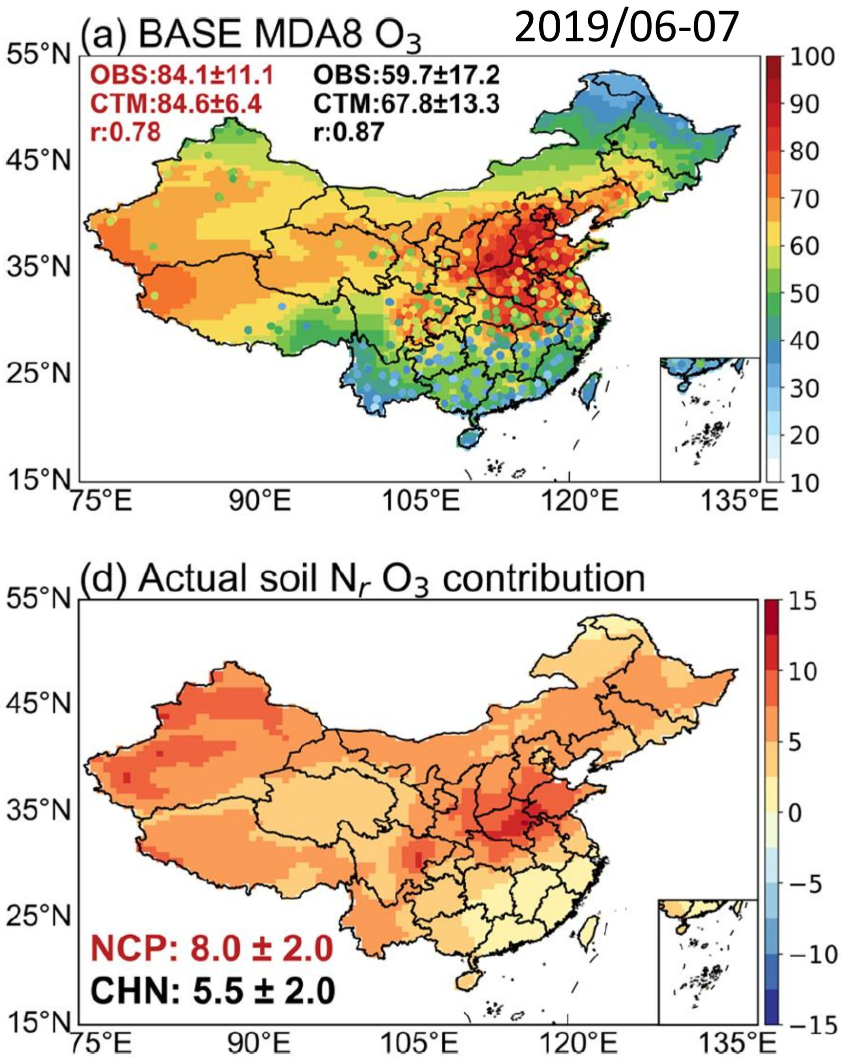
中国大气臭氧污染防治蓝皮书（2020）

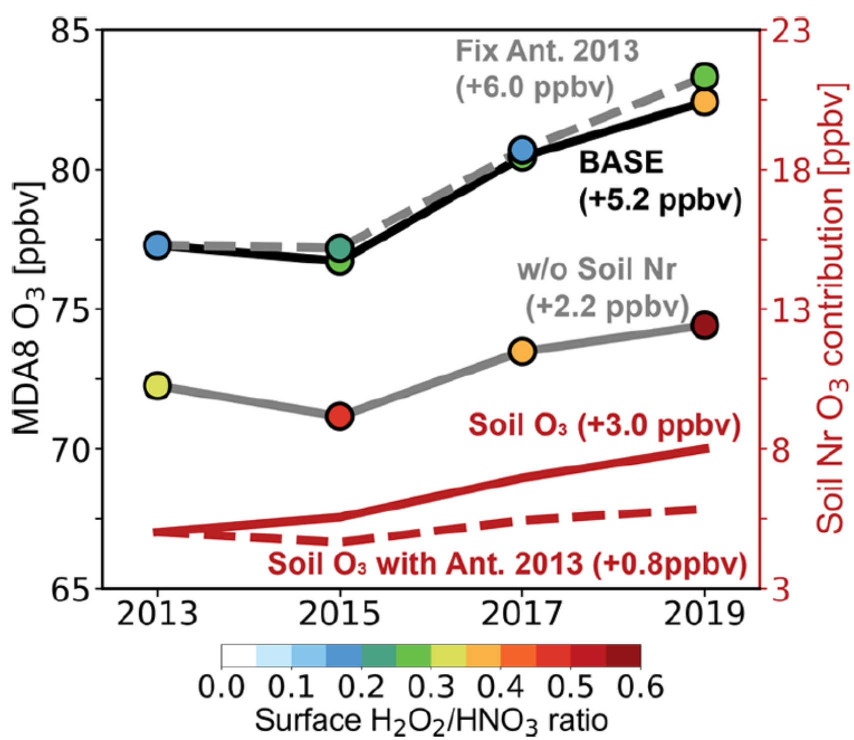
Drivers of Ozone Trend over China



Li et al., 2019, PNAS

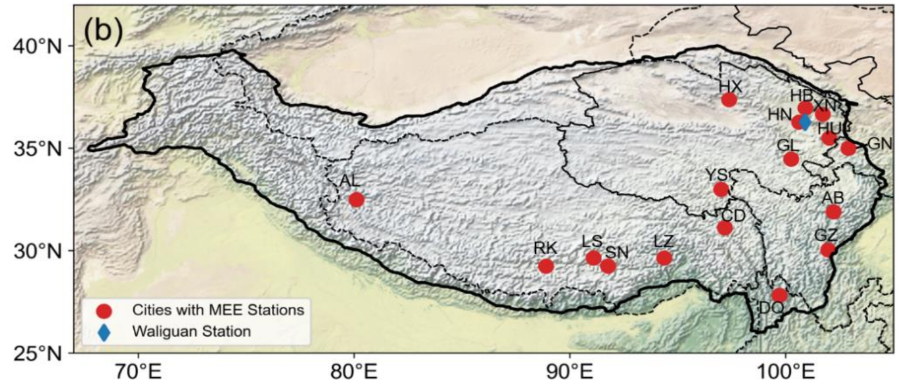
Drivers of Ozone Trend over China



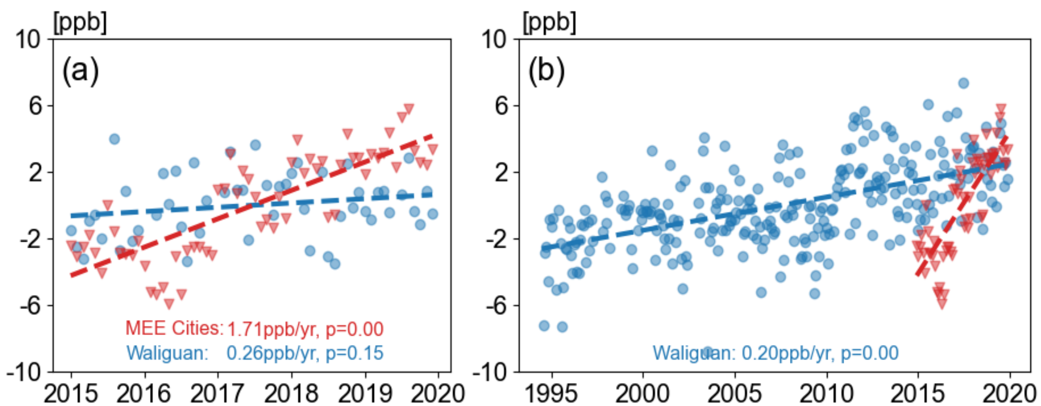


Tan et al., 2023, EST

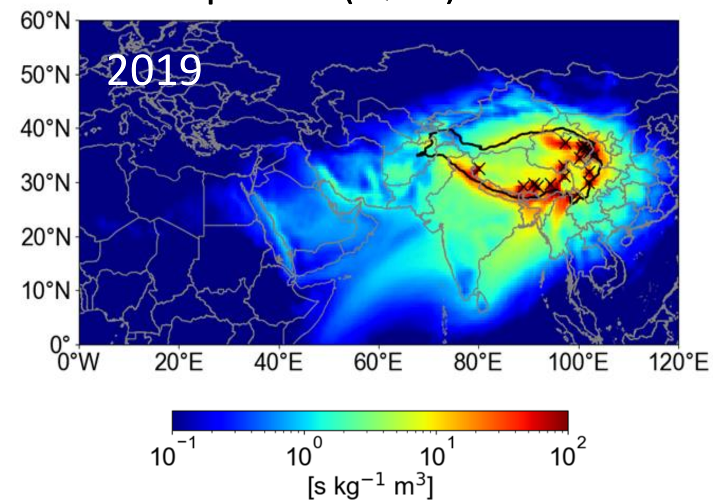
Rapid Ozone Growth over Tibet Plateau Caused by Local and Nonlocal Sources



Deseasonalized ozone growth

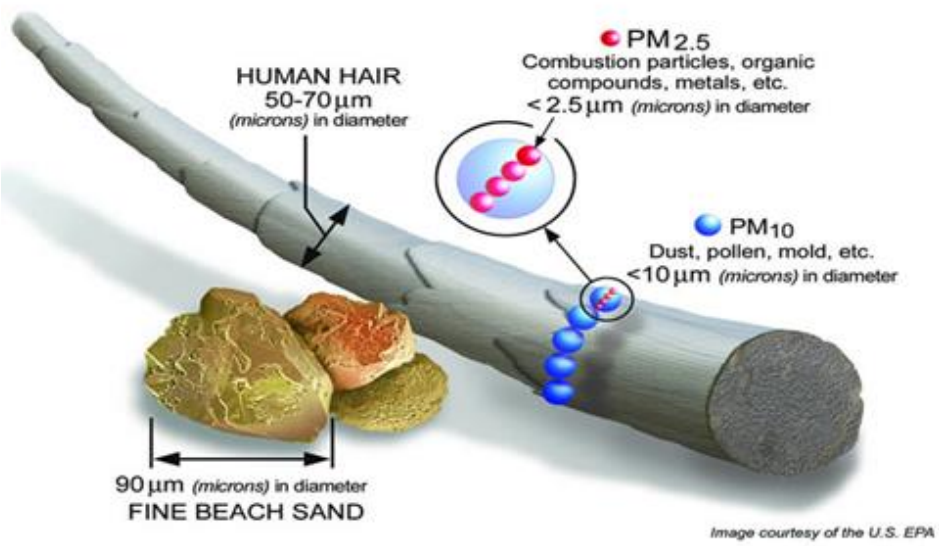


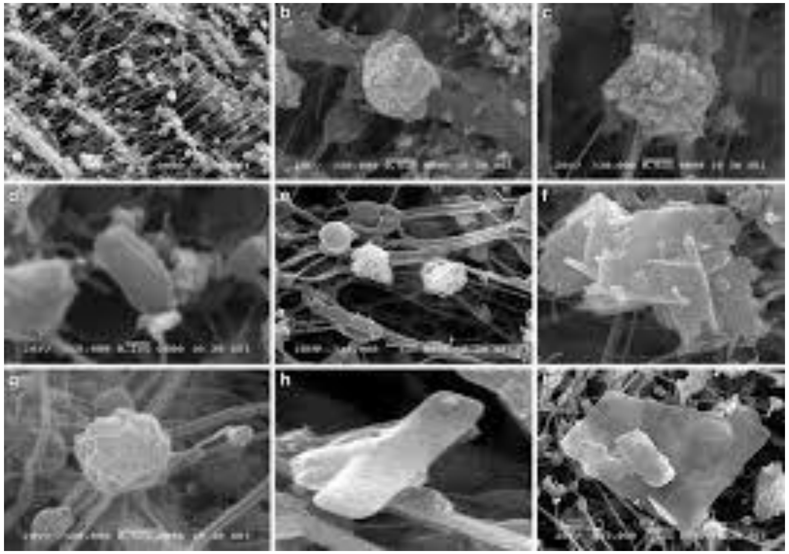
Quantity Emitted into Retroplume (QNR) for NOx

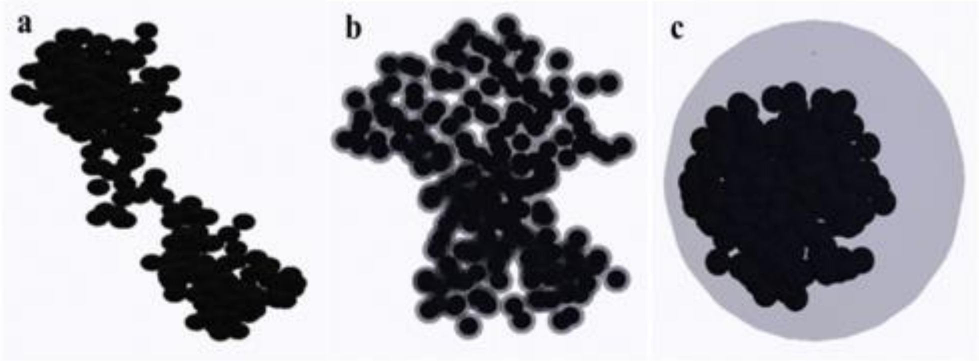


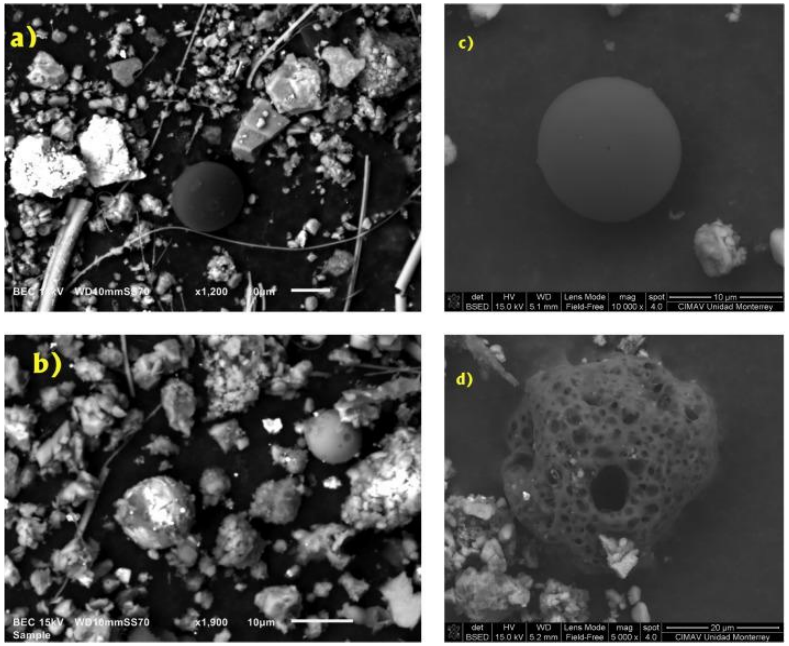
Xu et al., ACP, submitted

Particulate Matter Pollution: Morphology









The Great Smog of London, Dec 1952

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

Haze in Chinese City Clusters

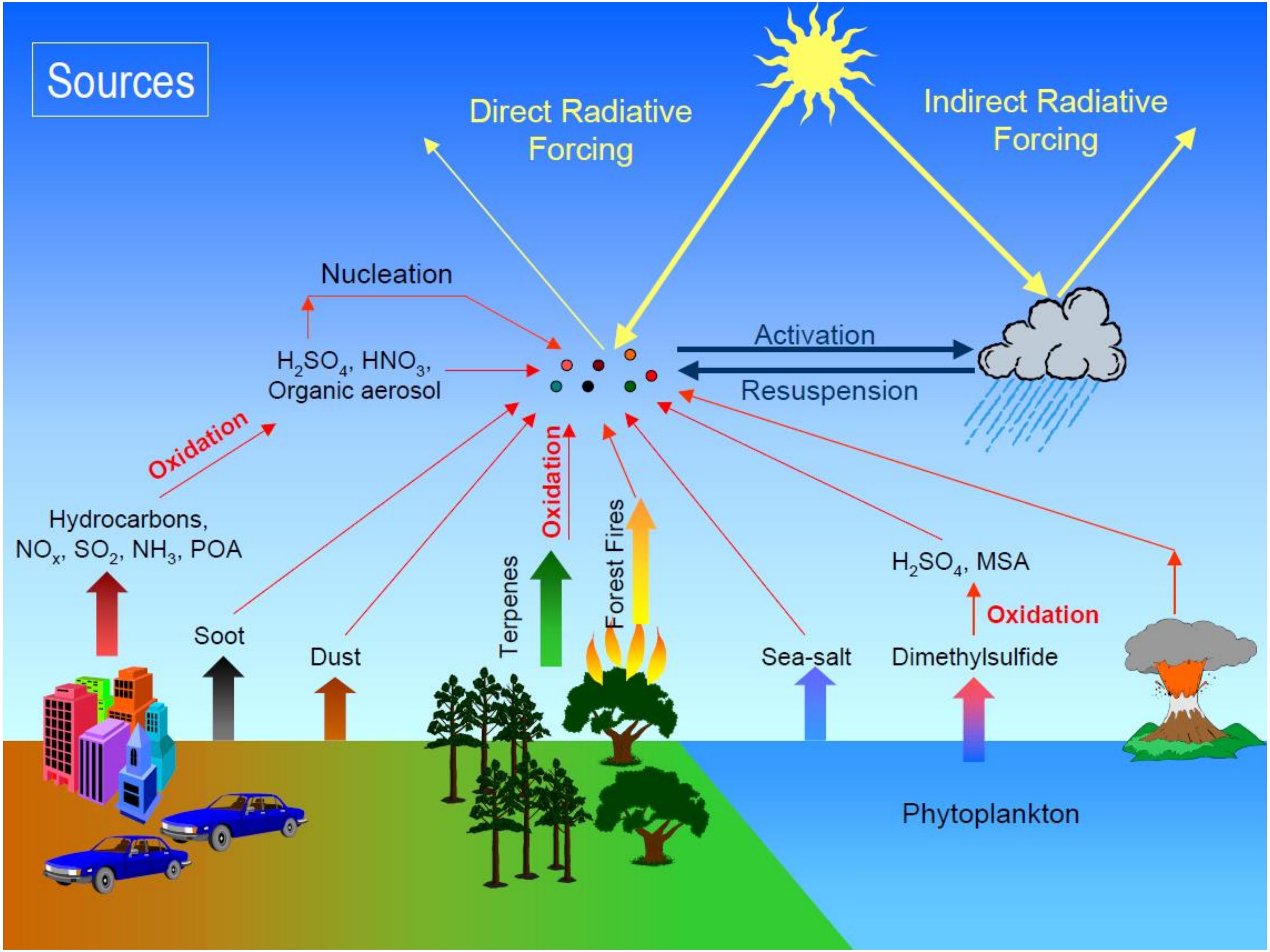
- Emissions of PM and precursors
- High humidity, sunlight
- Stagnant atmosphere
- Wind direction/speed

Tong Zhu

Haze in Beijing

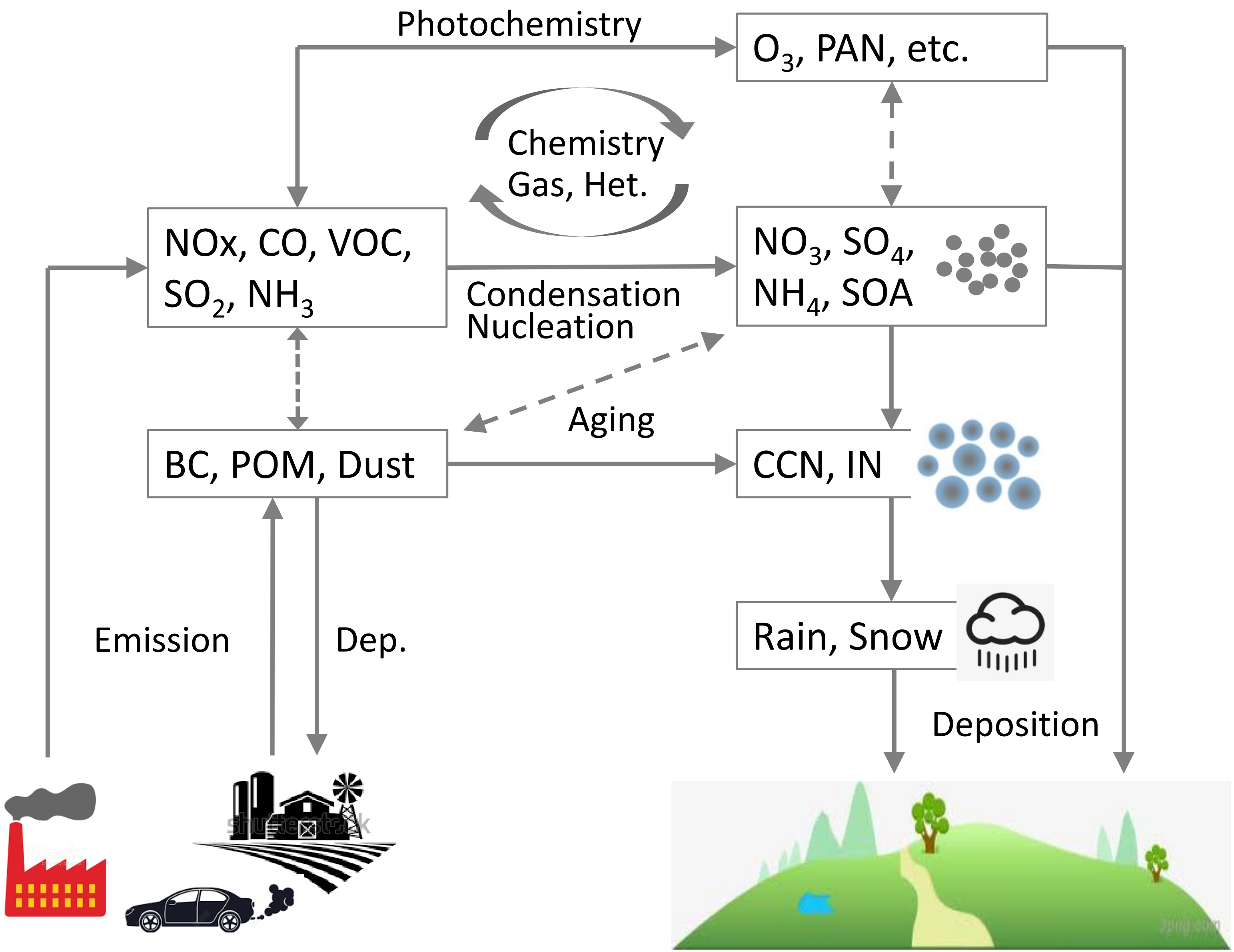
中青在线：2023年10月30日，北京遭遇雾霾天气 游客戴口罩游览天安门广场

PM Sources, Sinks, and Transformation



Tong Zhu

Emission-Chemistry-Transport-Deposition of PM



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

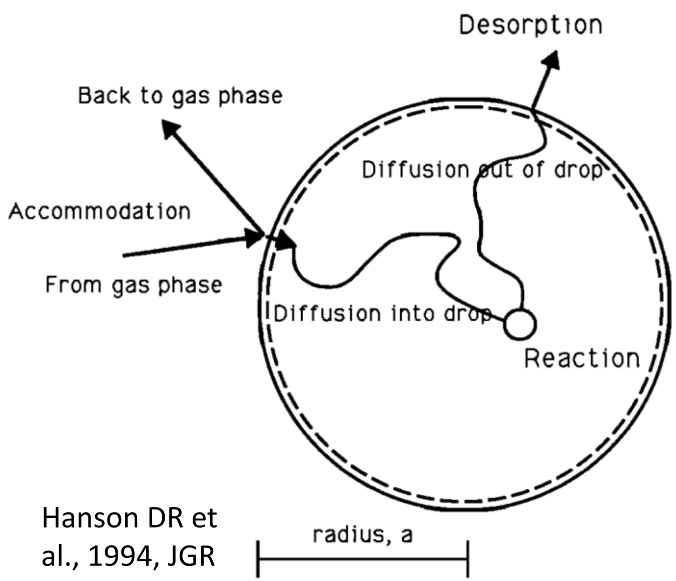
- **Secondary aerosols: mostly anthropogenic; mostly small**
  - **Sulfate** – anthropogenic; small
  - **Nitrate** – anthropogenic; typically small
  - **Ammonium** – anthropogenic; small
  - **SOA** – anthropogenic and natural; typically small; natural sources important mainly in summertime

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

Heterogeneous Process



Hanson DR et al., 1994, JGR

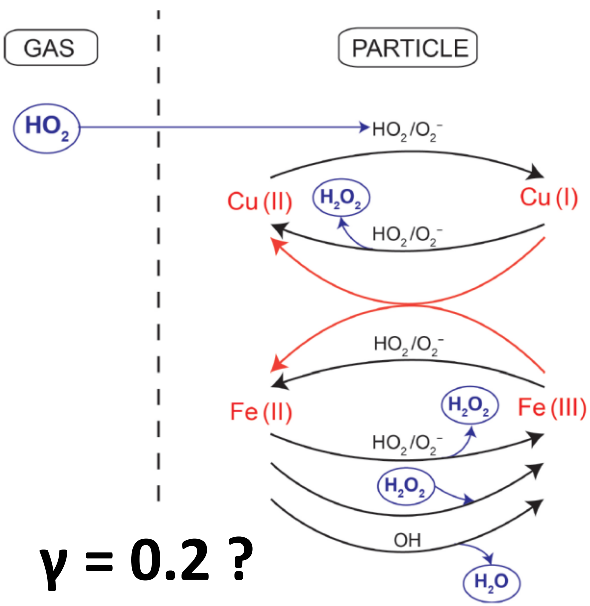
Gas ⟷ **Particle Surface** ⟷ **Particle Bulk**

(Effective) uptake coefficient, γ

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

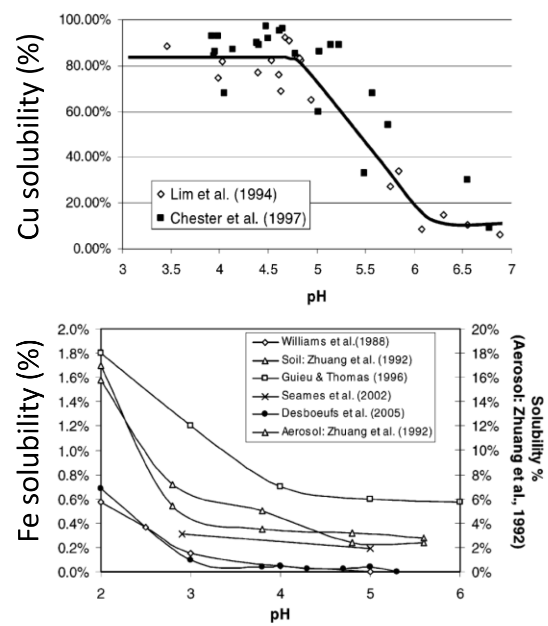
Heterogeneous Process: Roles of pH and TMI

HO_2 Uptake



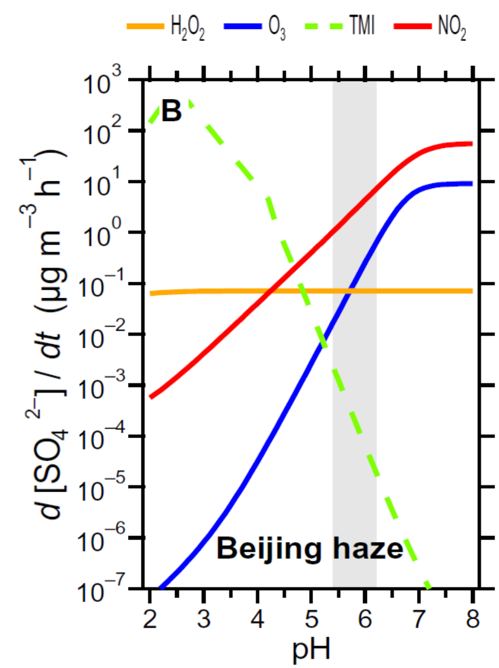
Mao JQ et al., 2013, ACP
Lin JT et al., 2012, ACP
Taketani F. et al., 2012, ACP

pH Dependence of TMI



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

Sulfate Formation



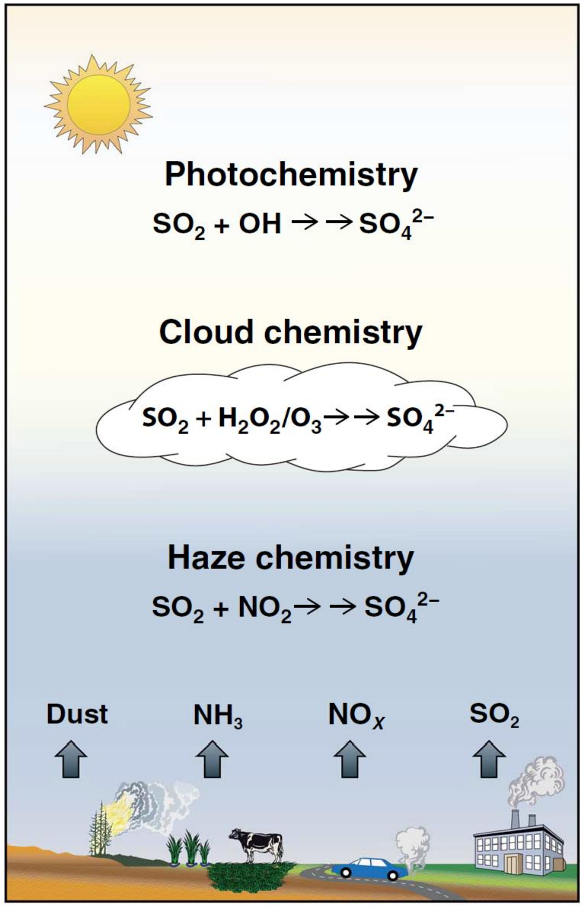
Cheng YF et al., 2016, SA
Wang GH et al., 2016, PNAS

- **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:

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



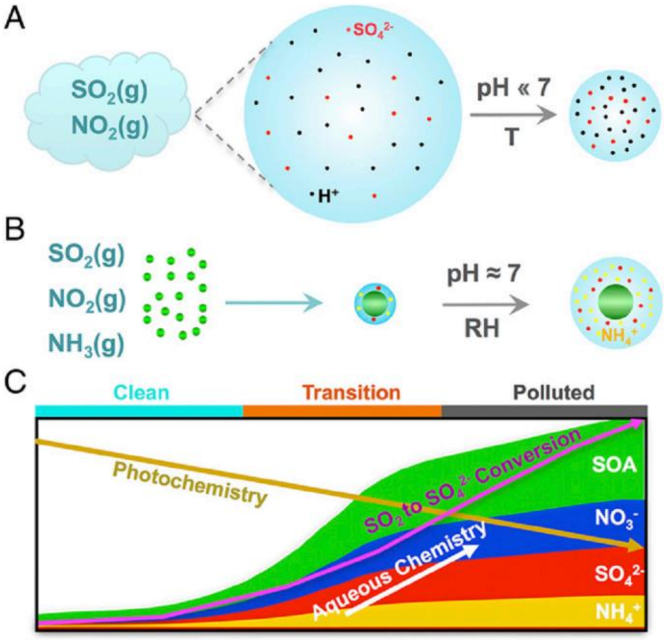
Cheng et al., 2017, Science Advance

Aerosol (small, easily acidified):

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

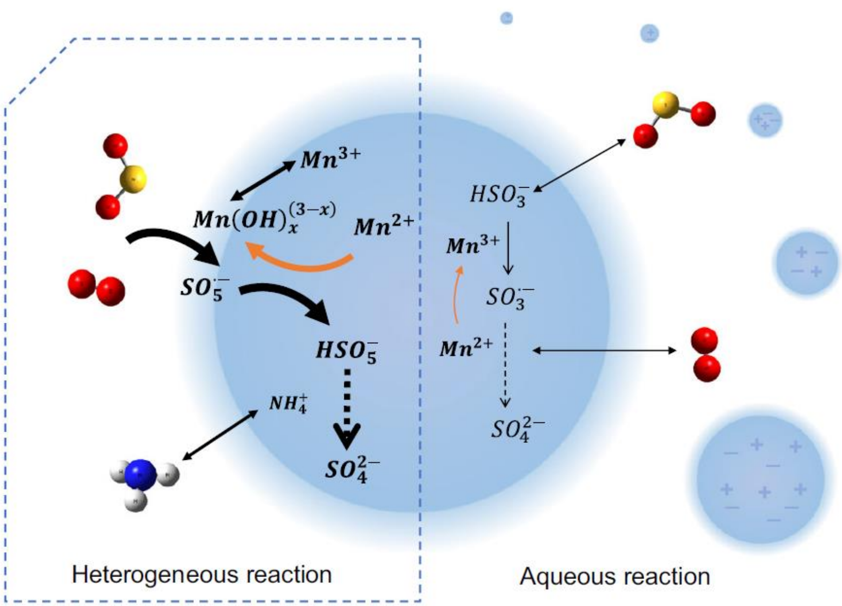
Cloud/fog (large):

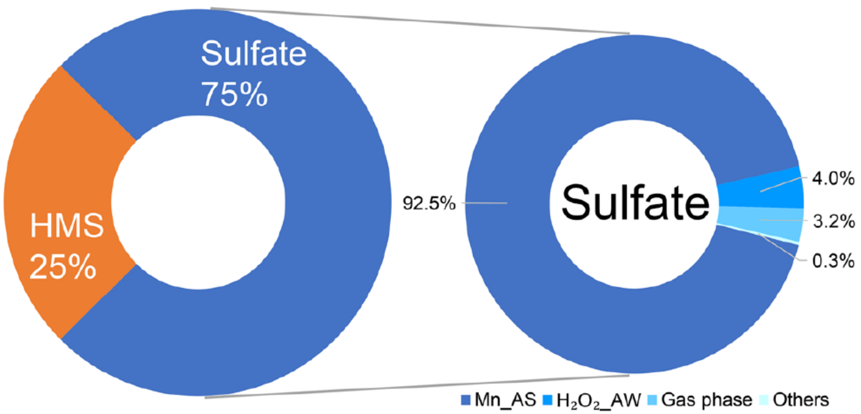
$$SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) + 2HONO(g).$$



Wang et al., 2016, PNAS

Mn-catalyzed Formation of Sulfate on Aerosol Surface





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

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

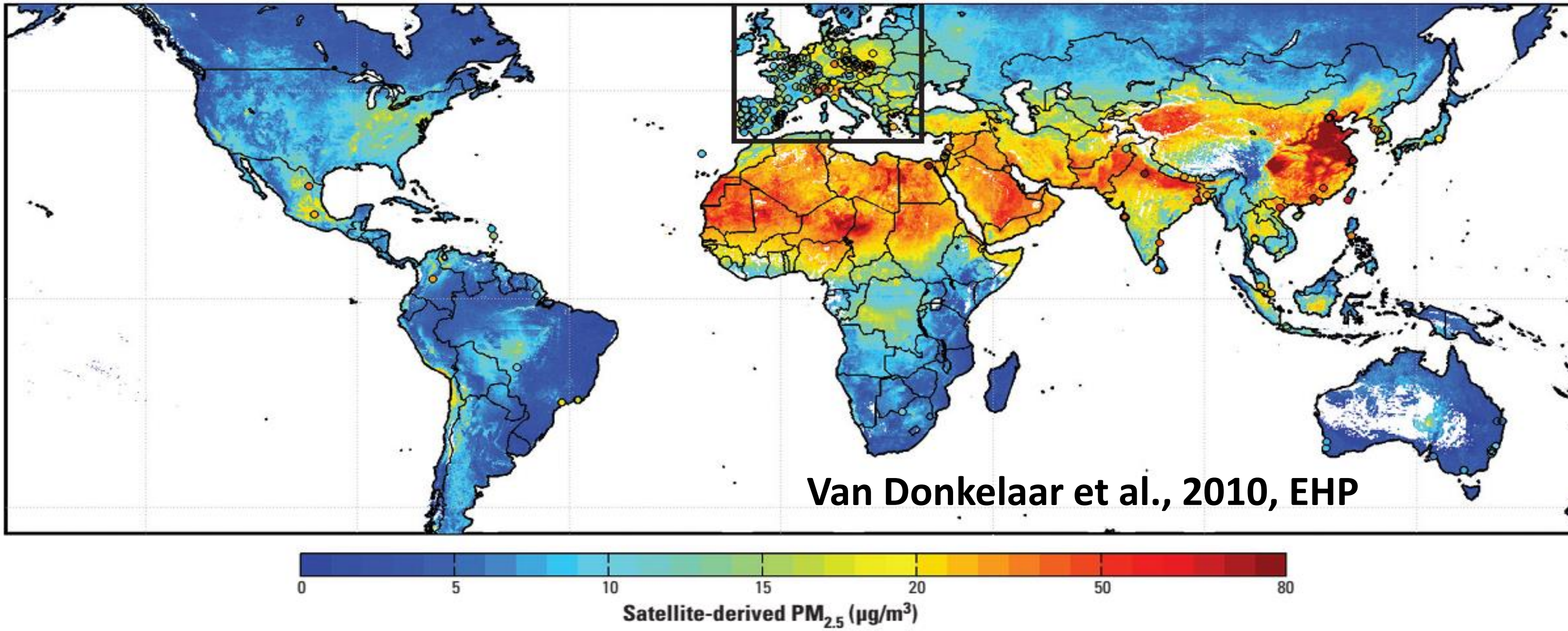
$$NH_3 + HSO_5^- + SO_2 + H_2O \rightarrow NH_4^+ + SO_4^{2-}.$$

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

Wang et al., 2021, Nature Communications

China Has World's Most Severe PM Pollution

Surface $PM_{2.5}$ concentration derived from satellite



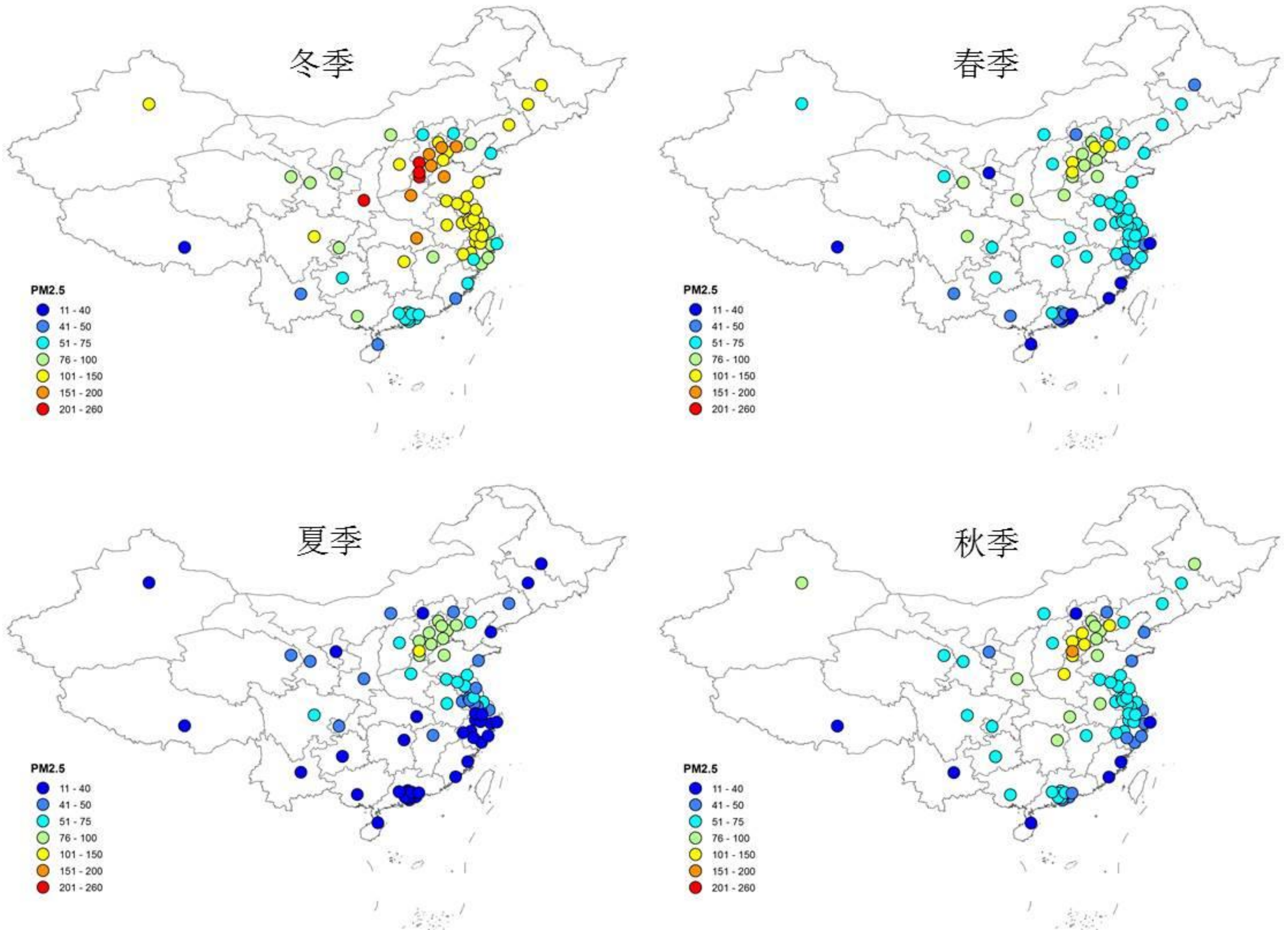
23,000,000 Chinese
live in areas with > 100 μg/m³

v.s.

Beijing in 2013：
90 μg/m³

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

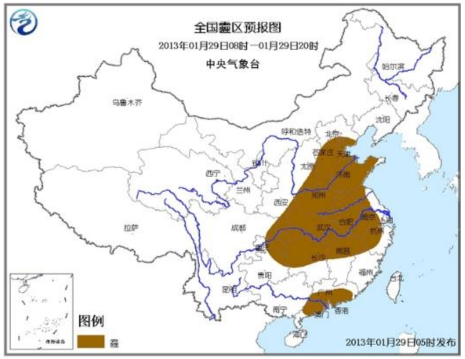
Seasonal Variation of $PM_{2.5}$ in China



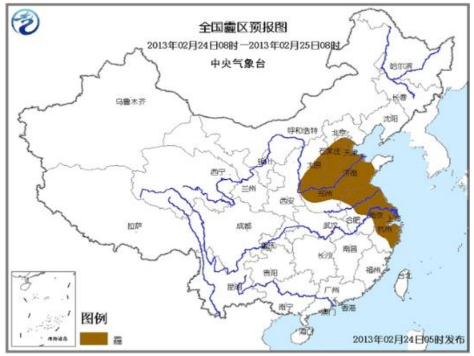
贺克斌，2014

Severe Haze in 2013

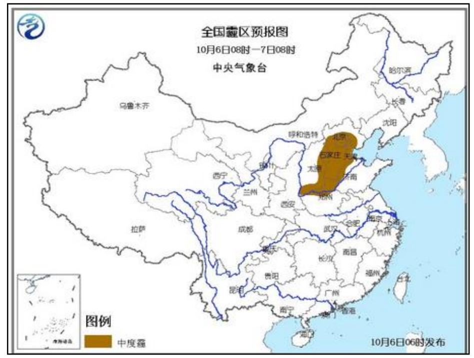
Jan 14-15, 2013



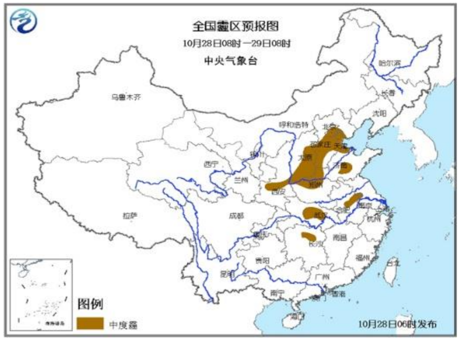
Jan 29, 2013



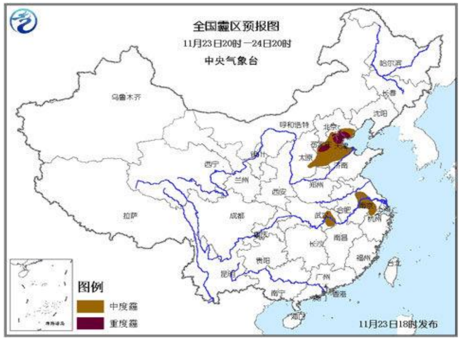
Feb 24-25, 2013



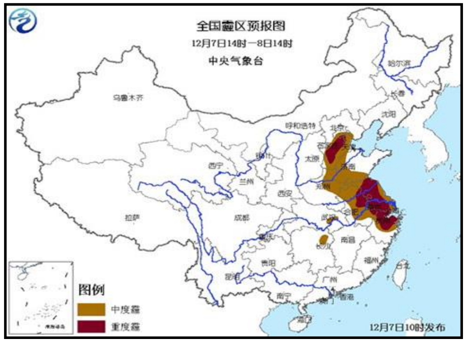
Oct 06-07, 2013



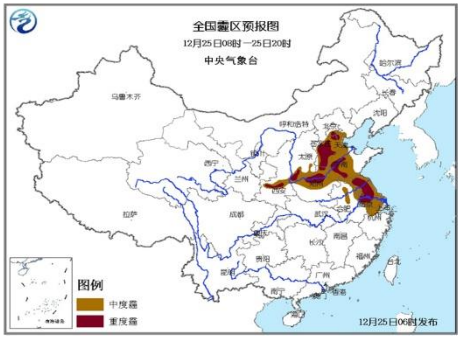
Oct 28-29, 2013



Nov 23-24, 2013



Dec 07-08, 2013

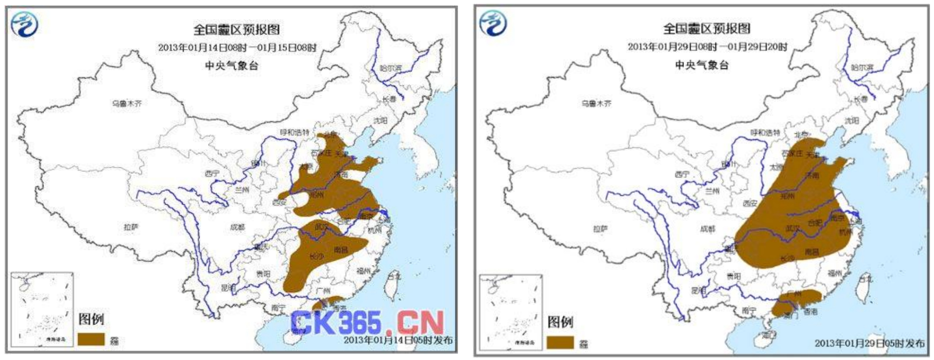


Dec 25, 2013

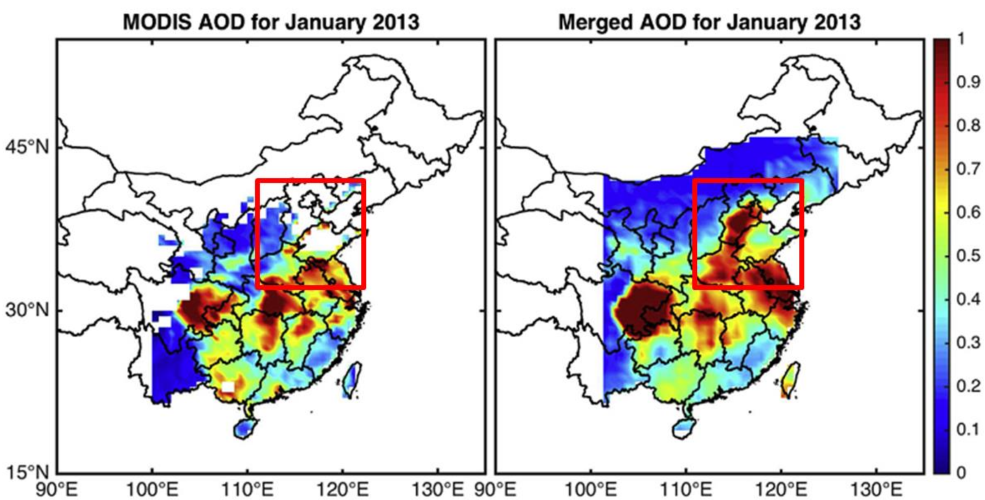
贺克斌，2014

Severe Haze in January 2013

Jan 14-15, 2013 Jan 29, 2013

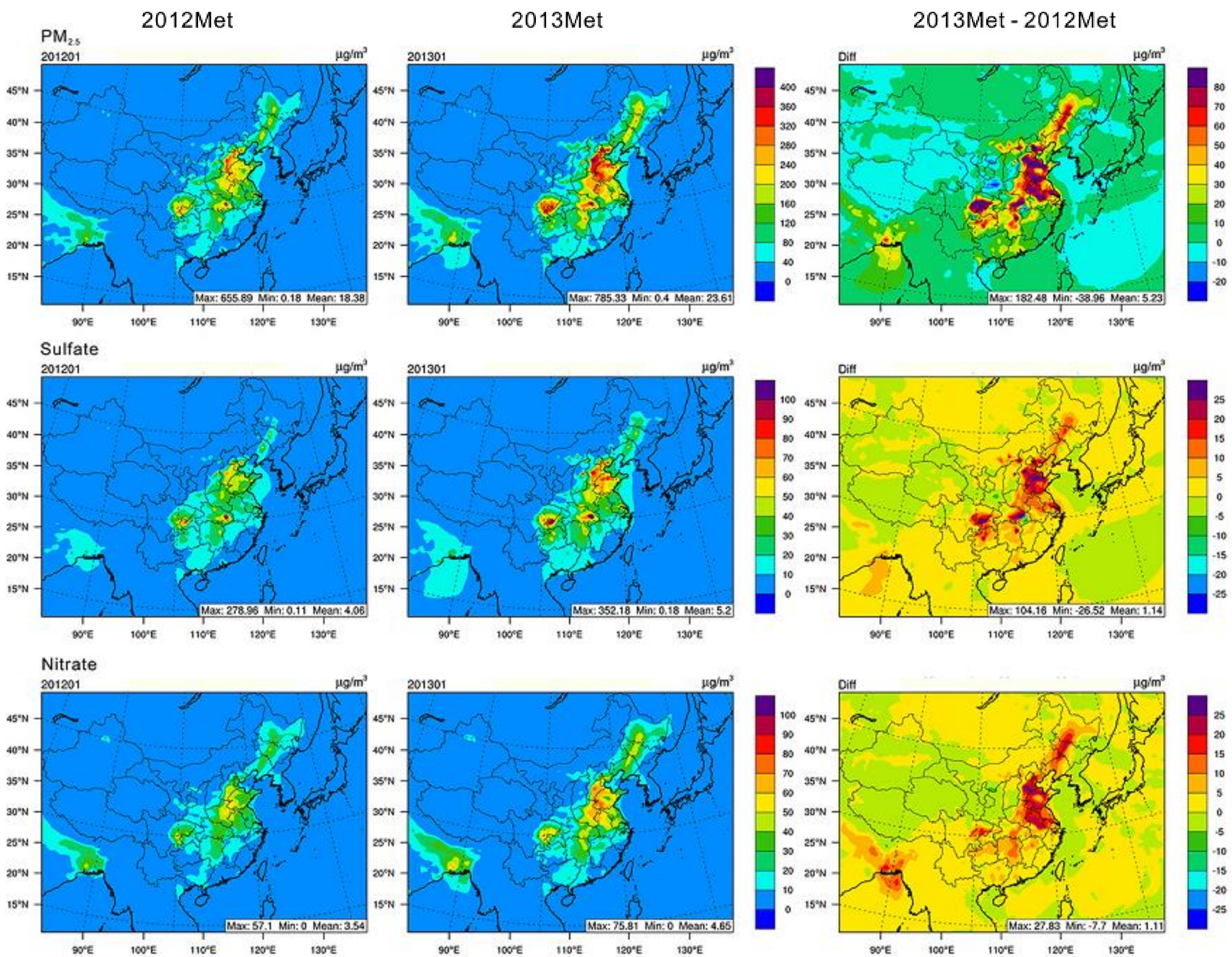


贺克斌，2014



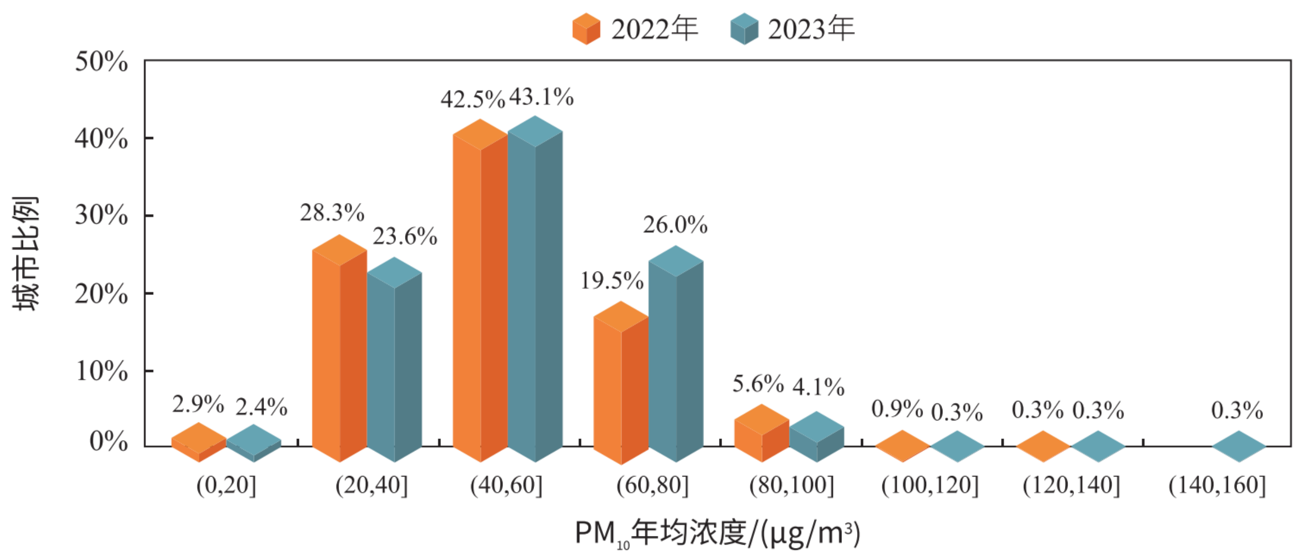
Lin and Li, AE, 2016

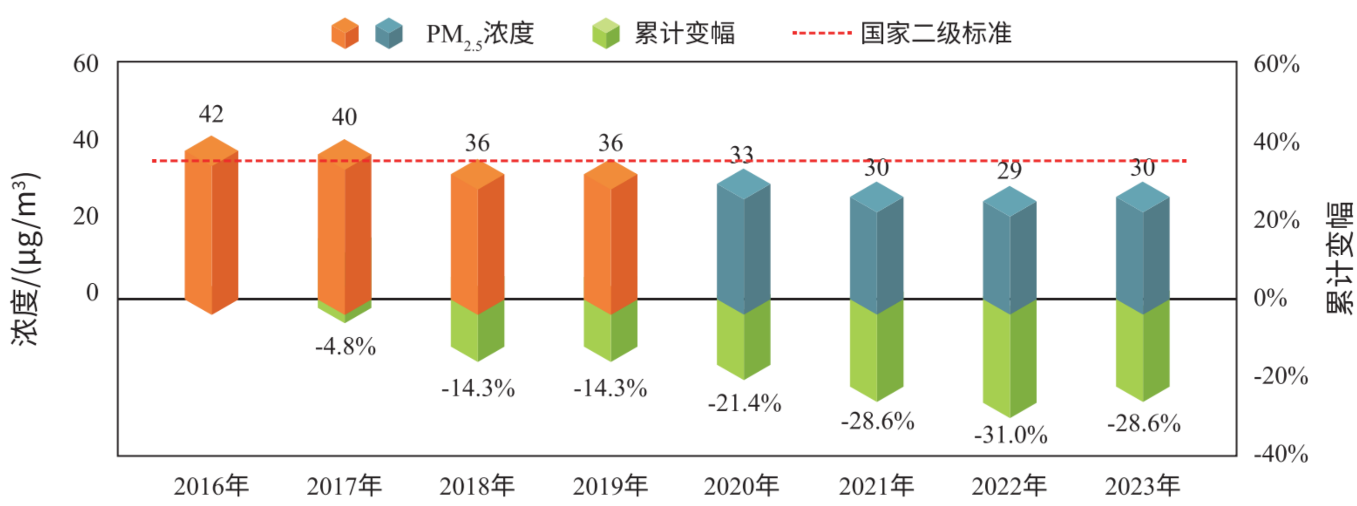
Contribution of Meteorology to Jan 2013 Haze



Zheng et al., 2015, ACP

$PM_{2.5}$ Pollution Changes in China

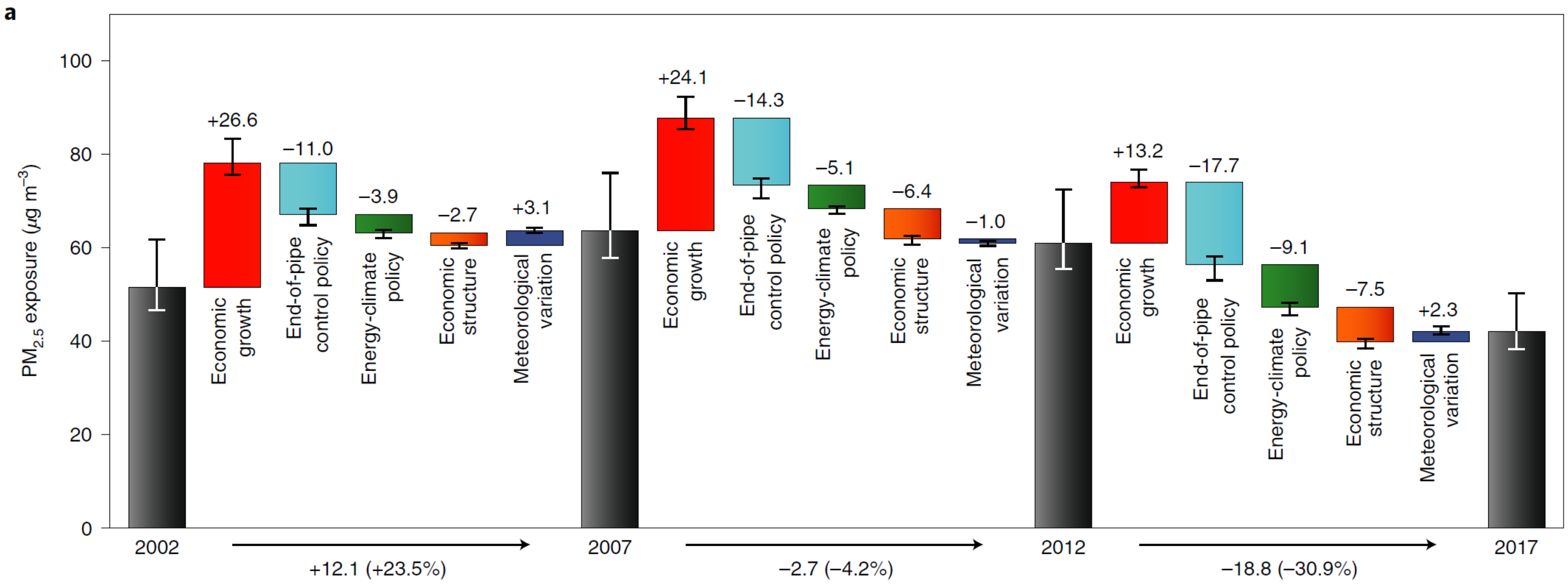




中国生态环境公报2023

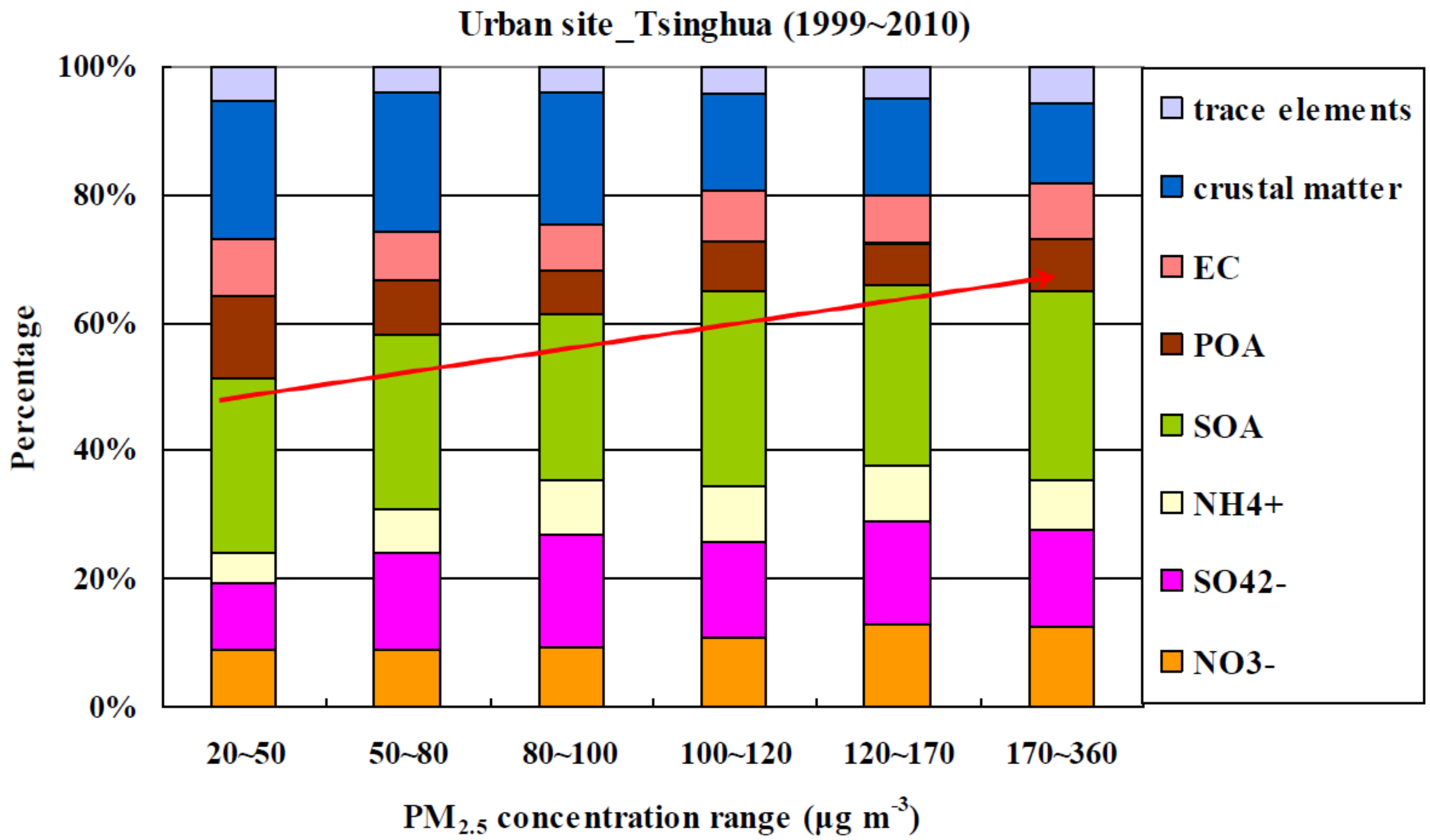
Drivers of $PM_{2.5}$ Pollution Trends over China

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



Geng et al., 2021, Nature Geoscience

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



Kebin He

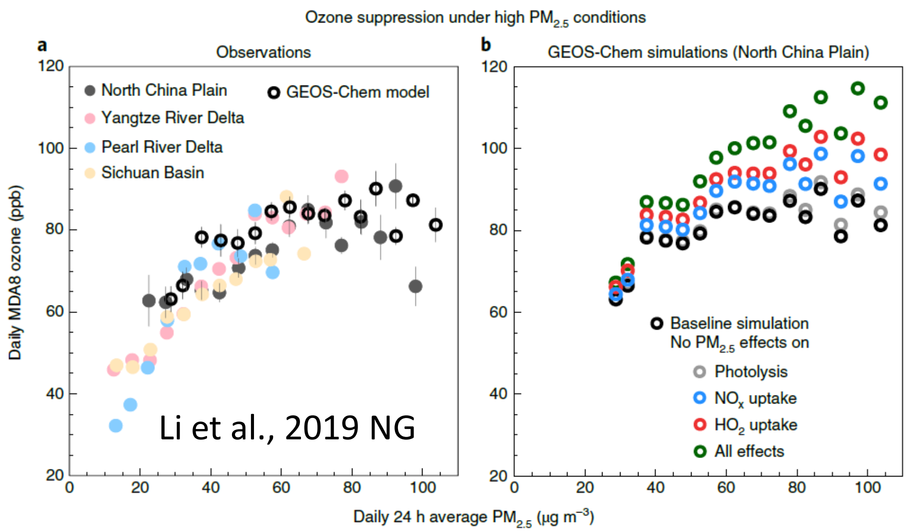
Interactions of Ozone and PM

Effects of ozone on PM:

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

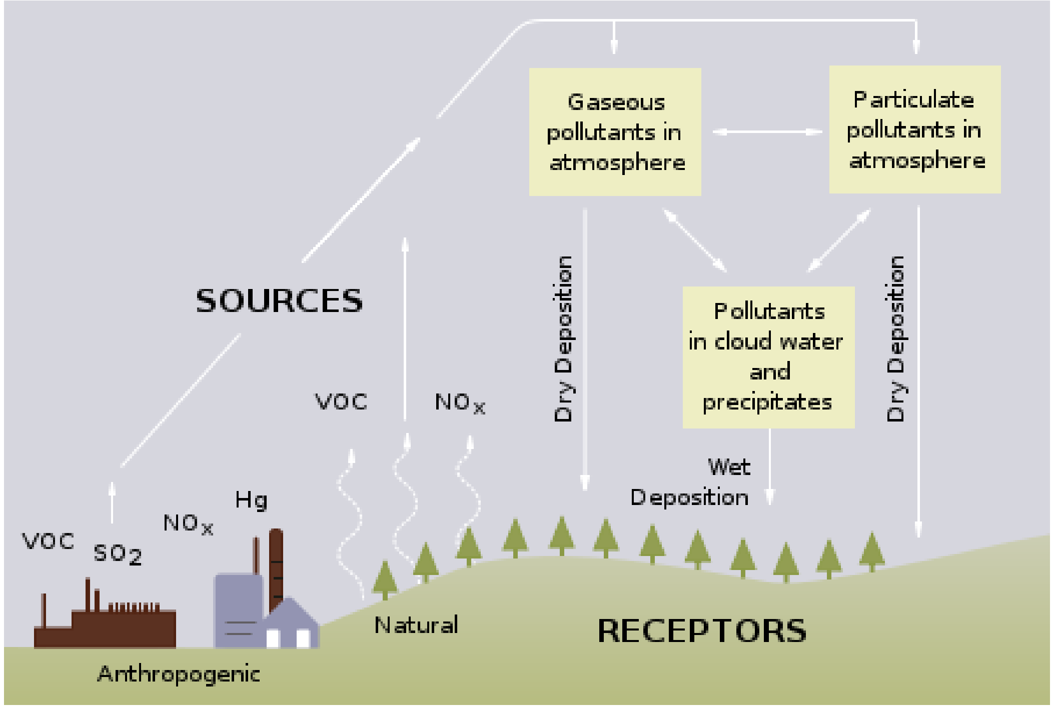
Effects of PM on ozone:

- ✓ Hetero. processes (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

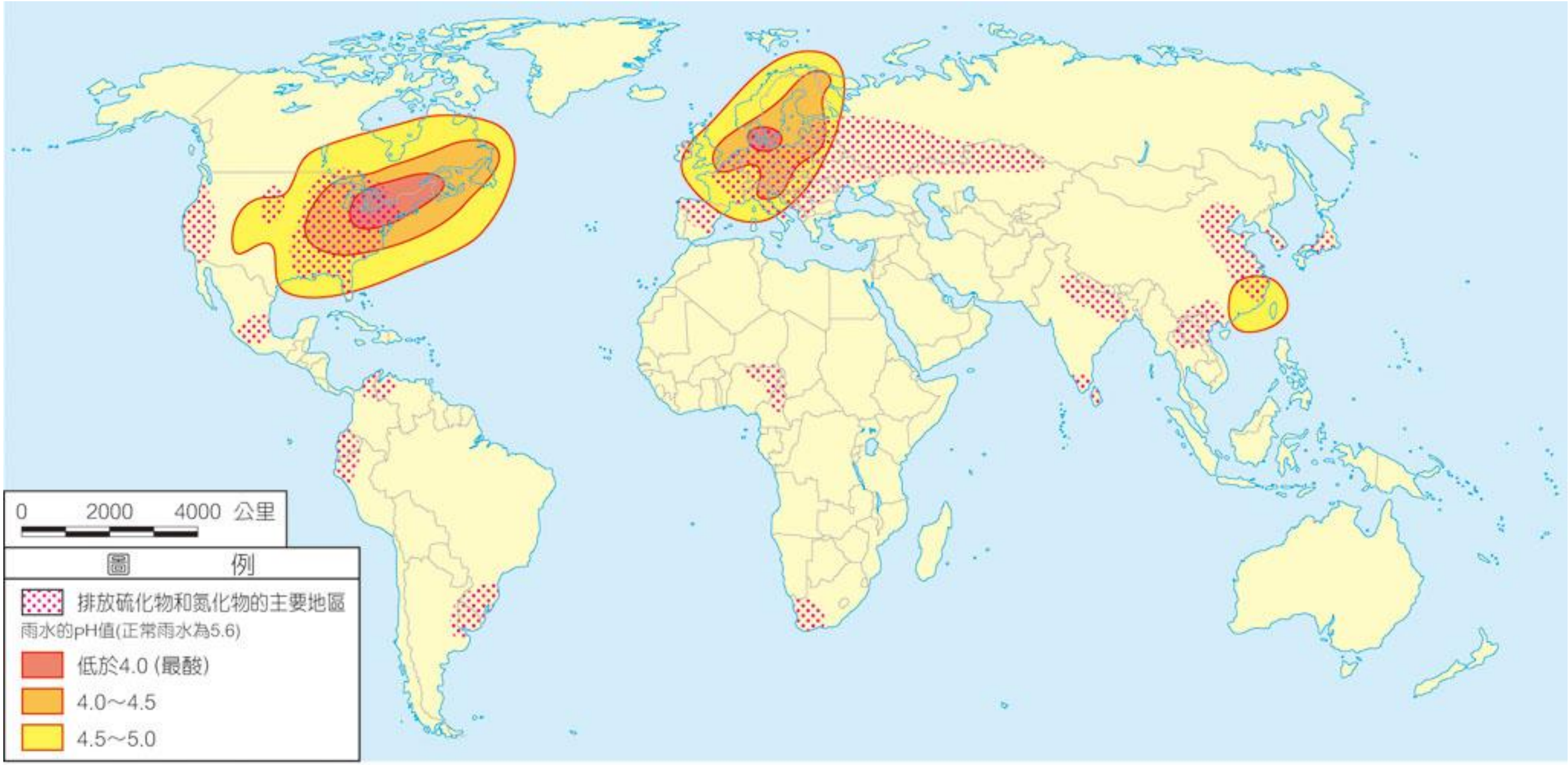
Acid Deposition



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

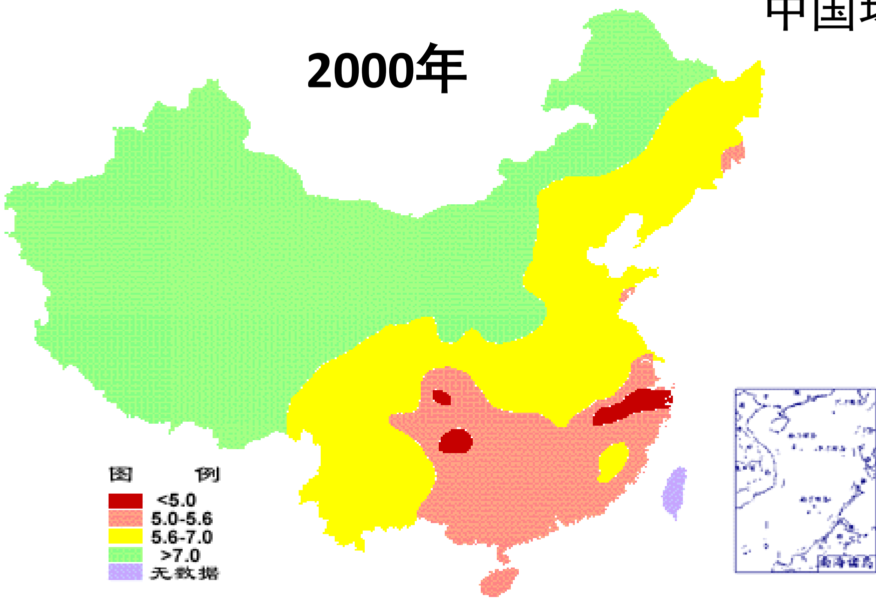
Acid Deposition



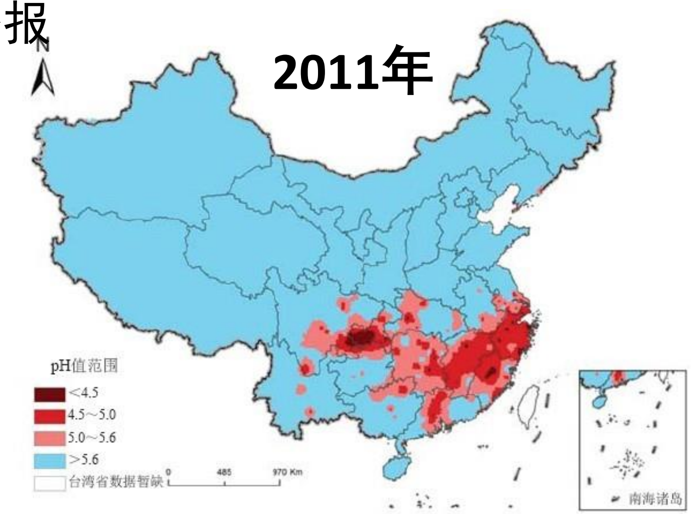
中国降水pH值分布

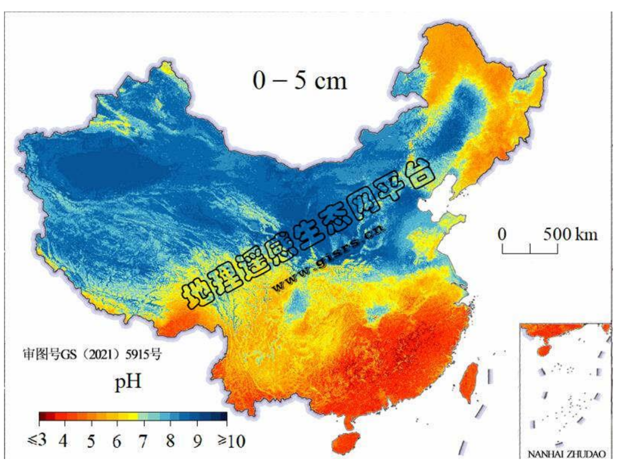
中国环境状况公报

2000年

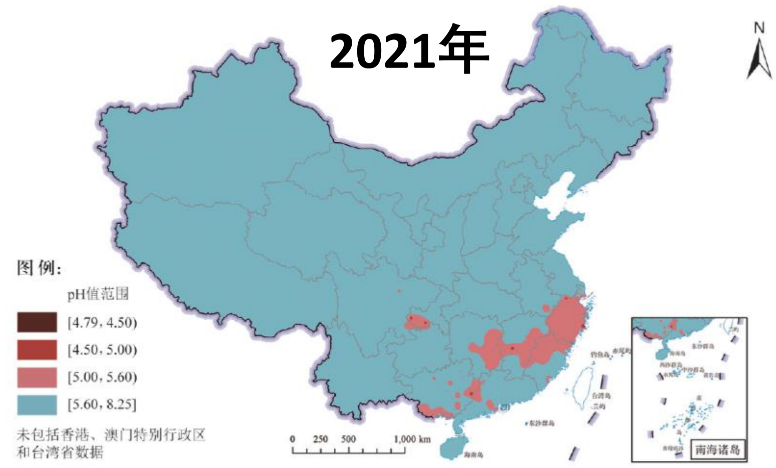


2011年





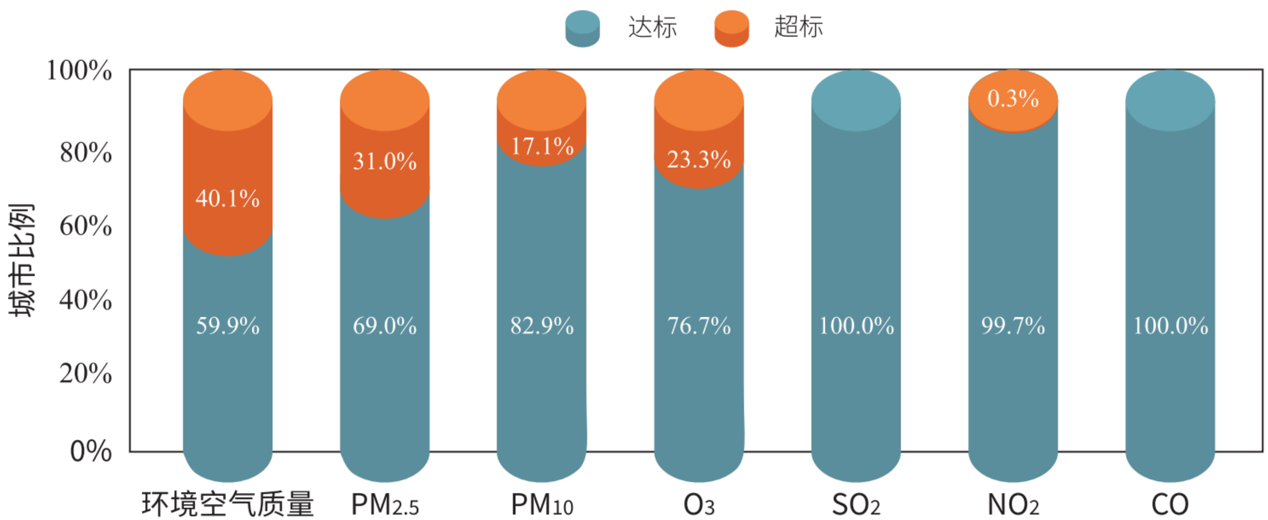
2021年

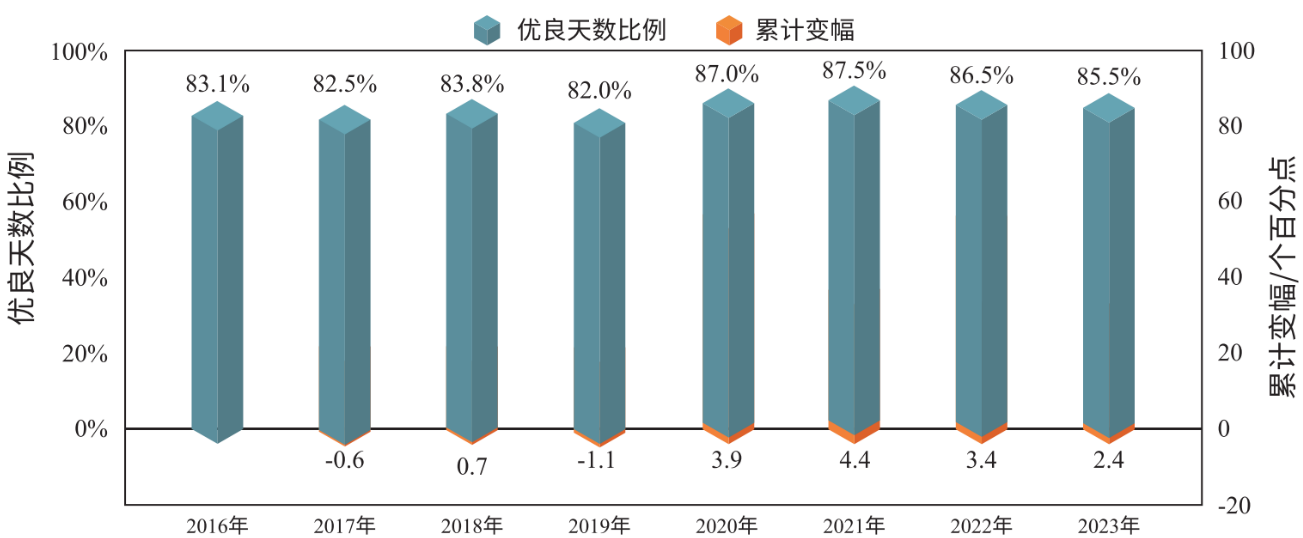


Quiz

1. **Impacts of NOx, CO and VOC on ozone production in urban, rural and background situations**
2. **Potential human influences on recent tropospheric OH and ozone 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? What would be trade-off or synergistic effects for ozone and PM under emission control?**

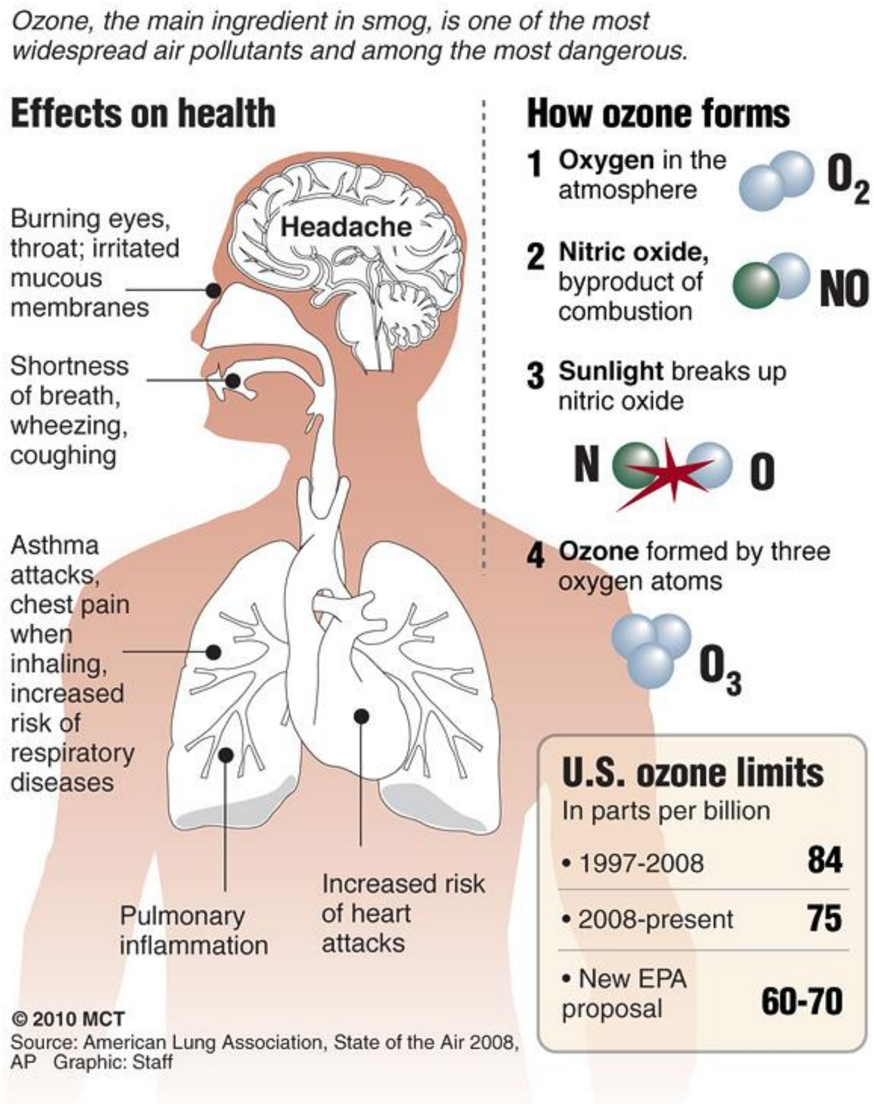
Air Quality Status in China



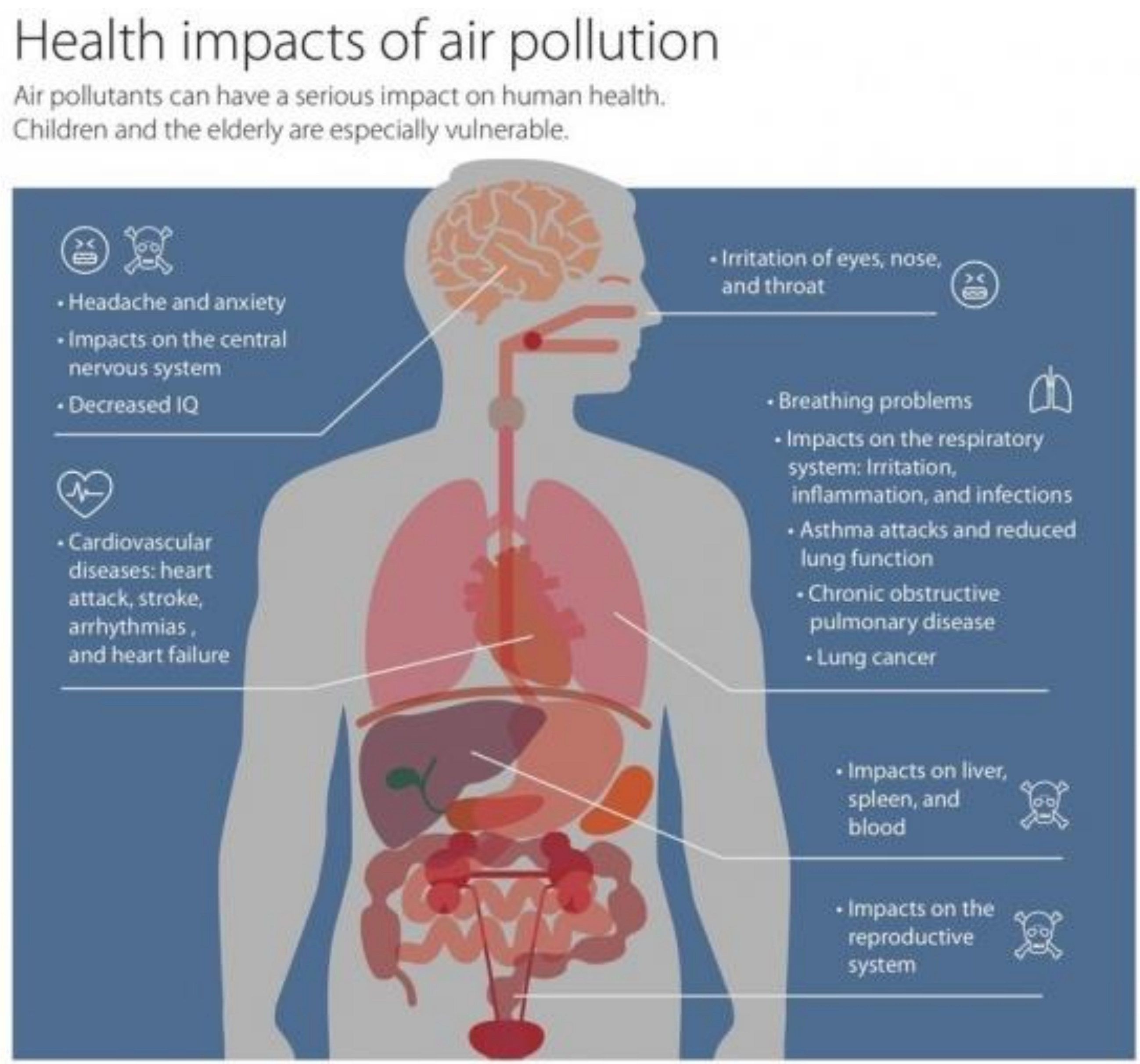


中国生态环境公报2023

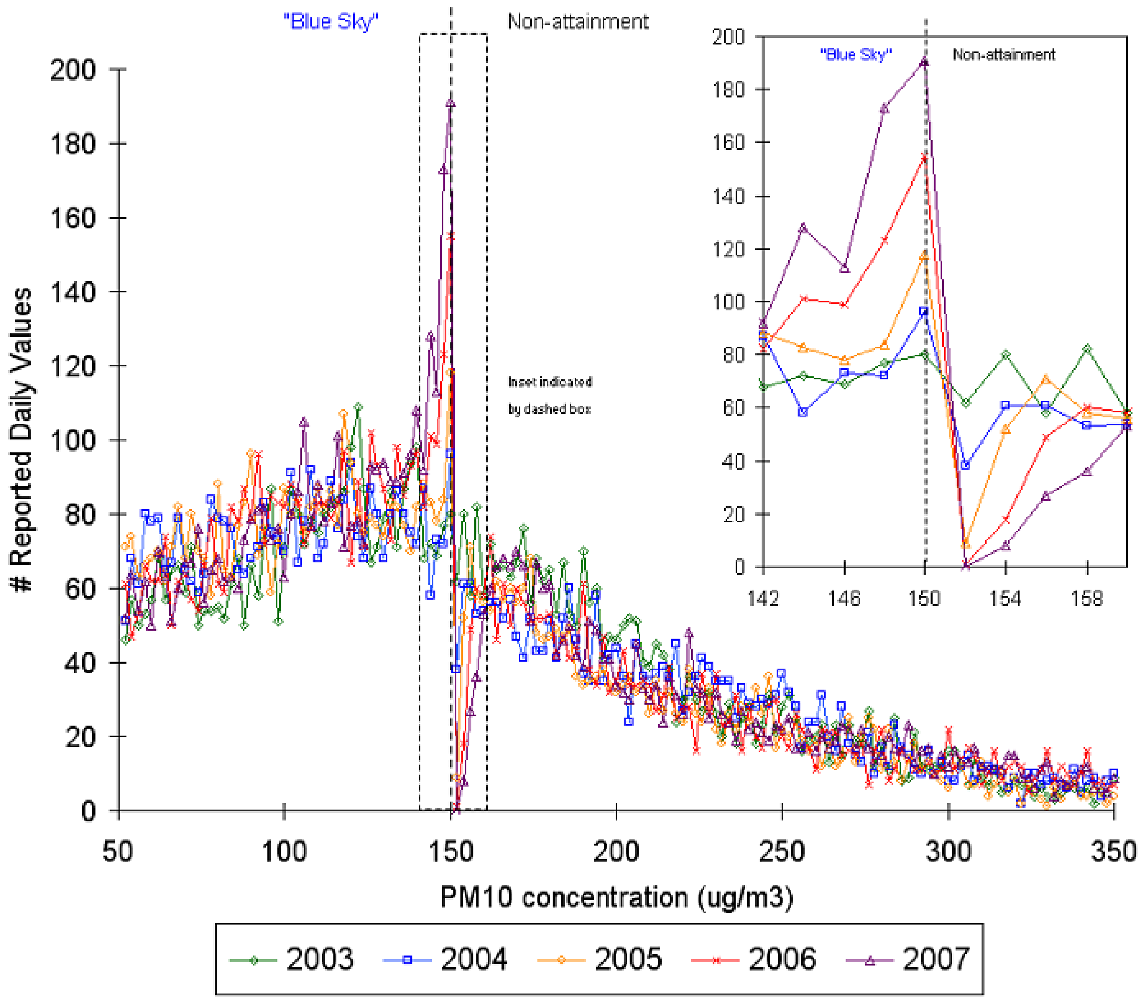
Health Impacts of Photochemical Smog



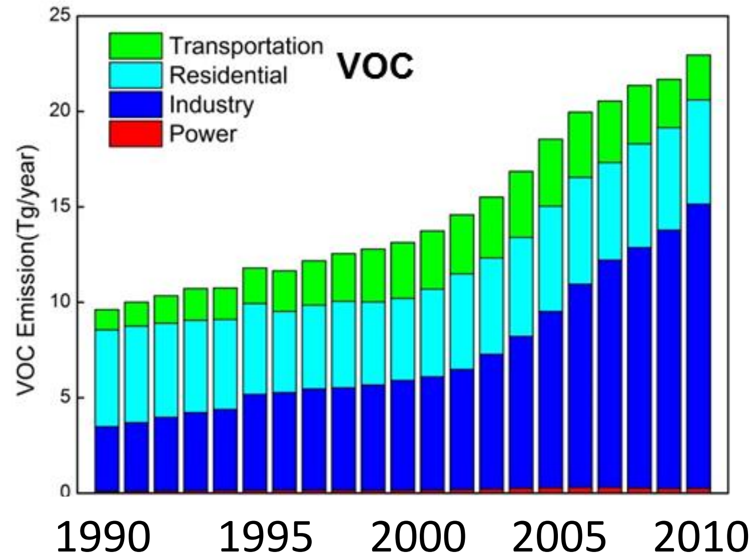
Health Impact of Air Pollution

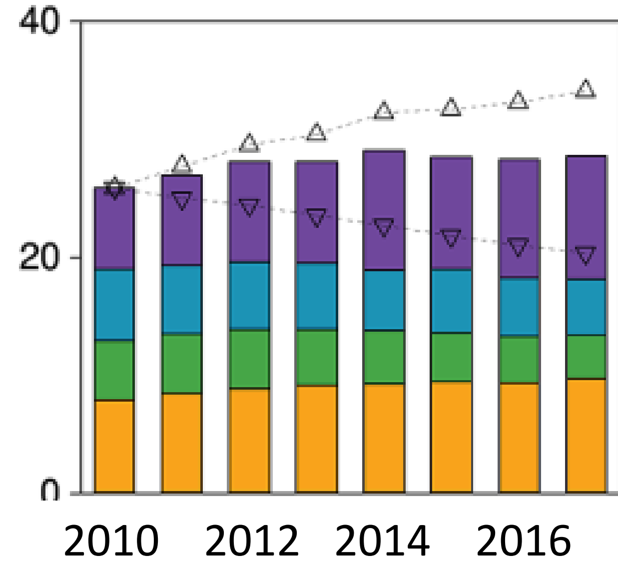


Ambient Air Quality Standards

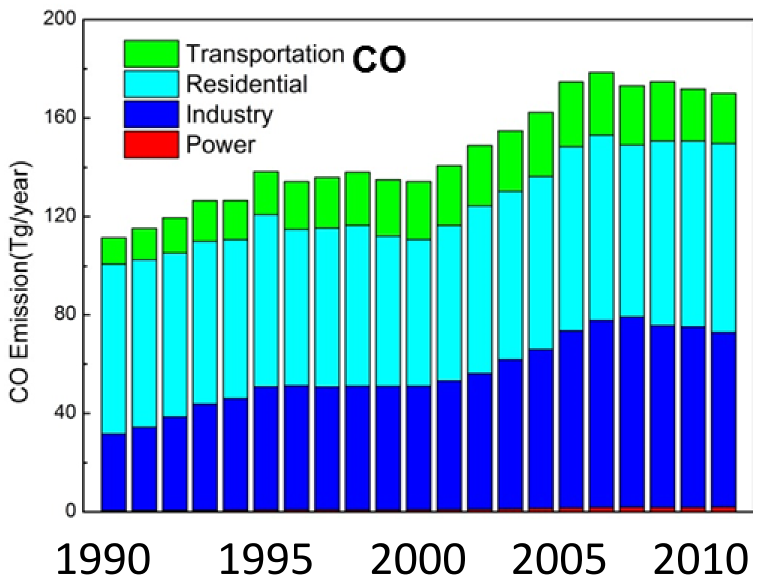


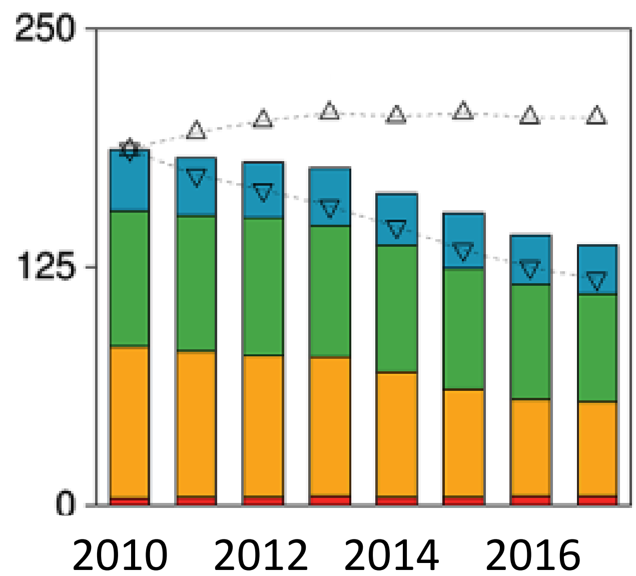
Anthropogenic Emissions in China: 1990-2010



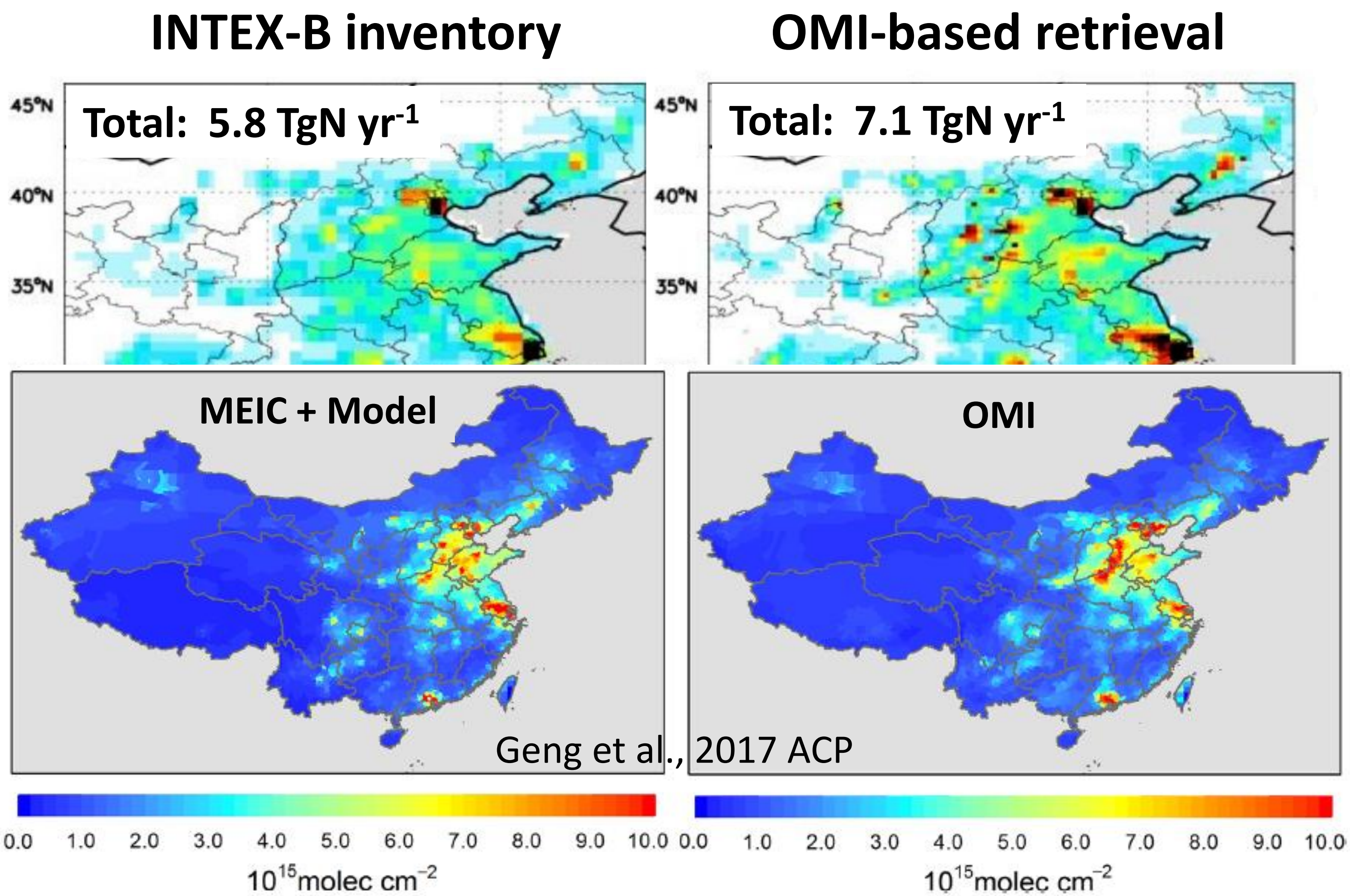


Source: MEIC



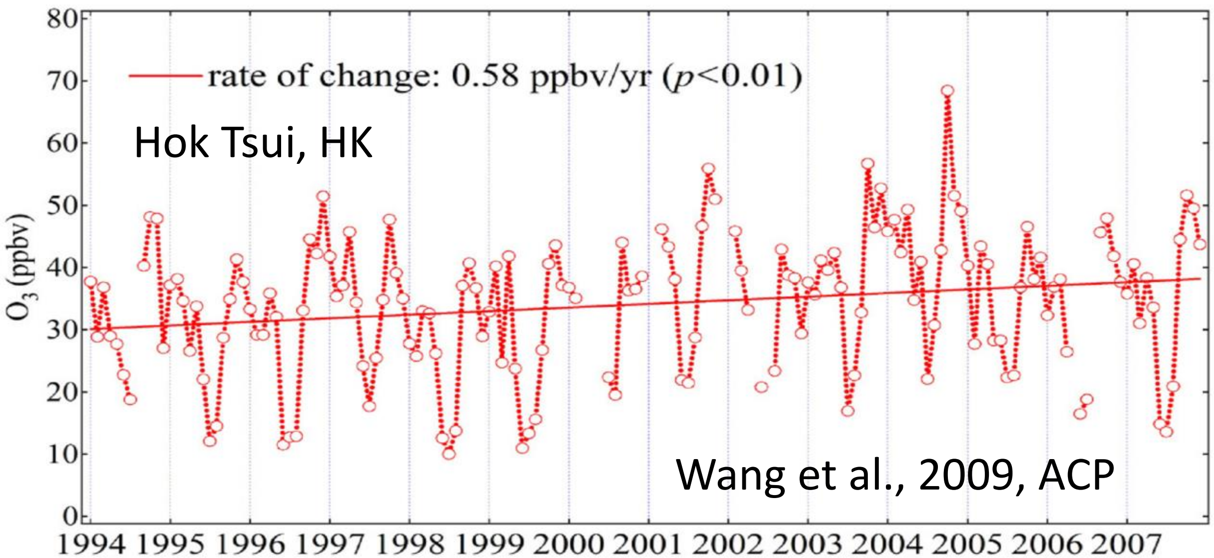


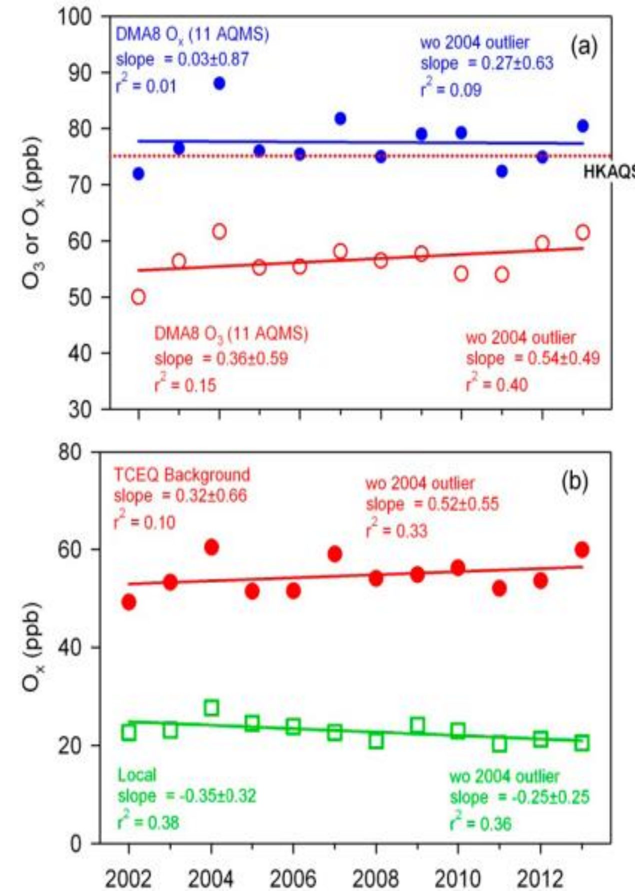
Satellite+Model Derived High-res (25 km) Emissions Reveal Urban Biases in Bottom-up Inventories



Geng et al., 2017 ACP

Background O_3 Concentrations are Increasing



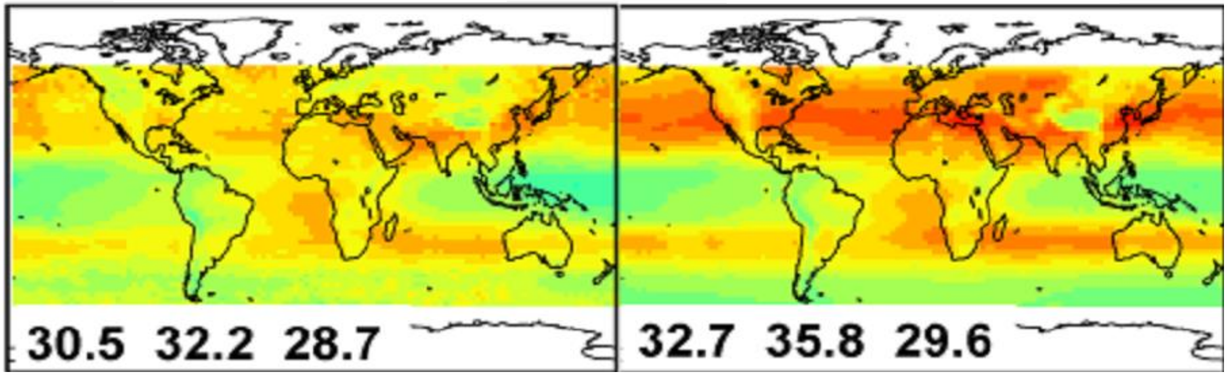


Xue et al., 2014, EST

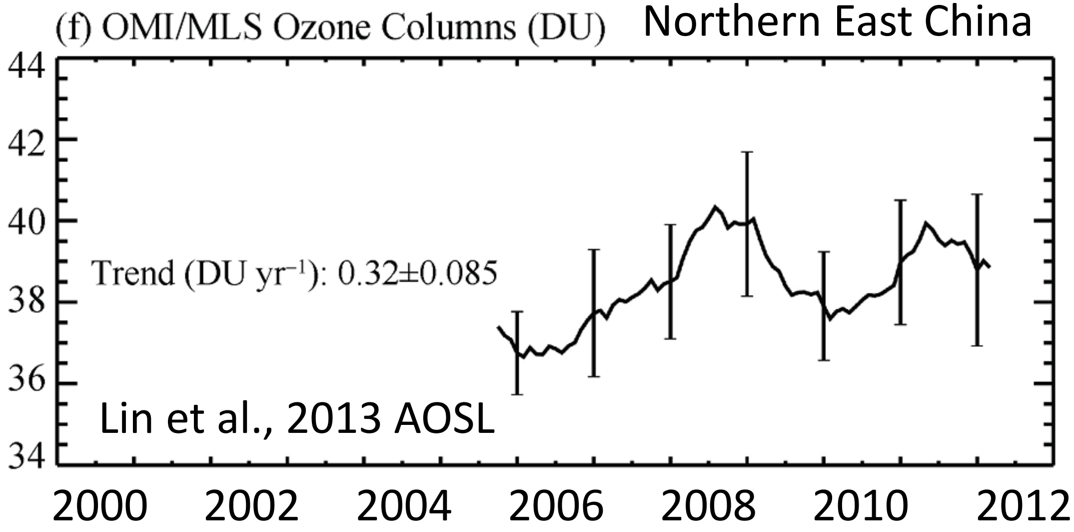
OMI-retrieved VCDs of Tropospheric Ozone

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

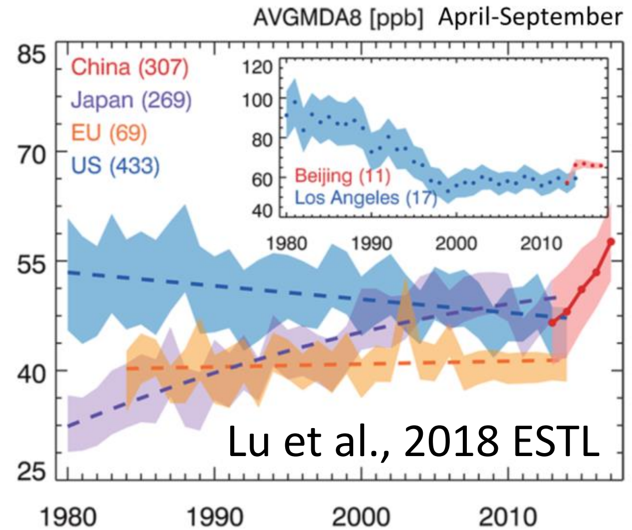
TCO, OMI/MLS TCO, OMI/Liu



Northern East China



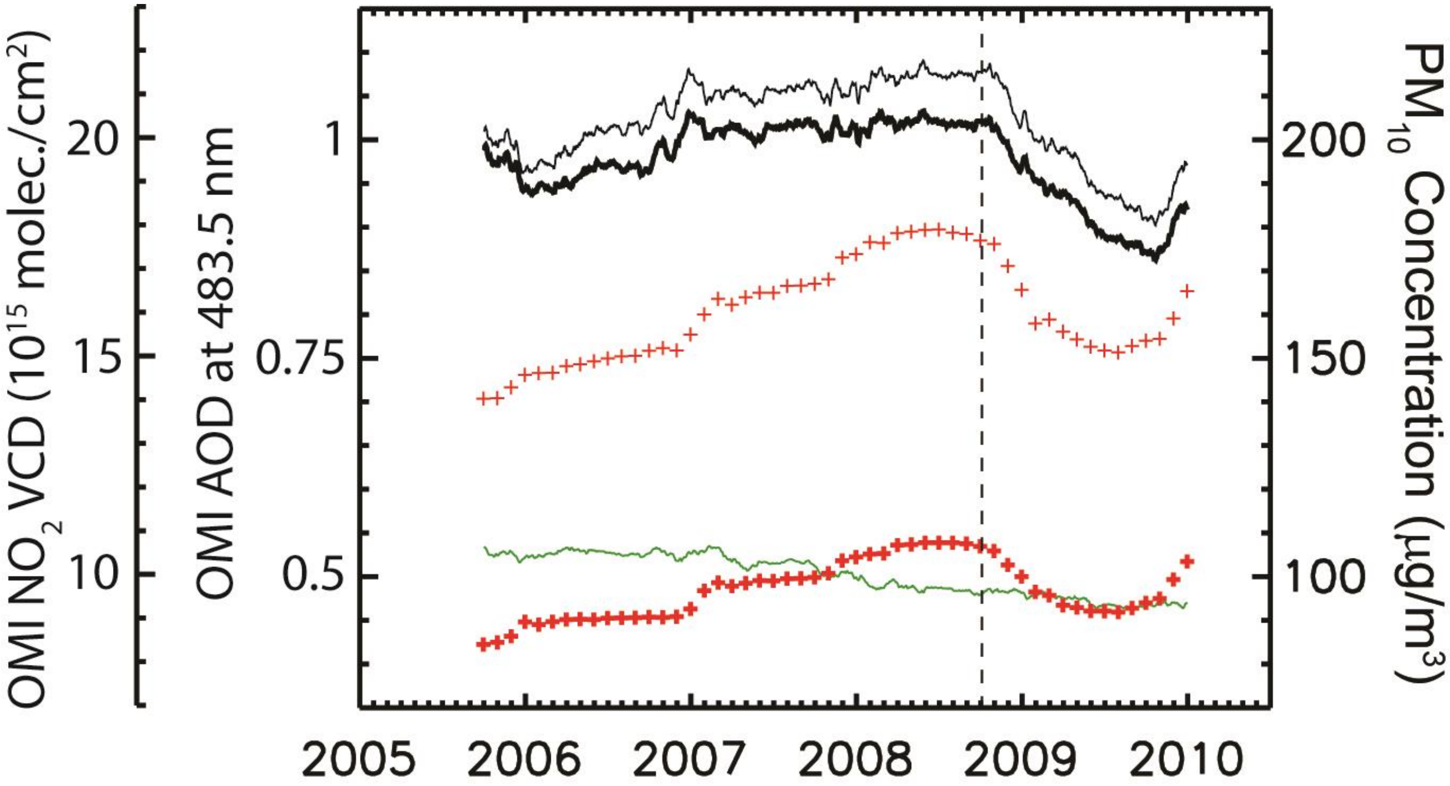
Lin et al., 2013 AOSL



Lu et al., 2018 ESTL

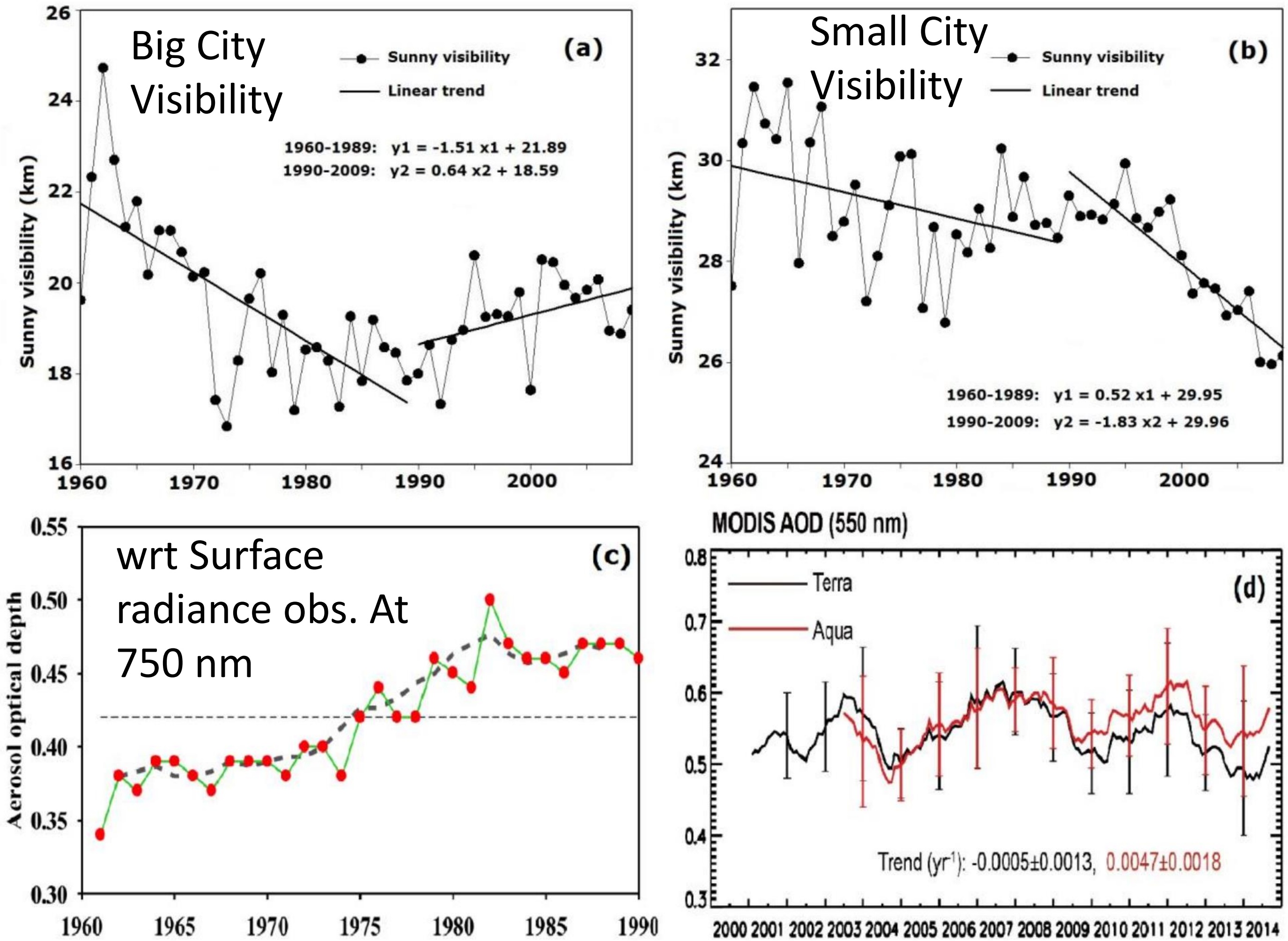
Trends of PM_{10} and AOD: 2005 – 2010

Northern East China



Lin et al., 2010

Trends of Visibility and AOD over China: 1960–2014



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

Air Pollution in China

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