Chapter 2

Sources, Sinks and Global Cycling of Air Pollutants

北京大学
PEKING UNIVERSITY

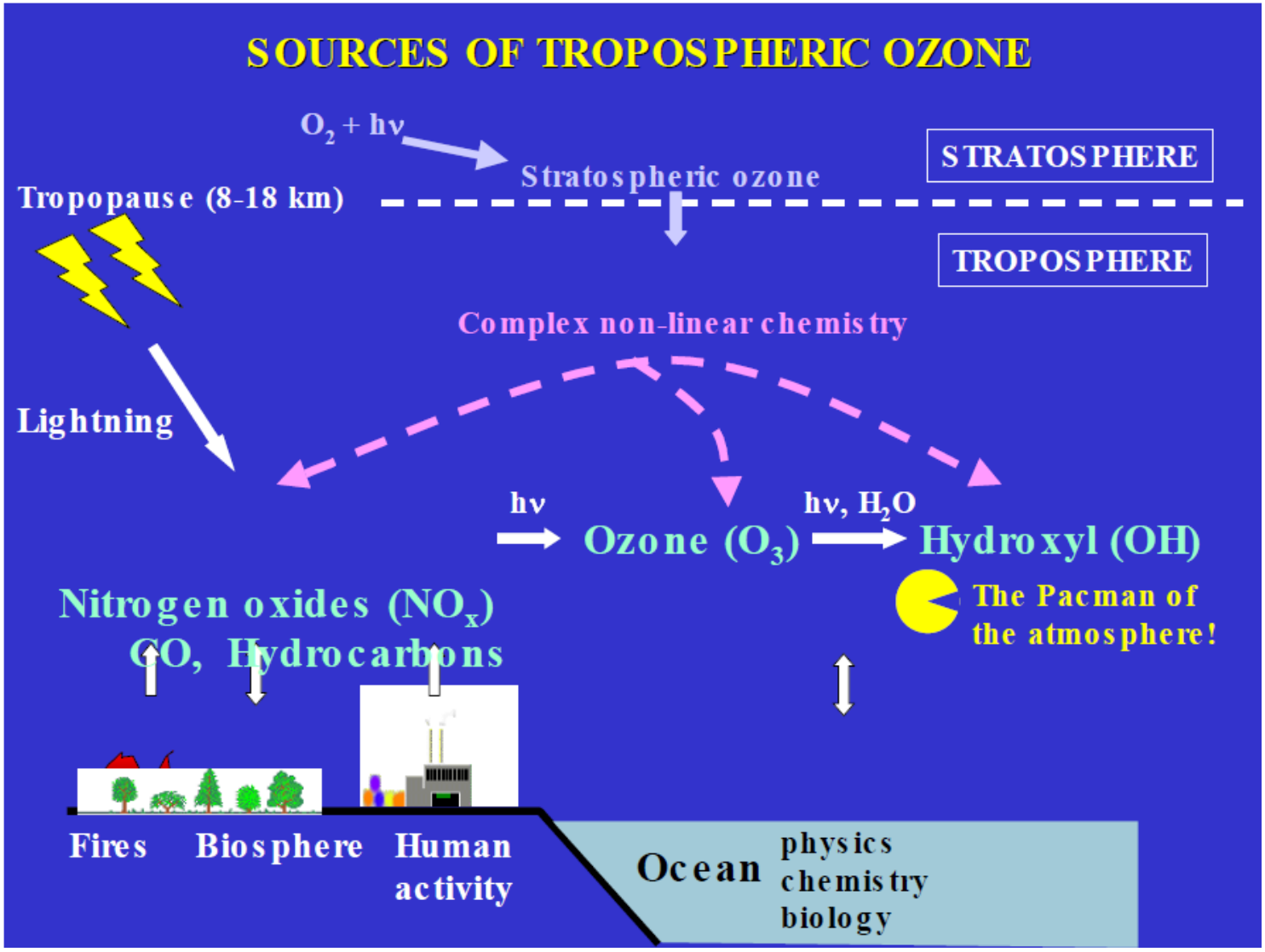
Quiz

1. How can climate change affect ozone and PM pollution (local production and transport)?
2. What factors determine the transboundary transport of air pollutants?
3. How to better design pollution control strategies in light of trade-related transboundary pollution?

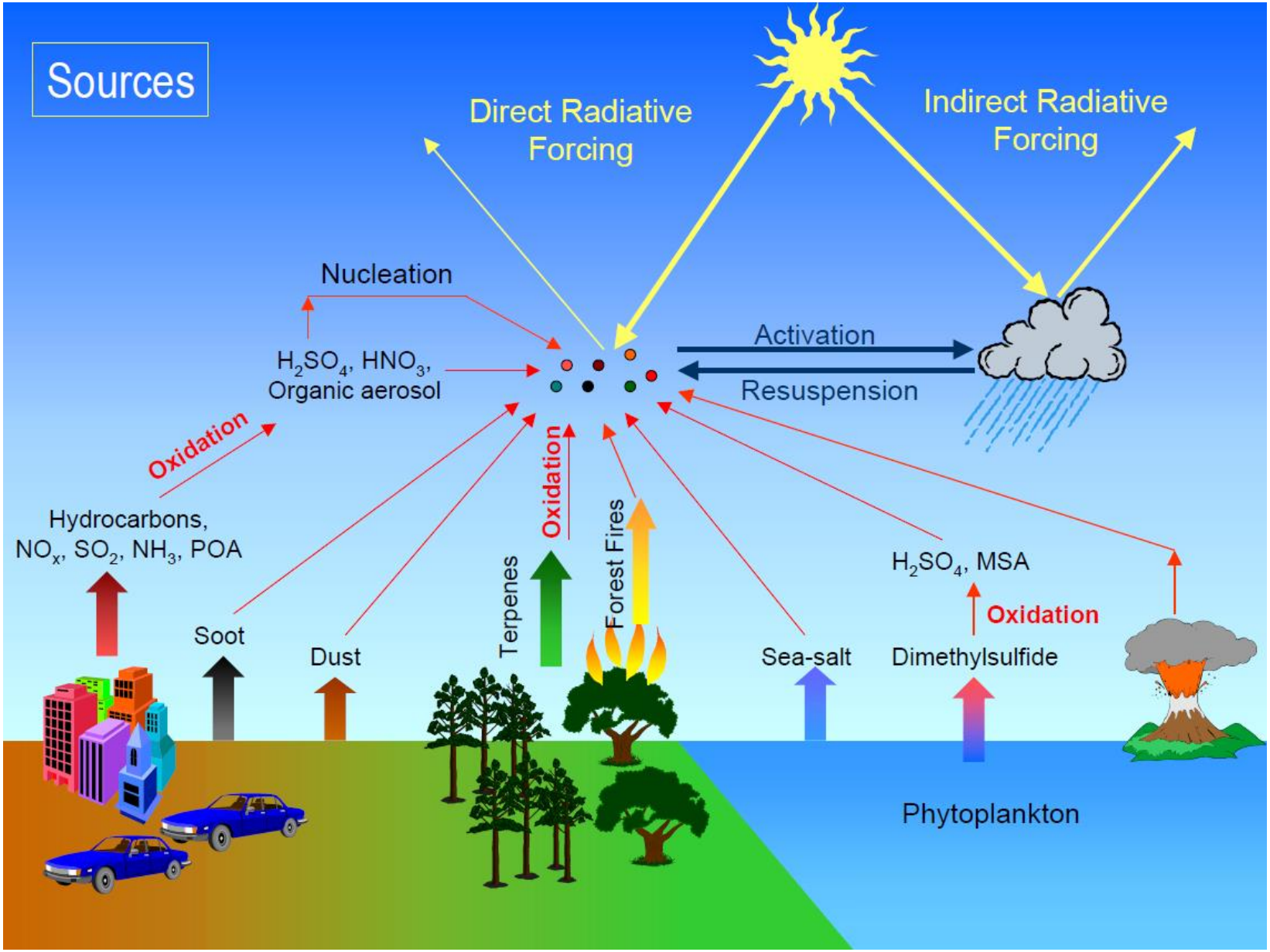
Key Chemical Species in the Troposphere

- **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

Sources of Tropospheric Ozone

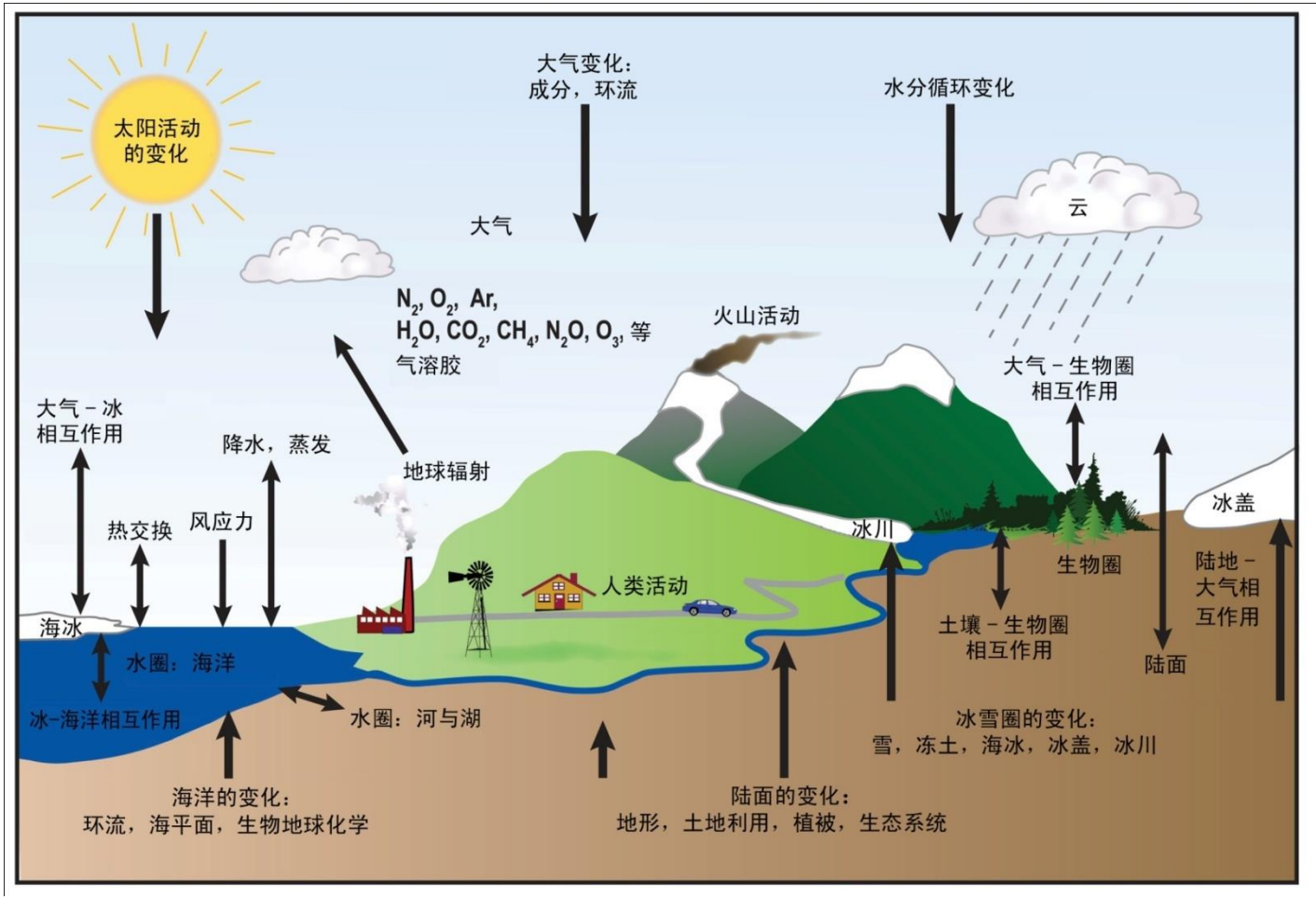


Sources of PM



地球系统中的气候和生地化循环

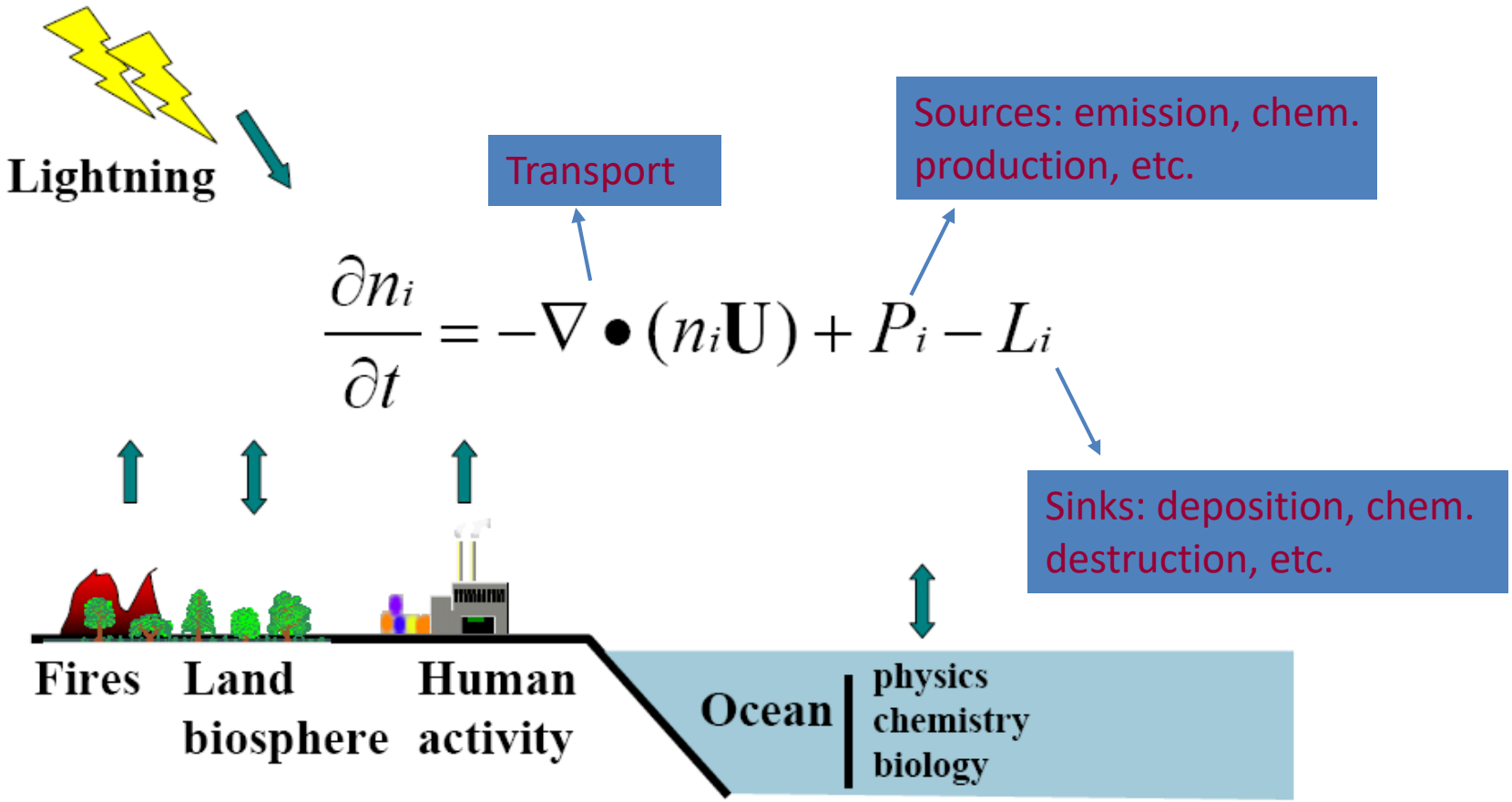
- 气候系统
- 碳循环
- 氮循环
- 硫循环



IPCC, 2013

Budget of Air Pollutants

AN ATMOSPHERIC CHEMIST'S VIEW OF THE WORLD

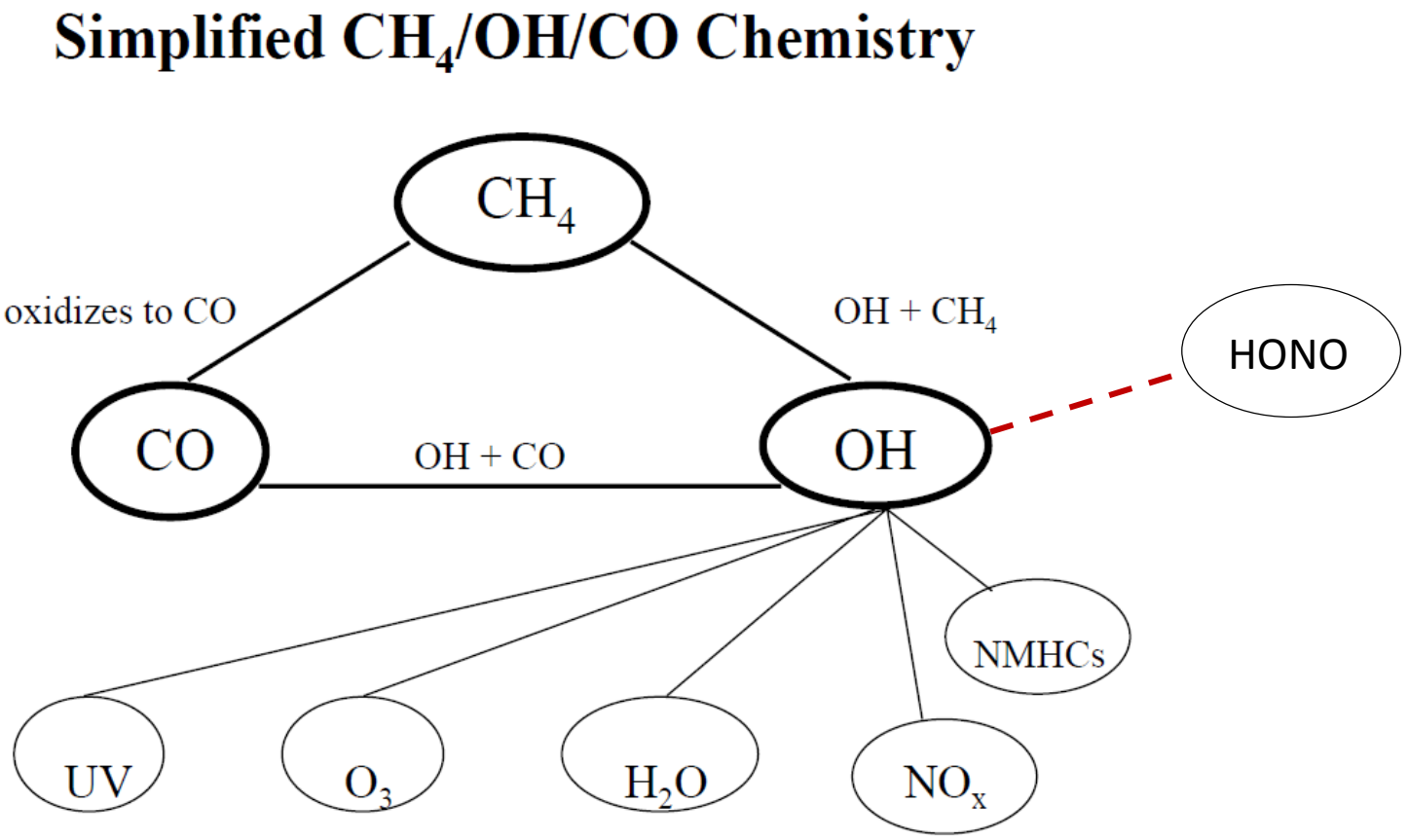


Modified from Don Wuebbles' Lecture

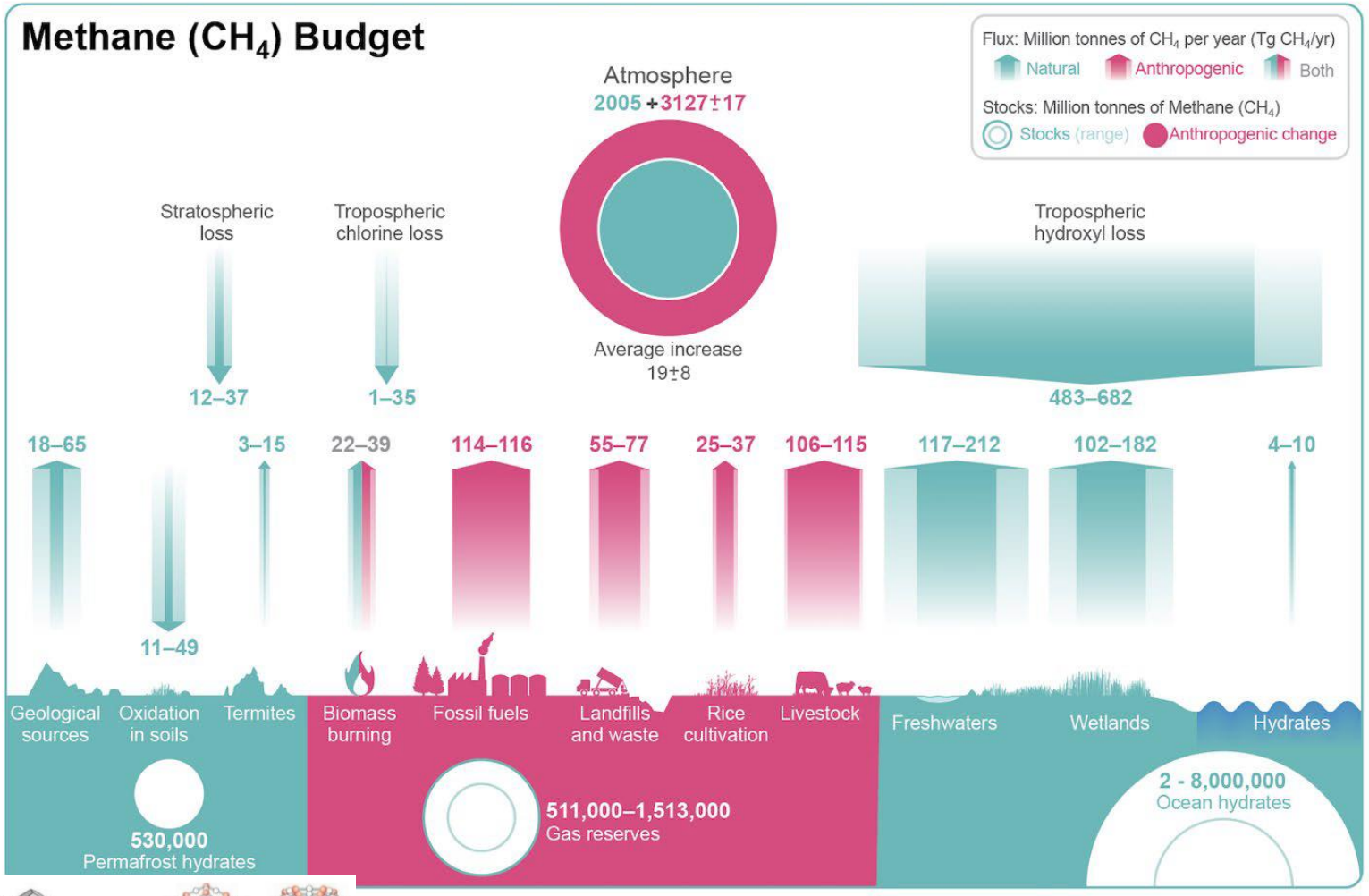
Characteristics of Emissions of Various Trace Species

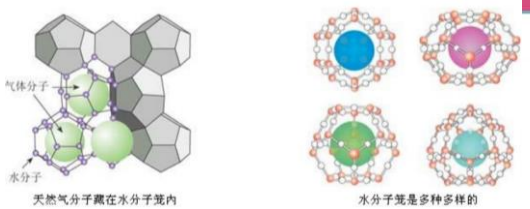
Species	From Combustion?	Source in comb.	Leakage from fuel	Microbial
CH4	Incomplete combustion	Fuel	Abundant	Abundant
CO, BC, POC	Incomplete combustion	Fuel	Little to None	Little to none
NMVOC	Incomplete combustion	Fuel	Abundant	Abundant
NOx	High-temp combustion	Fuel + air	None	Significant
NH3	Little ?	Fuel + additive	None	Mostly
SO2	Mostly	Fuel	None	Little

Roles of CH_4 and CO in Atmospheric Chemistry



Global Methane Cycle

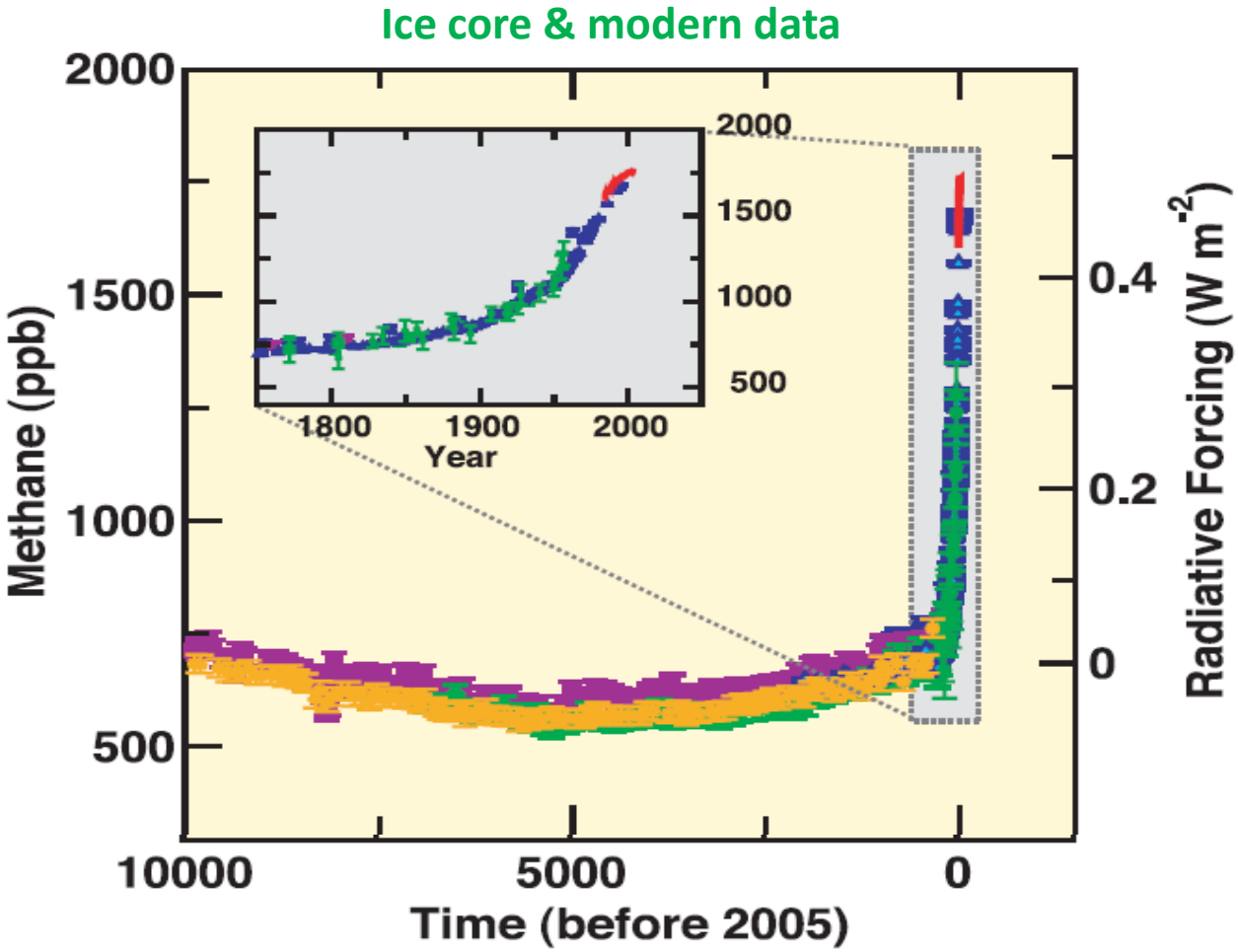




IPCC, 2021

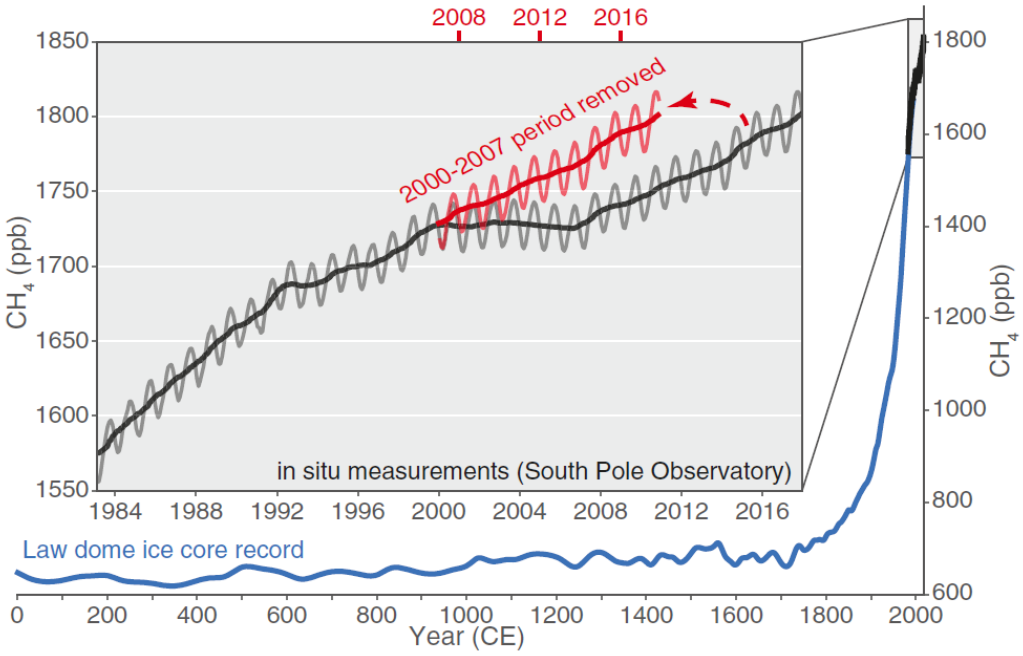
可燃冰：CH4水合物

Rapid Growth of CH_4 in the Industrial Era

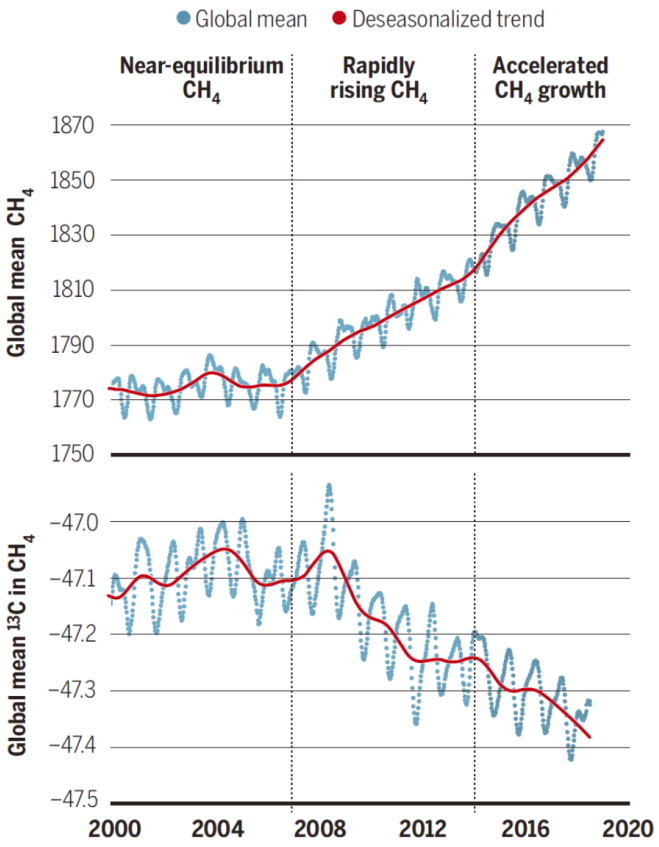


IPCC, 2007

Global CH_4 Growth

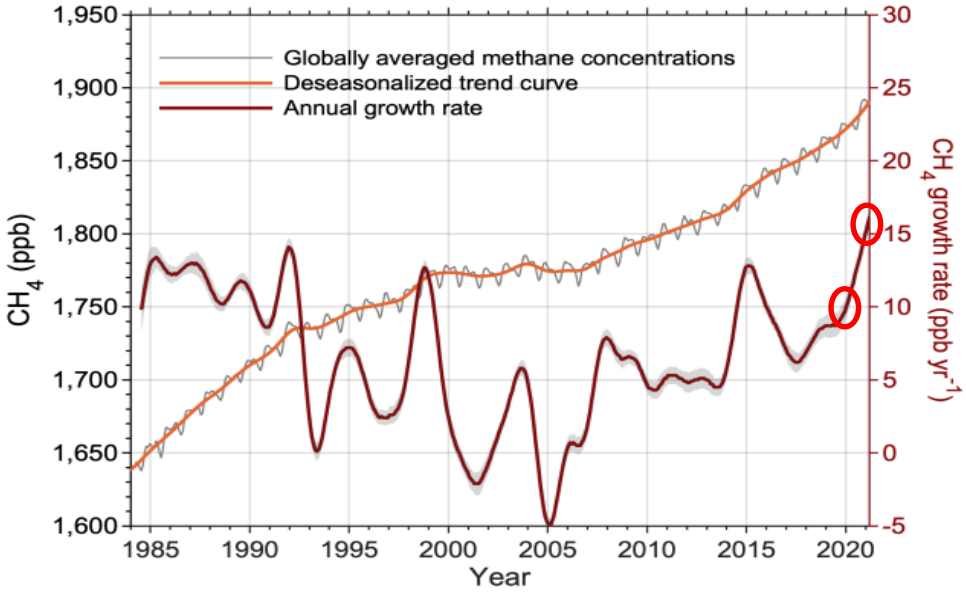


Turner et al., 2019, PNAS



Fletcher et al., 2019, Science

Enhanced Growth of CH_4 Associated with COVID

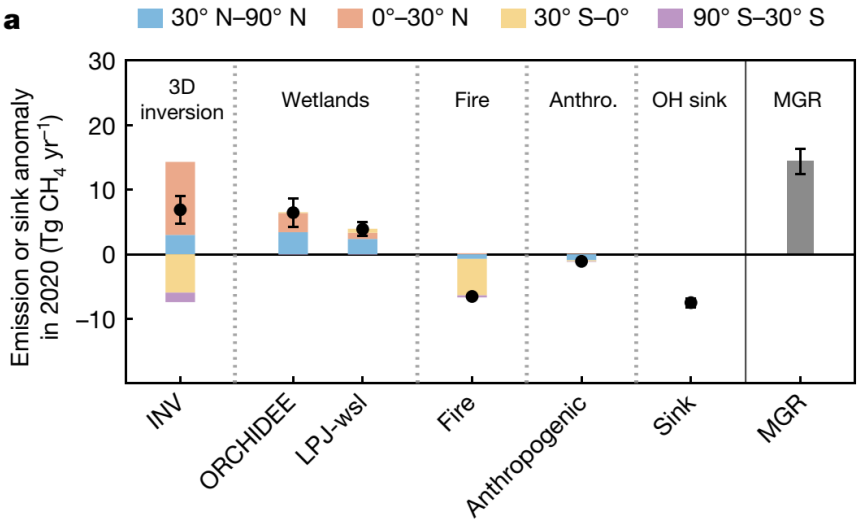


Growth rate:

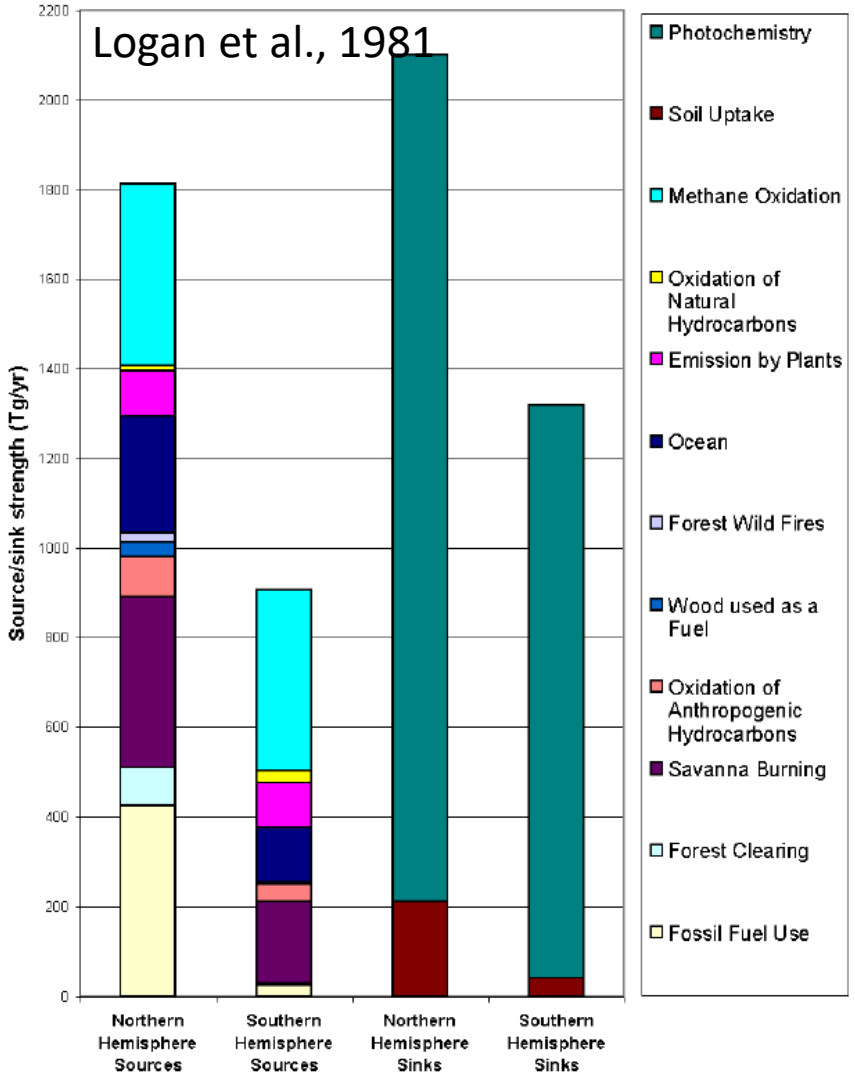
2020.1.1-2019.1.1: 9.9 ± 0.6 ppb yr^{-1}

2021.1.1-2020.1.1: 15.1 ± 0.4 ppb yr^{-1}

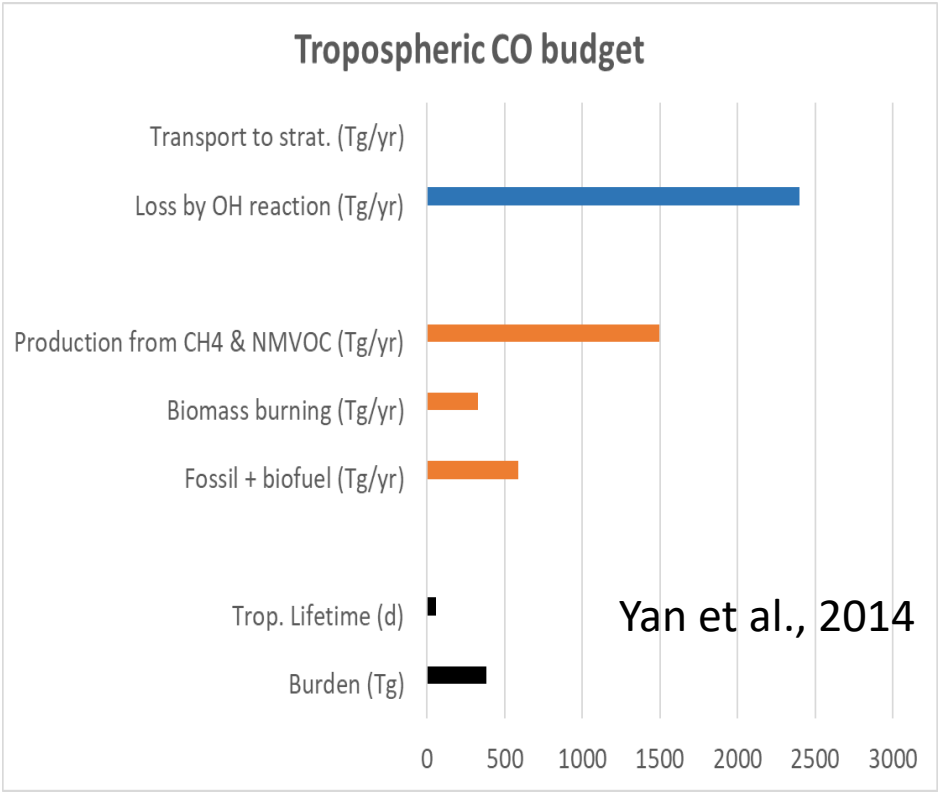
Peng et al., Nature, 2022



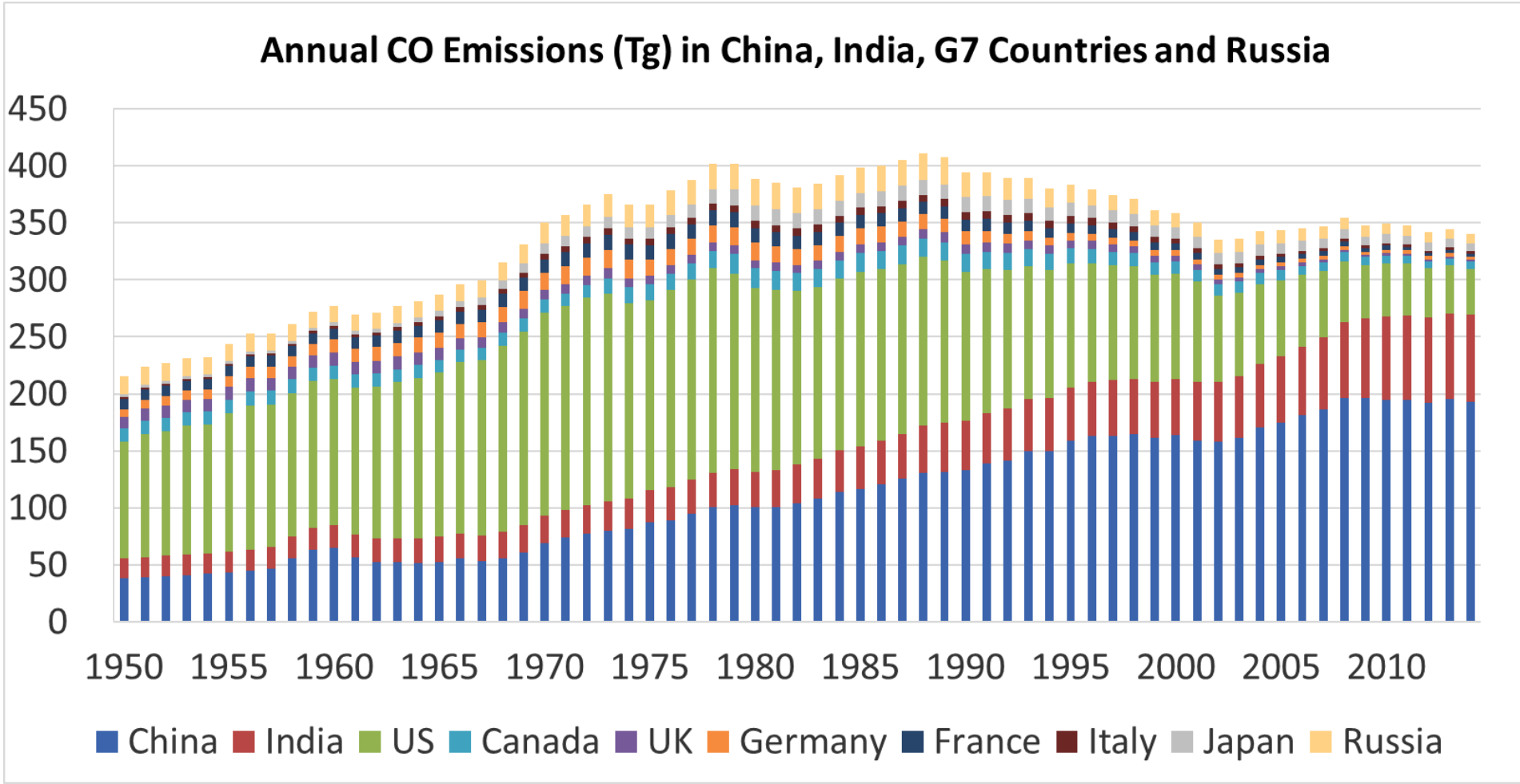
Global Budget of CO



CO sources and sinks in 2009

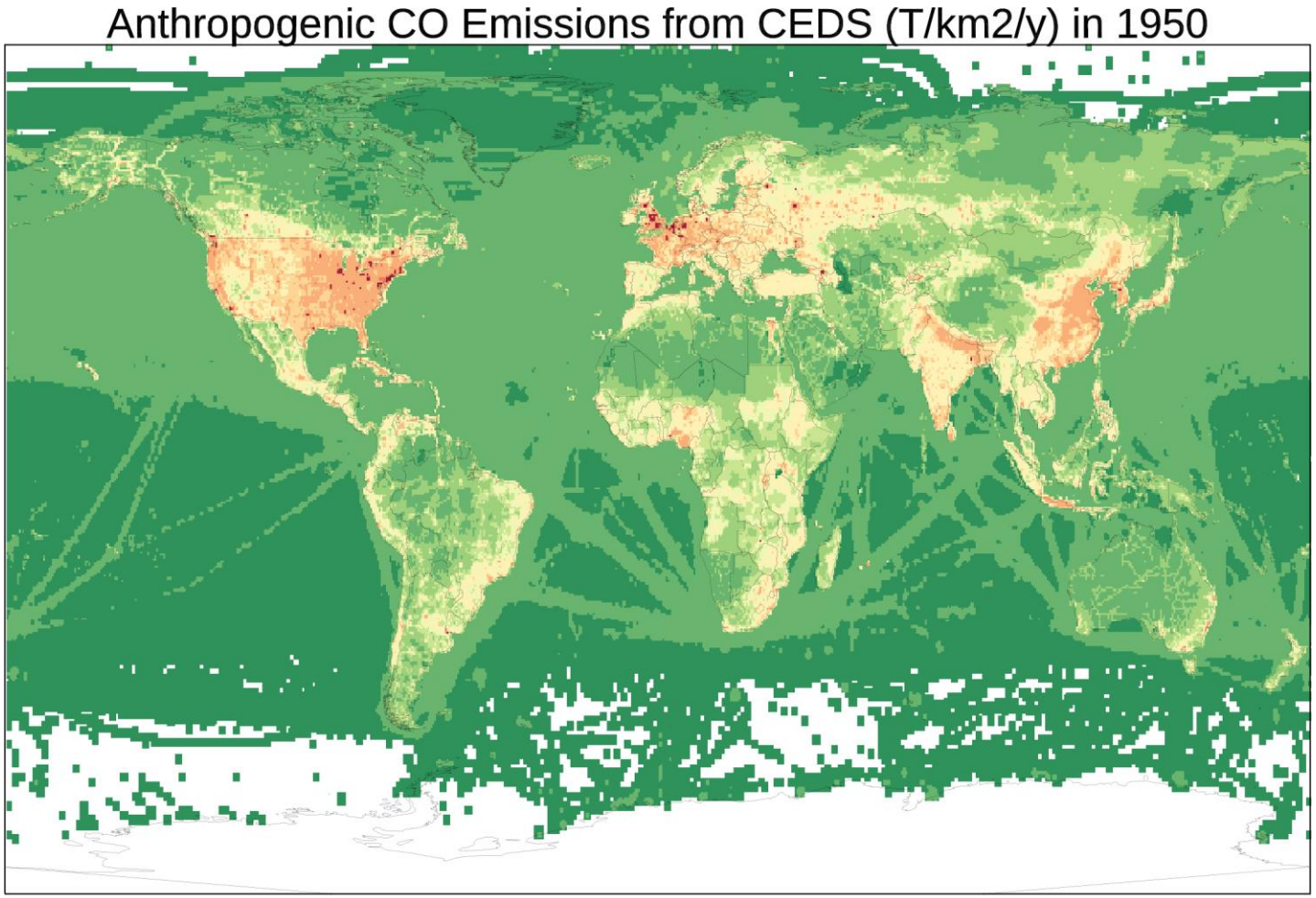


Anthropogenic Emissions of CO: 1950-2014



CEDS inventory

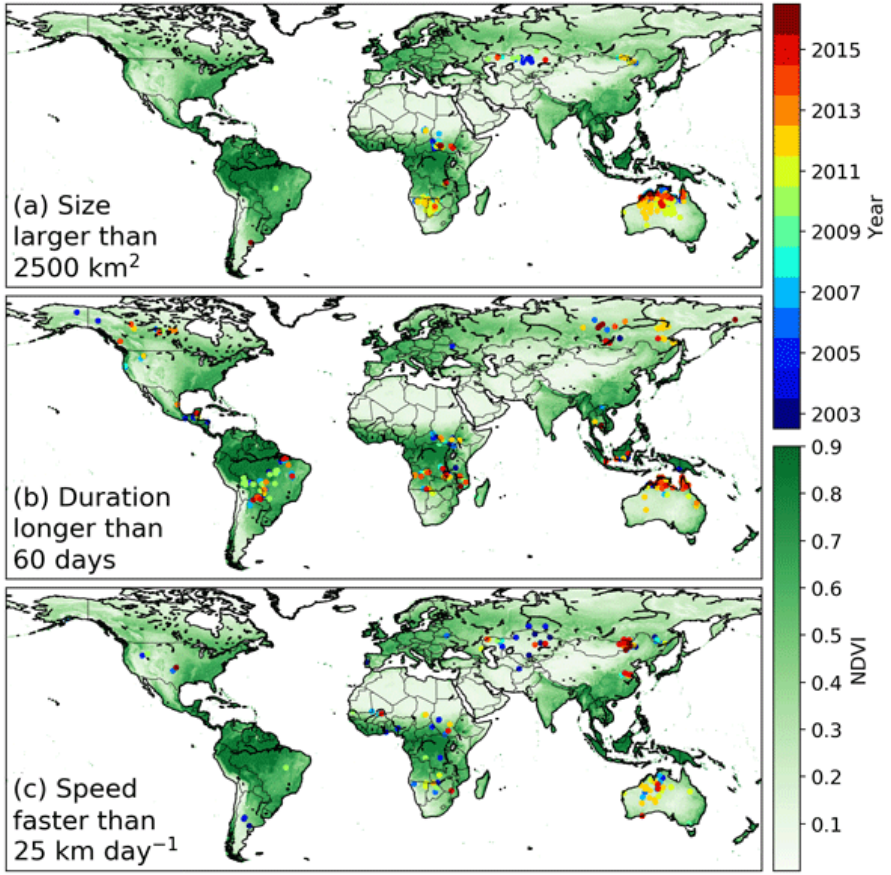
Anthropogenic Emissions of CO: 1950-2014



CEDS inventory

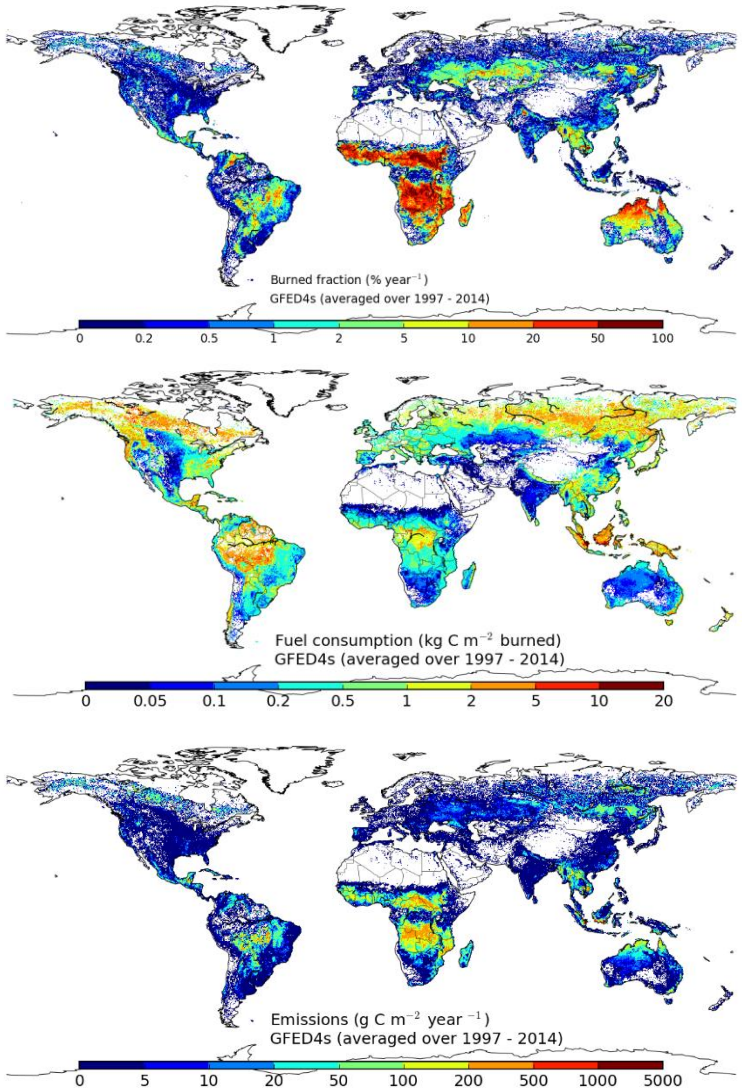
Biomass Burning Emissions of Carbon

Global fire atlas (2003-2016)

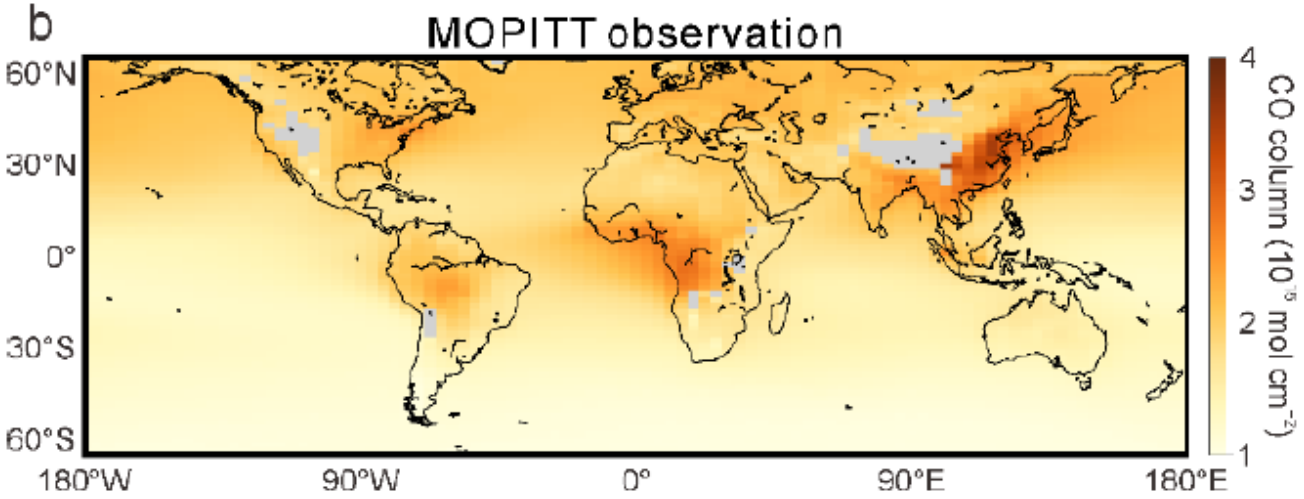


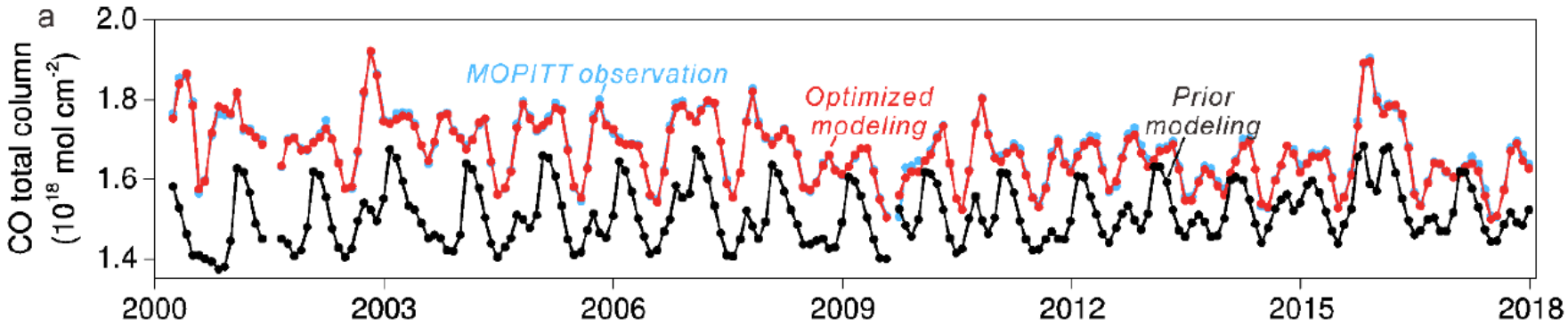
GFED4: http://www.globalfiredata.org

Global fire emissions (1997-2014)



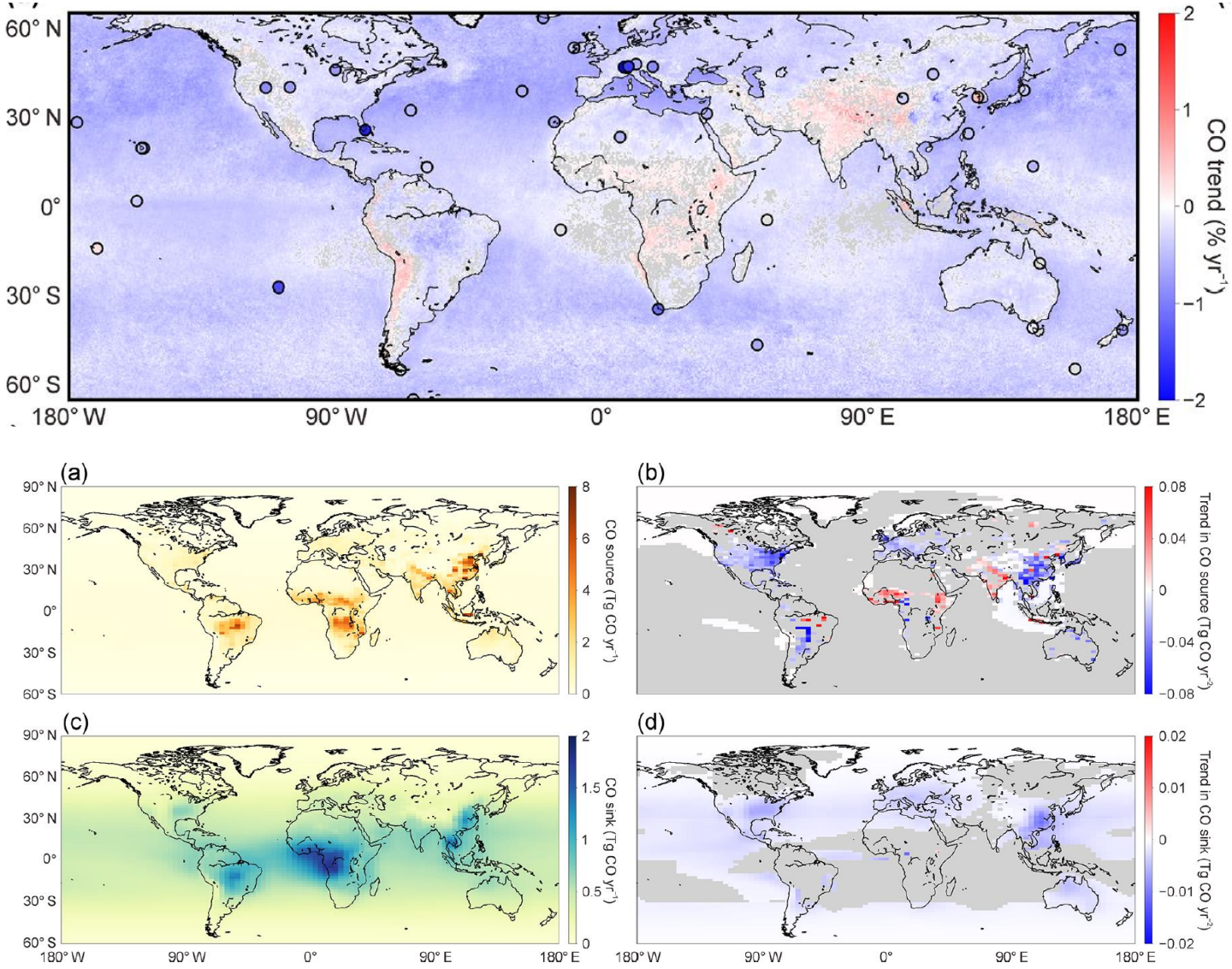
Tropospheric CO Column: 2000-2017





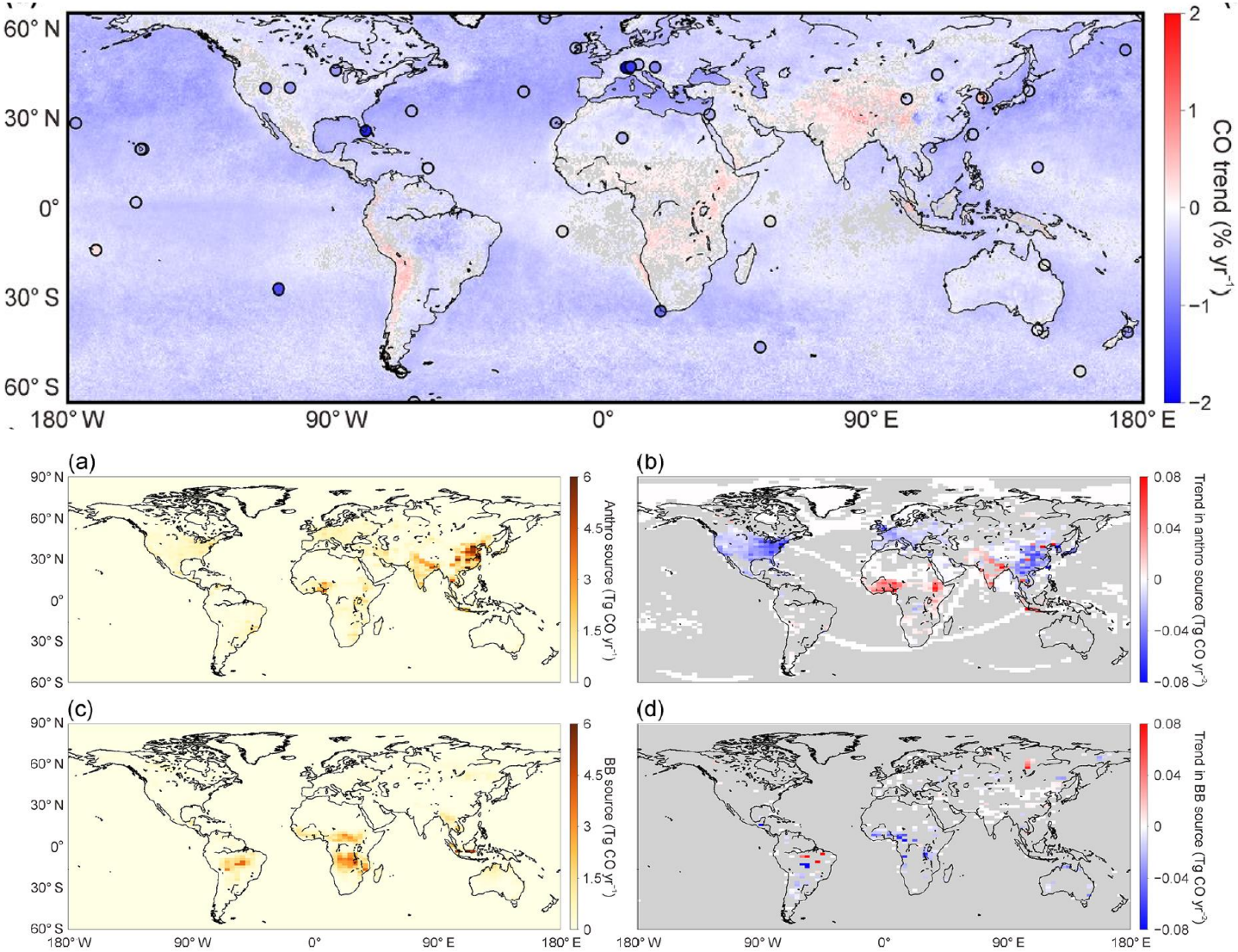
Zheng et al., 2019, ESSD

Trends of Tropospheric CO, Sources and Sinks: 2000-2017



Zheng et al., 2019, ESSD

Trends of Tropospheric CO and Emissions: 2000-2017



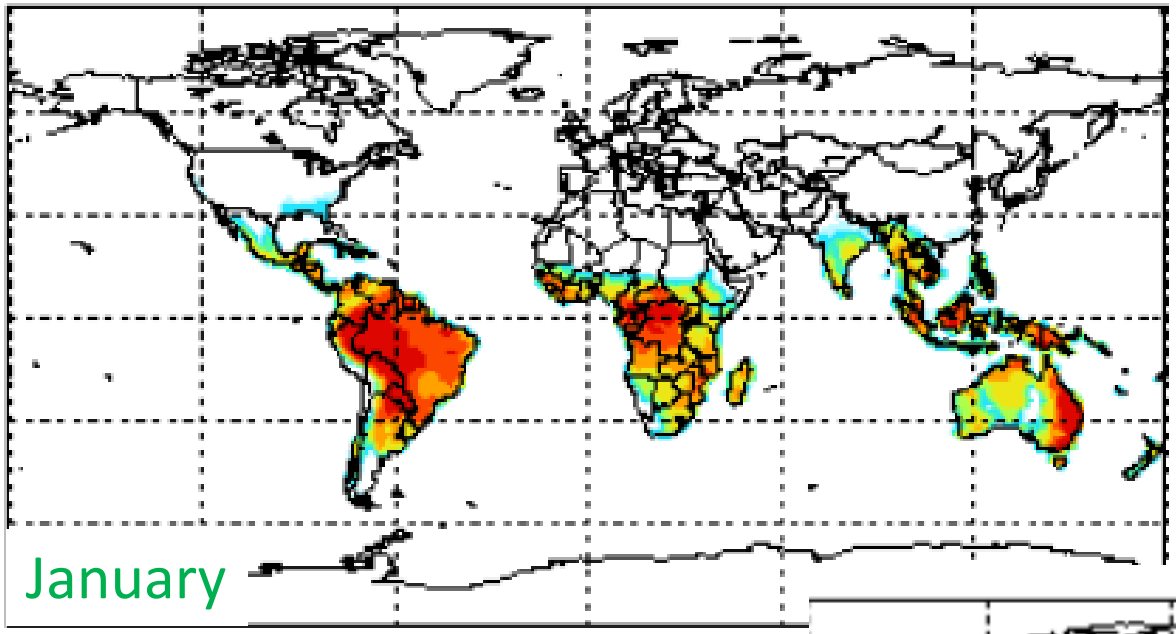
Zheng et al., 2019, ESSD

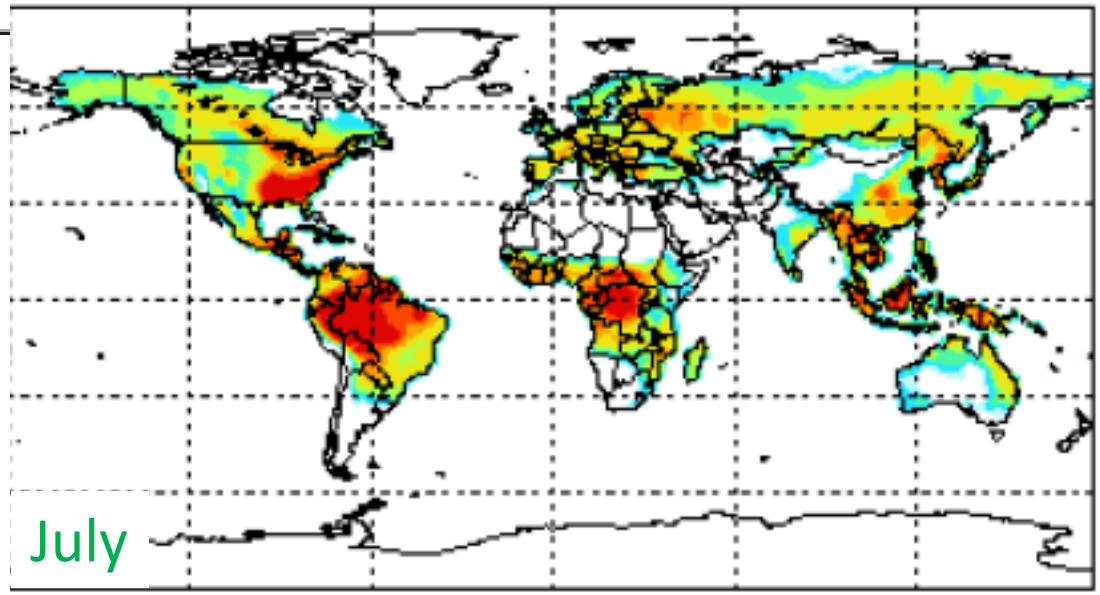
Global emissions of non-methane hydrocarbons

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

Brasseur et al., 1998

Biogenic Emissions of Isoprene

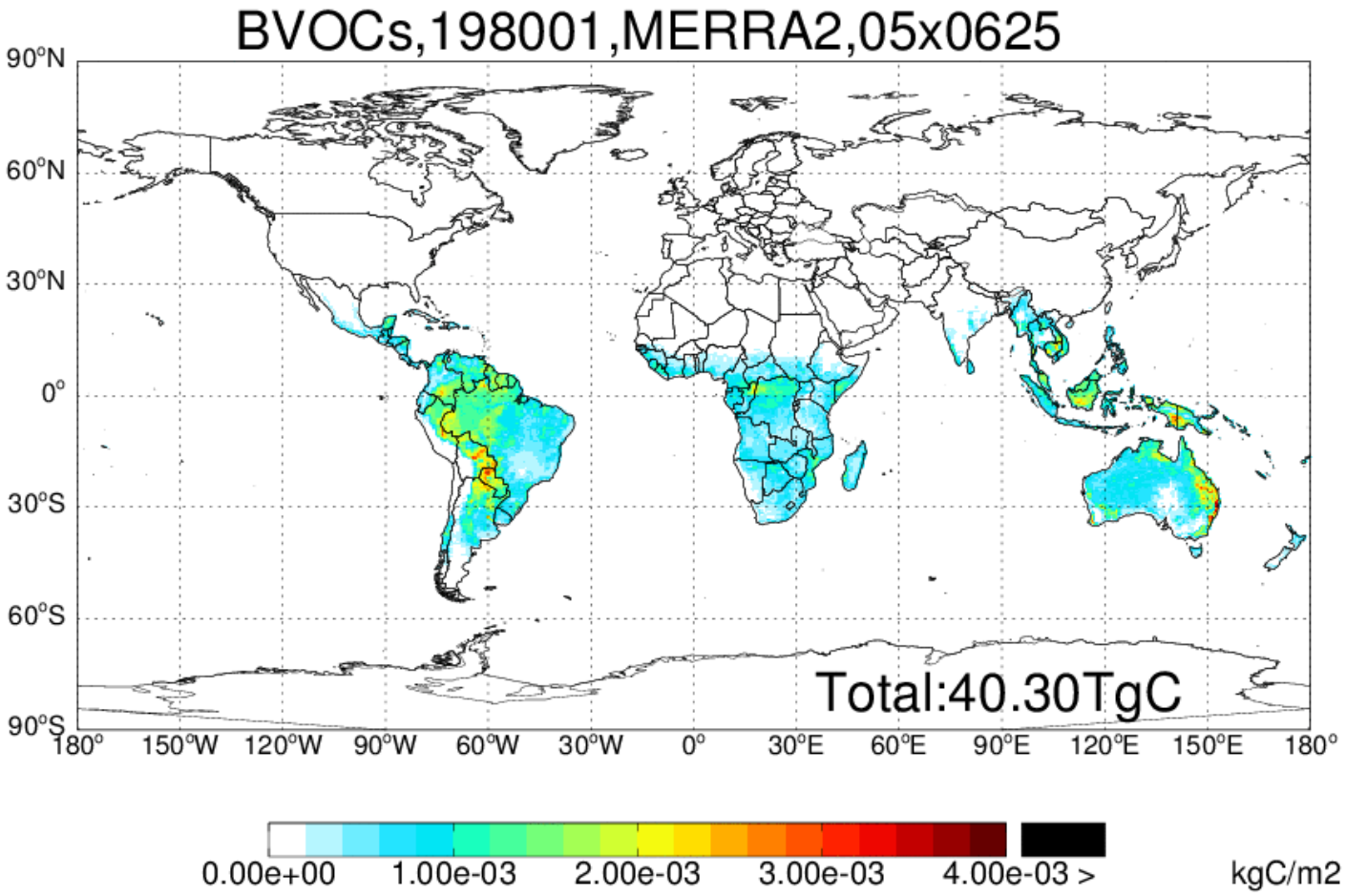




Isoprene:

- Emissions: most abundant
- Reactivity: among the highest

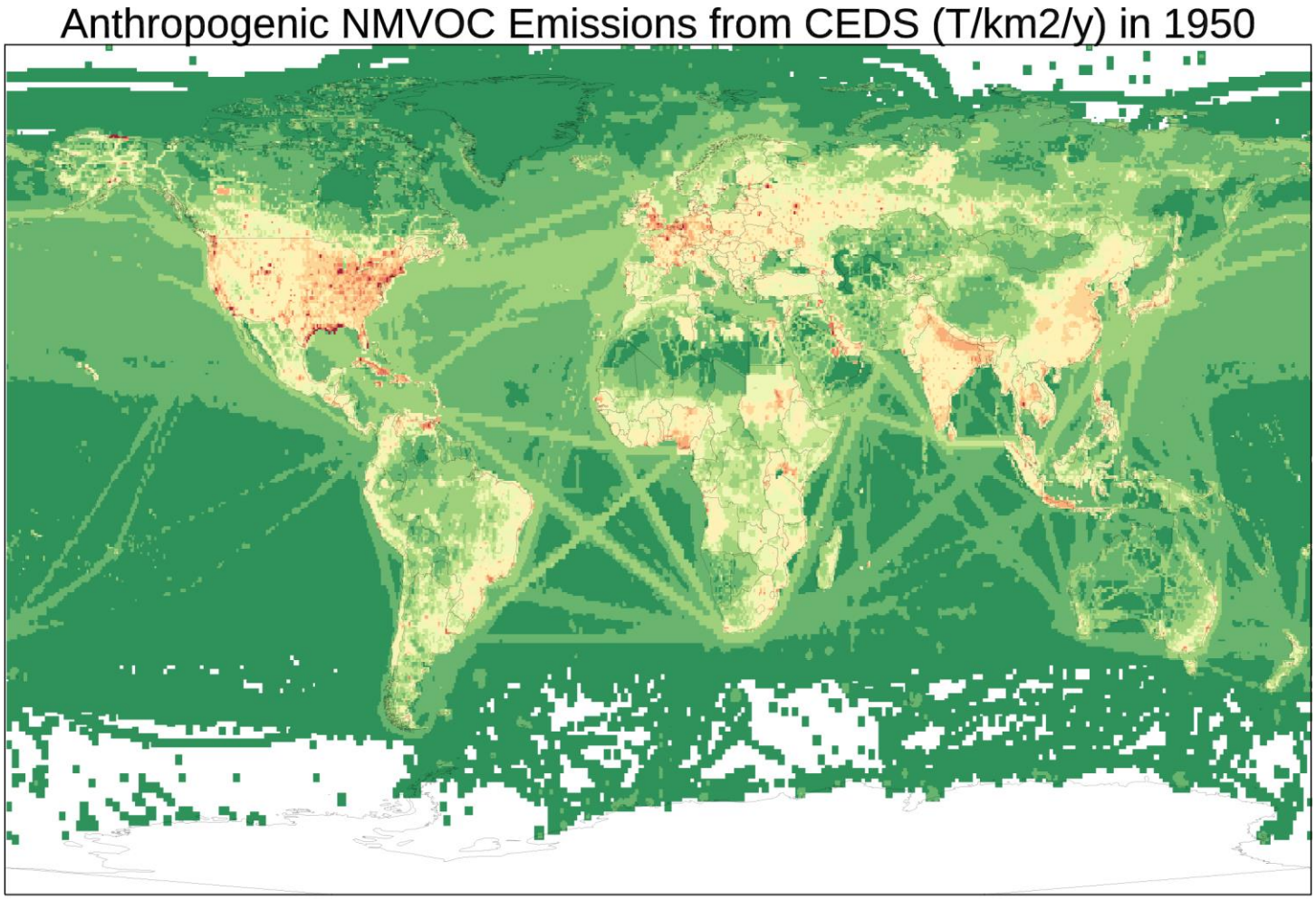
Biogenic NMVOC Emissions Since 1980



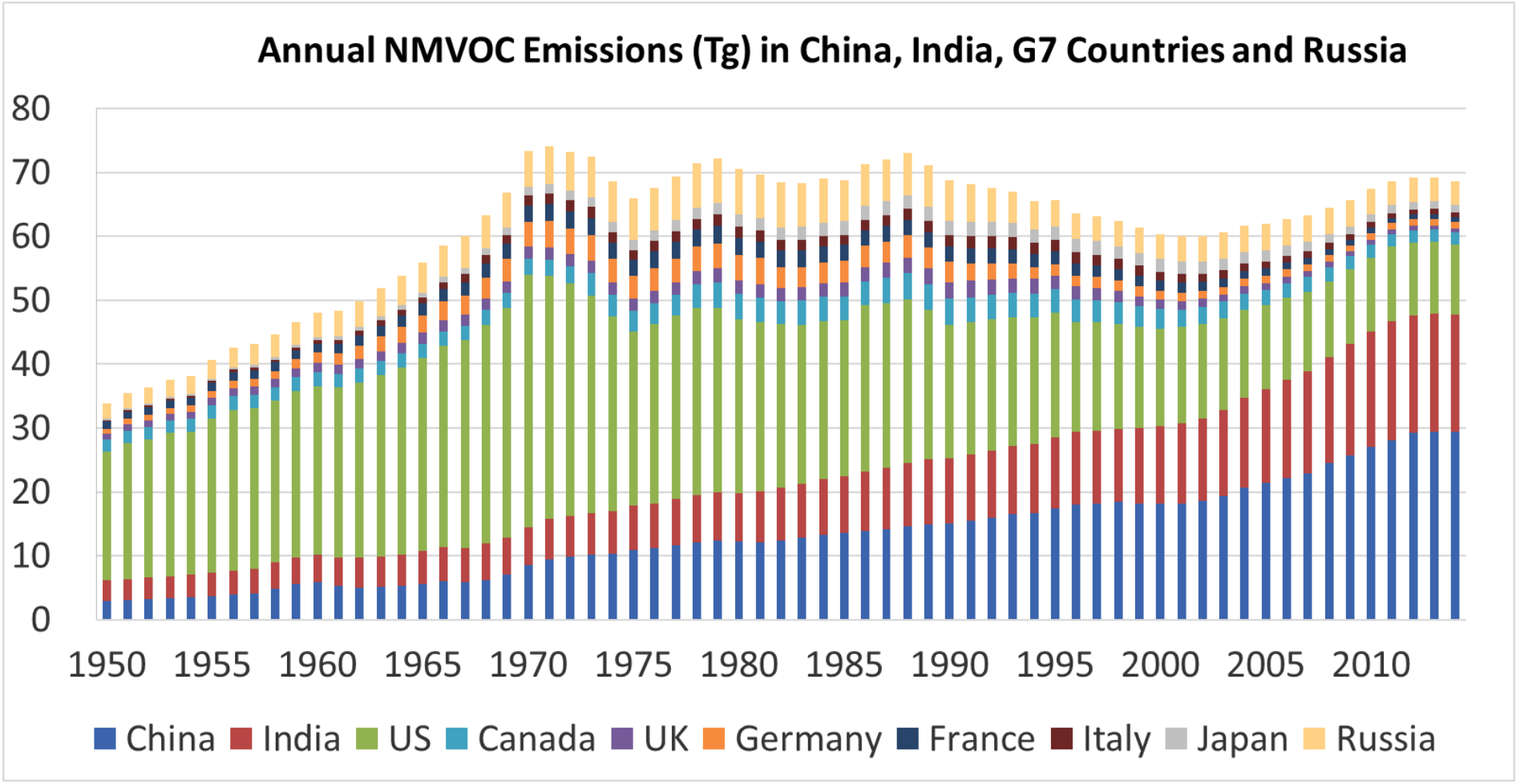
Temporal res : hourly
Horizontal res: 25 or 50 km

Weng HJ et al., 2020, SD

Anthropogenic NMVOC Emissions: 1950-2014

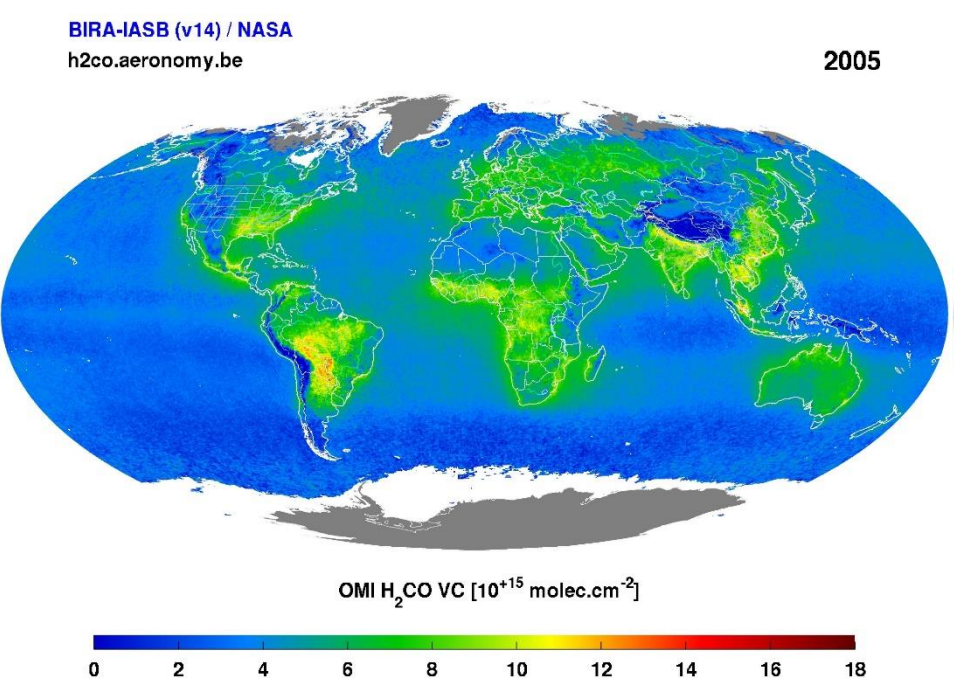


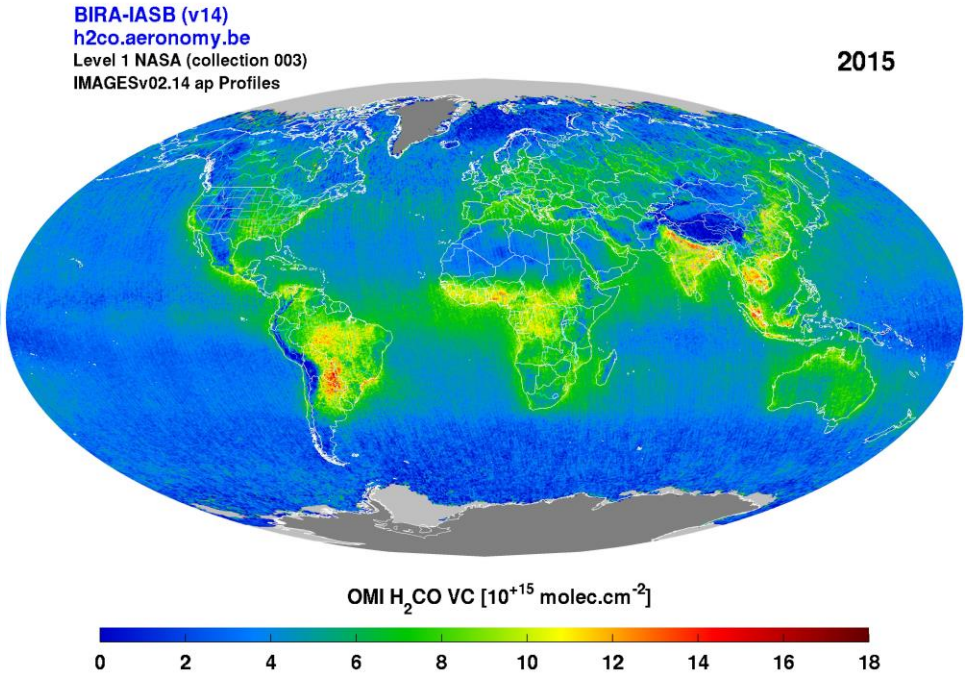
Anthropogenic Emissions of NMVOC: 1950-2014



CEDS inventory

Tropospheric HCHO Column: 2005-2015



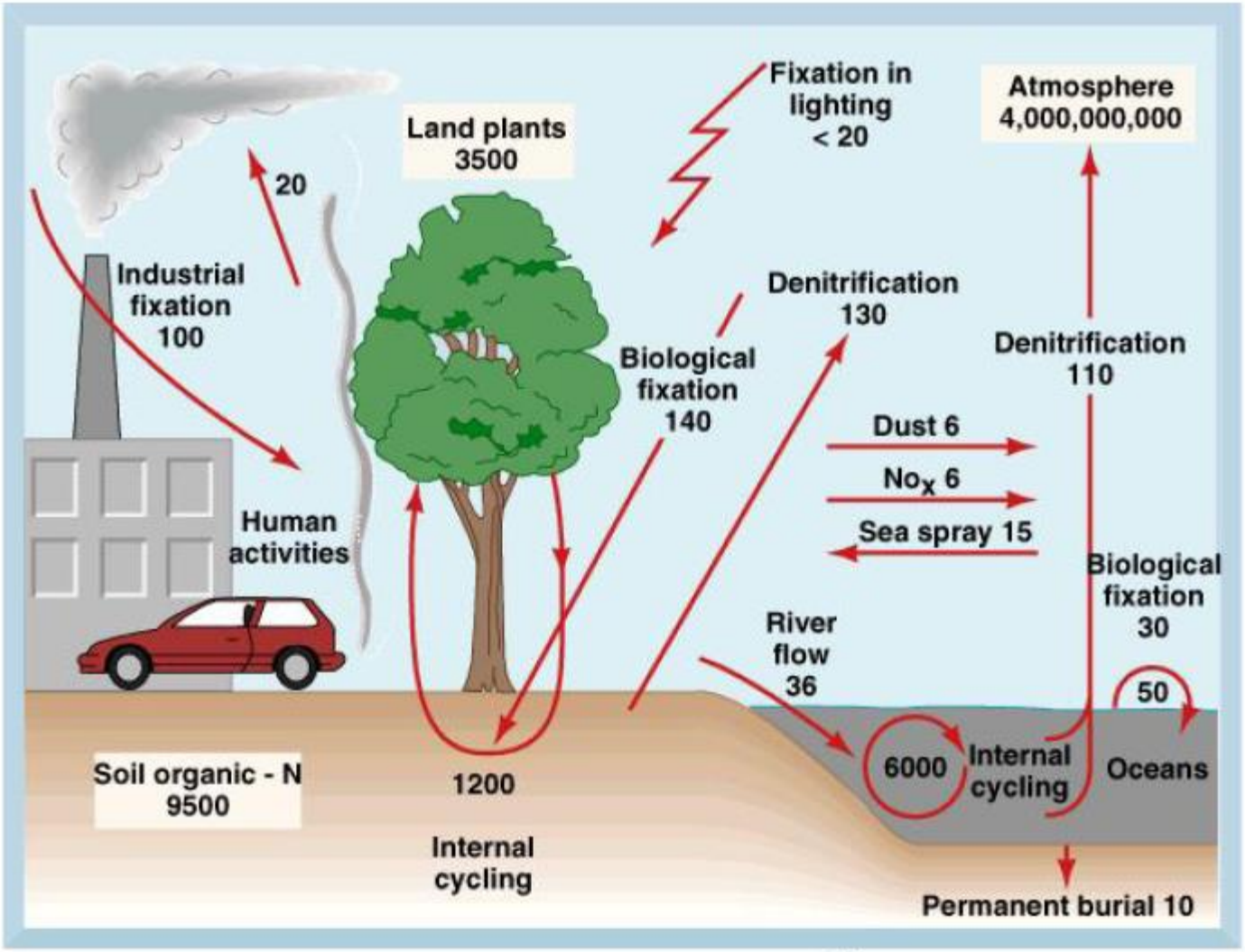


www.temis.nl

Global Nitrogen Cycle

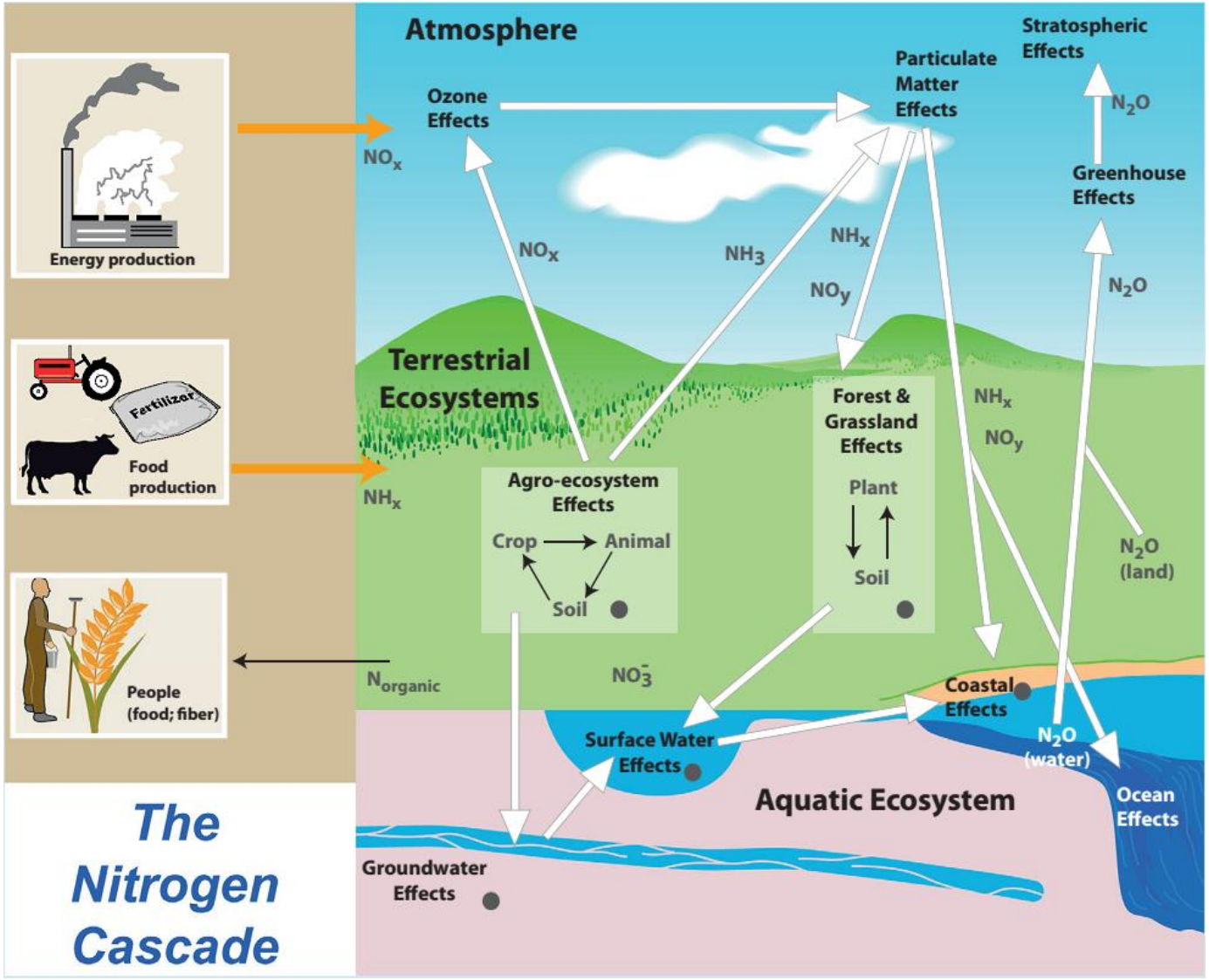
- Good: Important nutrition for agriculture, ecosystem
- Bad: Precursor of ozone, aerosols
- Bad: Adverse effects on air quality, climate, and acid deposition
- Species: NOx, NOy, NH3, NH4, N2O

Global Nitrogen Cycle



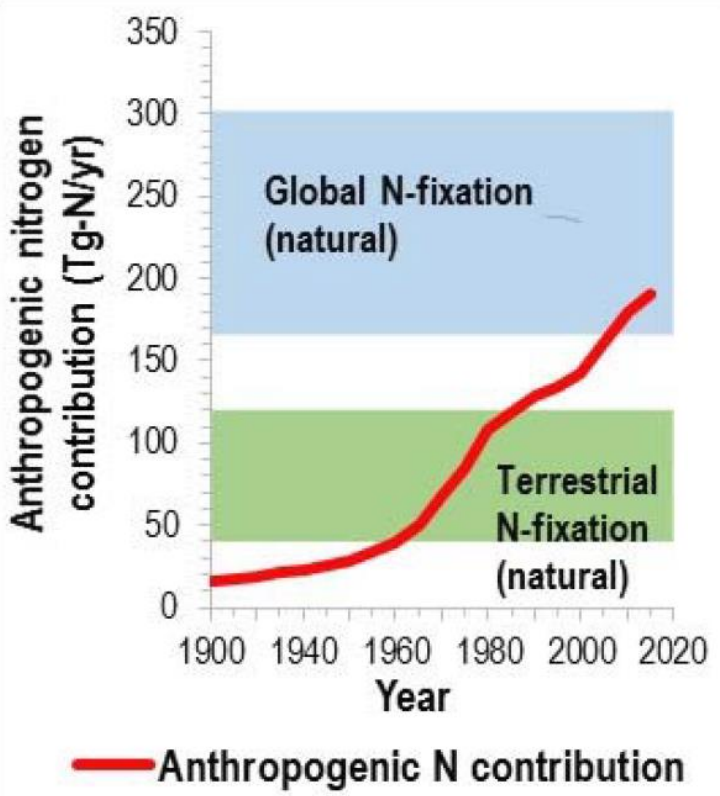
The global nitrogen cycle. Pools (□)and annual (→) flux in $10^{12}gN_2$. Note that the industrial fixation of nitrogen is nearly equal to the global biological fixation. (*SOURCE:* Data from Söderlund, and T. Rosswall, 1982 , O. Hutzinger (ed.), *The Handbook of Environmental Chemistry,* Vol 1, Pt. B., Springer-Verlag New York, Inc., New York).

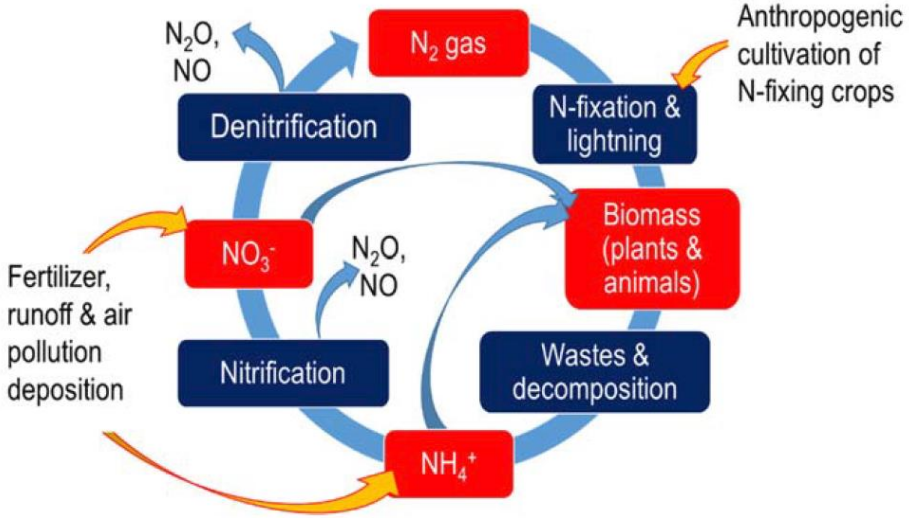
Global Nitrogen Cascade

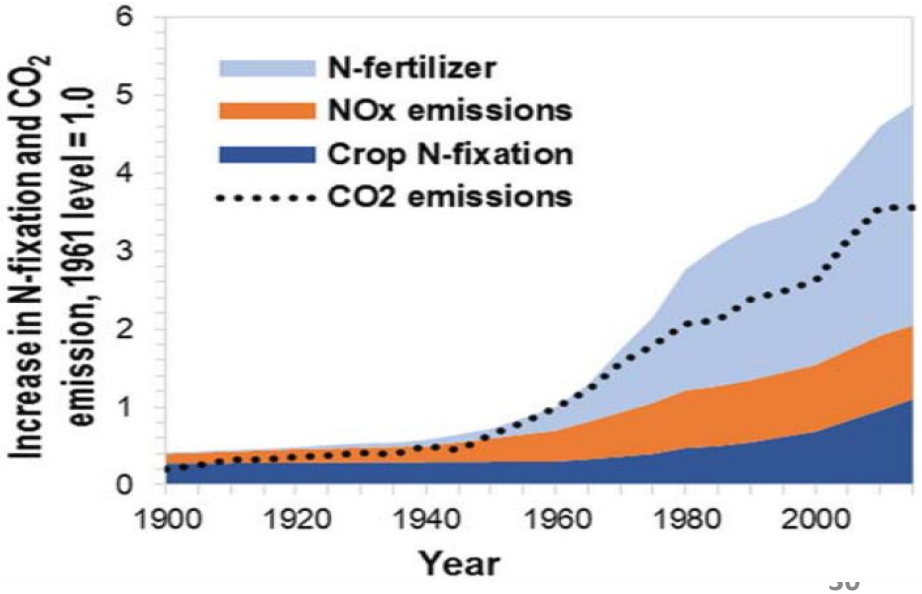


IPCC, 2013

Global Reactive Nitrogen Creation







Battye et al., 2017

NOx Emissions by Source

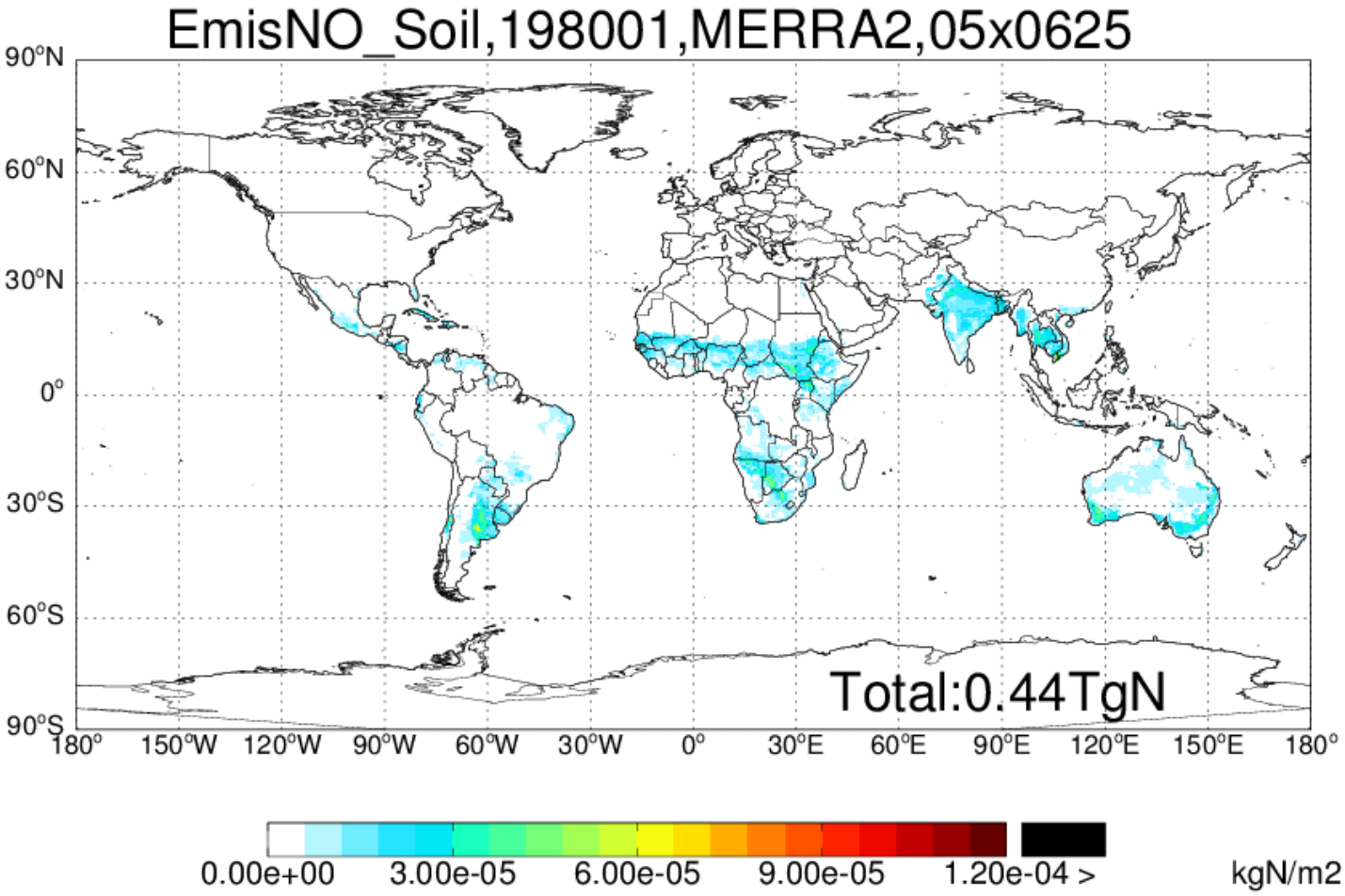
NOx Budget

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
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**

China has used excessive fertilizer in agriculture (32.6 vs 11.6 in US in 2010), leading to significant emis of nitrogen from soil

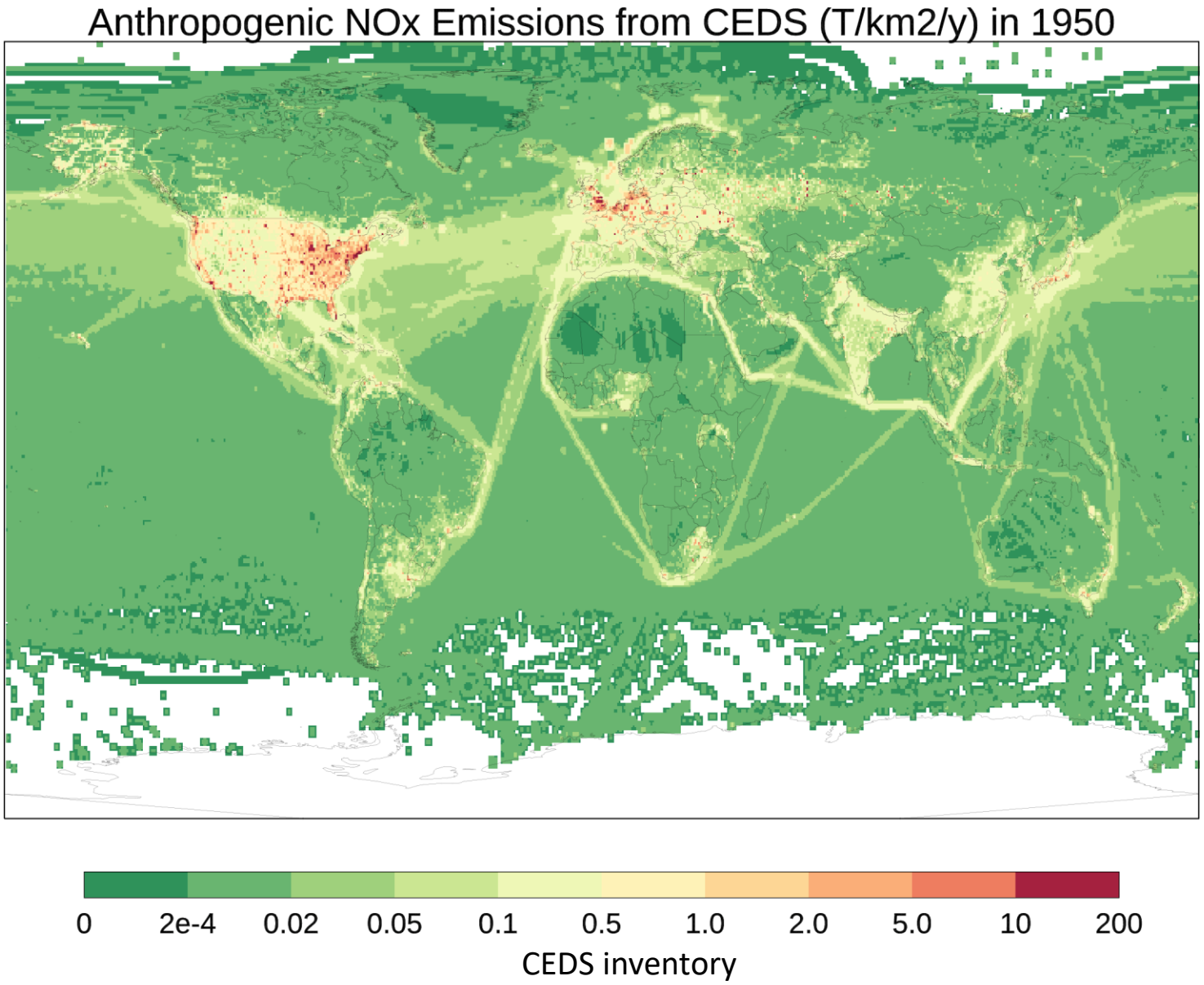
Soil NOx Emissions Since 1980



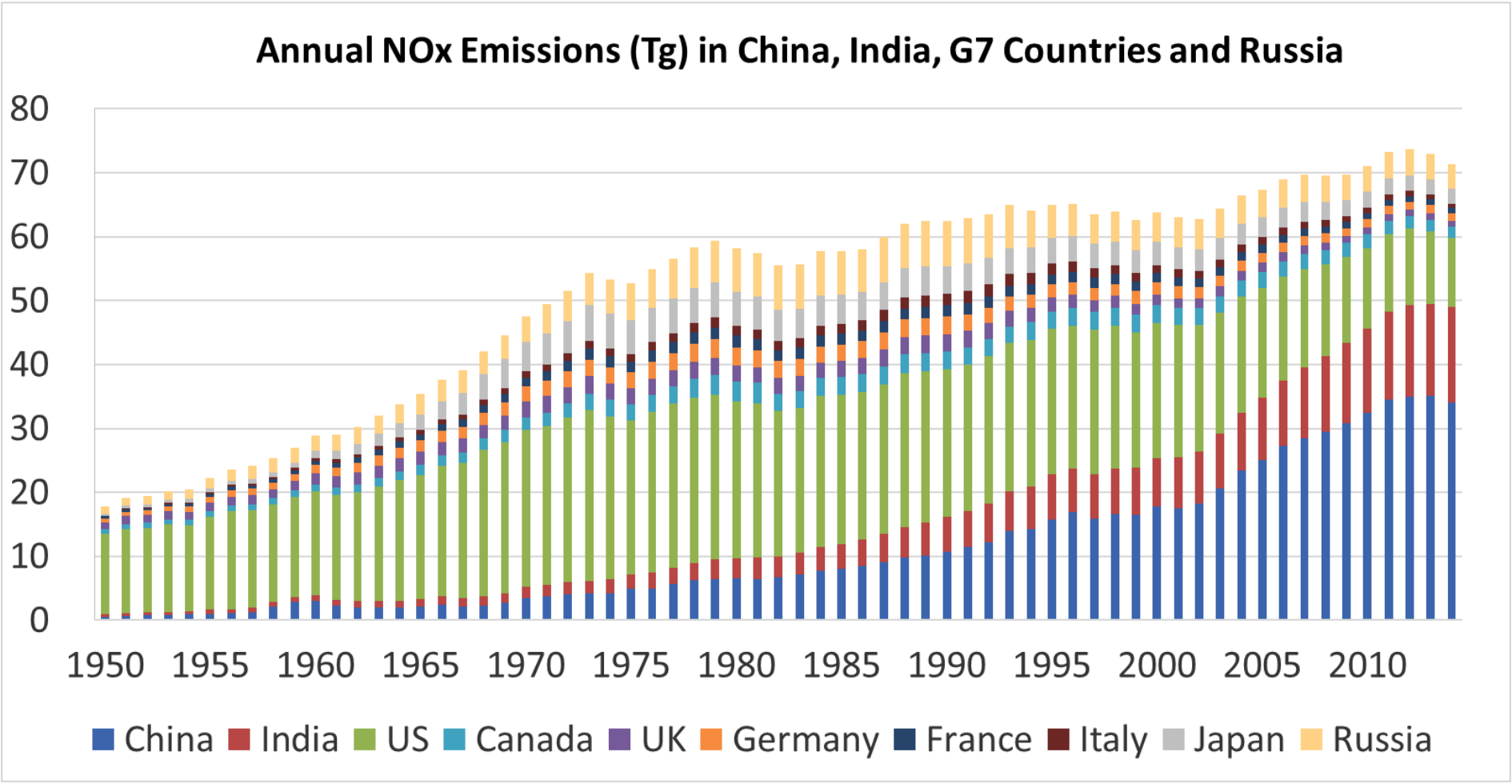
Temporal res : hourly
Horizontal res: 25 or 50 km

Weng HJ et al., 2020, SD

Anthropogenic NOx Emissions: 1950-2014

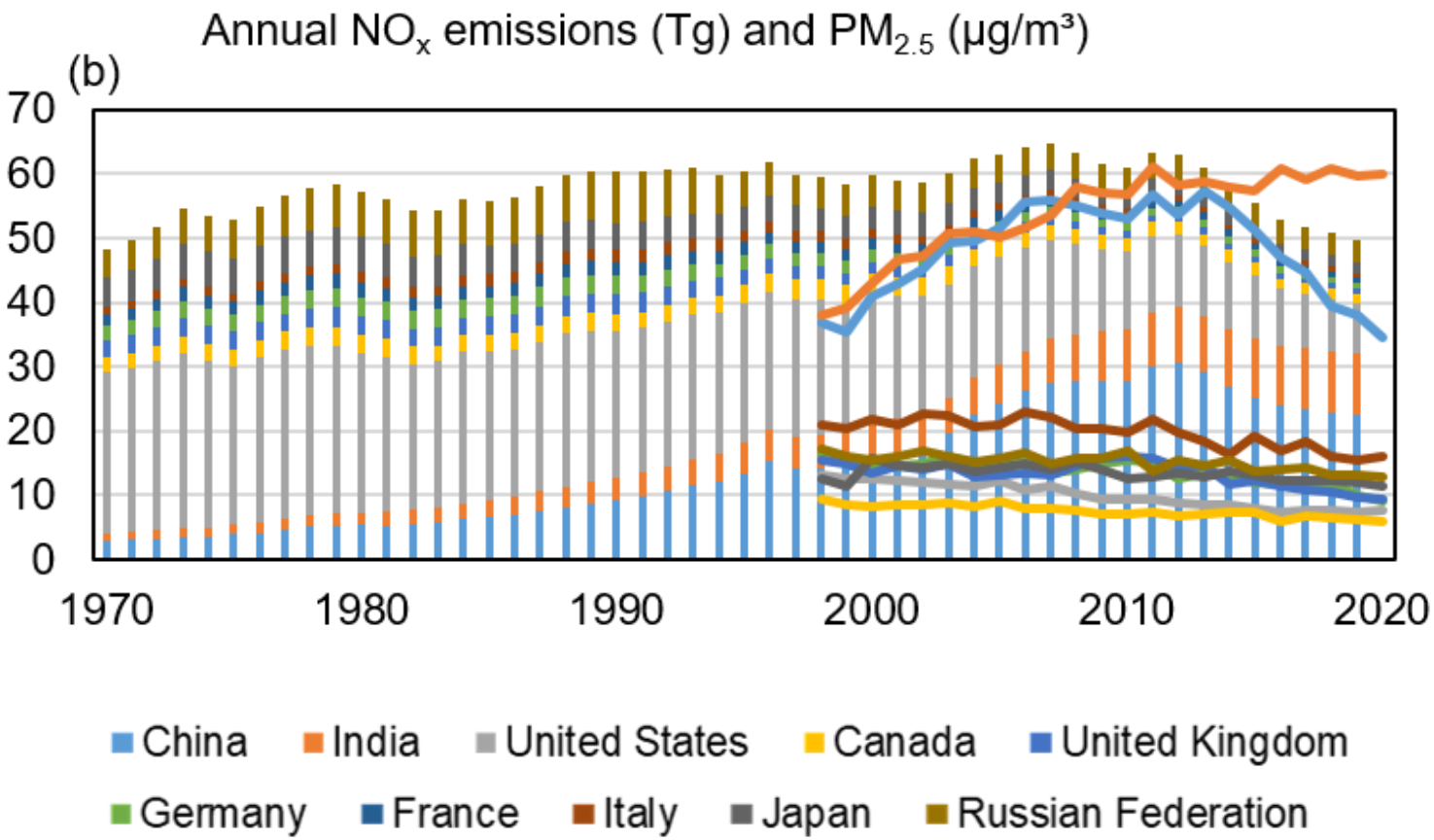


Anthropogenic Emissions of NOx: 1950-2014



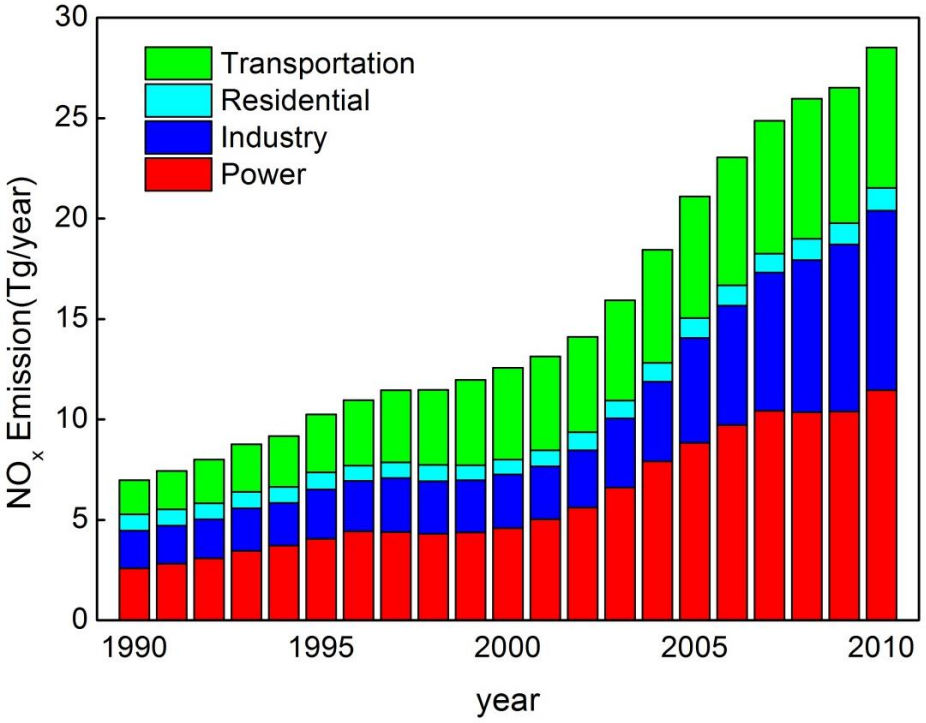
CEDS inventory

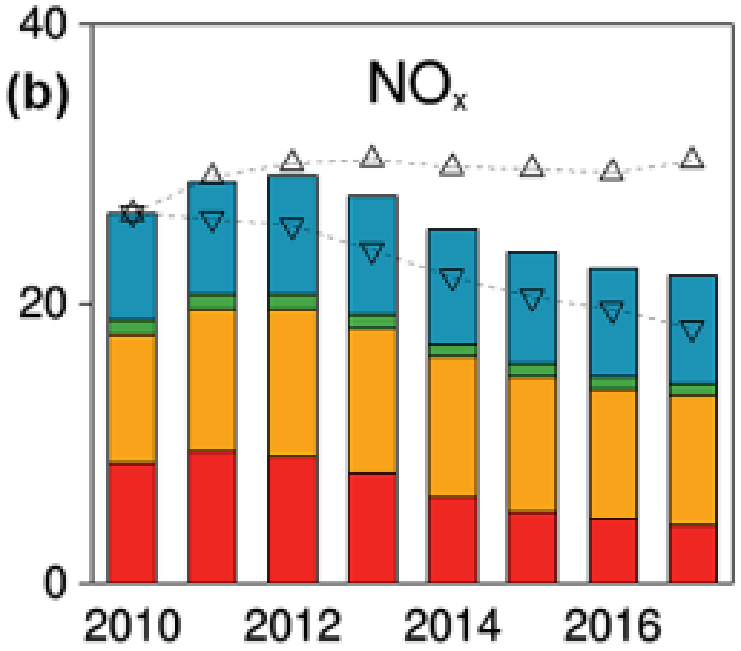
Anthropogenic Emissions of NOx: 1970-2019



CEDS-GBD-Map

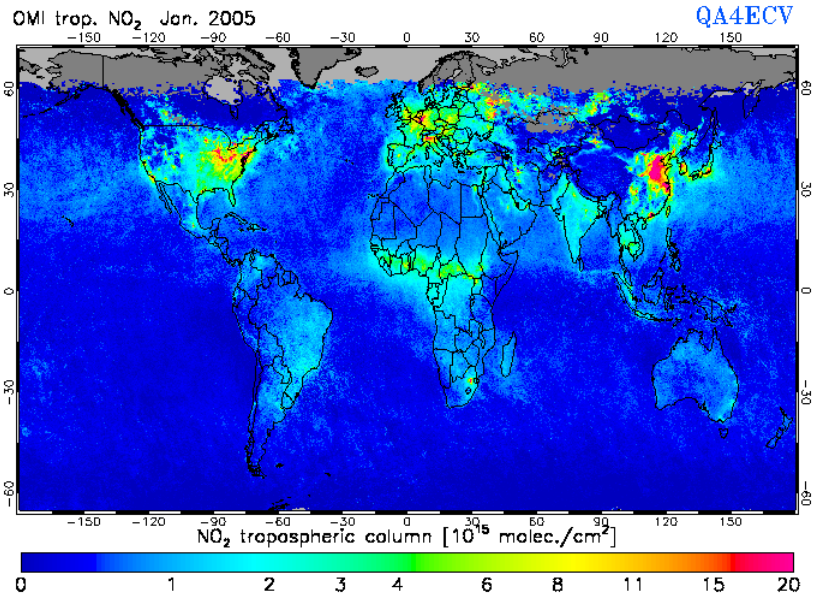
1990-2017 emission trends in MEIC database: NOx

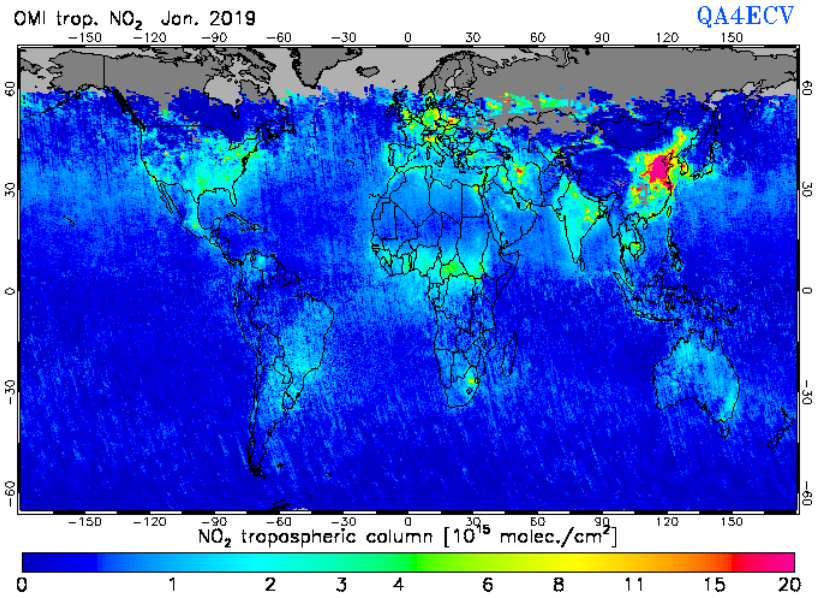


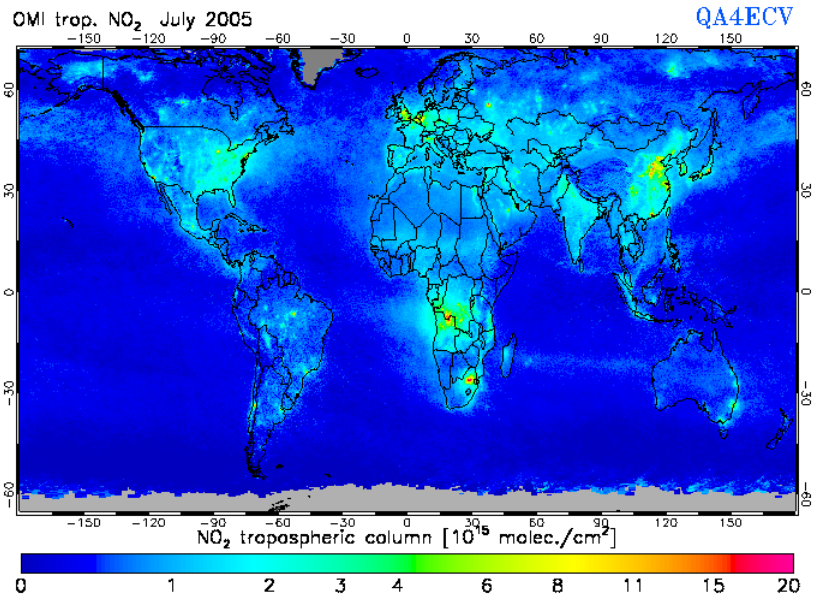


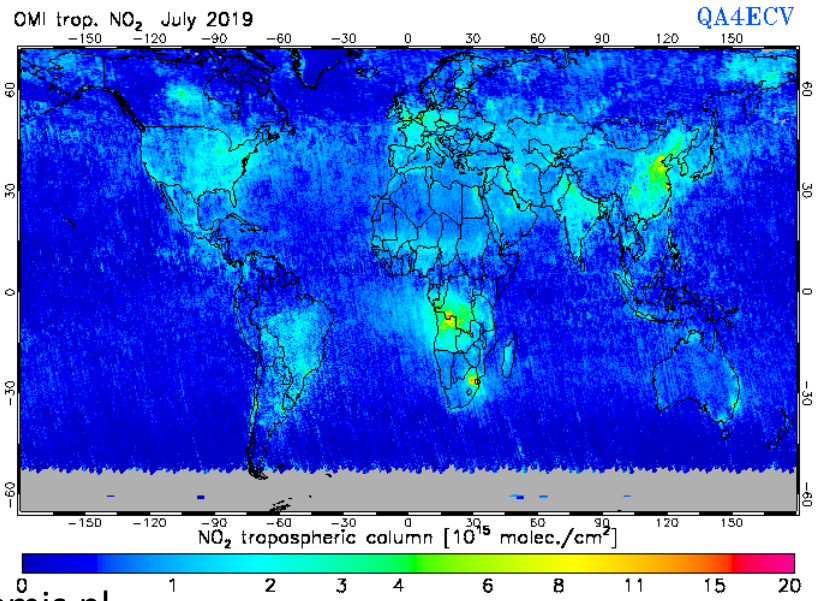
Qiang Zhang; Zheng et al., 2018

Tropospheric NO_2 Column: 2005-2019

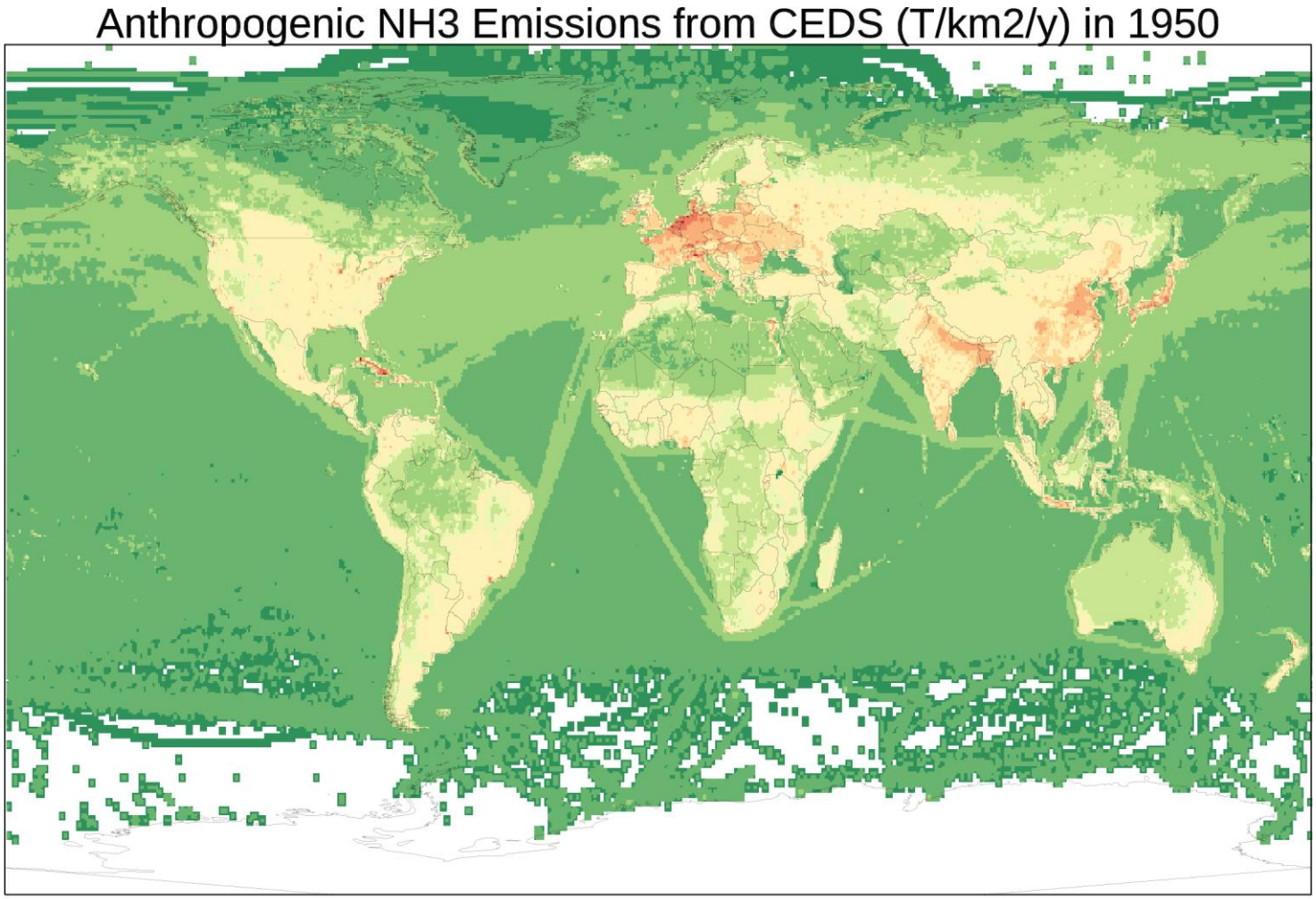




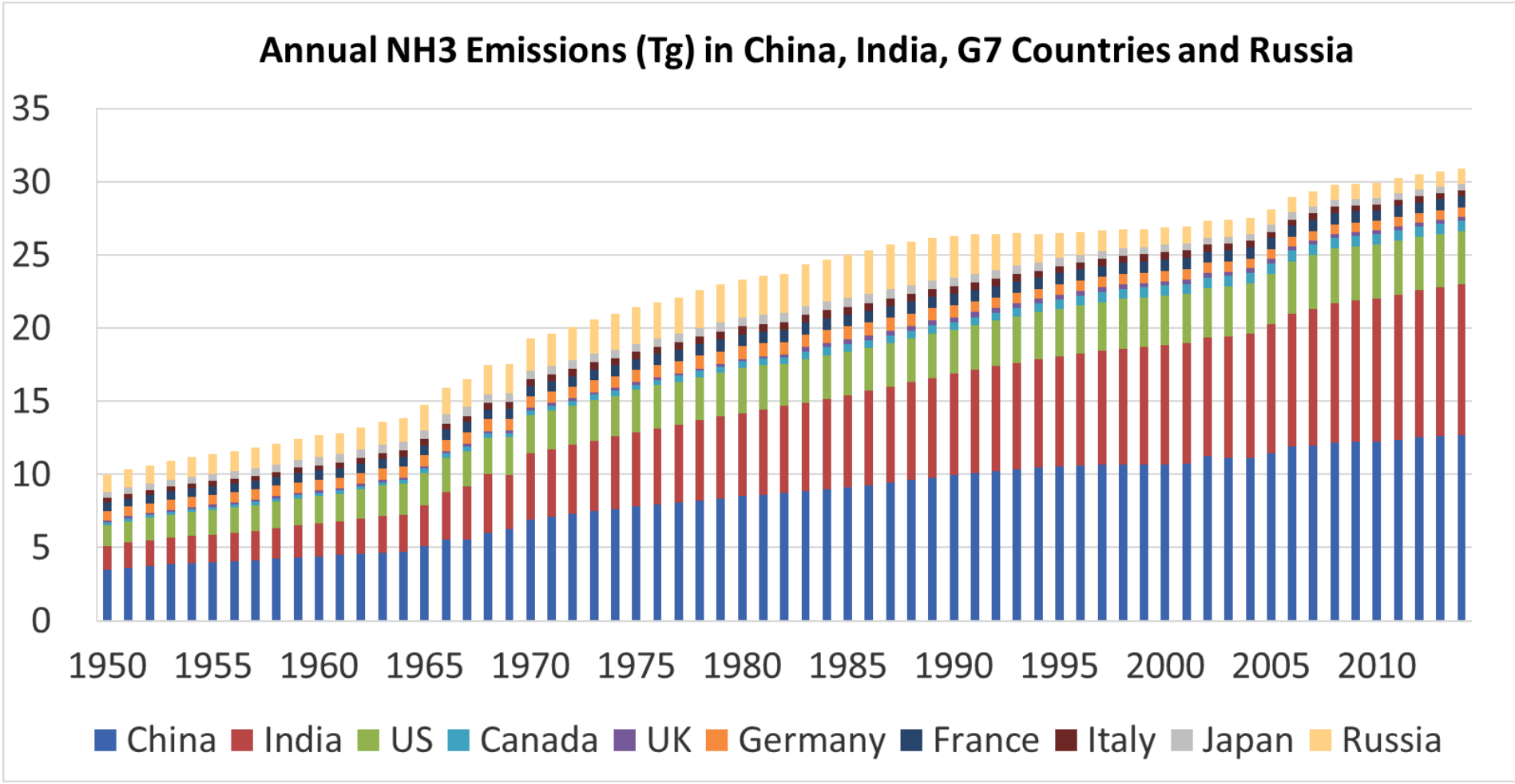




Anthropogenic NH_3 Emissions: 1950-2014



Anthropogenic Emissions of NH_3: 1950-2014



CEDS Inventory

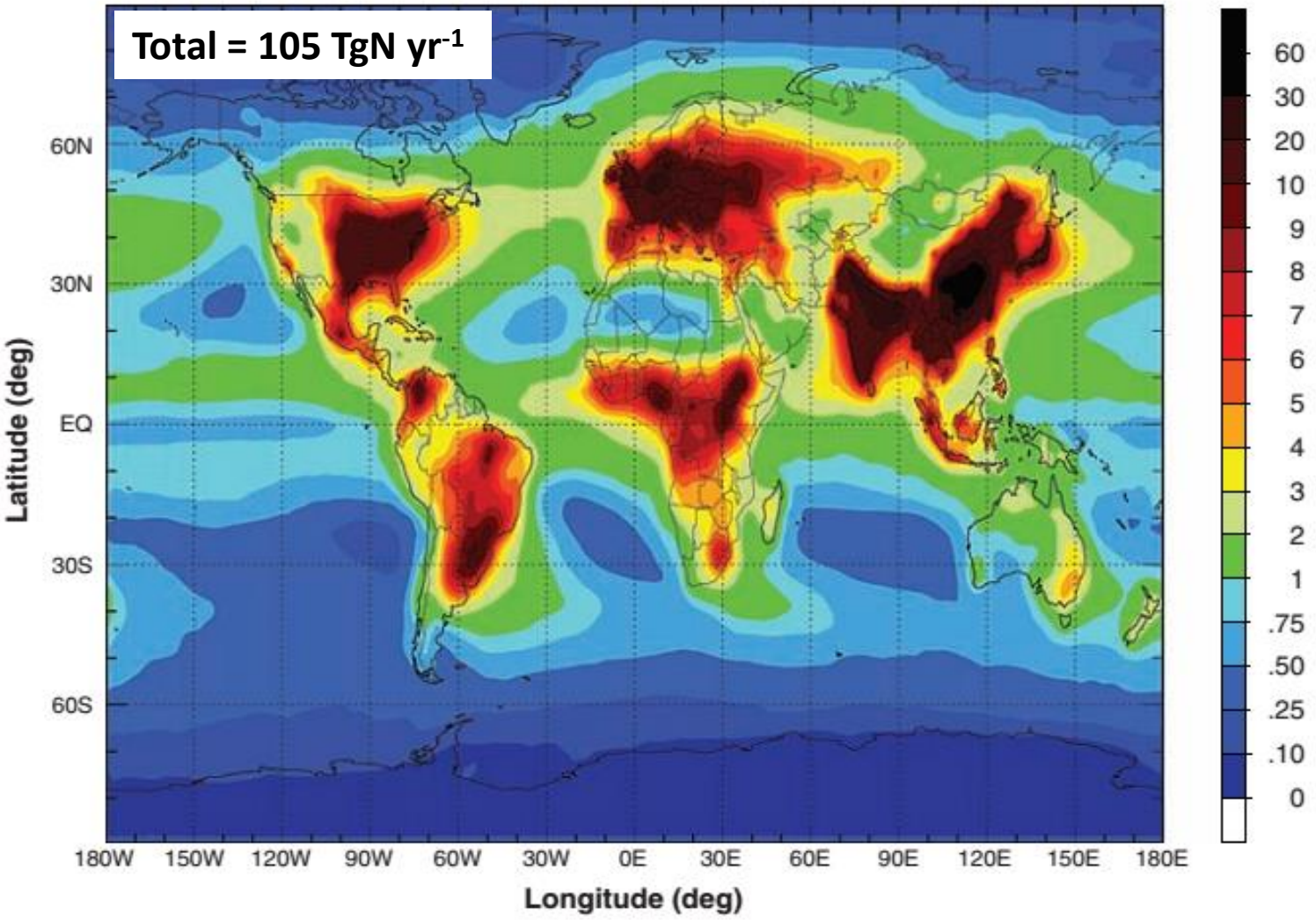
Large Uncertainty in Chinese Anthropogenic NH_3 Emissions

References	Base year	Fertilizer application	Livestock waste	Human	Others[2]	Total
Yan et al. (2003)	1995	4.32	2.48[3]	0.21		7.01
Streets et al. (2003)	2000	6.8	5.17	1.63		13.6
Li and Li (2012)	2004	1.82	8.30	1.67	0.21	12.0
Wang et al. (2009)	2005	4.3	8.82	0.26		13.38
Zhang et al. (2011)	2005	4.31				
Dong et al. (2010)	2006	8.68	6.61	0.65	0.14	16.08
Huang et al. (2012)	2006	3.2	5.3	0.2	1.1	9.8
Cao et al. (2010)	2007	3.62	9.58		2.8	16.0
EDGAR	2008	8.1	3.1	0.1		11.3
Xu et al. (2016)	2008	3.3	3.8[3]	0.7	0.6	8.4
Paulot et al. (2014) (MASAGE)	2008	3.6	5.8	0.8		10.2
Kurokawa et al. (2013) (REAS v2)	2008	9.46	2.88	1.81	0.85	15.0
Zhao et al. (2013)	2010	9.82	7.36	1.12		18.3
Fu et al. (2015)	2011	3				
Kang et al. (2016)	2012	2.8	4.99	0.12	1.71	9.62
Zhang et al. (2017)	2008	5.05	5.31	1.30[4]		11.7

Zhang et al., 2017, ACP

Global Nitrogen (NOy+NHx) Deposition

NOy+NHx deposition in 2000 (kg N ha^{-1} yr^{-1})



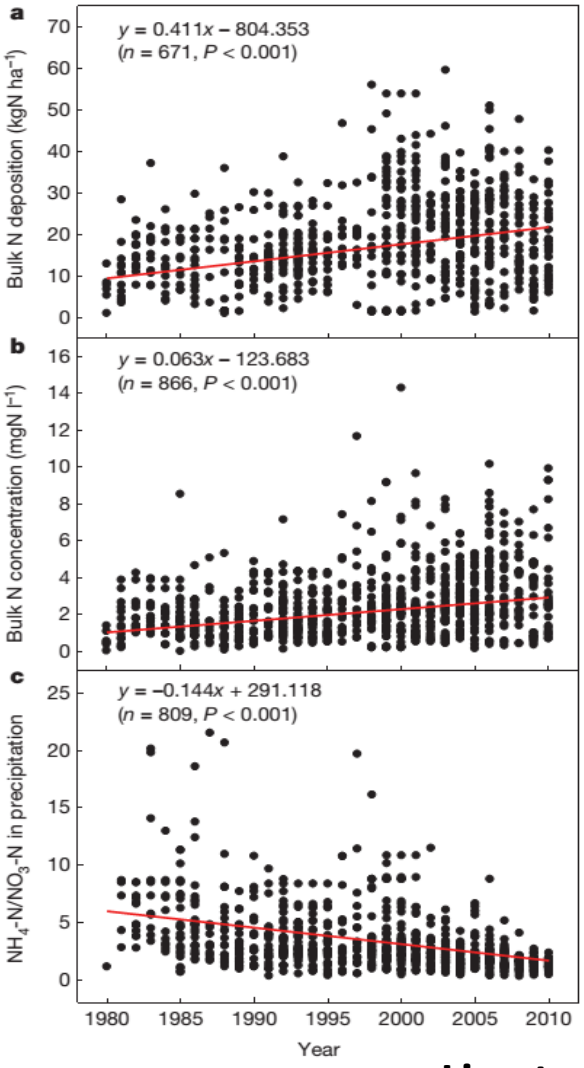
Dentener et al., 2006, GBC; Galloway et al., 2008, Science

Increasing Bulk N Deposition in China

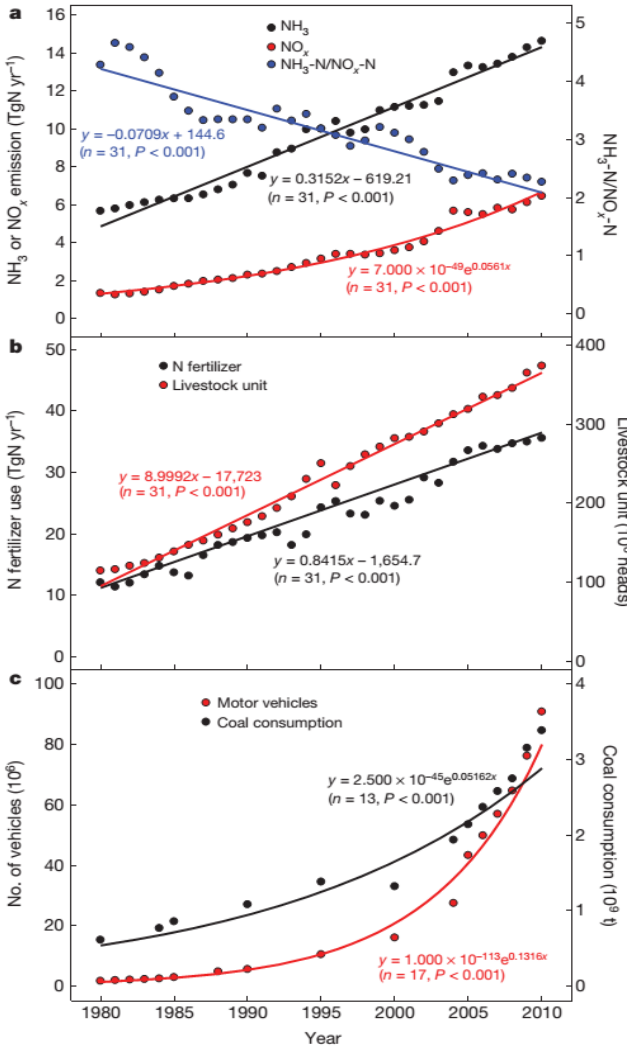
Wet + some Dry

Mostly inorganic

Deposition



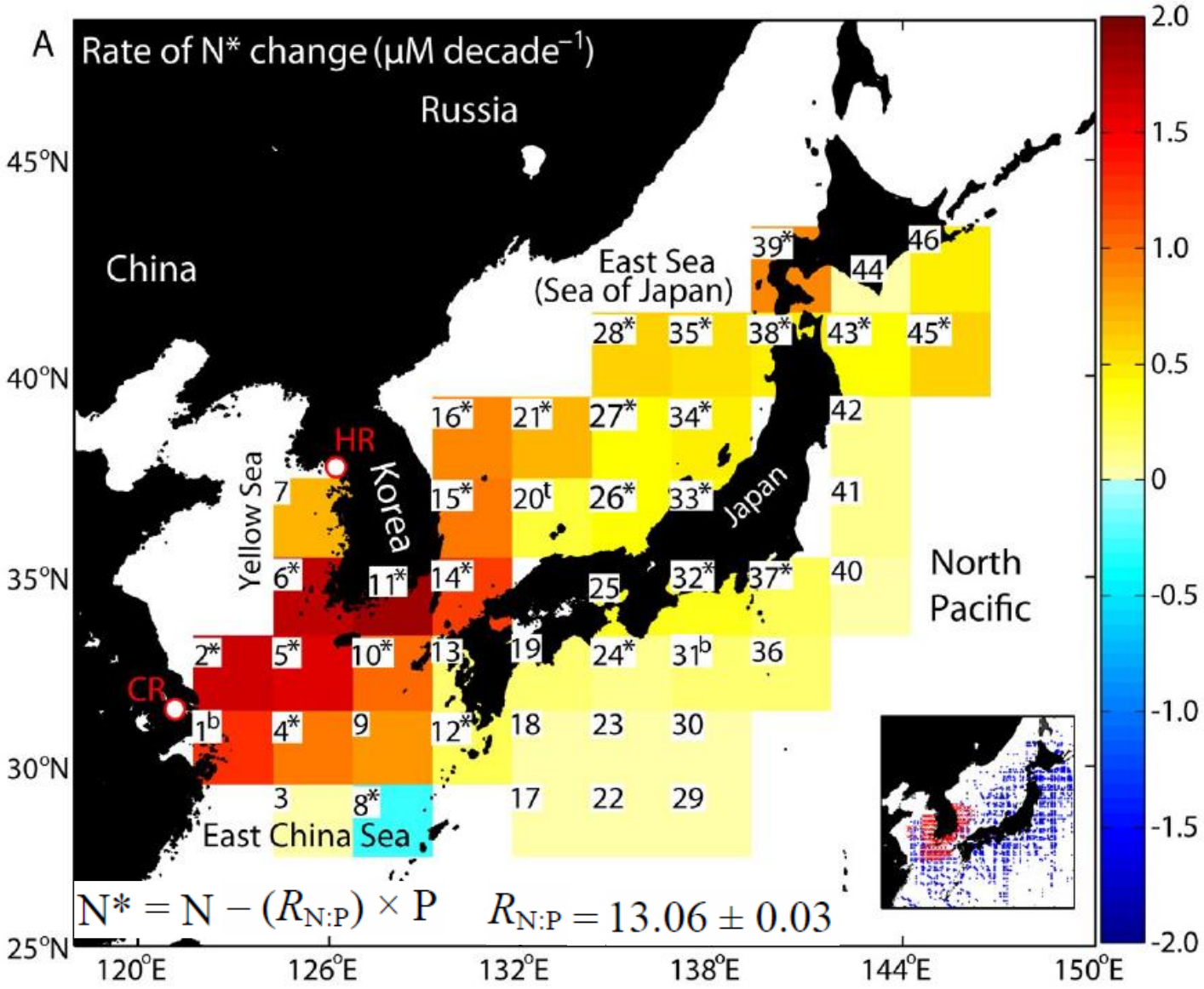
Emissions



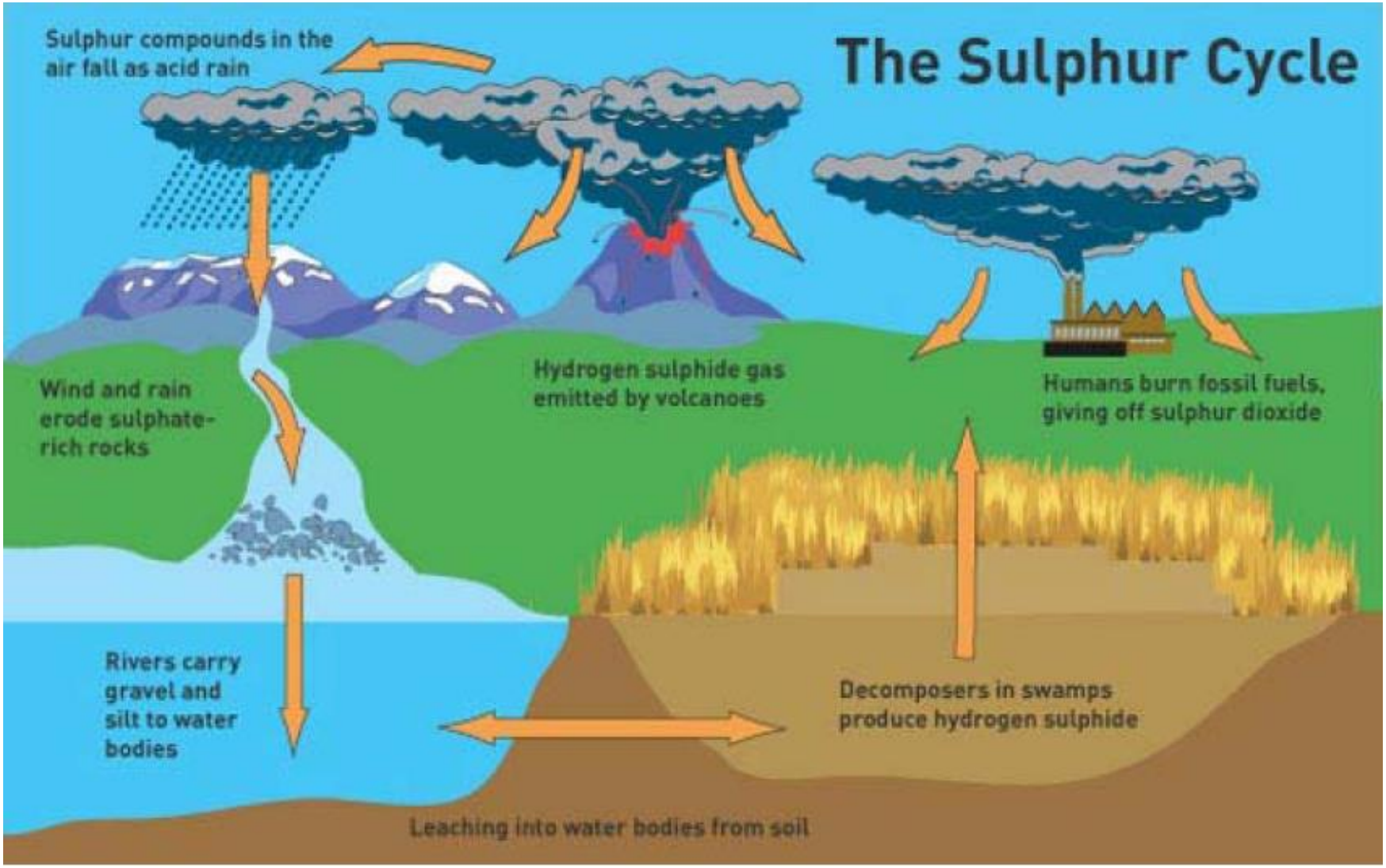
Liu et al., 2013, Nature

N* Concentration in the Ocean: 1980-2010

Kim et al., 2011, Science



Global Sulfur Cycling



Sulfur Species

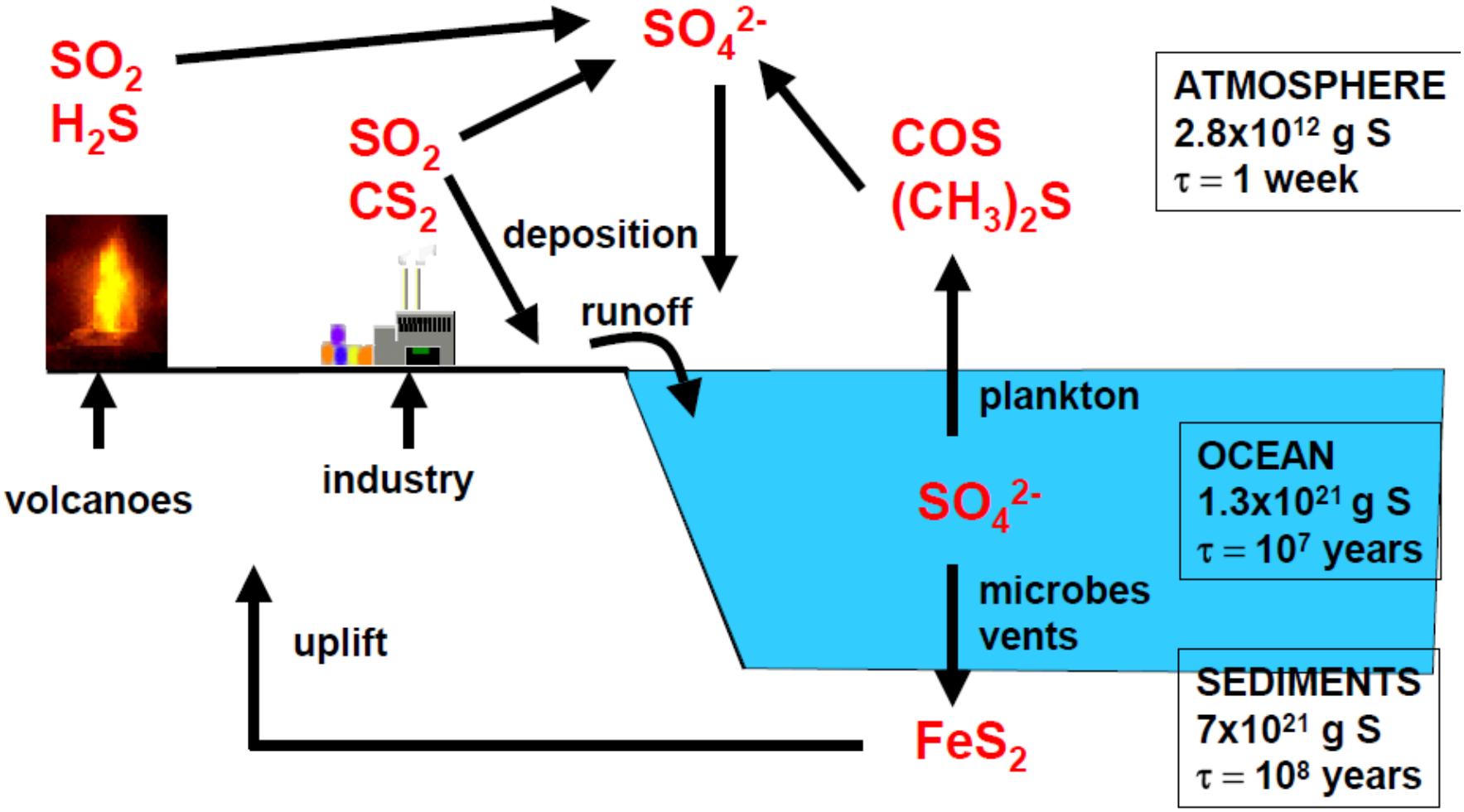
OXIDATION STATES OF SULFUR

S has 6 electrons in valence shell ⇨ oxidation states from –2 to +6

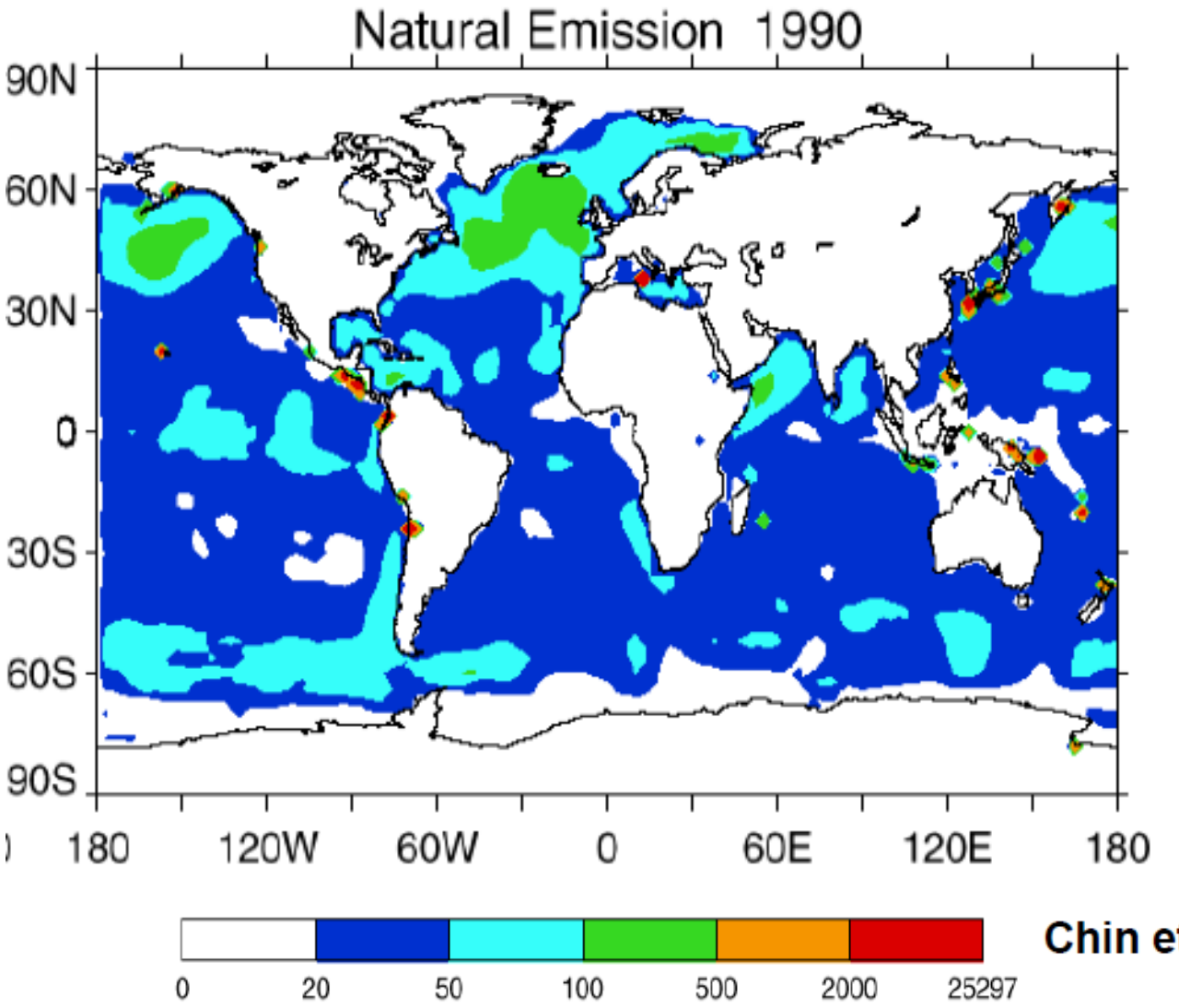
Increasing oxidation number (oxidation reactions)

-2	+4	+6
FeS_2 Pyrite H_2S Hydrogen sulfide $(CH_3)_2S$ Dimethylsulfide (DMS) CS_2 Carbon disulfide COS Carbonyl sulfide	SO_2 Sulfur dioxide	H_2SO_4 Sulfuric acid SO_4^{2-} Sulfate

Global Sulfur Cycle

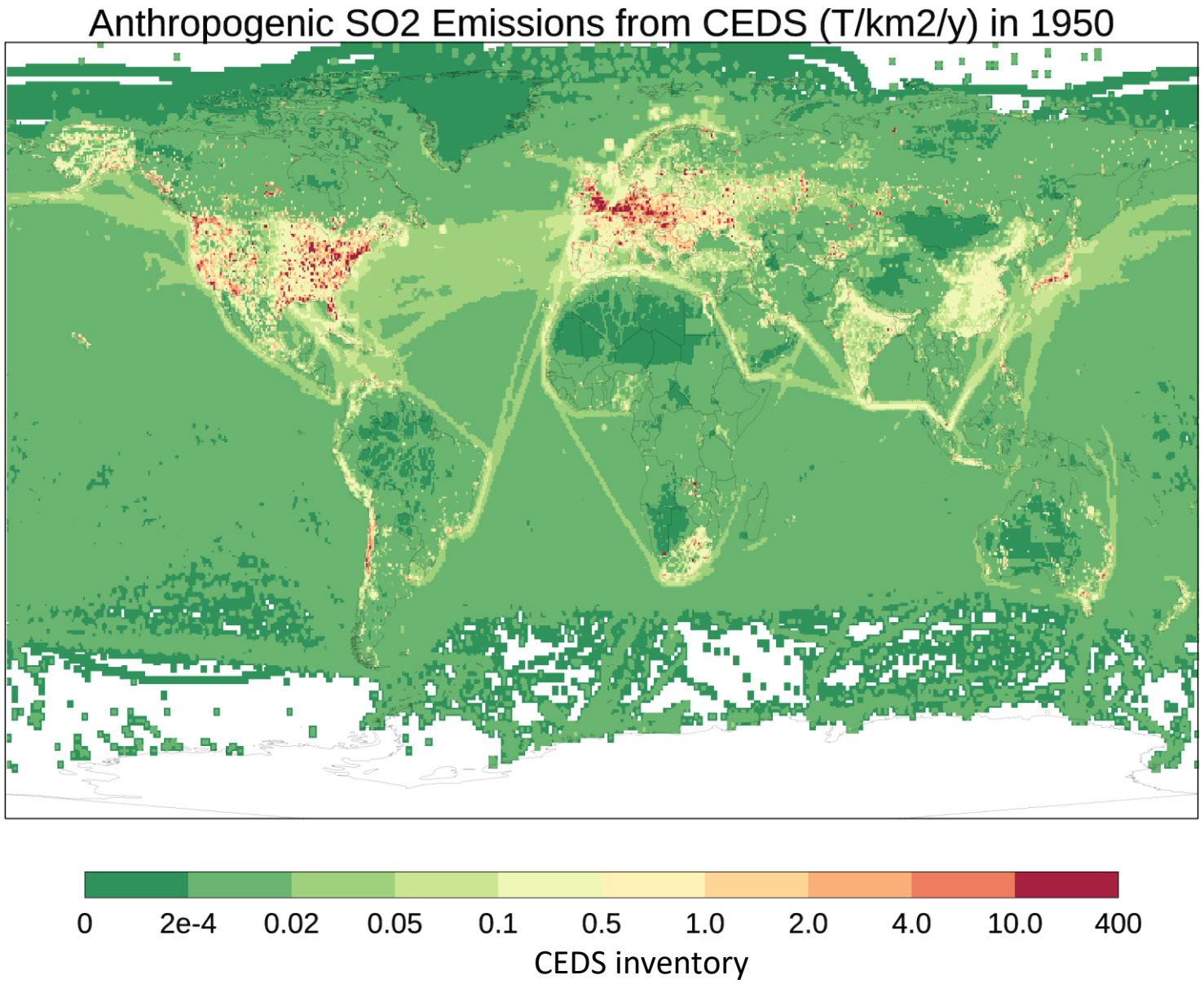


Natural Sulfur Emissions

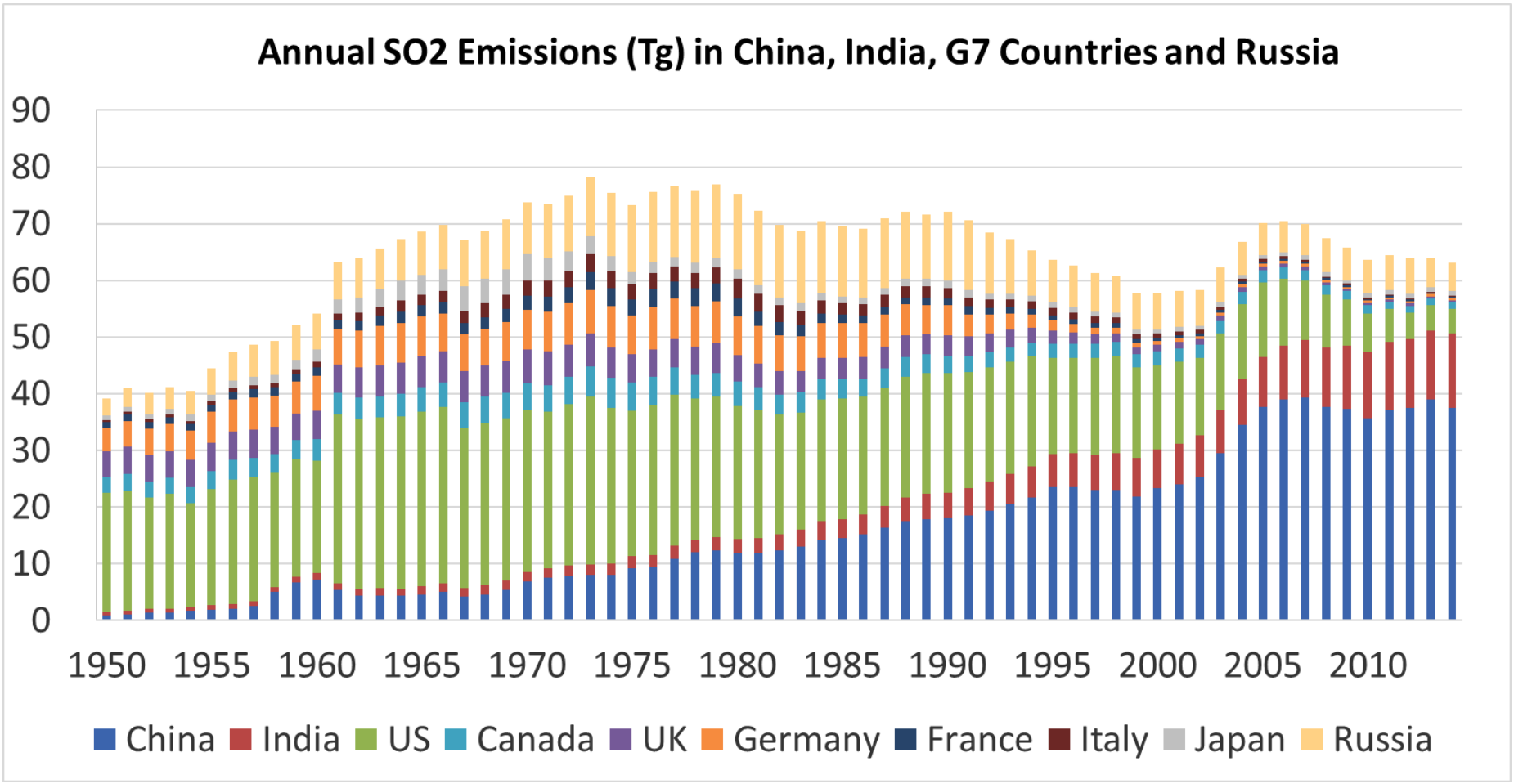


Chin et al. [2000]

Anthropogenic SO_2 Emissions: 1950-2014

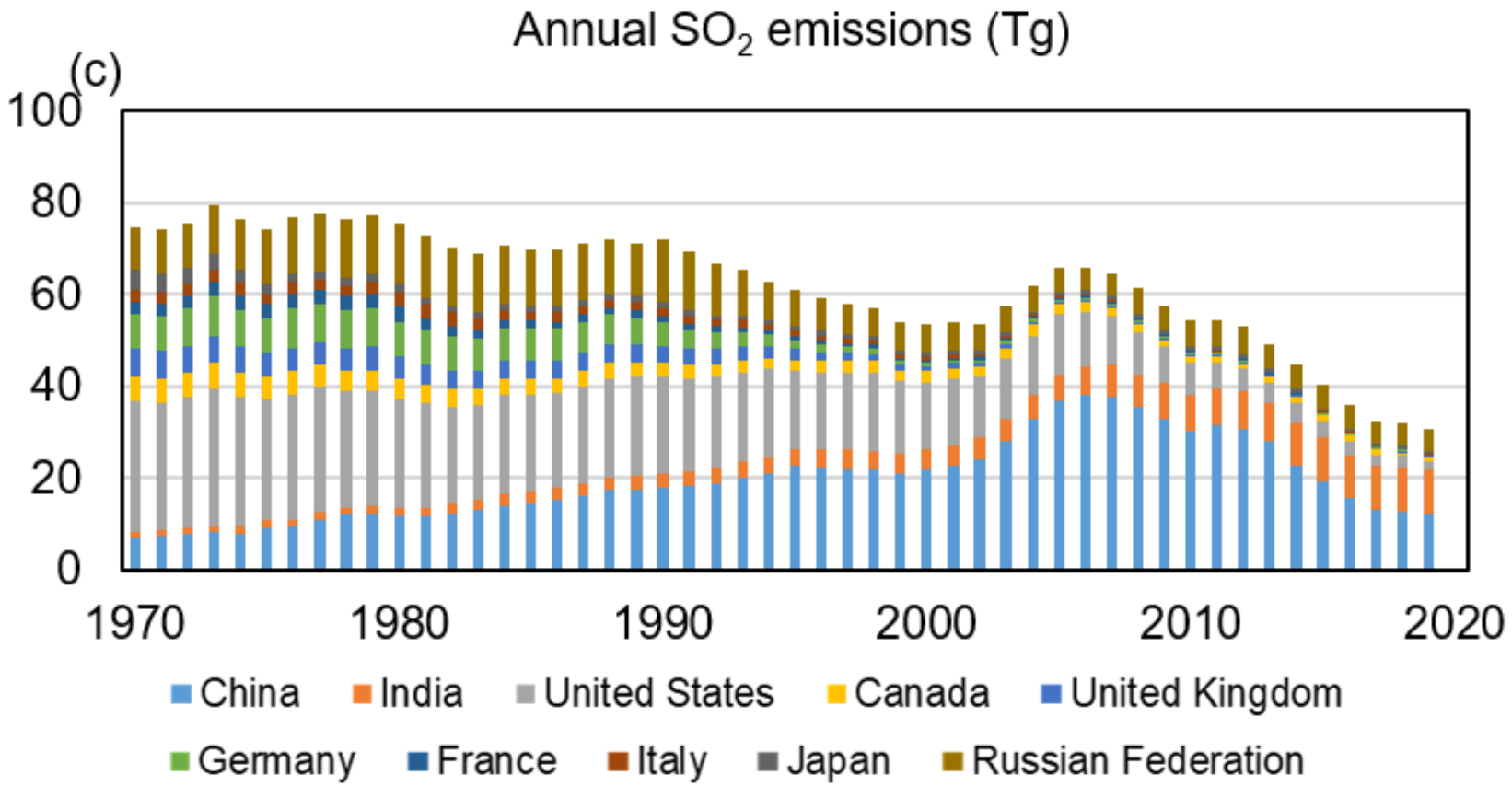


Anthropogenic Emissions of SO_2: 1950-2014



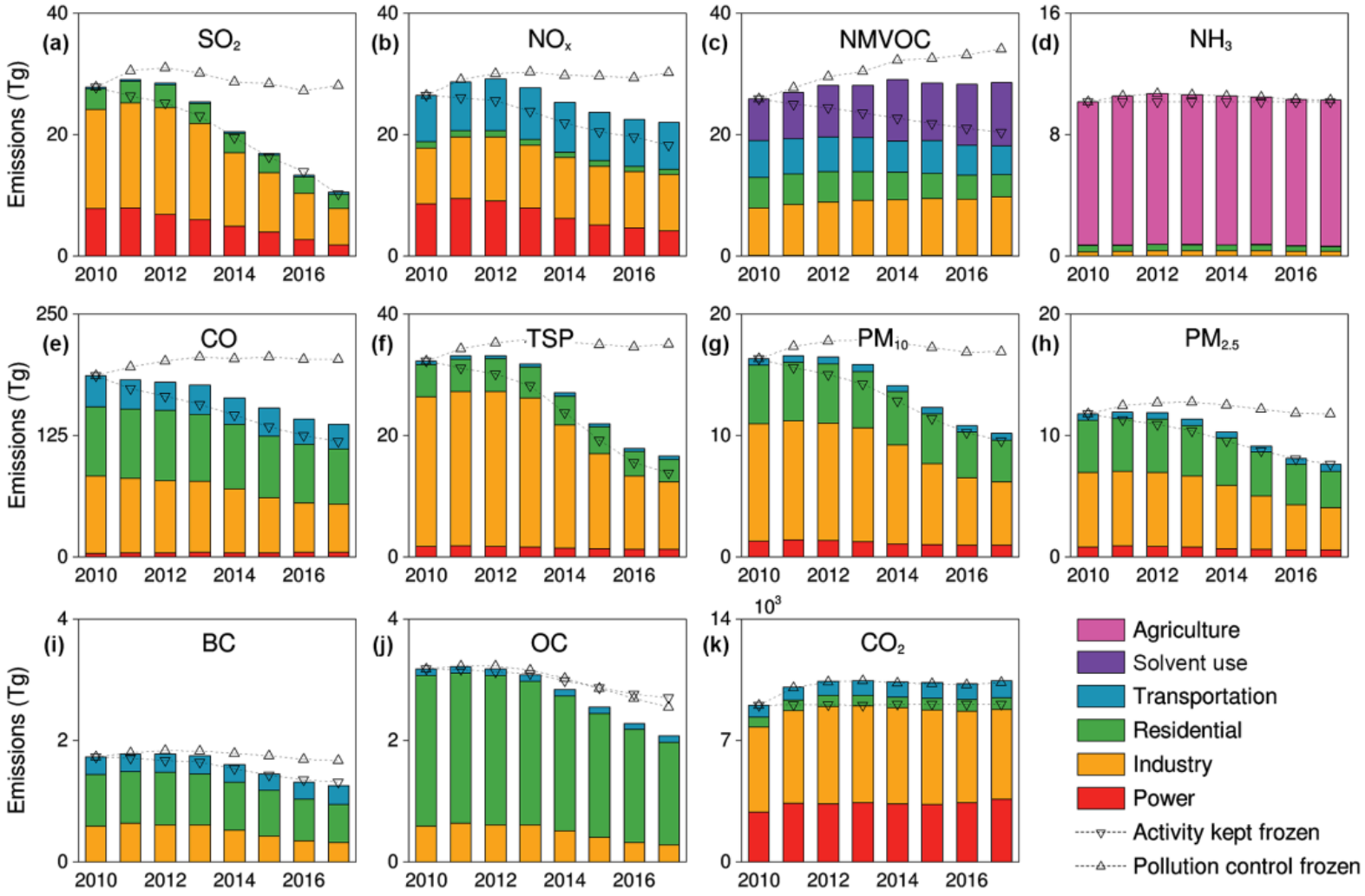
CEDS inventory

Anthropogenic Emissions of SO_2: 1970-2019



CEDS-GBD-Map

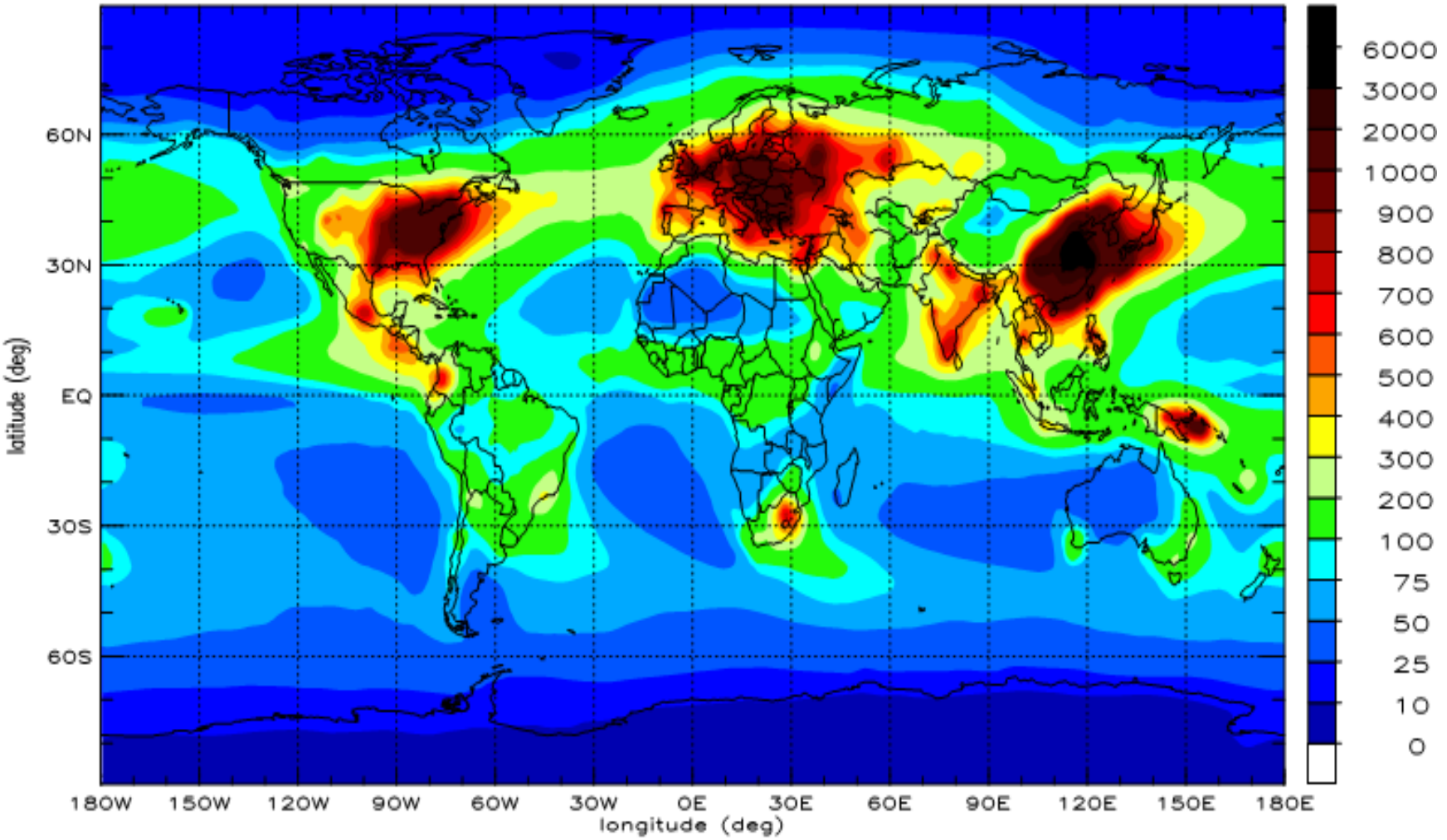
Anthropogenic Emissions in China: 2010-2017



Zheng et al., ACP, 2018

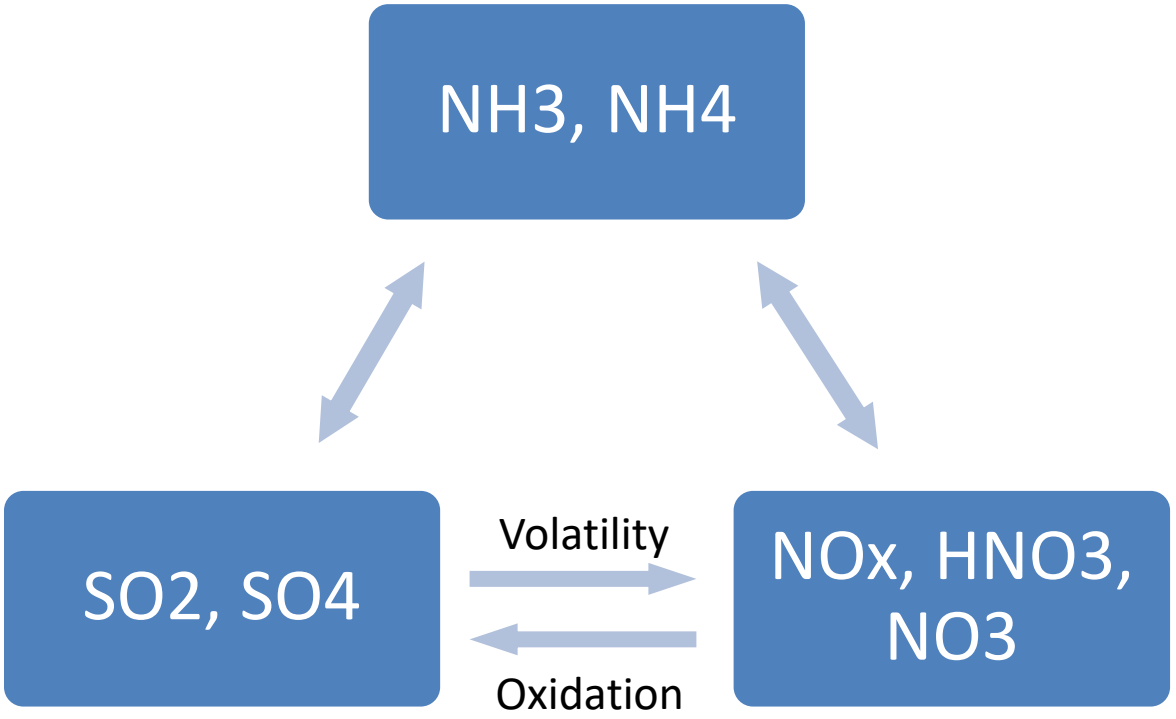
Global Sulfur Deposition

SOx deposition in 2000 (mg S m^{-2} yr^{-1})

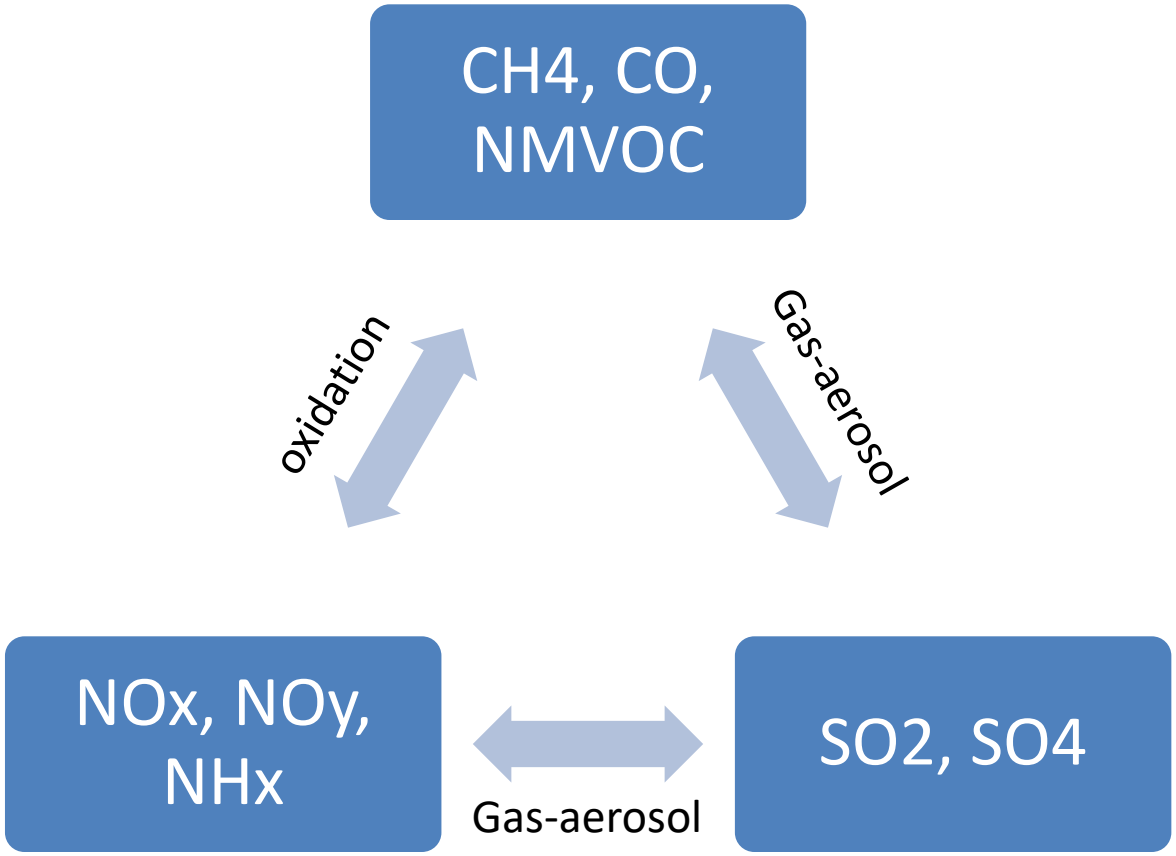


Dentener et al., 2006, GBC

Sulfate-Nitrate-Ammonium Interactions



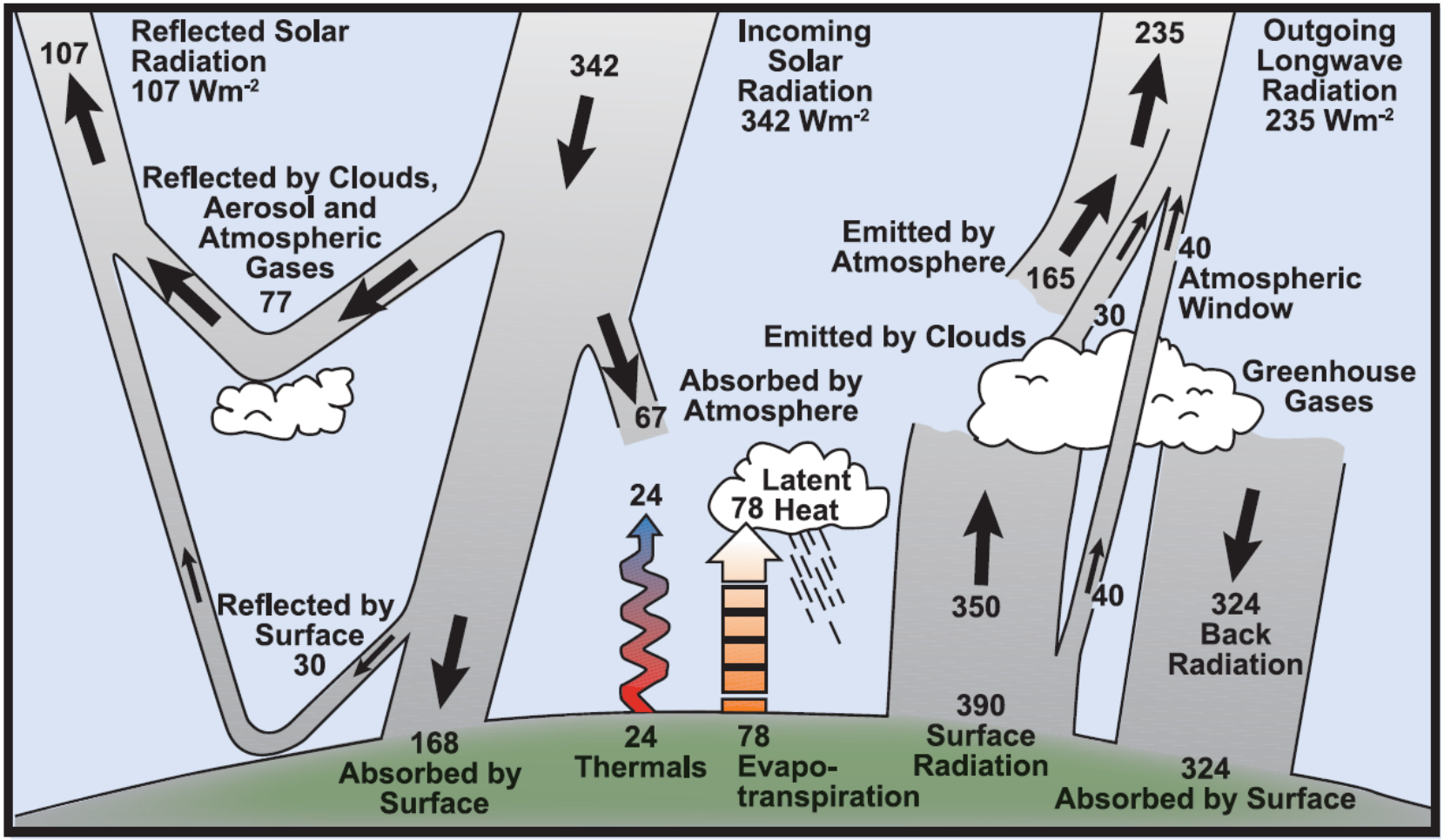
Carbon-Nitrogen-Sulfur Interactions

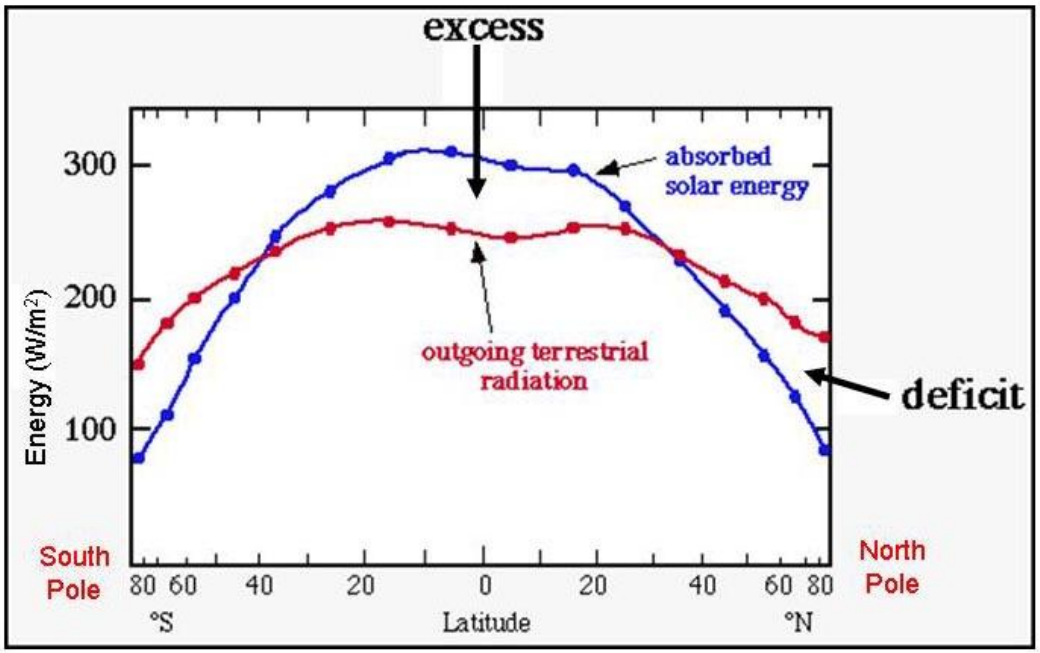


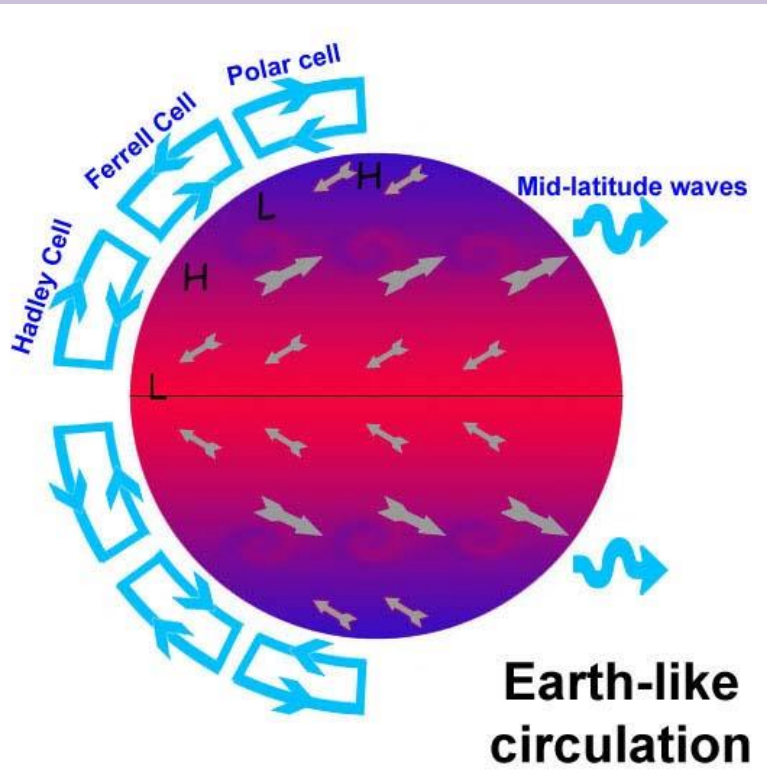
Quiz

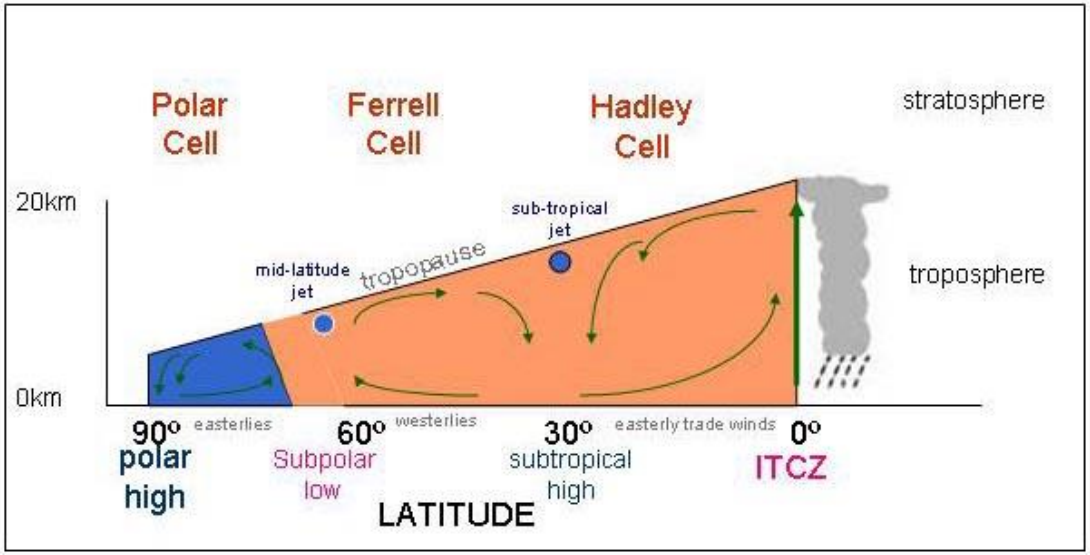
1. Causes of slowdown and resumption of CH4 growth
2. Causes of horizontal distribution in sulfur emissions from oceans
3. Why does deposition of N and S resemble their emissions

Energy Budget of Earth Climate



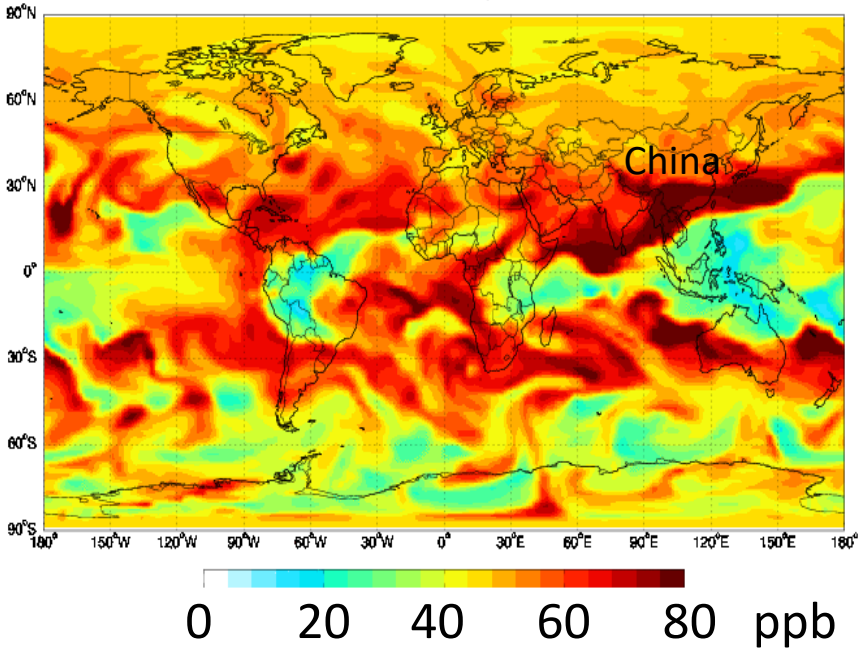

excess
absorbed solar energy
outgoing terrestrial radiation
deficit
Energy (W/m²)
300
200
100
South Pole
North Pole
80 60 40 20 0 20 40 60 80
°S
Latitude
°N


Polar cell
Ferrell Cell
Hadley Cell
Mid-latitude waves
H
L
H
L
Earth-like circulation

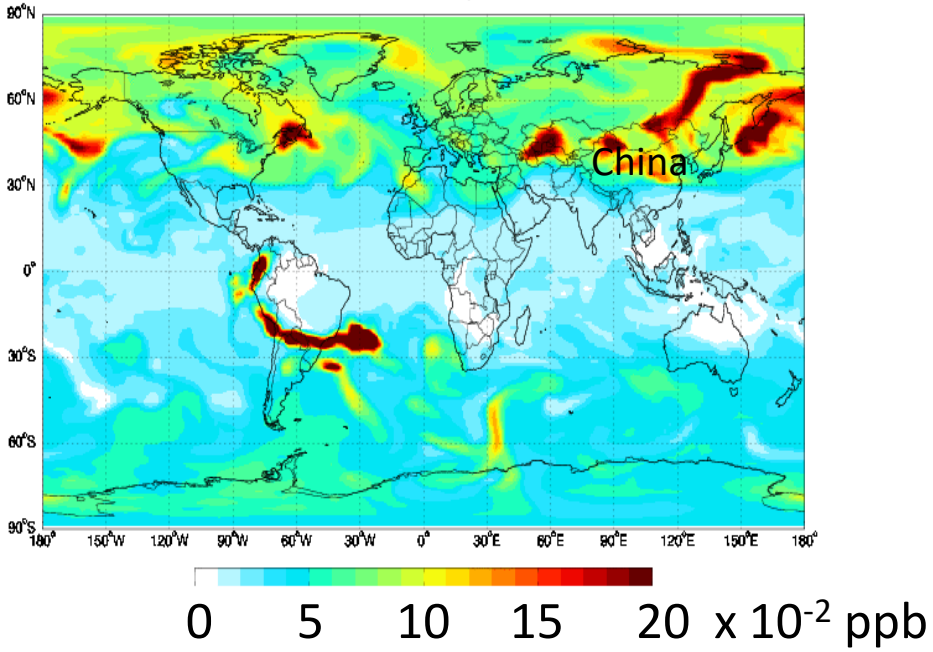

Polar Cell
Ferrell Cell
Hadley Cell
stratosphere
troposphere
20km
0km
sub-tropical jet
mid-latitude jet
tropopause
90° easterlies
polar high
60° westerlies
Subpolar low
30° easterly trade winds
subtropical high
0°
ITCZ
LATITUDE

Atmospheric Pollution Transport

Ozone in Mid-Trop. in Jan 2009



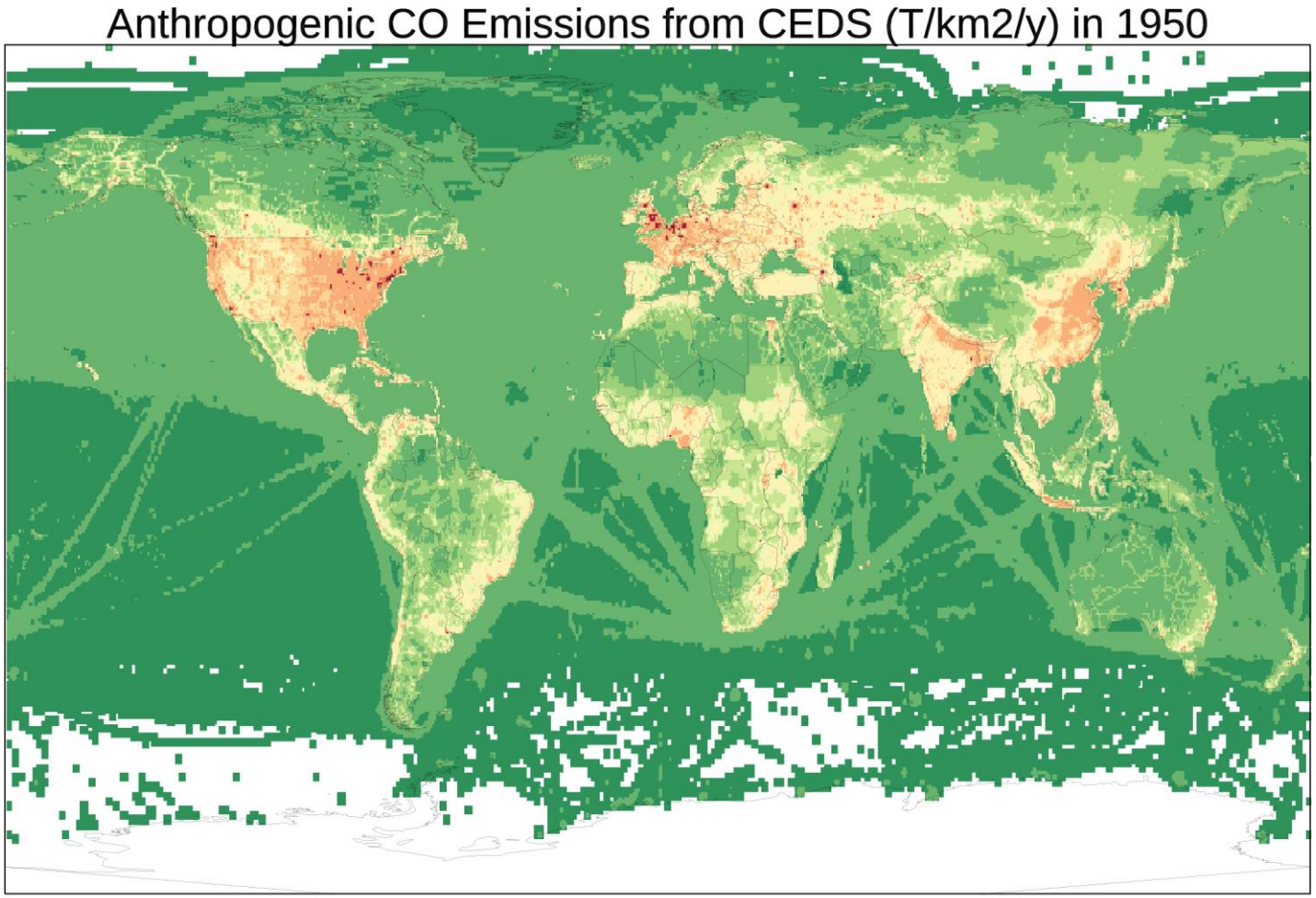
Sulfate in Mid-Trop. in Jan 2009



- **Both local sources and transport of pollution are obvious**
- **The extent of transport depends on emissions, chemistry, etc.**
- **China is both a *source* and a *receptor* region**

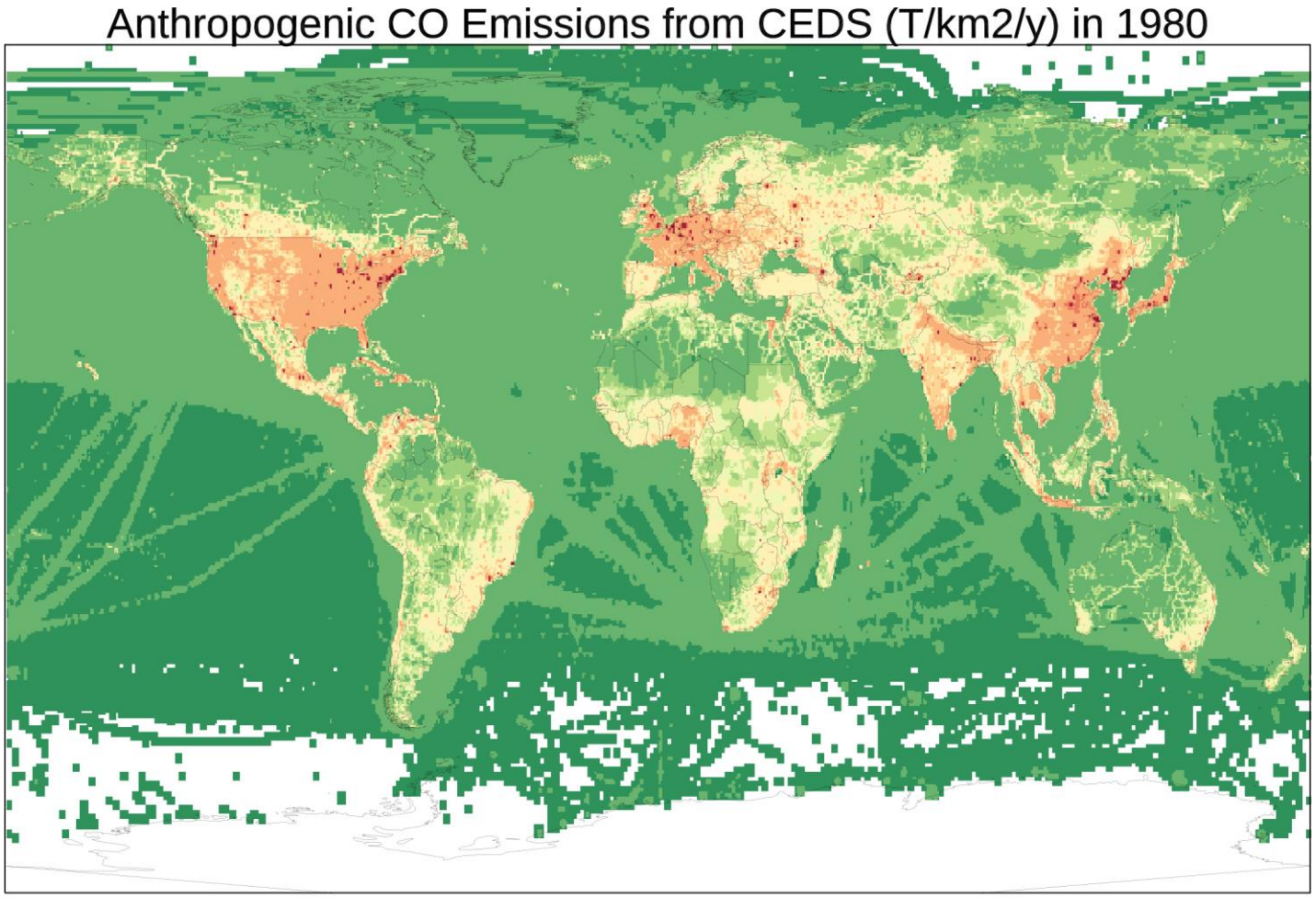
Yan et al., 2014 ACP; 2016 ACP

Anthropogenic Emissions of CO: 1950-2014

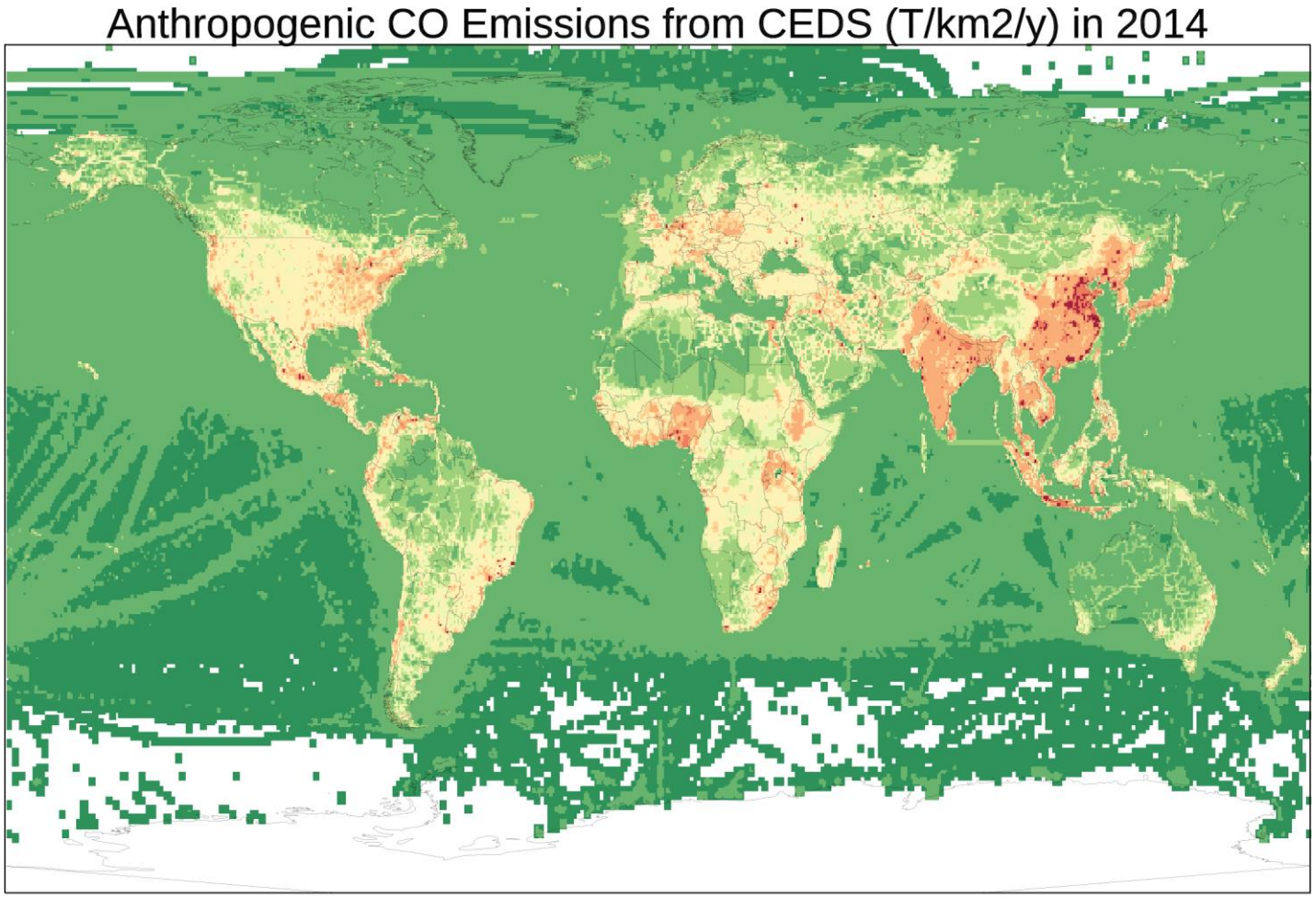


CEDS inventory

Anthropogenic Emissions of CO: 1950-2014

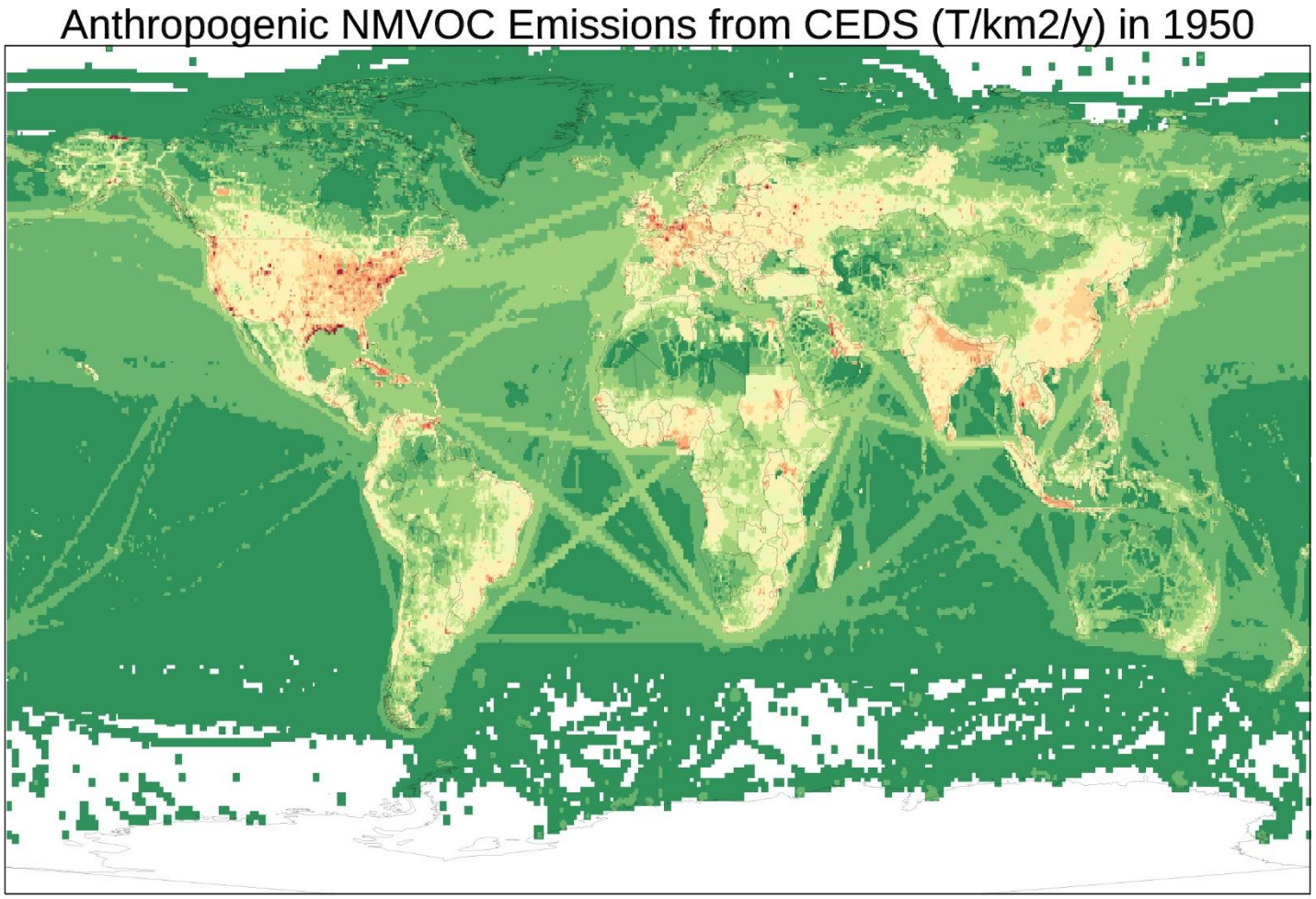


Anthropogenic Emissions of CO: 1950-2014

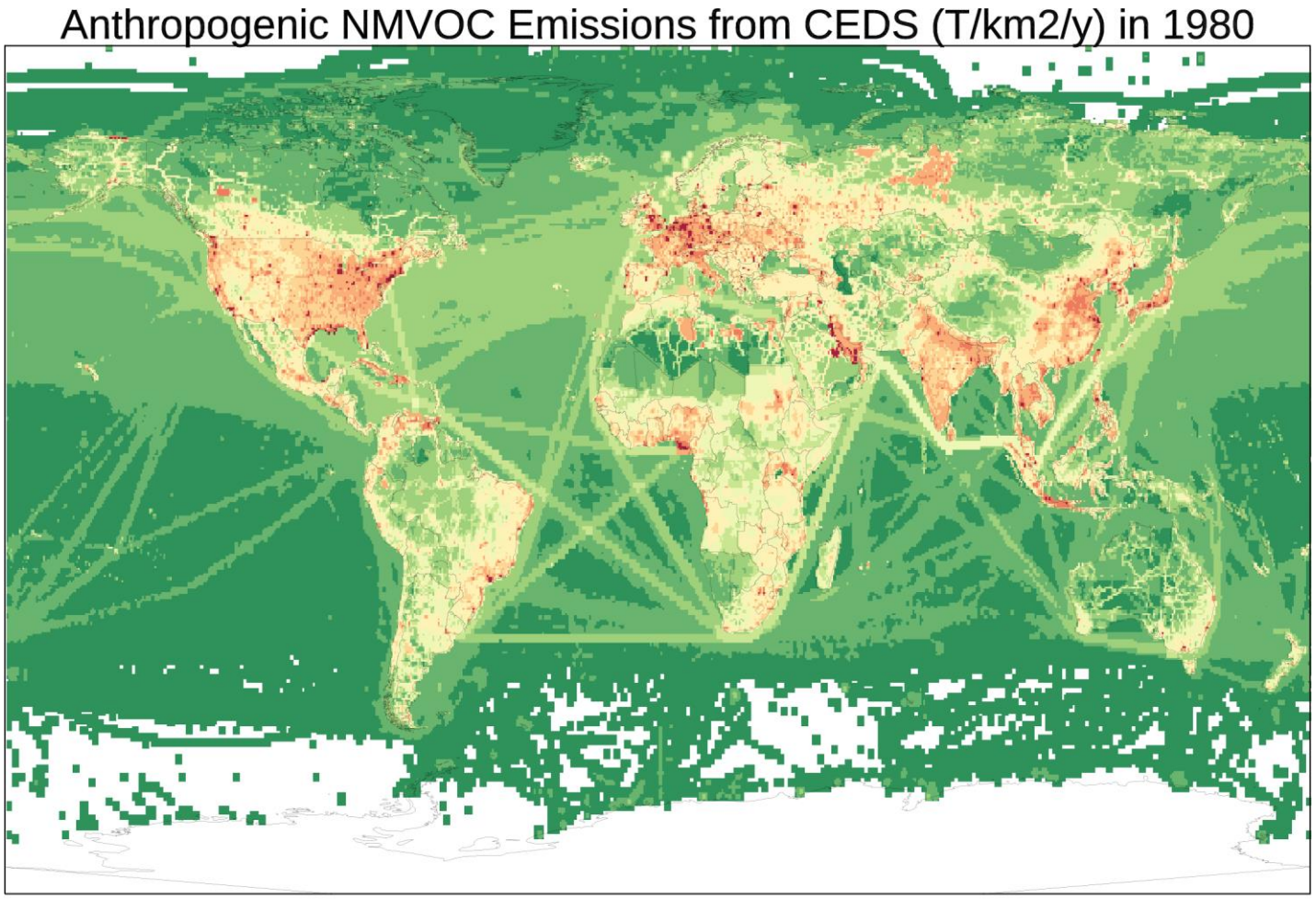


CEDS inventory

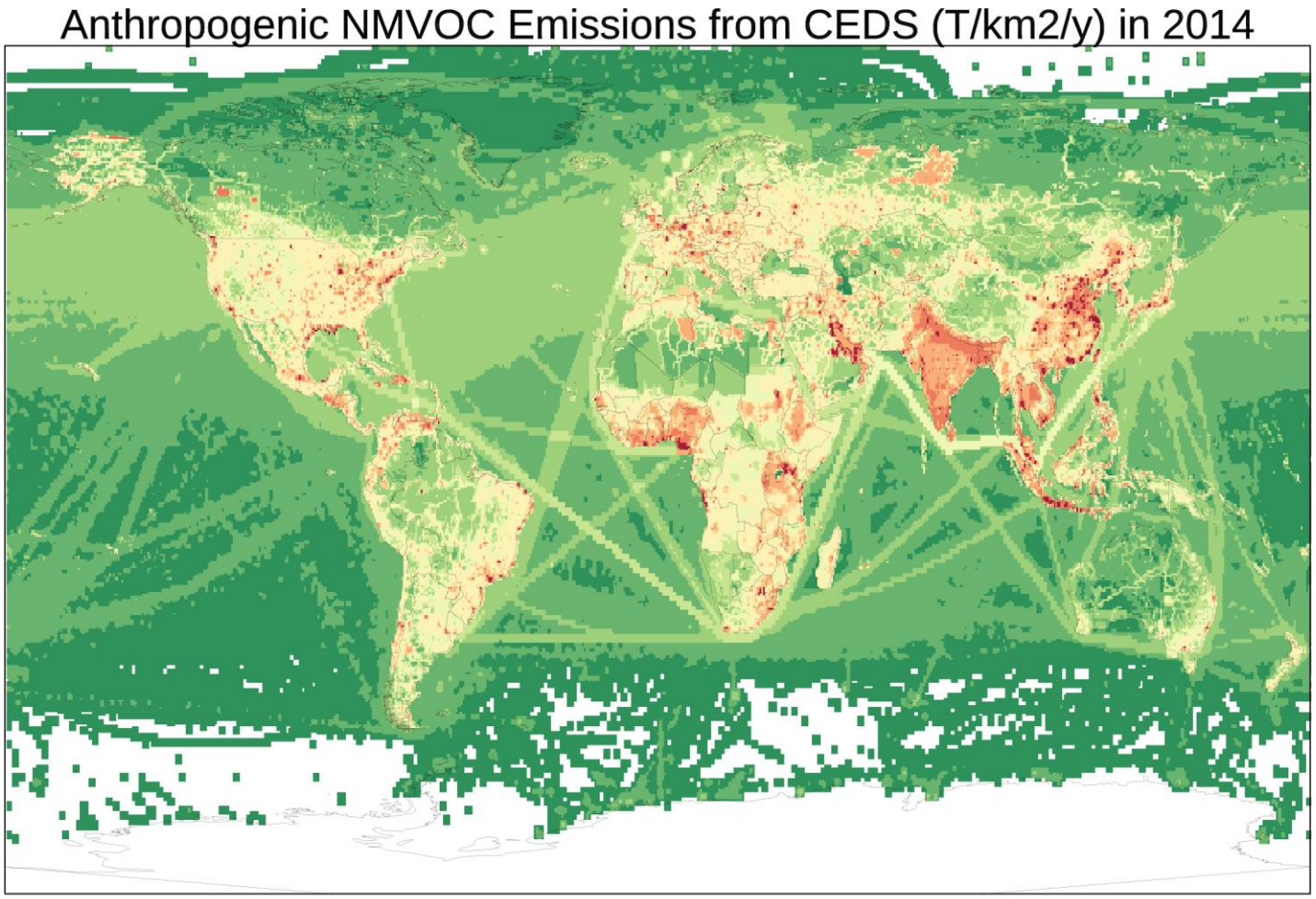
Anthropogenic NMVOC Emissions: 1950-2014



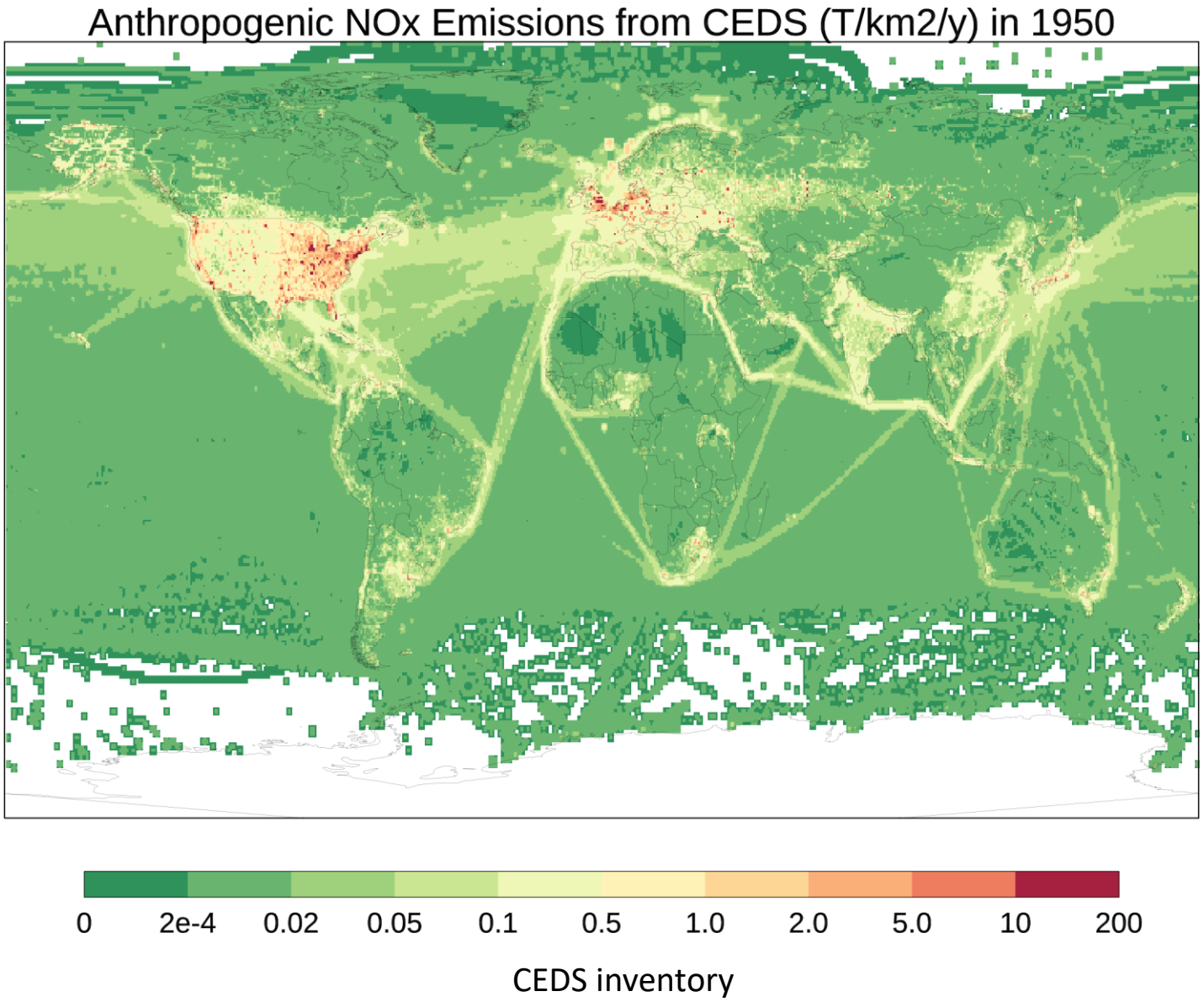
Anthropogenic NMVOC Emissions: 1950-2014



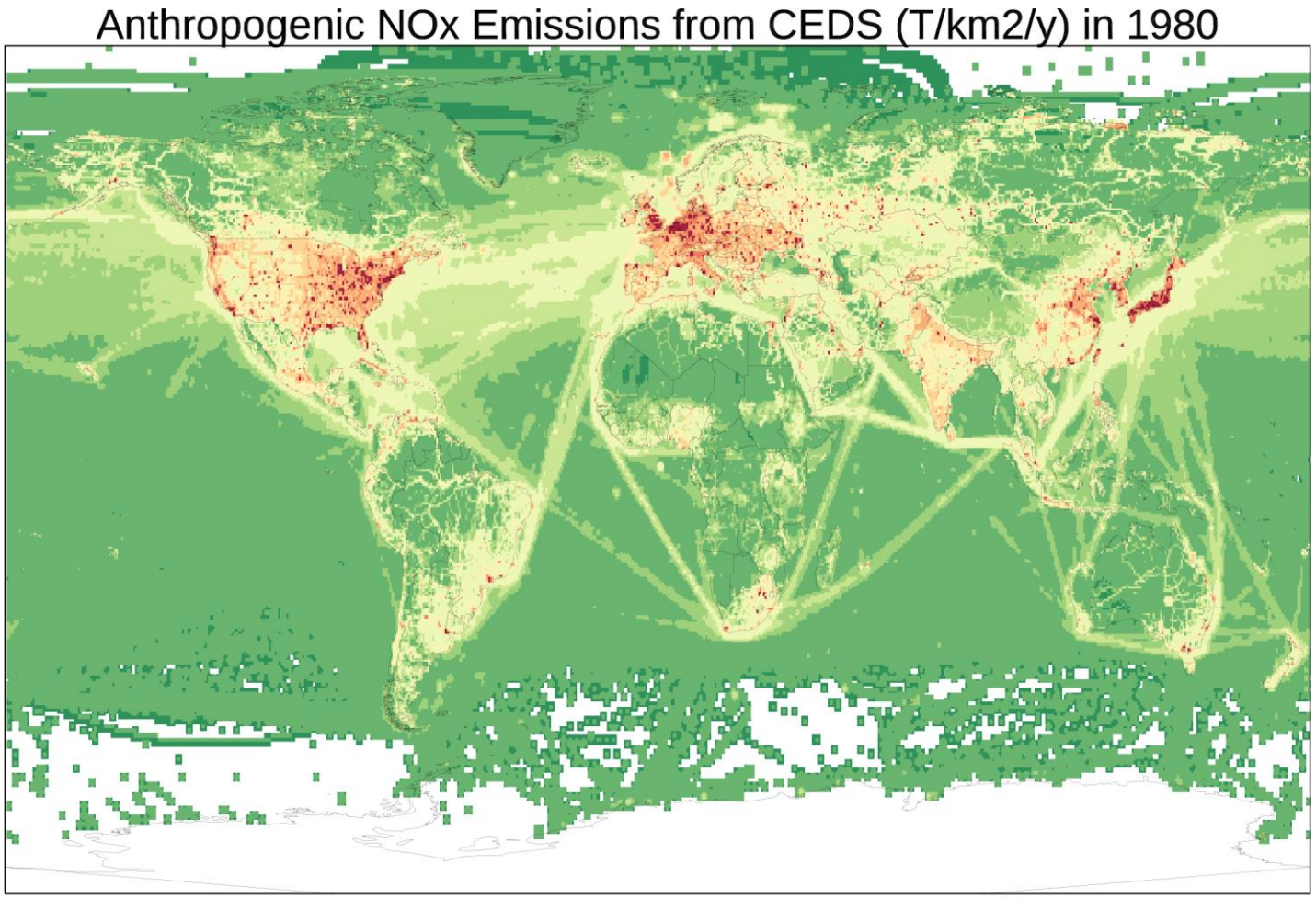
Anthropogenic NMVOC Emissions: 1950-2014



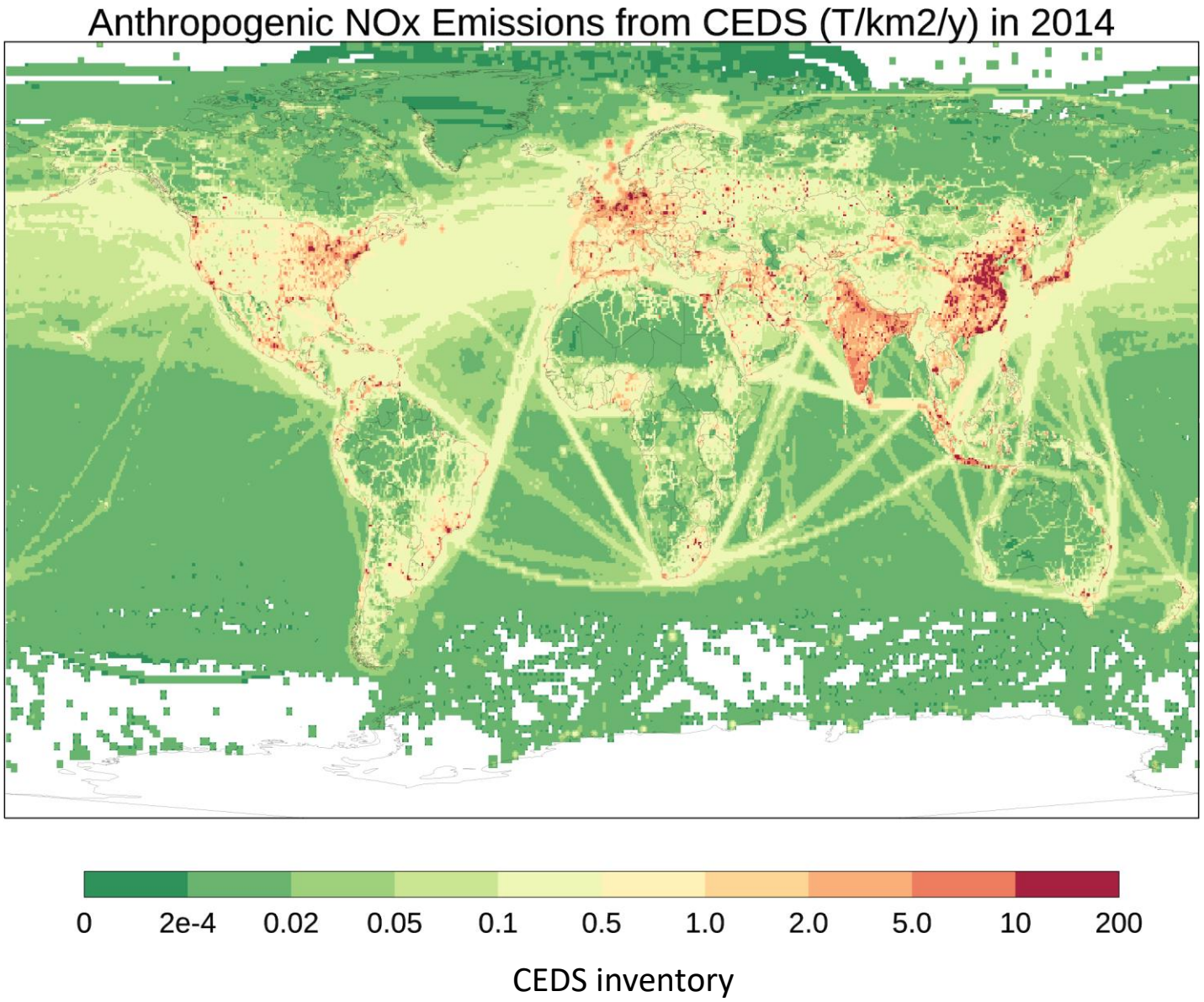
Anthropogenic NOx Emissions: 1950-2014



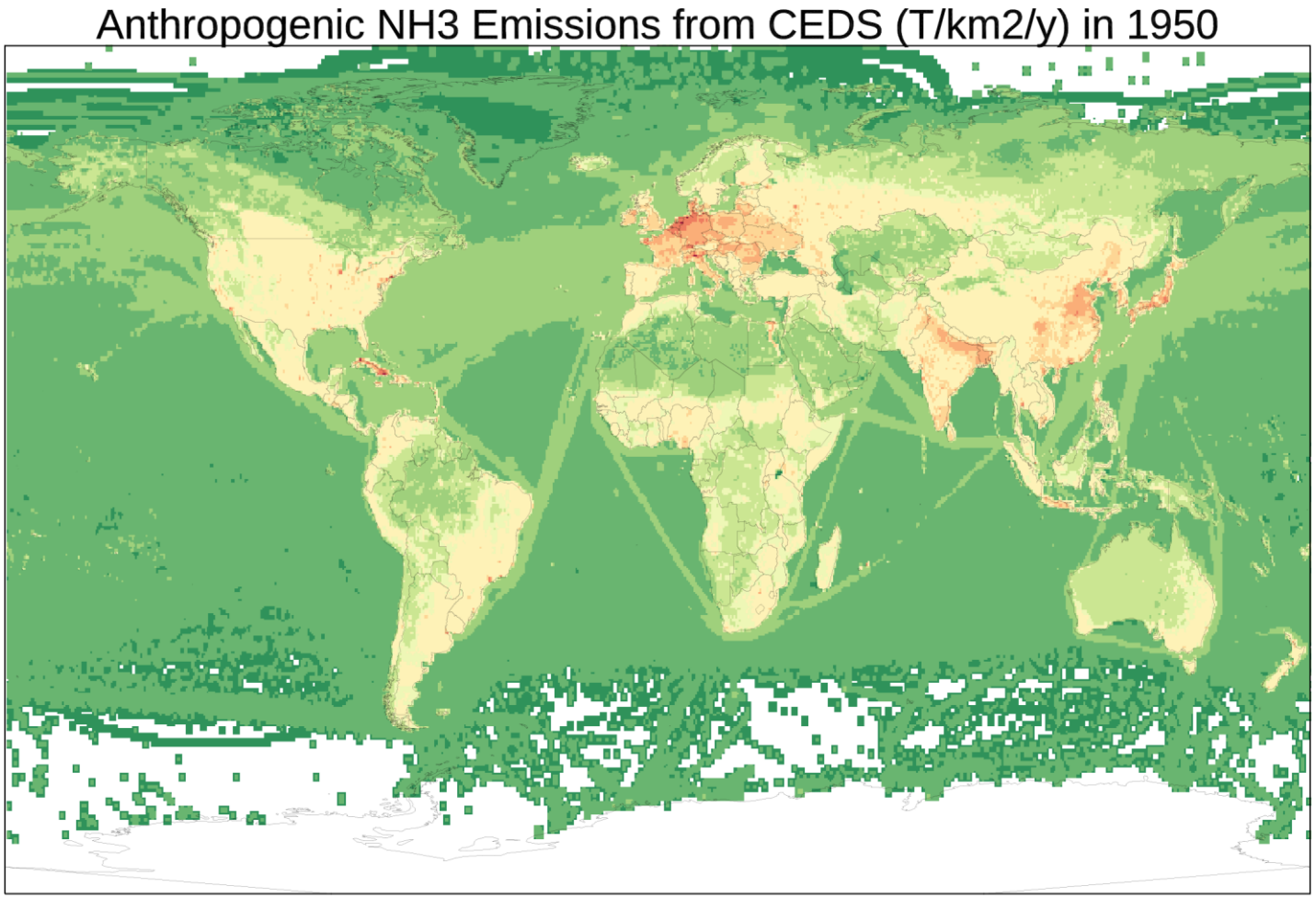
Anthropogenic NOx Emissions: 1950-2014



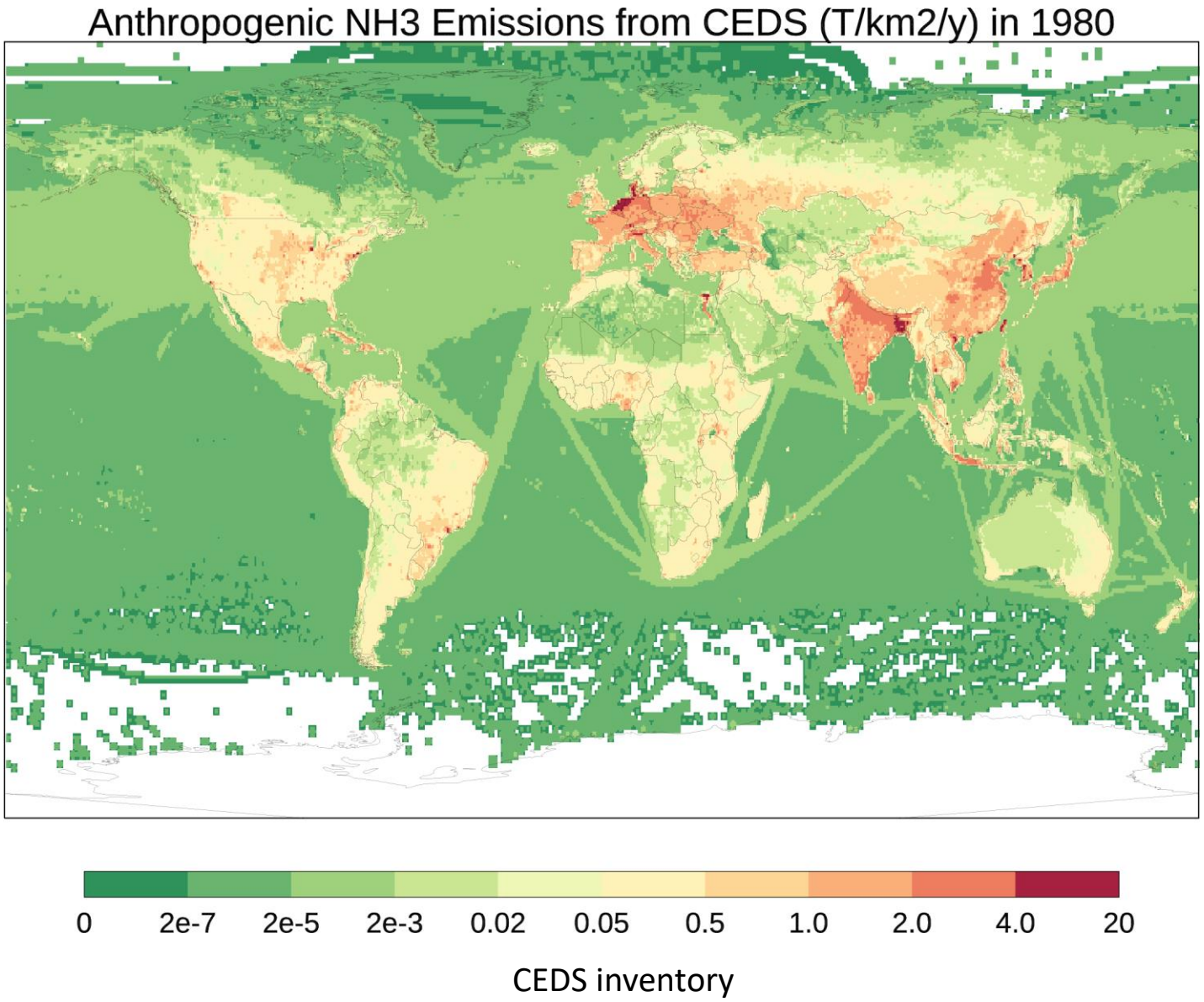
Anthropogenic NOx Emissions: 1950-2014



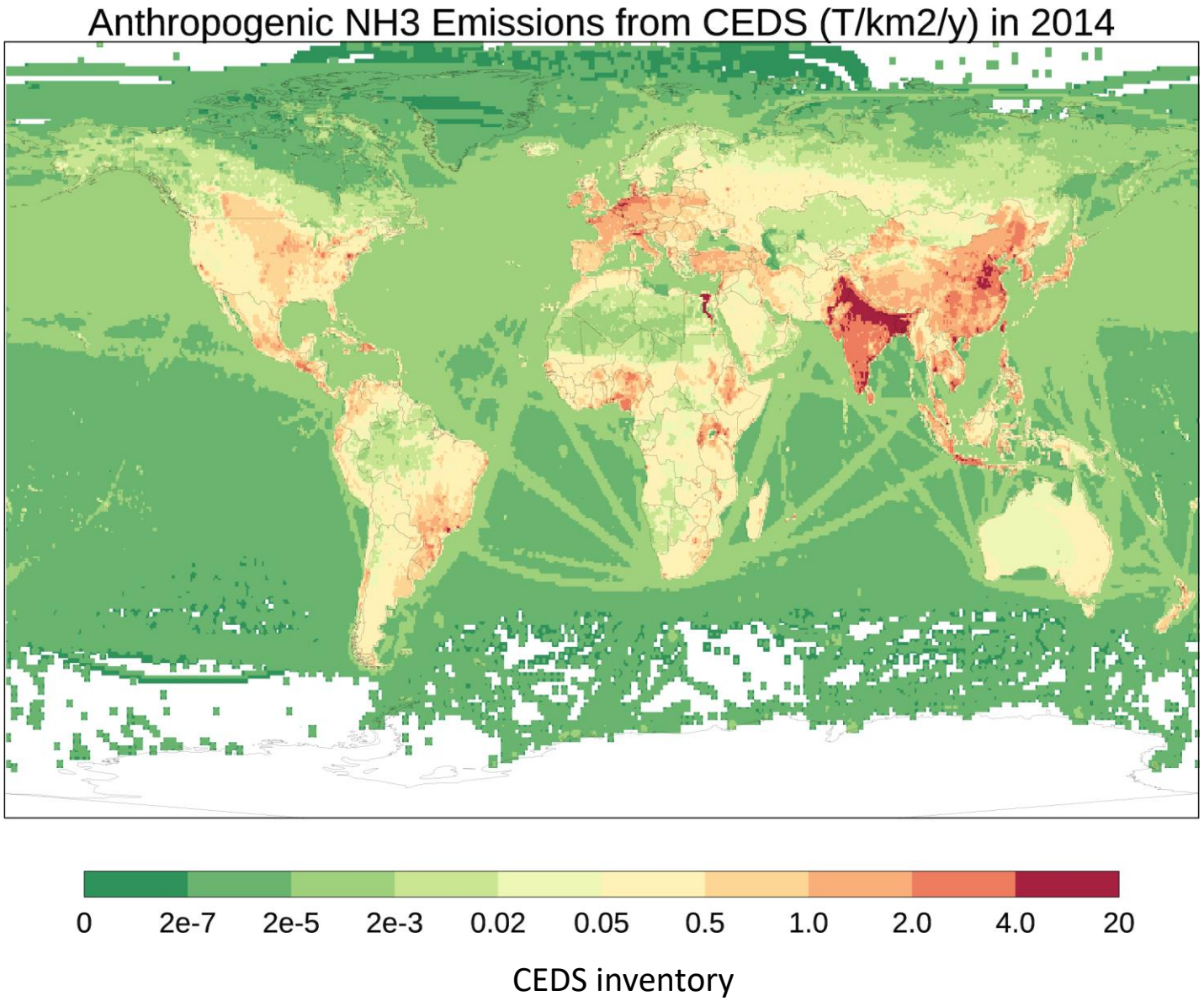
Anthropogenic NH_3 Emissions: 1950-2014



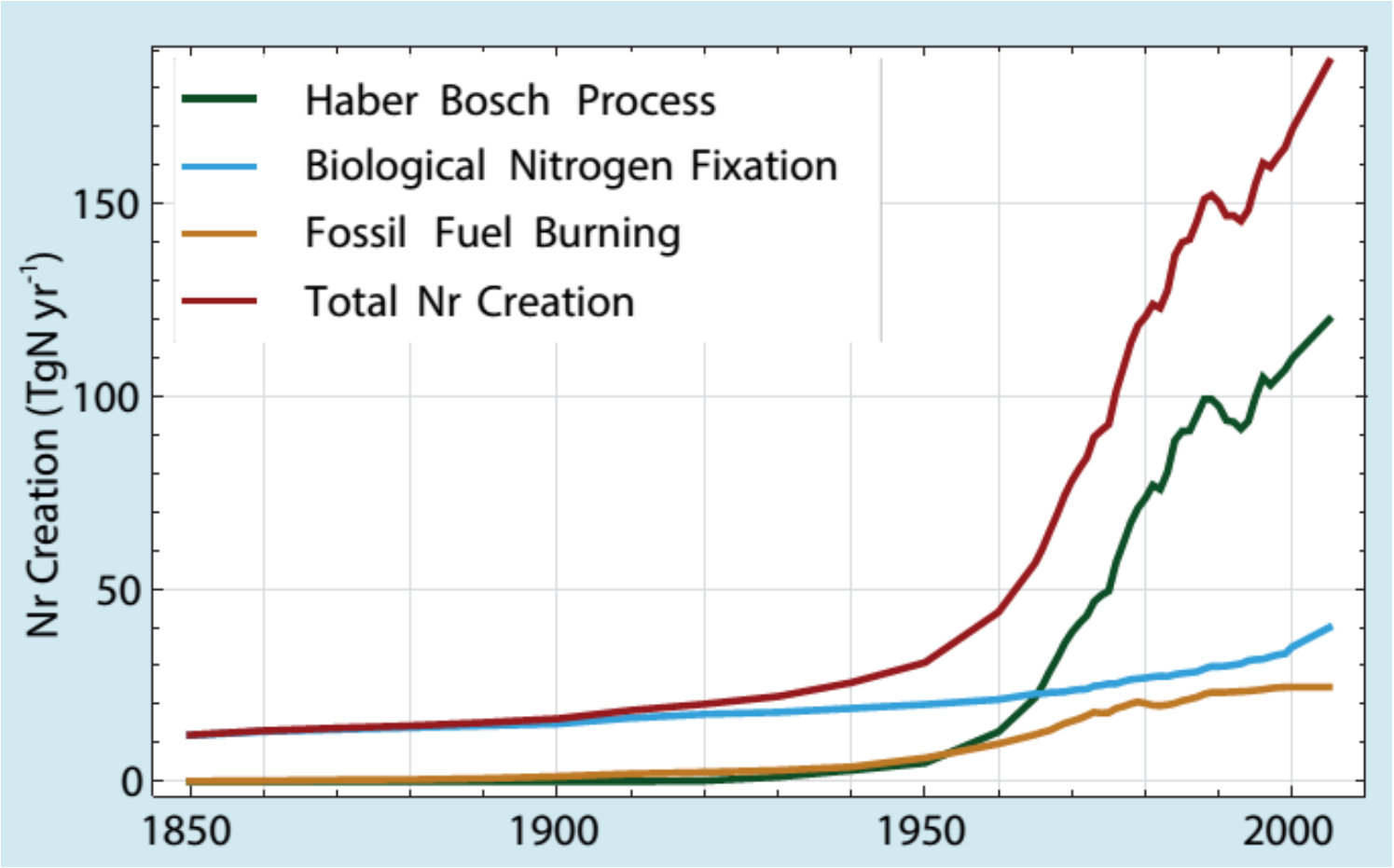
Anthropogenic NH_3 Emissions: 1950-2014



Anthropogenic NH_3 Emissions: 1950-2014

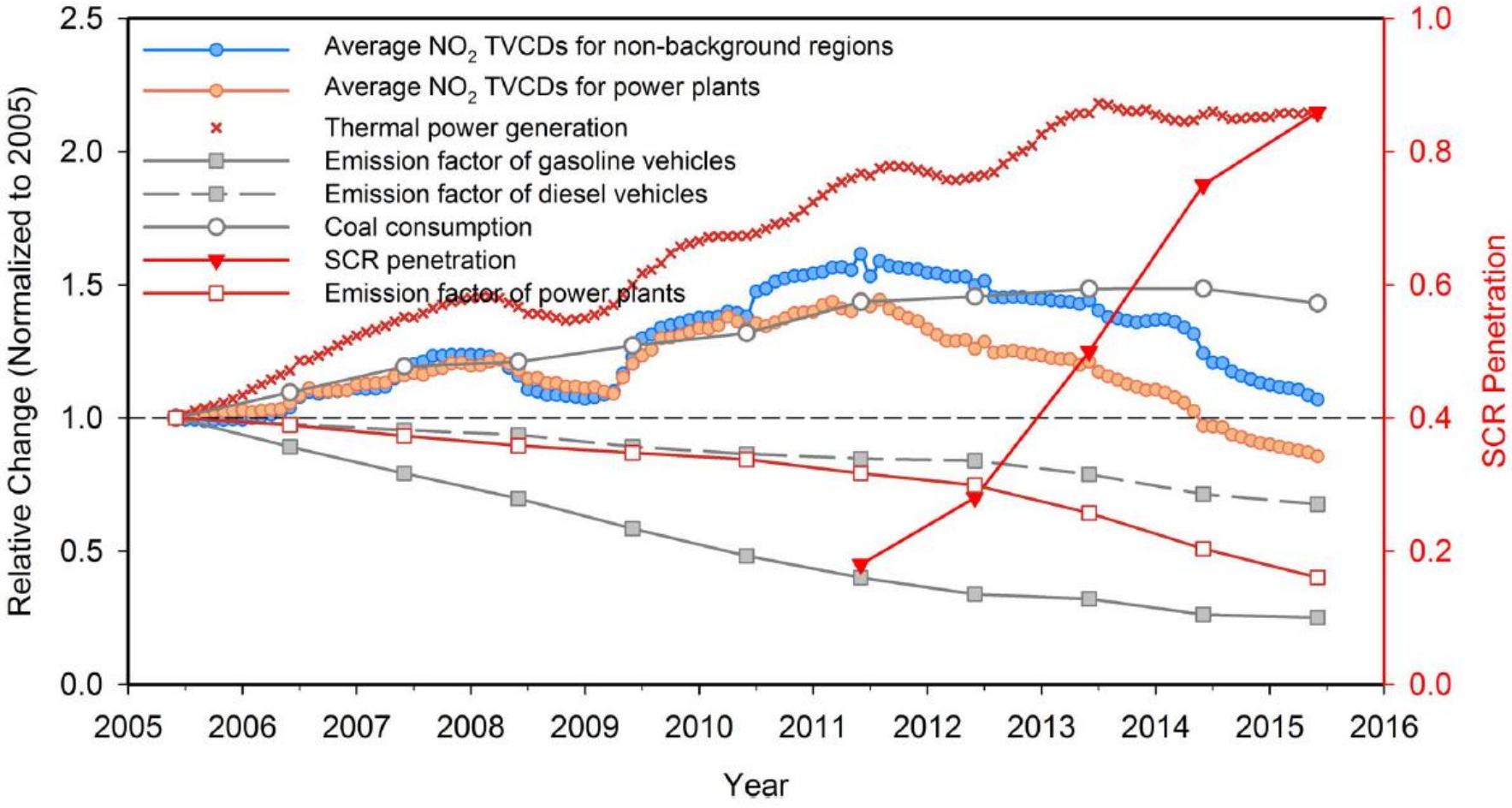


Global Reactive Nitrogen Creation by Human



IPCC, 2013

Recent Reduction in NOx Emissions Over China



Liu et al., 2016, ERL

Global Nitrogen Cycle: Past, Present and Future

Inorganic N deposition

mg N m^{-2} yr^{-1}

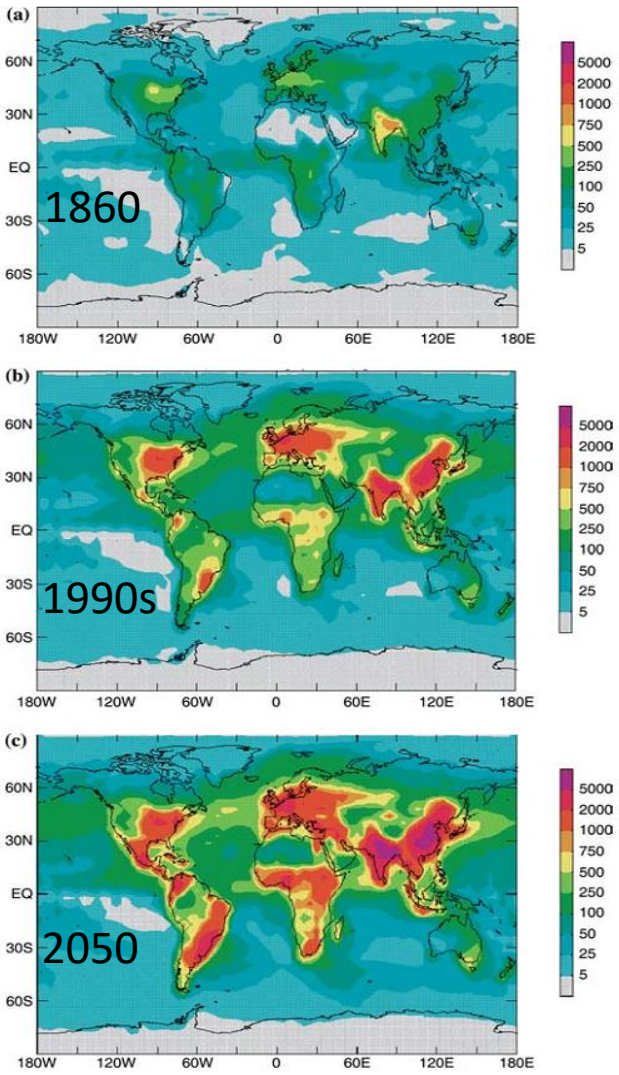


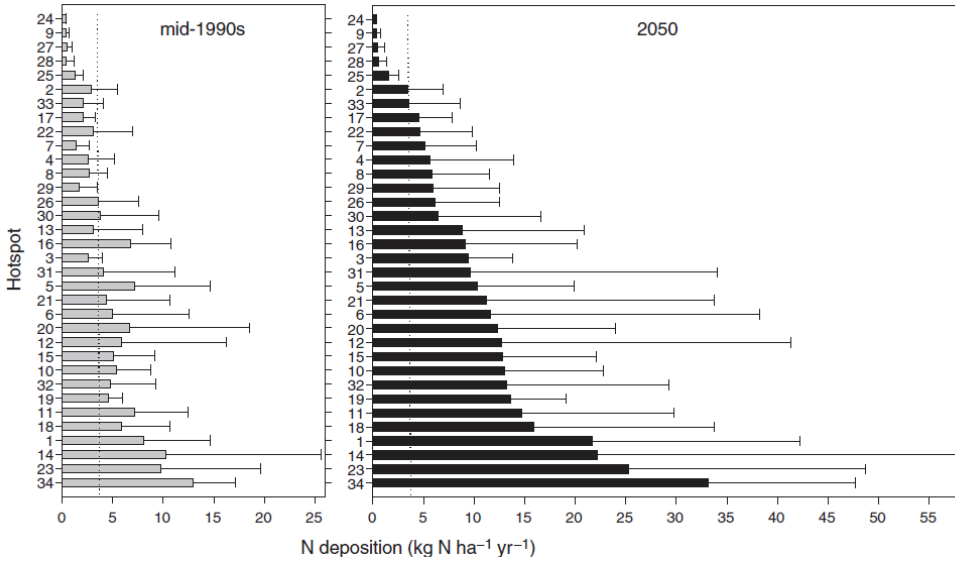
Table 1. Global Nr creation and distribution, Tg N yr^{-1}

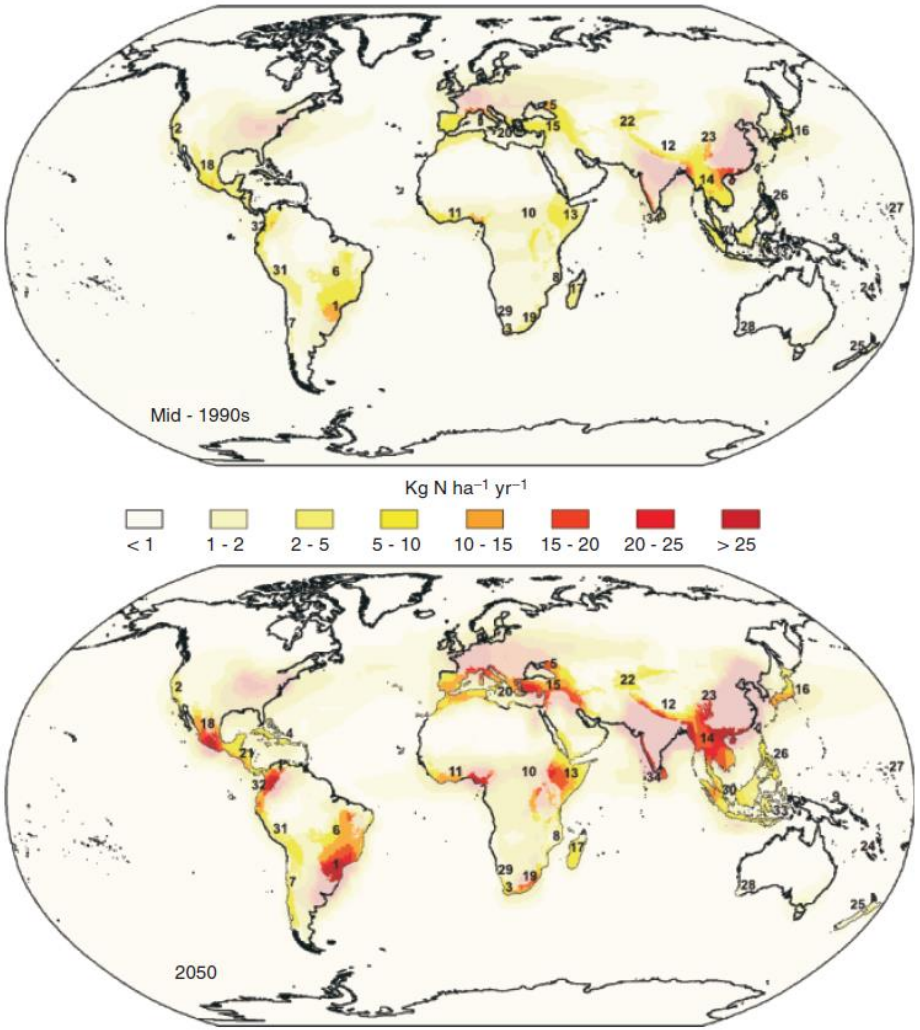
	1860	Early-1990s	2050
Nr creation			
Natural			
Lightning	5.4	5.4	5.4
BNF-terestrial	120	107	98
BNF-marine	121	121	121
Subtotal	246	233	224
Anthropogenic			
Haber-Bosch	0	100	165
BNF-cultivation	15	31.5	50
Fossil fuel combustion	0.3	24.5	52.2
Subtotal	15	156	267
Total	262	389	492
Atmospheric emission			
NO_x			
Fossil fuel combustion	0.3	24.5	52.2
Lightning	5.4	5.4	5.4
Other emissions	7.4	16.1	23.9
NH_3			
Terrestrial	14.9	52.6	113
Marine	5.6	5.6	5.6
N_2O			
Terrestrial	8.1	10.9	13.1 ±
Marine	3.9	4.3	5.1
Total (NO_x and NH_3)	13.1	46	82
Atmospheric deposition			
NO_y			
Terrestrial	6.6	24.8	42.2
Marine	6.2	21	36.3
Subtotal	12.8	45.8	78.5
NH_x			
Terrestrial	10.8	38.7	83
Marine	8	18	33.1
Subtotal	18.8	56.7	116.1
Total	31.6	103	195
Riverine fluxes			
Nr input into rivers	69.8	118.1	149.8
Nr export to inland systems	7.9	11.3	11.7
Nr export to coastal areas	27	47.8	63.2
Denitrification			
Continental			
Terrestrial		67	95
Riverine		47.8	63.2
Subtotal	98	115	158
Estuary and shelf			
Riverine nitrate	27	47.8	63.2
Open ocean nitrate	145	145	145
Subtotal	172	193	208

Galloway et al., 2004, Biogeochemistry

Nitrogen Deposition in Biodiversity Hotspots

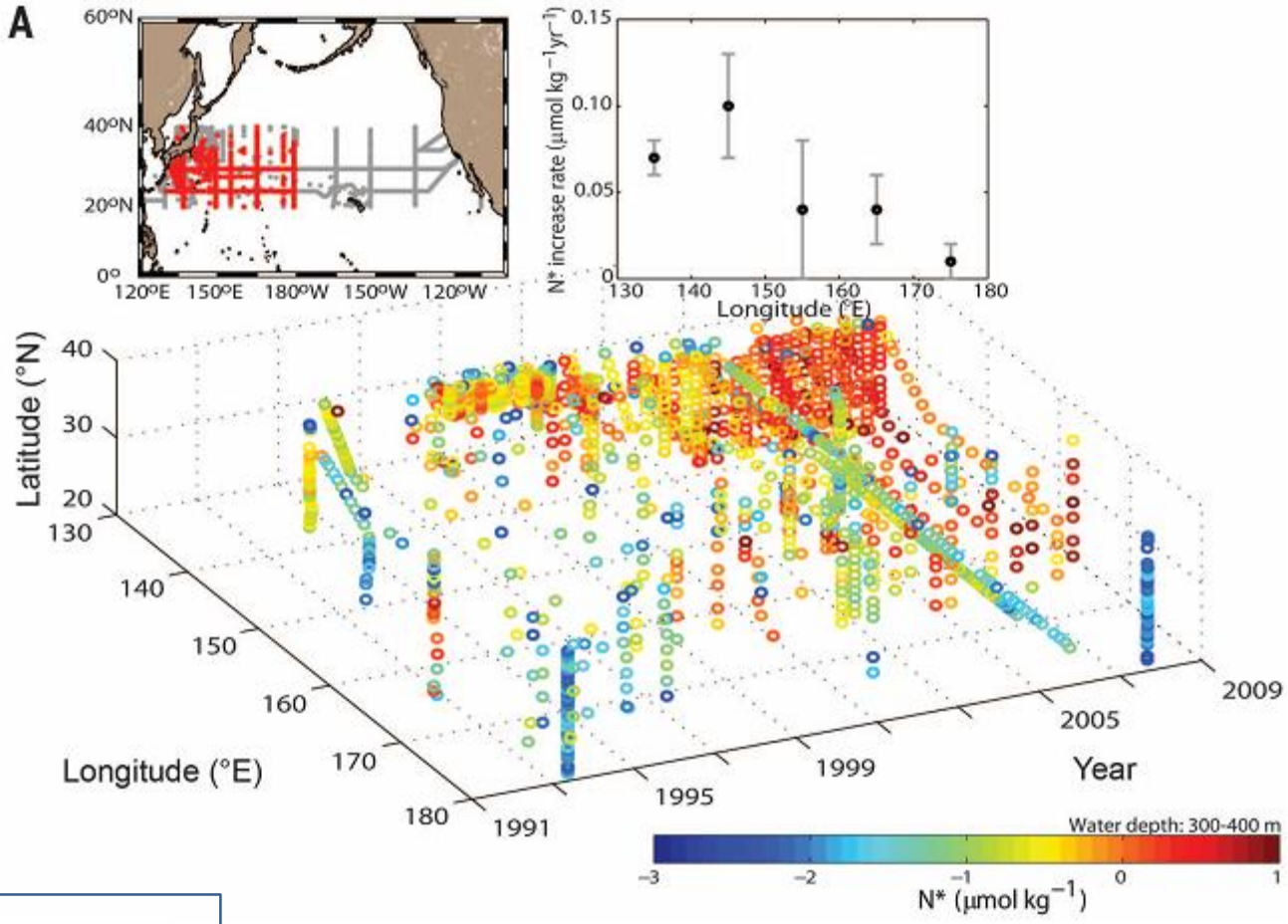
- **Setting a threshold of N deposition(15 kg N ha^{-1} yr^{-1}), Phoenix et al. simulated the impacts of atmospheric N deposition on the 34 world biodiversity hotspots in 1990s and 2050 (based on TM3)**





Phoenix et al., 2006, GCB

Increasing Atmospheric N Deposition in the Pacific Ocean

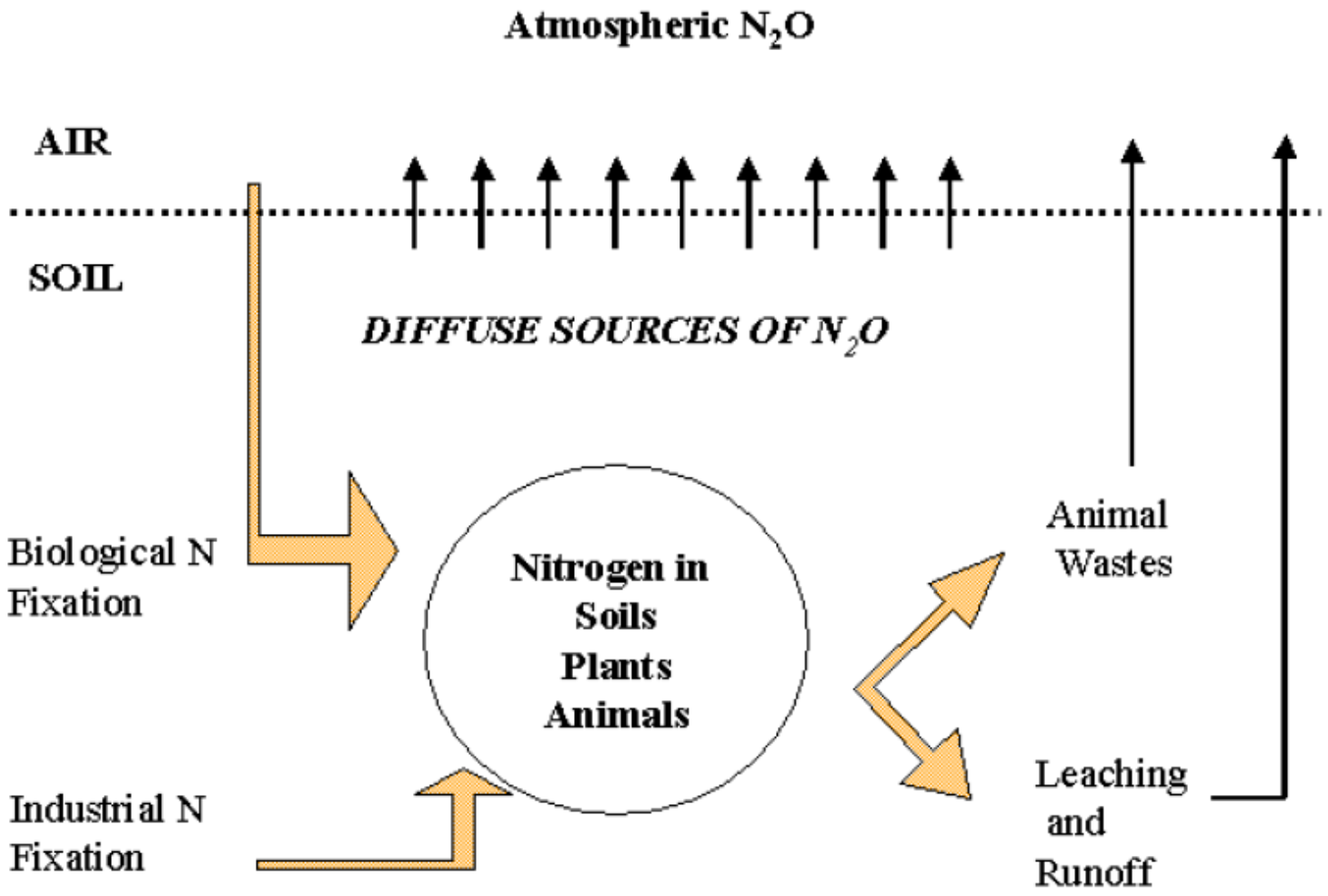


$$N^* = N - R_{N:P} \times P$$

$R_{N:P}$ = Redfield ratio = 16

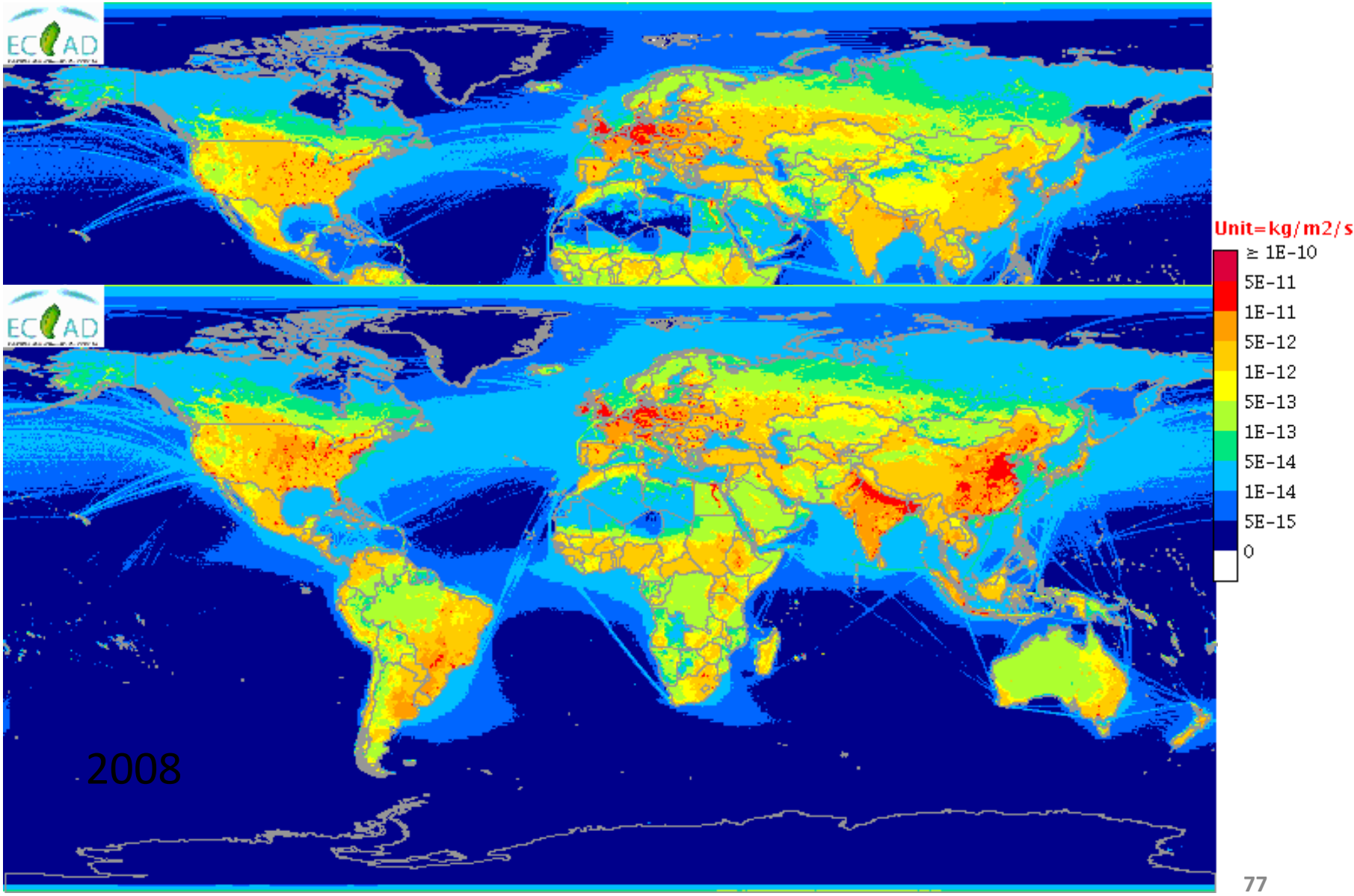
Kim et al., 2014, Science

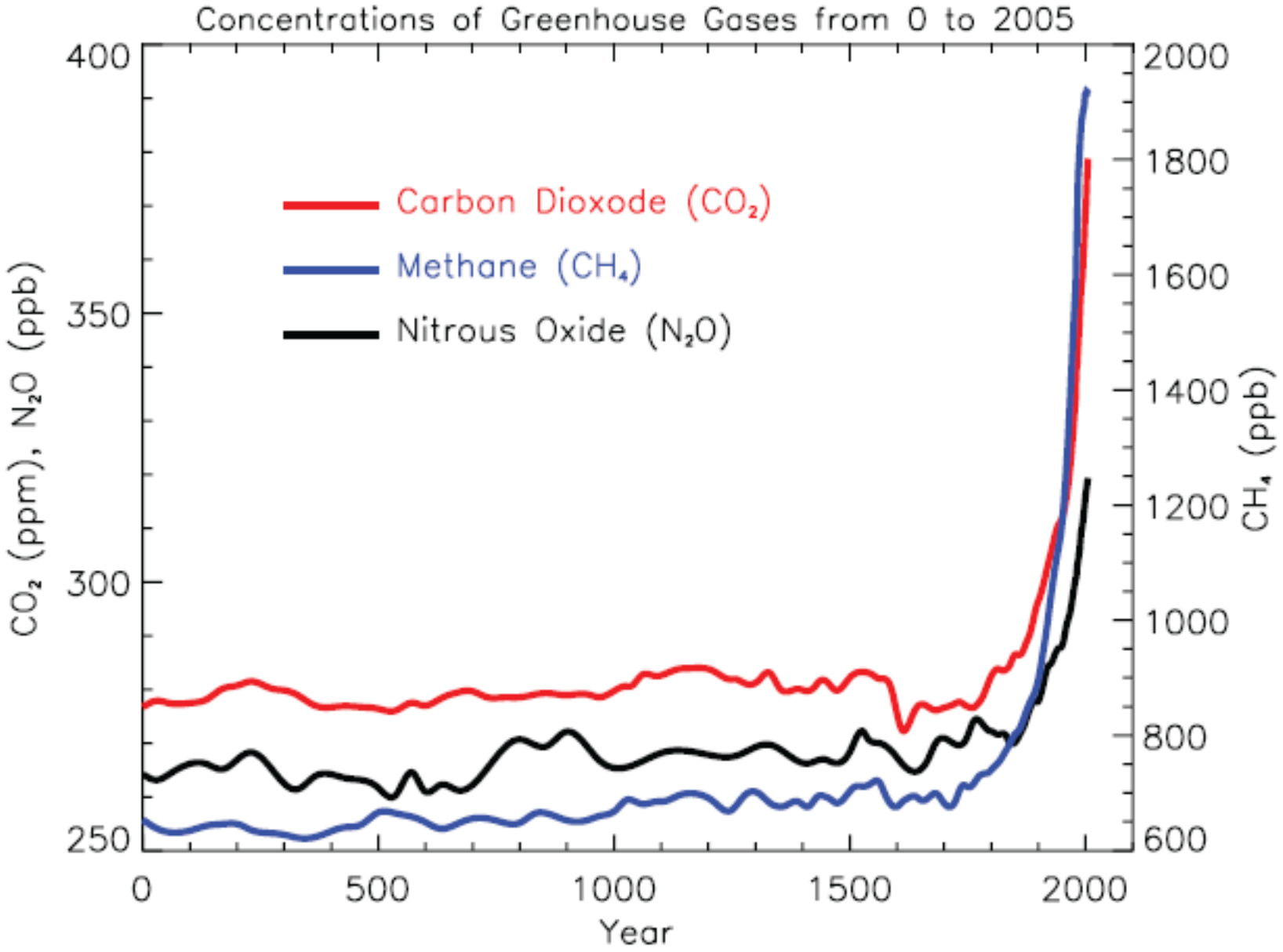
N_2O Emitted from Agriculture and Biosphere



Soil processes involved in the formation of N_2O from agriculture

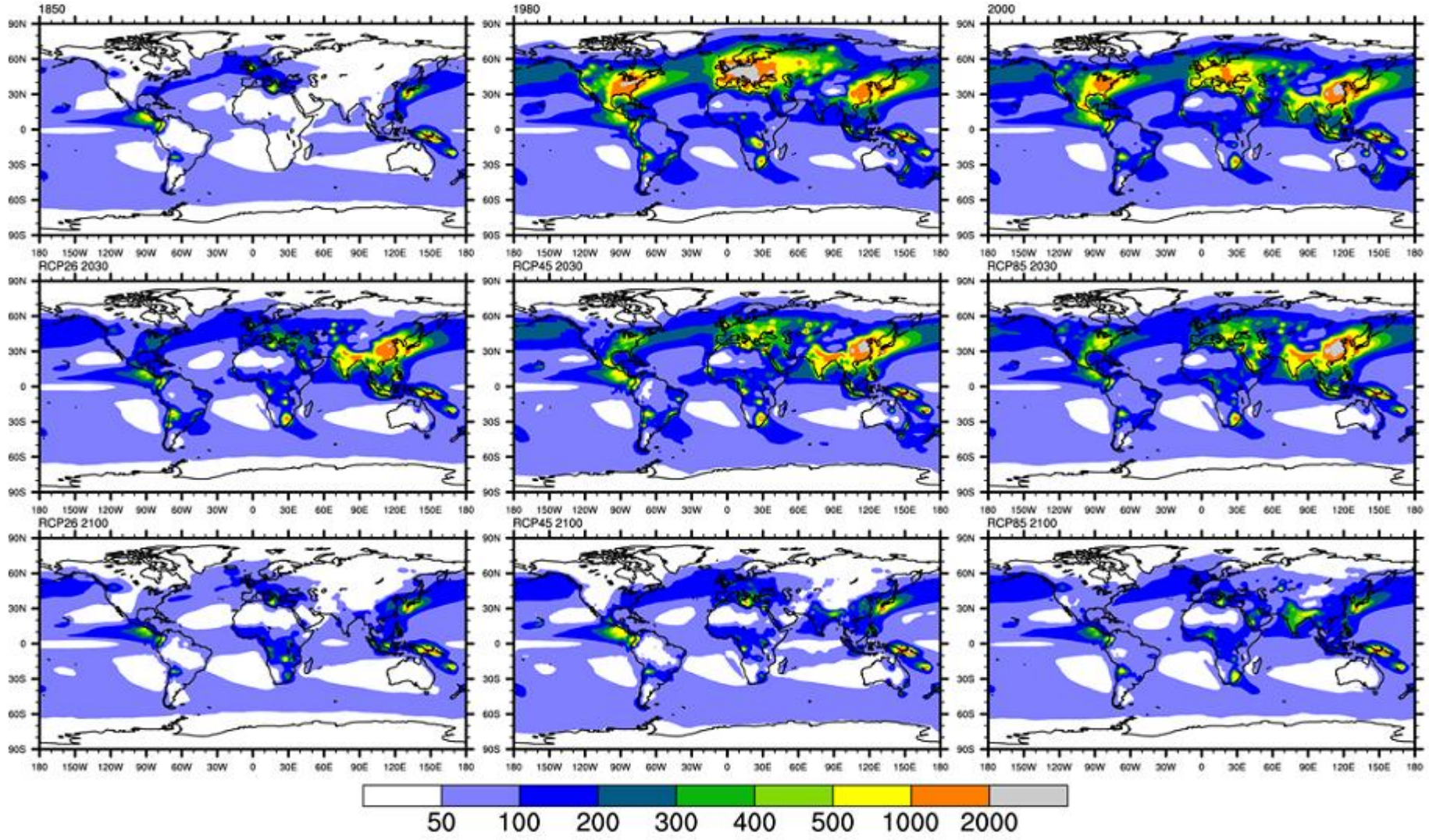
N_2O Emissions: 1970-2008 (EDGAR v4.2)




Concentrations of Greenhouse Gases from 0 to 2005
Carbon Dioxode (CO_2)
Methane (CH_4)
Nitrous Oxide (N_2O)
CO_2 (ppm), N_2O (ppb)
CH_4 (ppb)
Year
400
350
300
250
2000
1800
1600
1400
1200
1000
800
600
0
500
1000
1500
2000

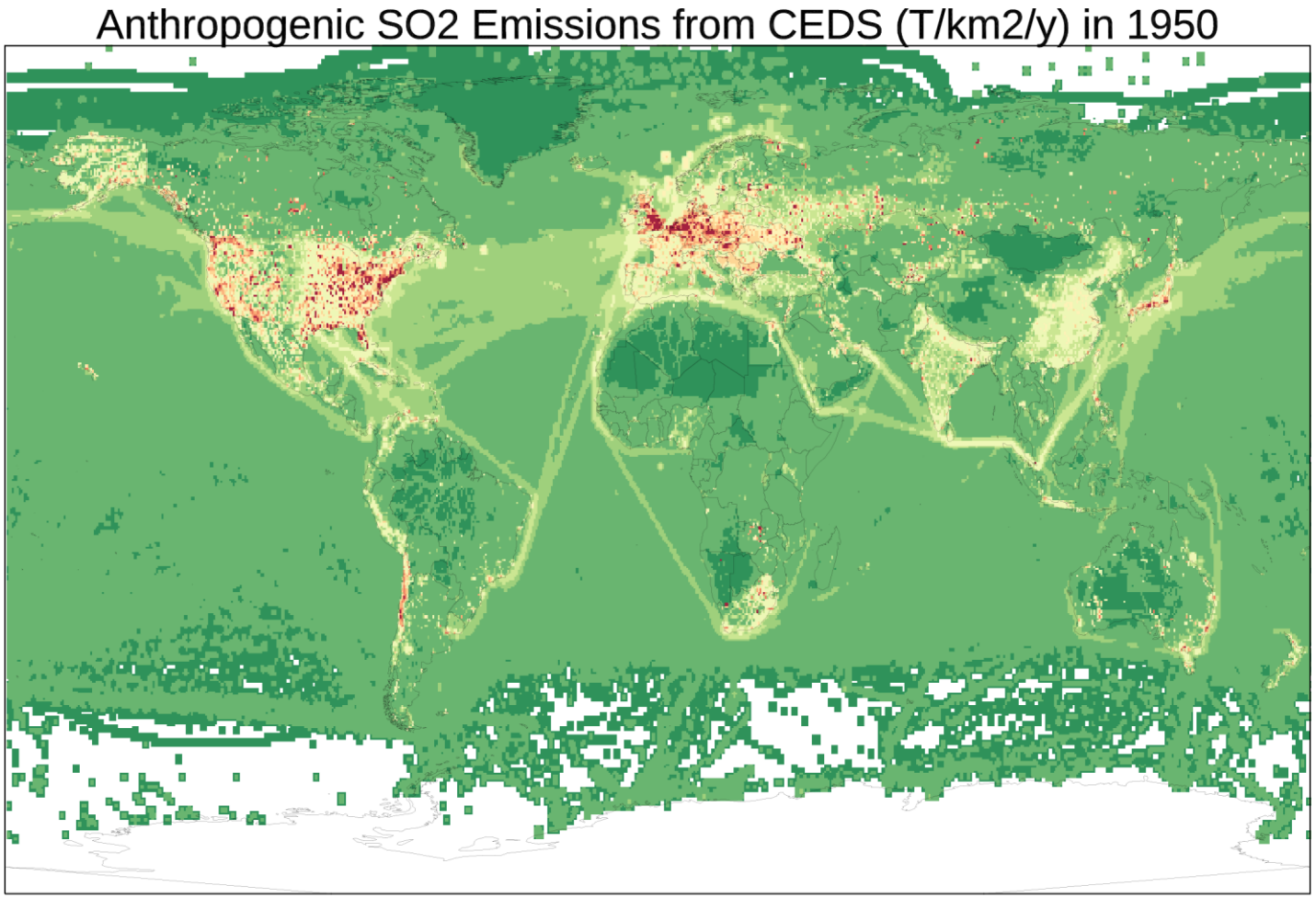
Global Sulfur Deposition: Past, Present and Future

SOx deposition in 1850, 1980, 2000, 2030 and 2100 (mg S m^{-2} yr^{-1})

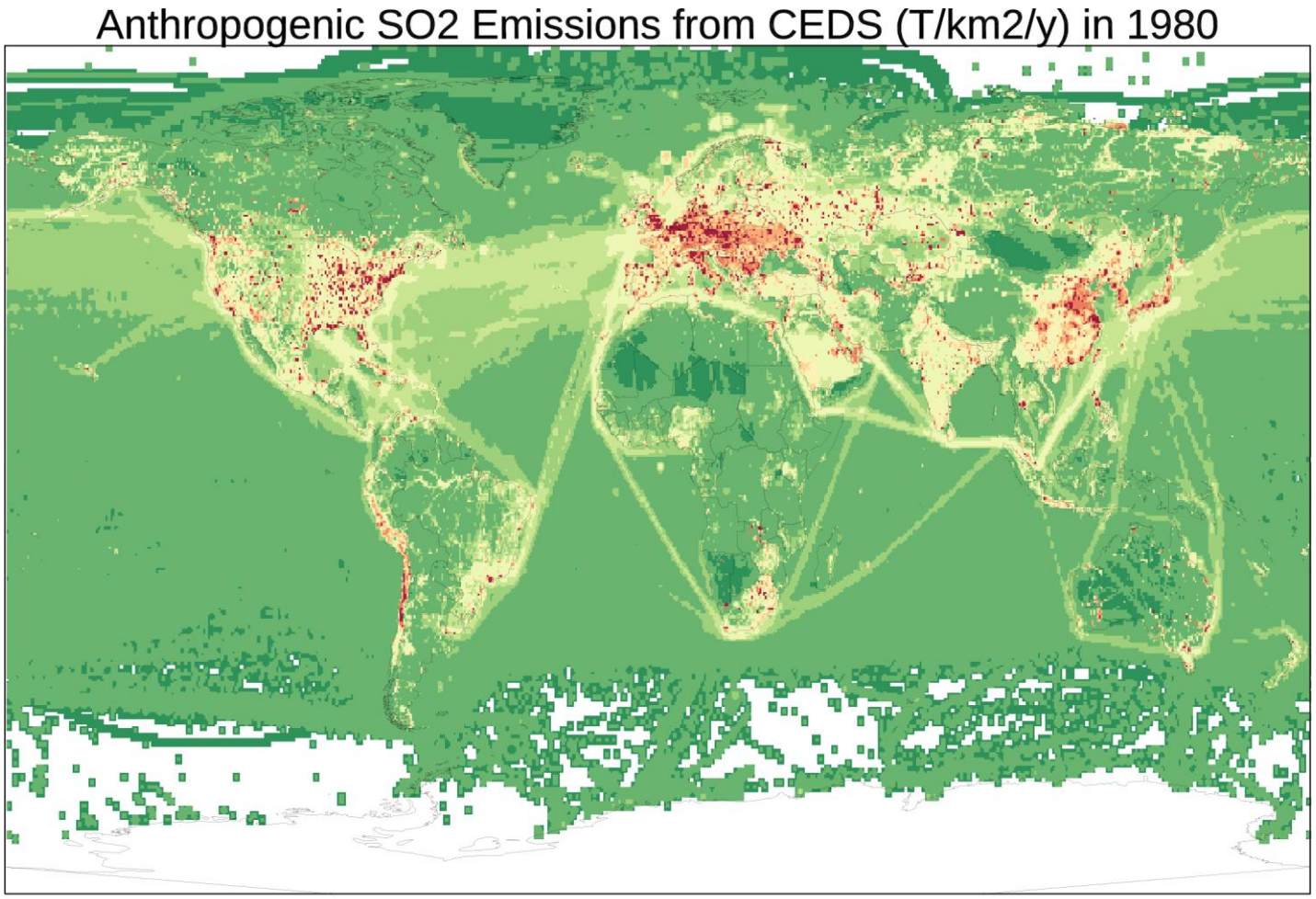


Lamarque et al., 2013, ACP

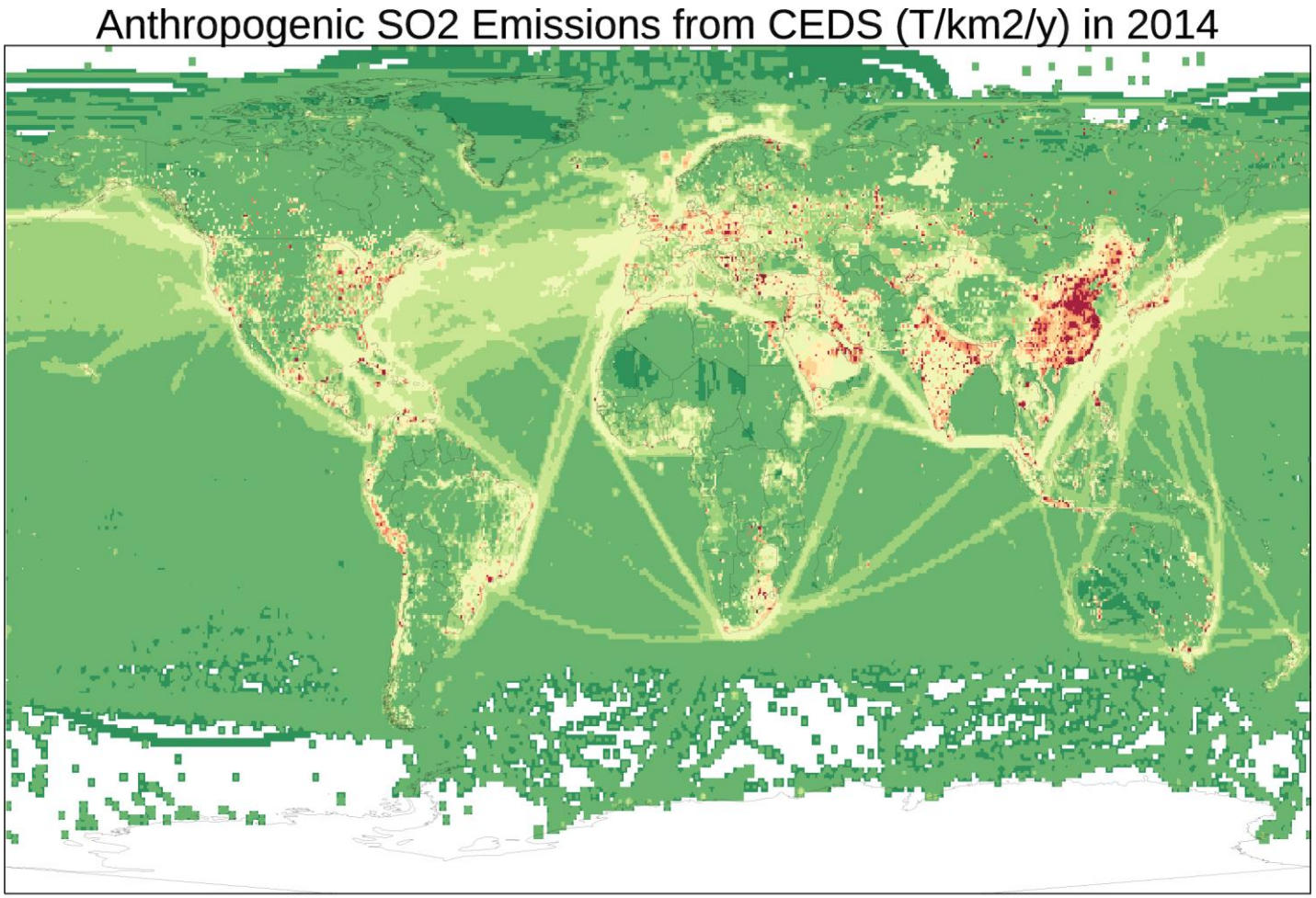
Anthropogenic SO_2 Emissions: 1950-2014



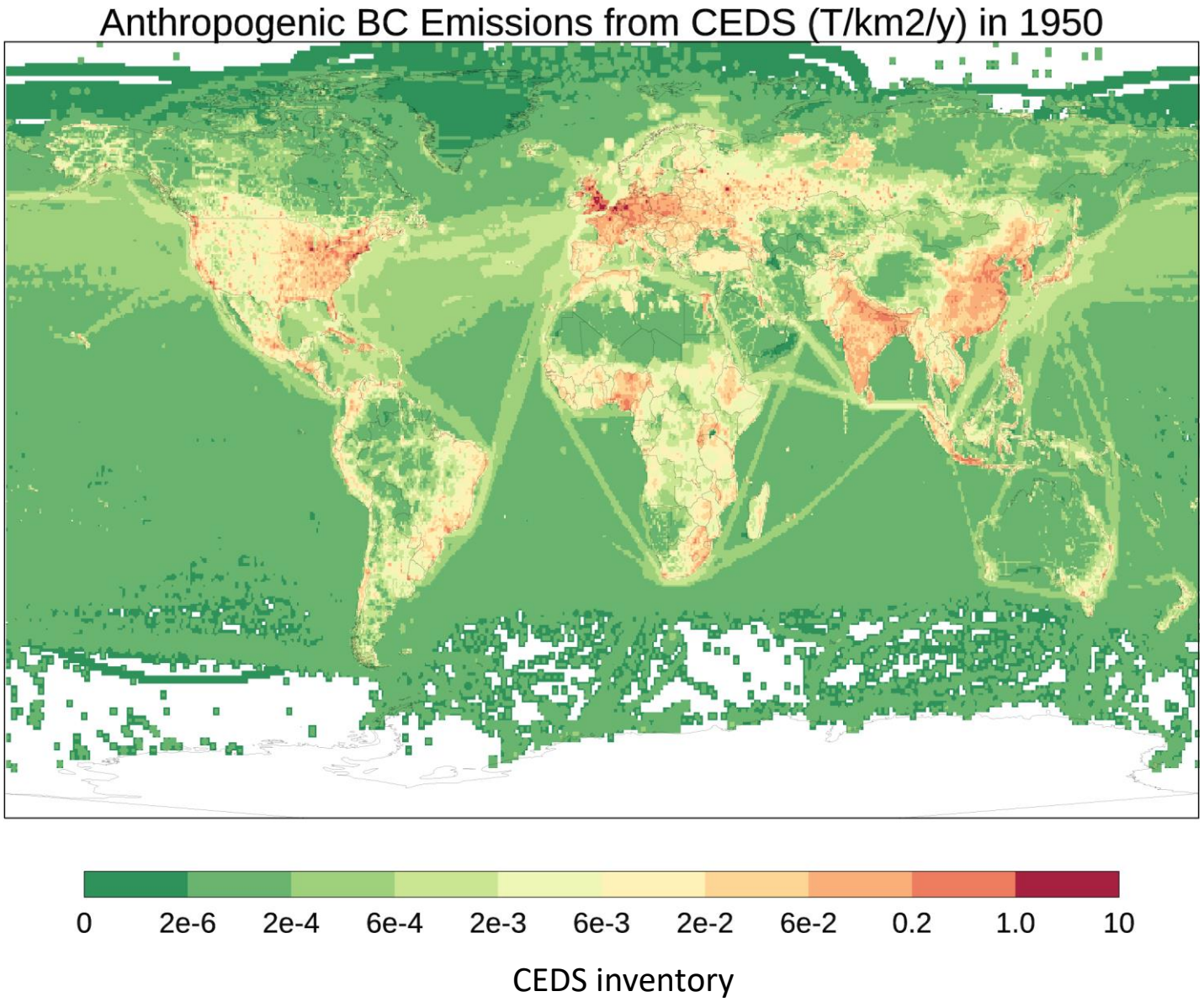
Anthropogenic SO_2 Emissions: 1950-2014



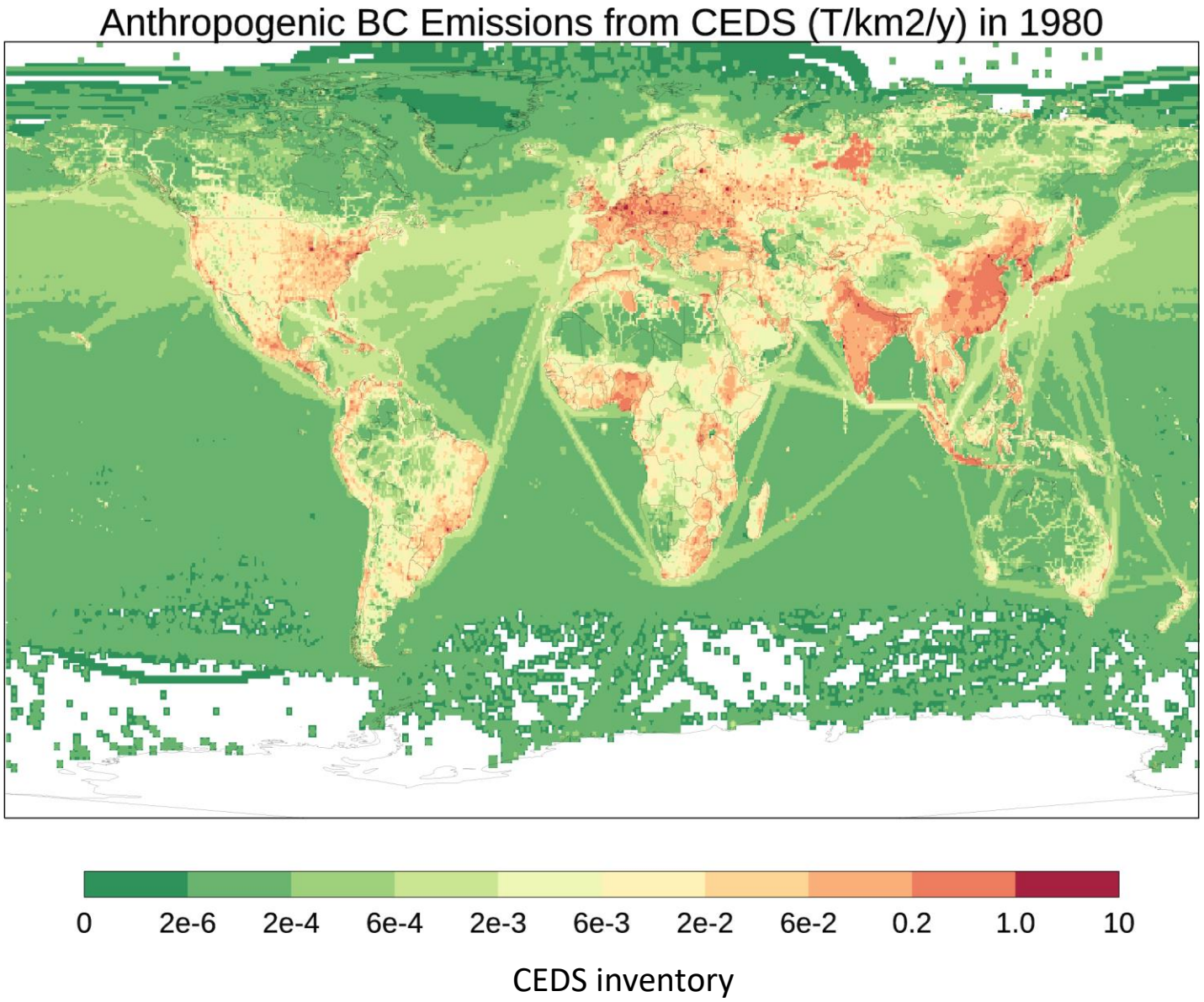
Anthropogenic SO_2 Emissions: 1950-2014



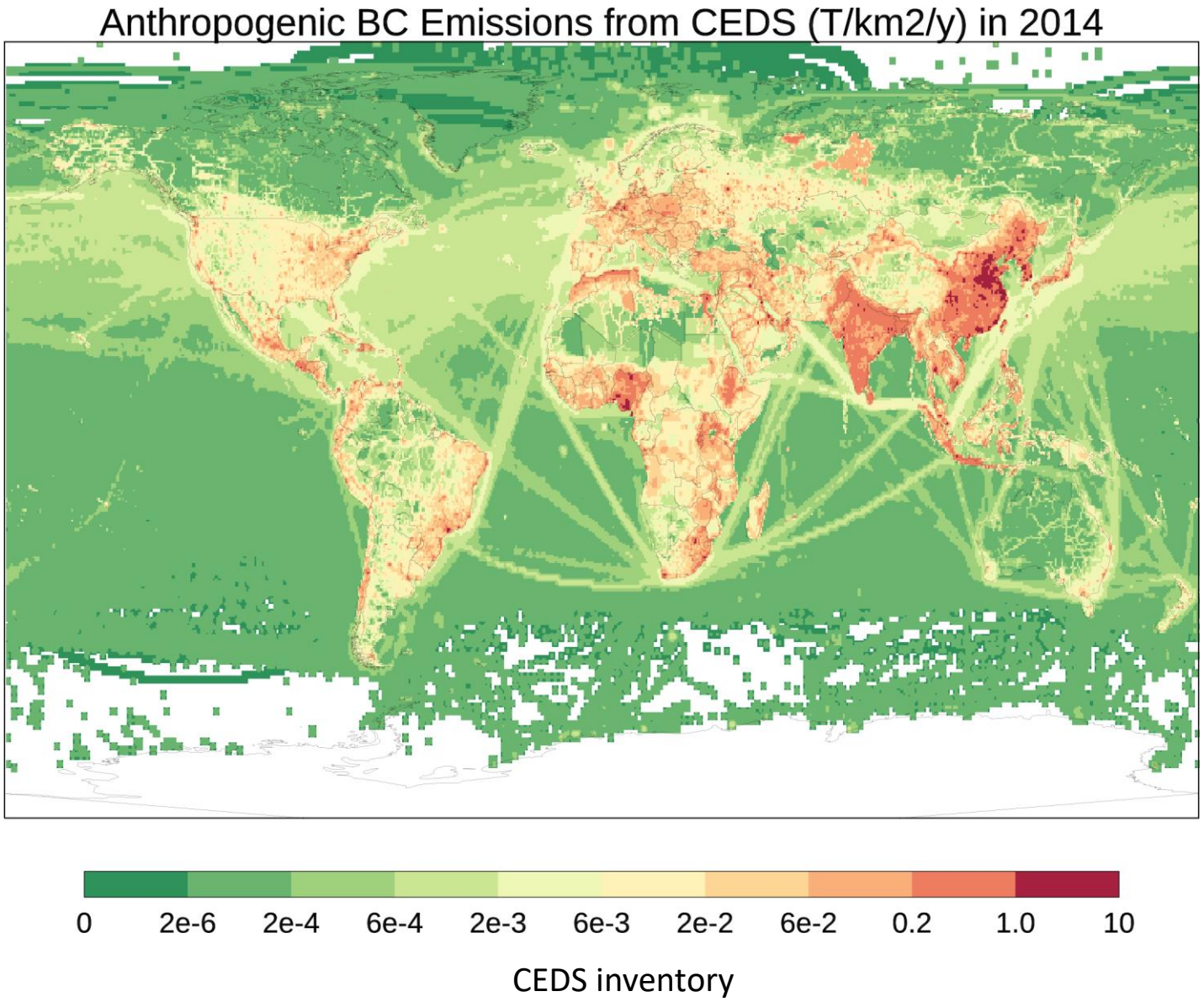
Anthropogenic BC Emissions: 1950-2014



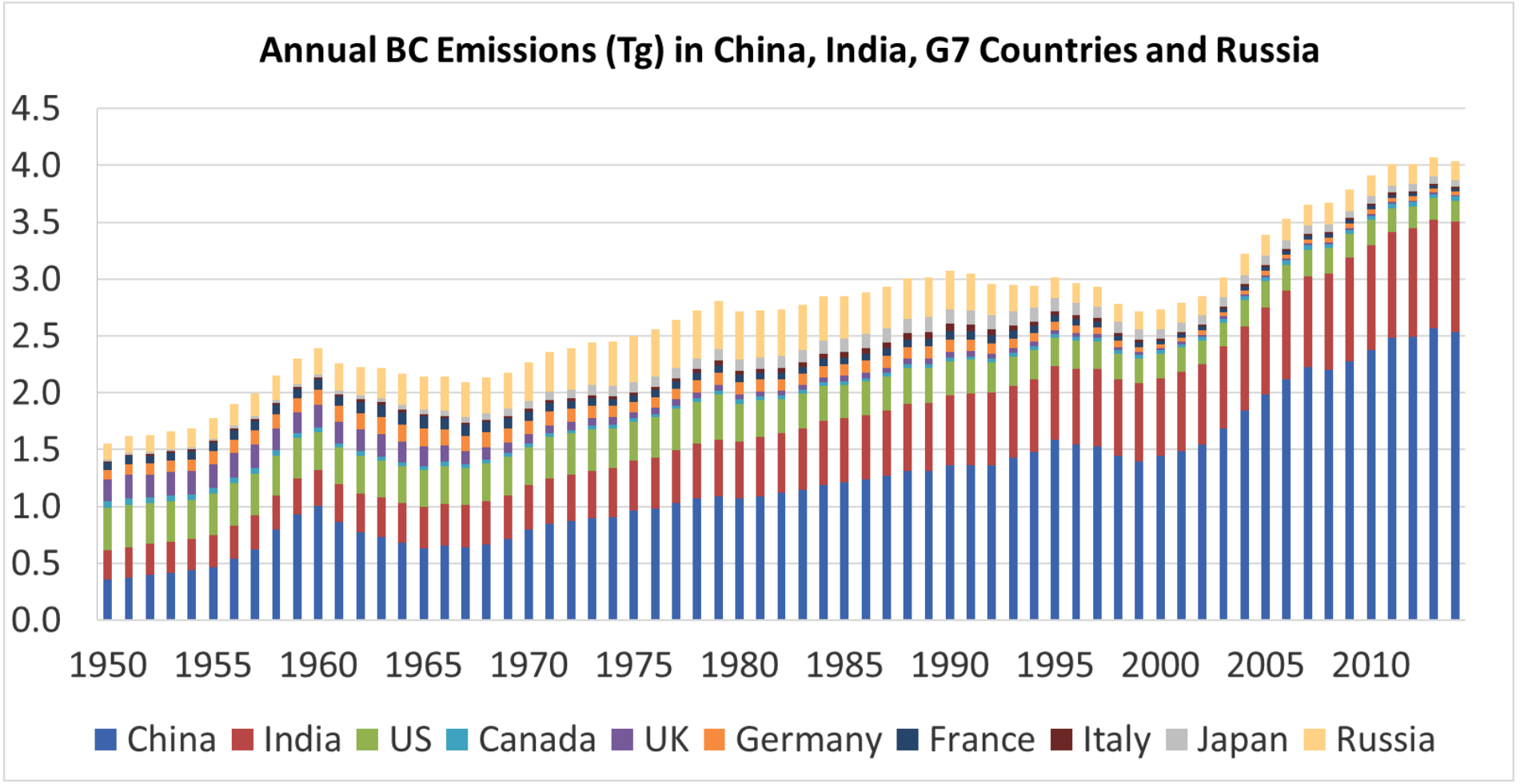
Anthropogenic BC Emissions: 1950-2014



Anthropogenic BC Emissions: 1950-2014

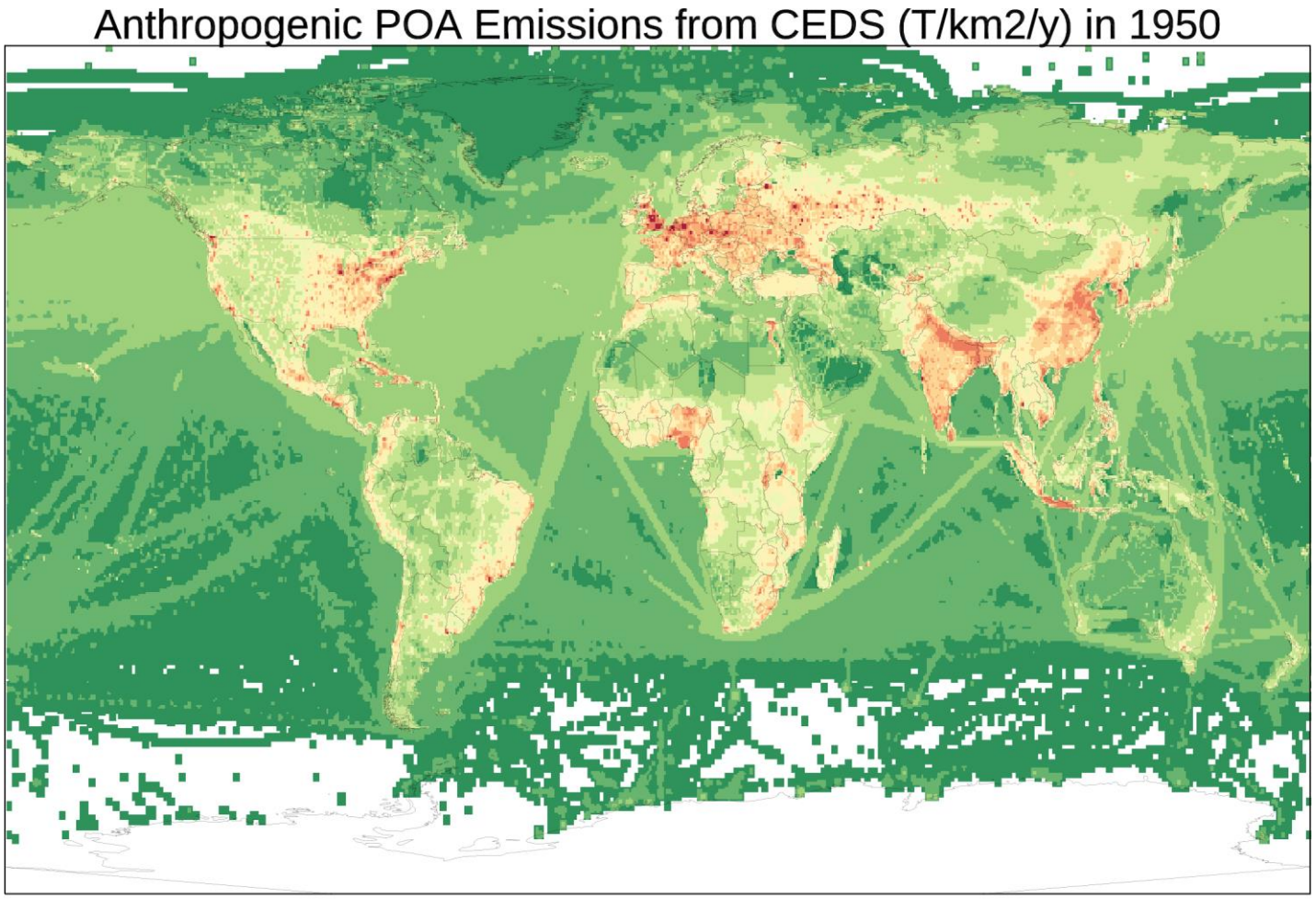


Anthropogenic Emissions of BC: 1950-2014



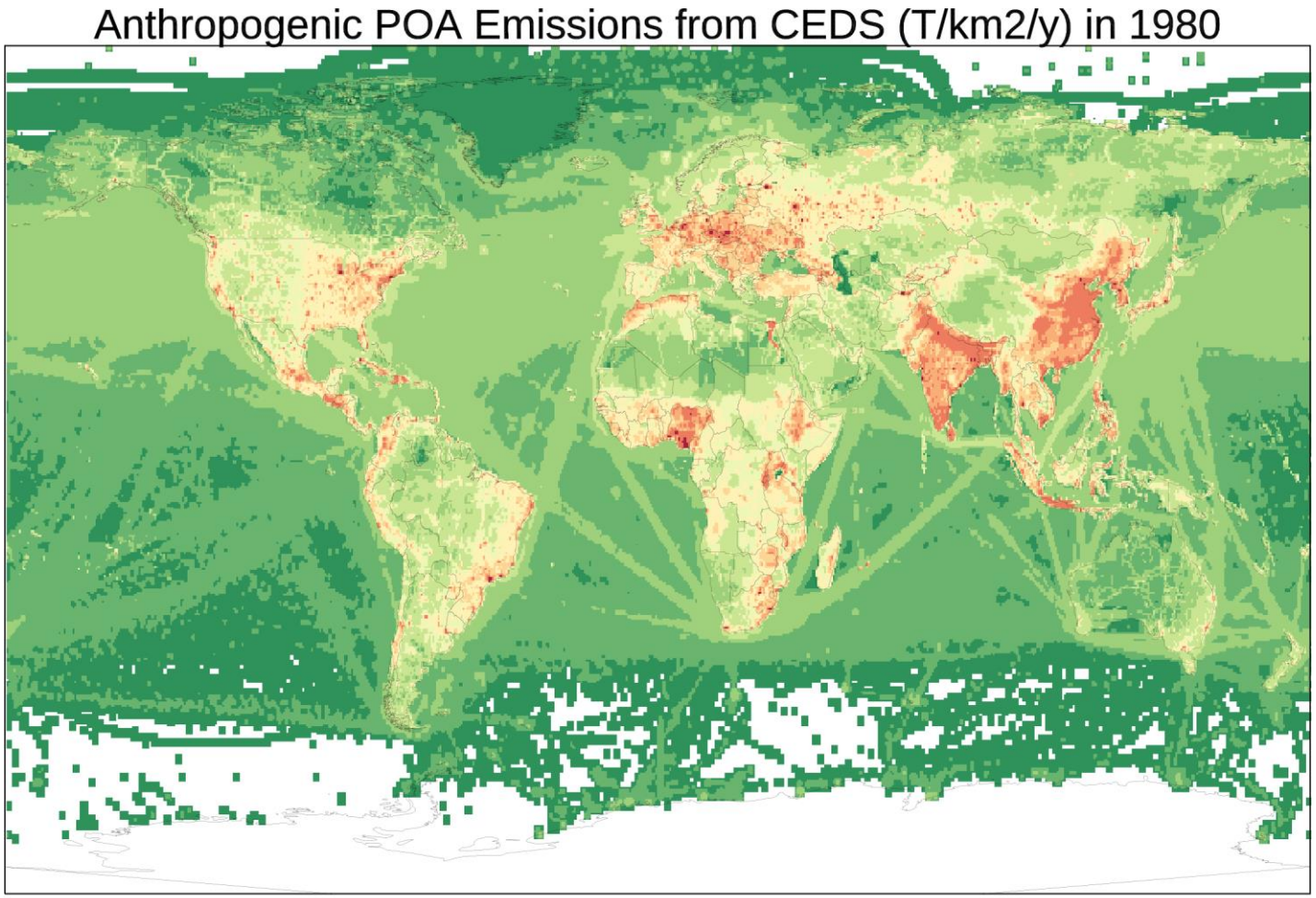
CEDS inventory

Anthropogenic POA Emissions: 1950-2014



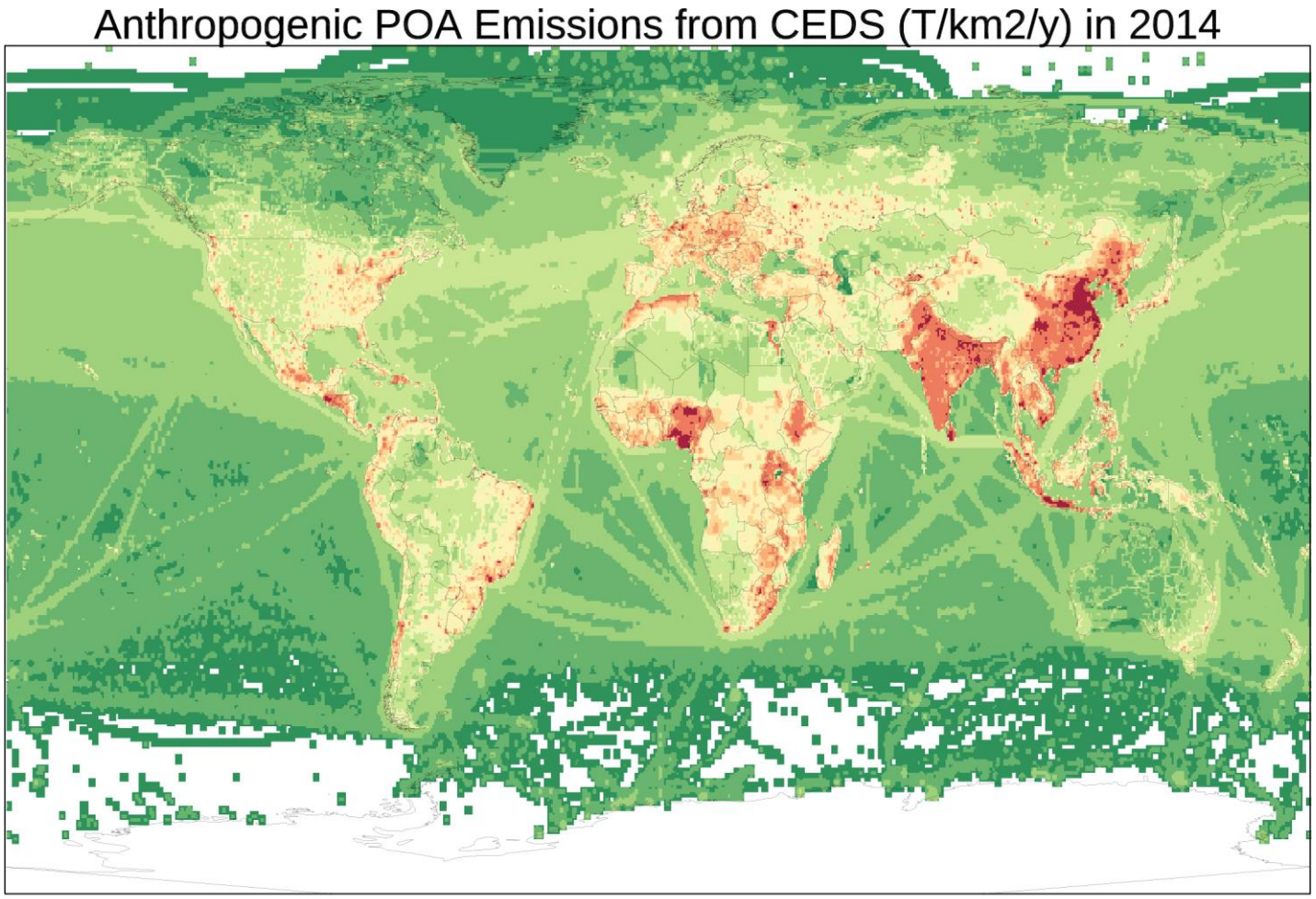
POA = 2.1 * POC

Anthropogenic POA Emissions: 1950-2014



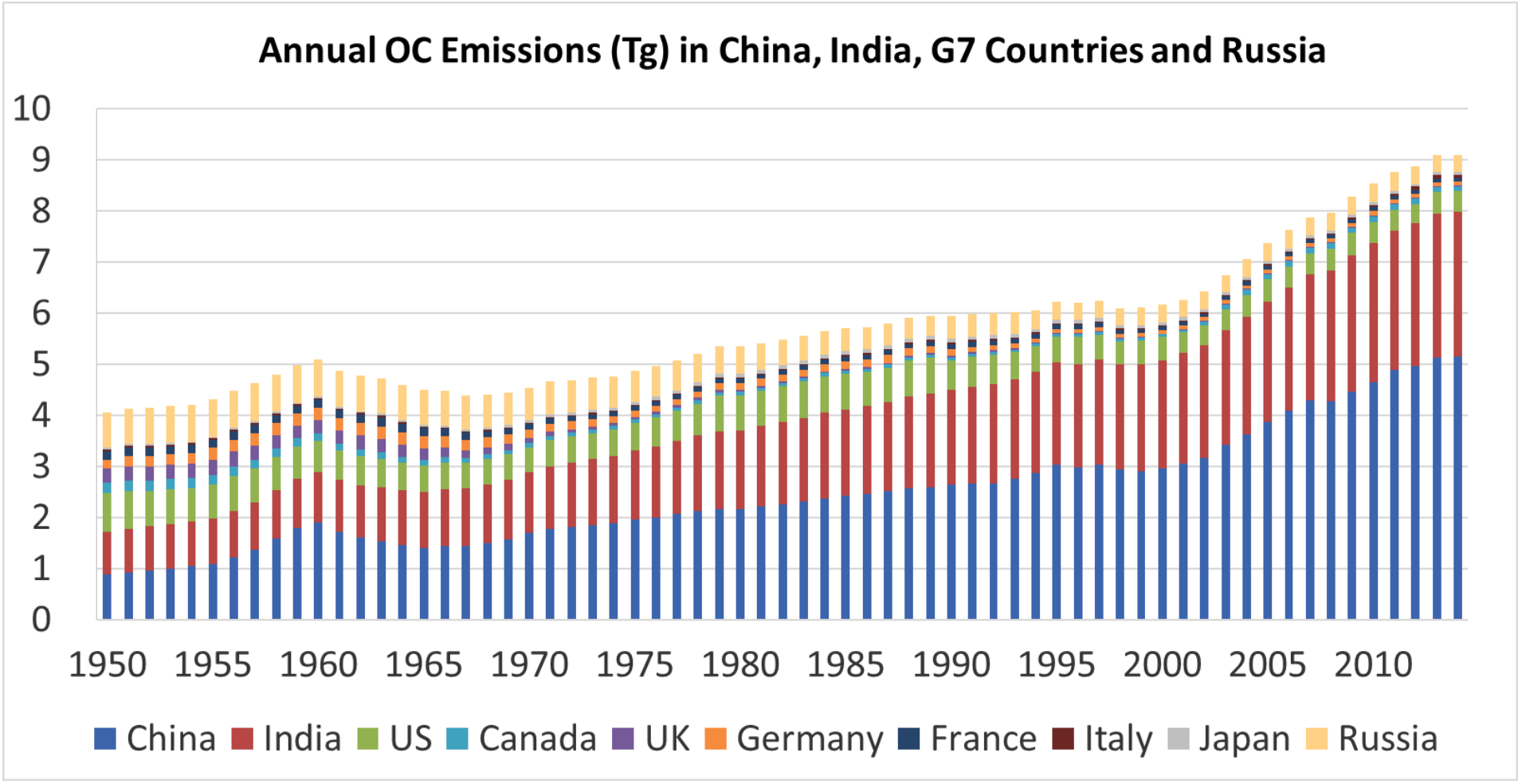
POA = 2.1 * POC

Anthropogenic POA Emissions: 1950-2014



POA = 2.1 * POC

Anthropogenic Emissions of POC: 1950-2014



CEDS inventory