Making sense of air quality

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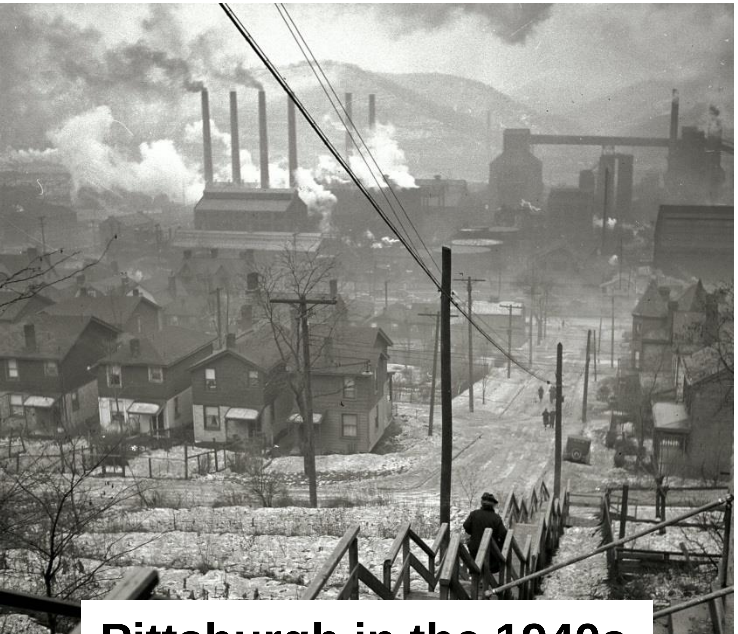
The industrial revolution and air pollution



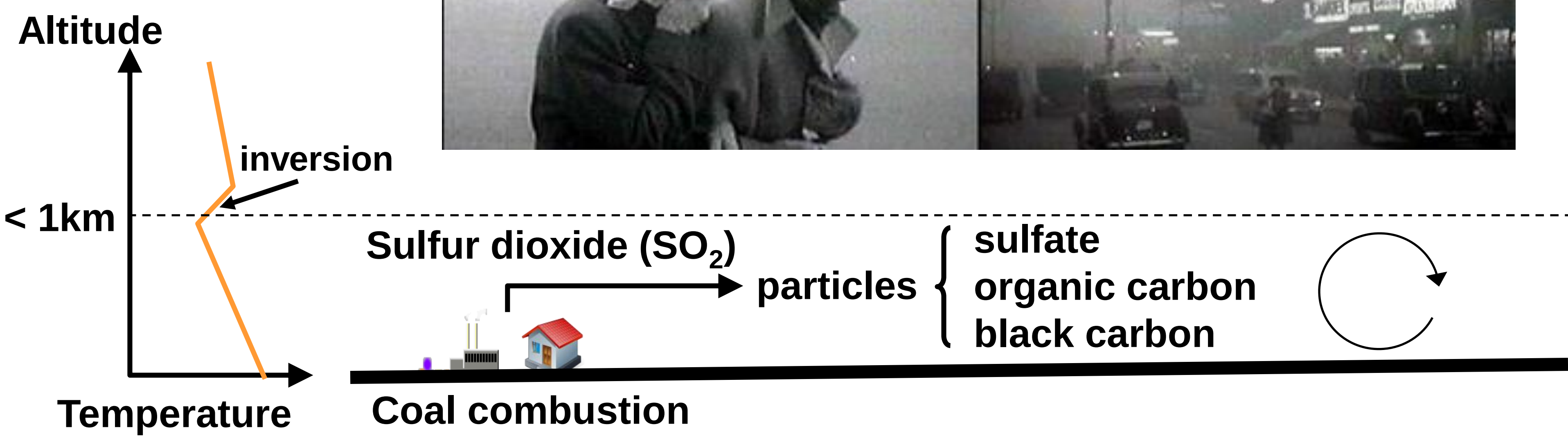
Pittsburgh in the 1940s

"Make great efforts to build China into a strong and prosperous industrialized country under the leadership of the Party and chairman Mao!"

London fog

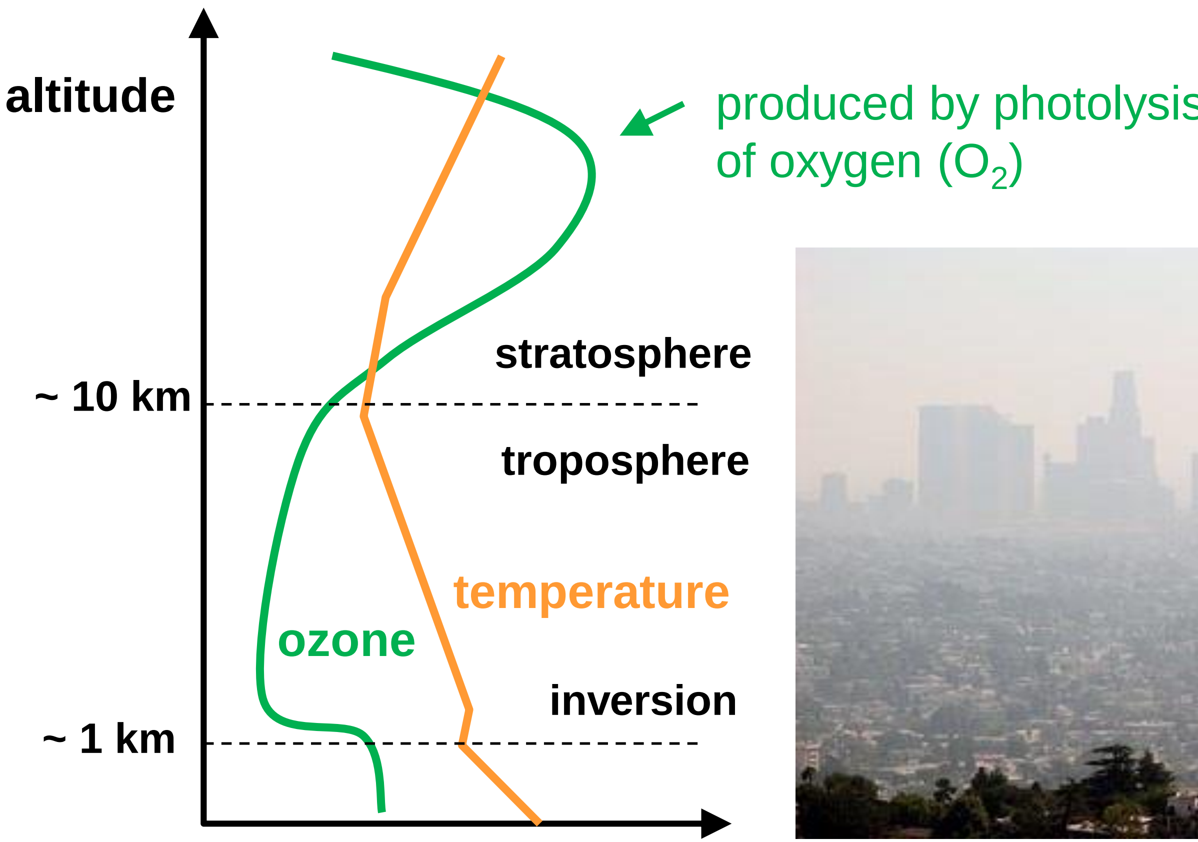
Aerosols a.k.a. particulate matter (PM) from domestic+industrial coal combustion

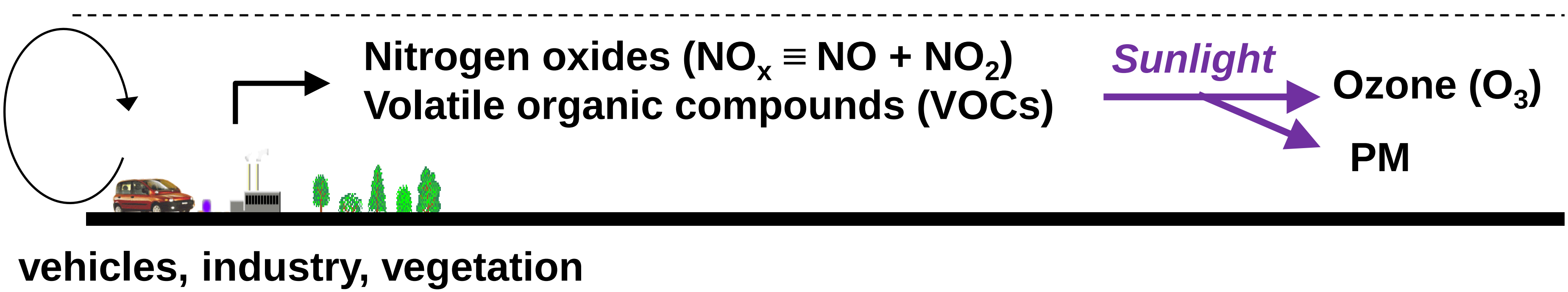
"Killer fog" of December 1952 resulted in 10,000 excess deaths



Los Angeles smog

Respiratory problems, vegetation damage due to high surface ozone

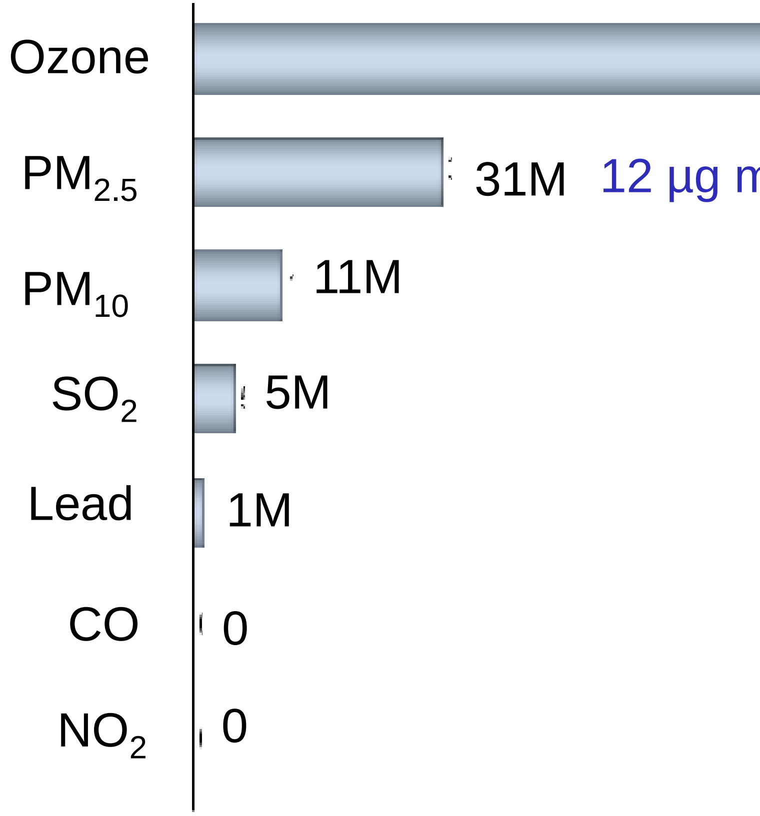


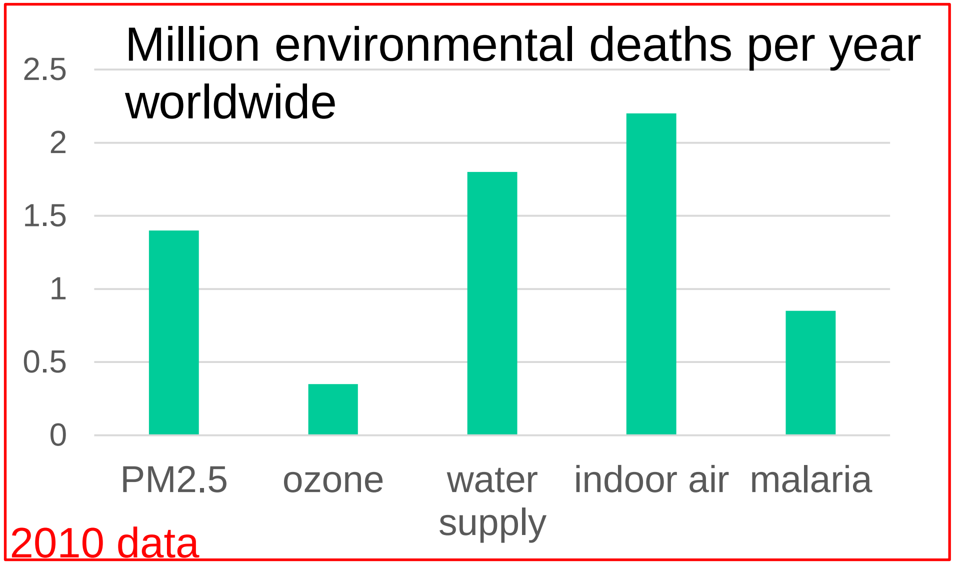


AIR POLLUTION TODAY:

Ozone and fine particulate matter ($PM_{2.5}$) are the major pollutants

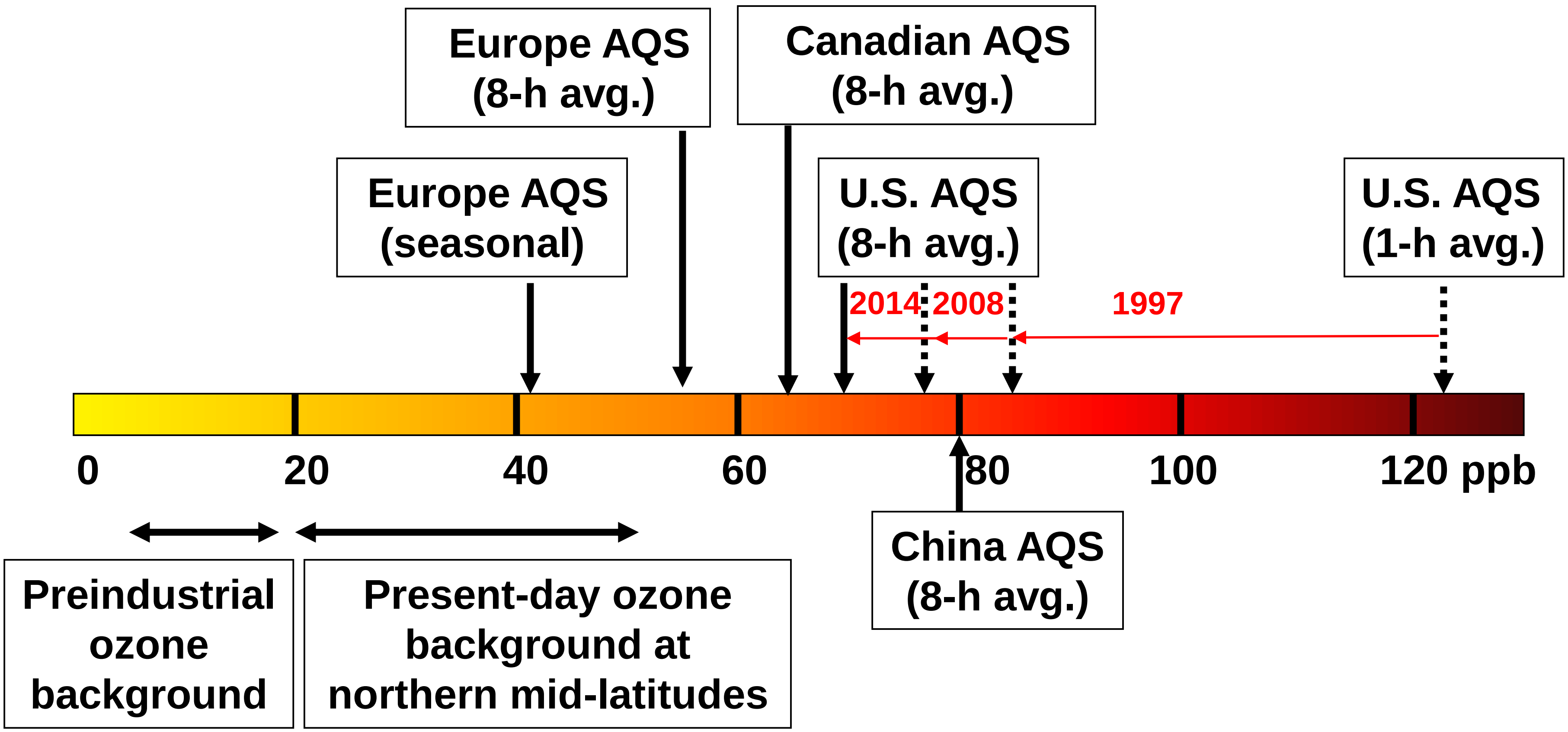
US population exposed to air pollutants
in excess of national ambient air quality standards (NAAQS), 2015



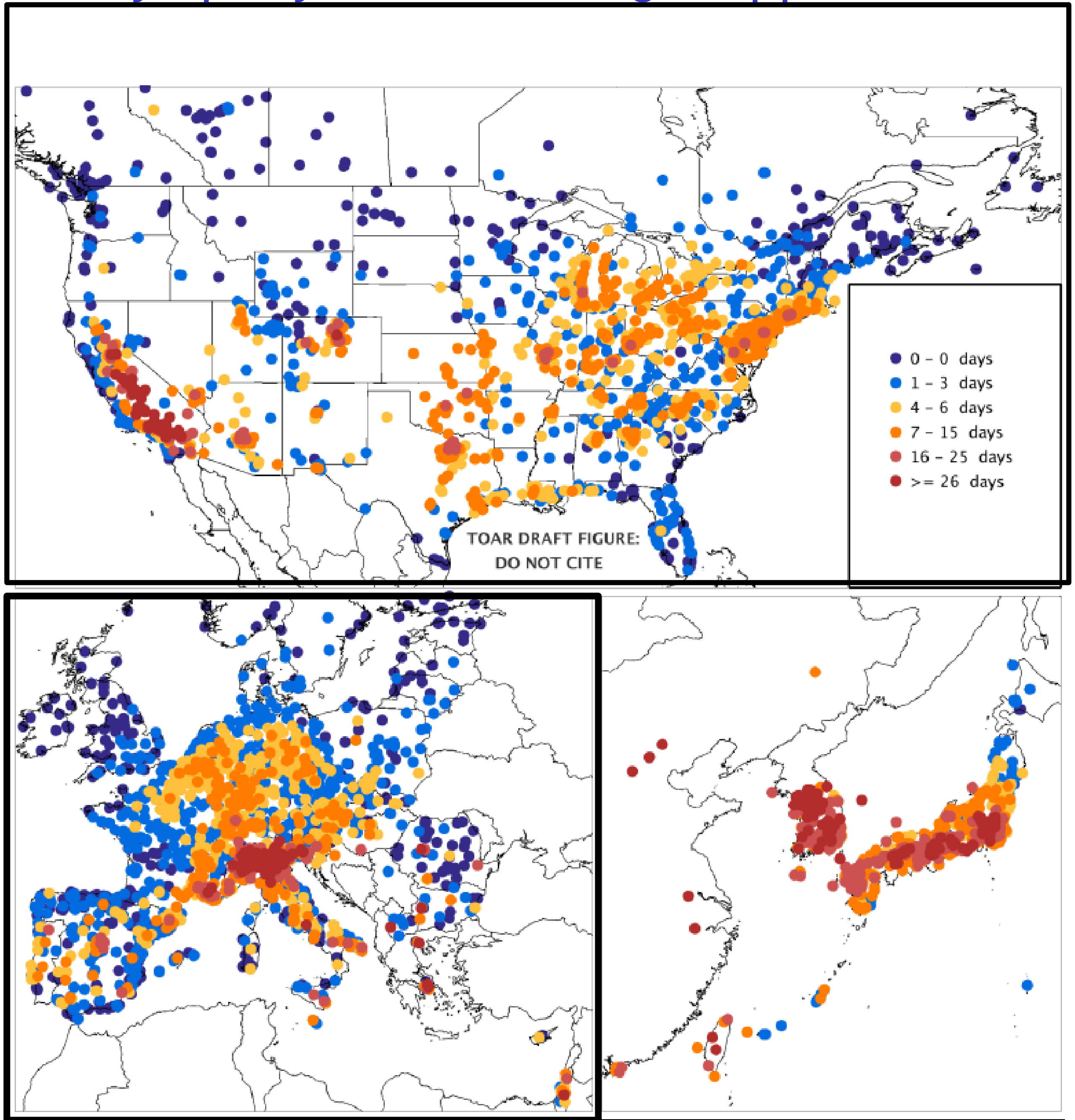


US EPA [2017], OECD [2012]

Ozone air quality standards in the US and in the world



Days per year exceeding 70 ppb ozone standard, 2010-2014



TOAR [2017]

How to control ozone pollution?

Decrease emissions of nitrogen oxides ($NO_x \equiv NO + NO_2$)
and/or volatile organic compounds (VOCs)

NO_x: efficient combustion (power plants, vehicles)
VOCs: inefficient combustion (vehicles, fires), industry, vegetation

…but complicated by non-linear dependence

Ozone production mechanism:

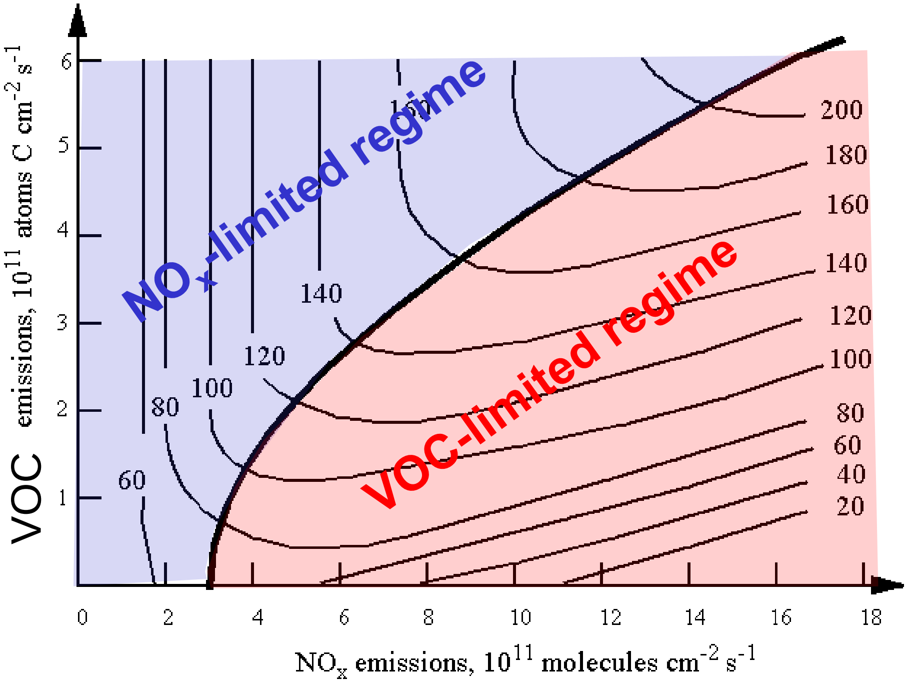
$$RH + OH \xrightarrow{O_2} RO_2 + H_2O \quad (1)$$

$$RO_2 + NO \longrightarrow RO + NO_2 \quad (2)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \quad (3)$$

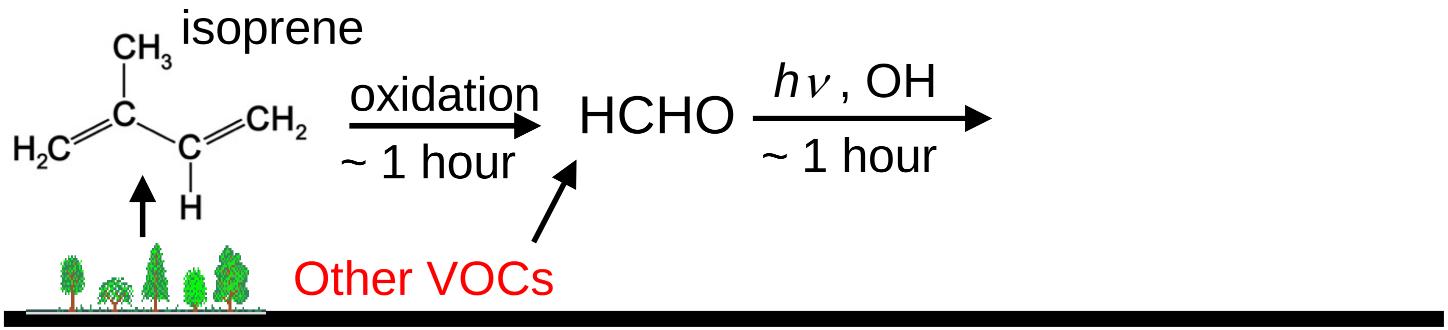
Ozone production can be limited by reaction (1) (VOC-limited regime) or reaction (2) (NO_x-limited regime)

Ozone (ppb) vs. NO_x and VOC emissions

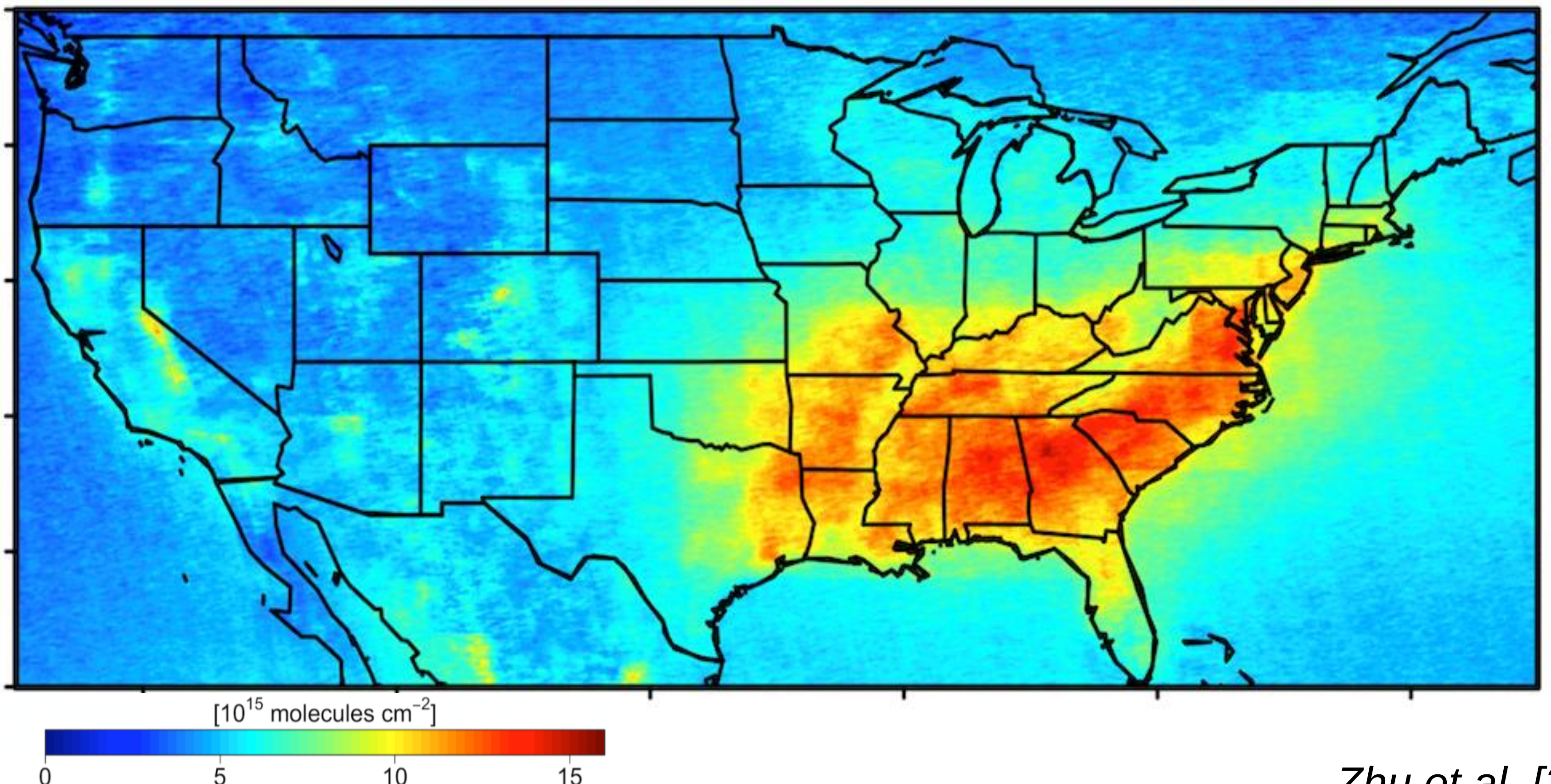


Sillman et al. [1988]

US is NO_x-limited due to high emissions of biogenic isoprene



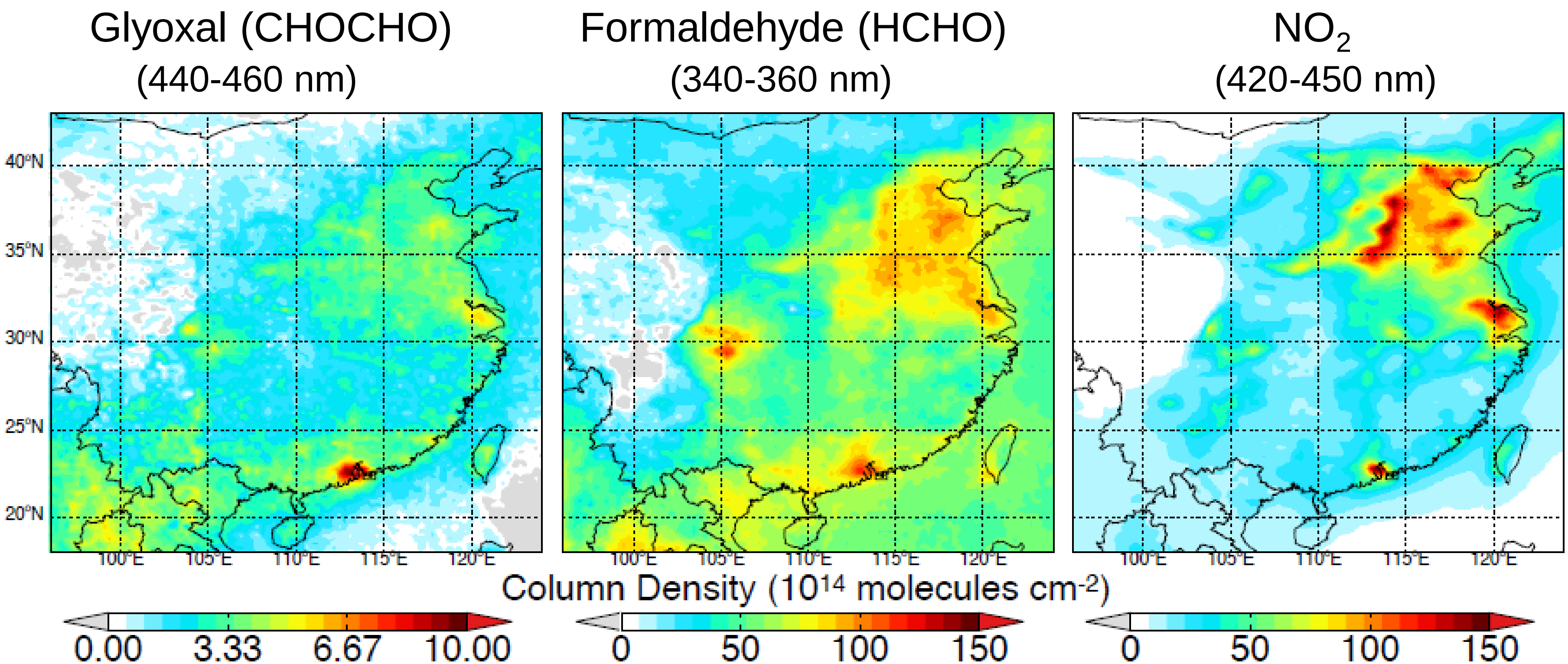
OMI satellite observations of formaldehyde (HCHO) columns, May-Aug 2005-2014



Zhu et al. [2017]

China is more complicated: high anthropogenic VOCs

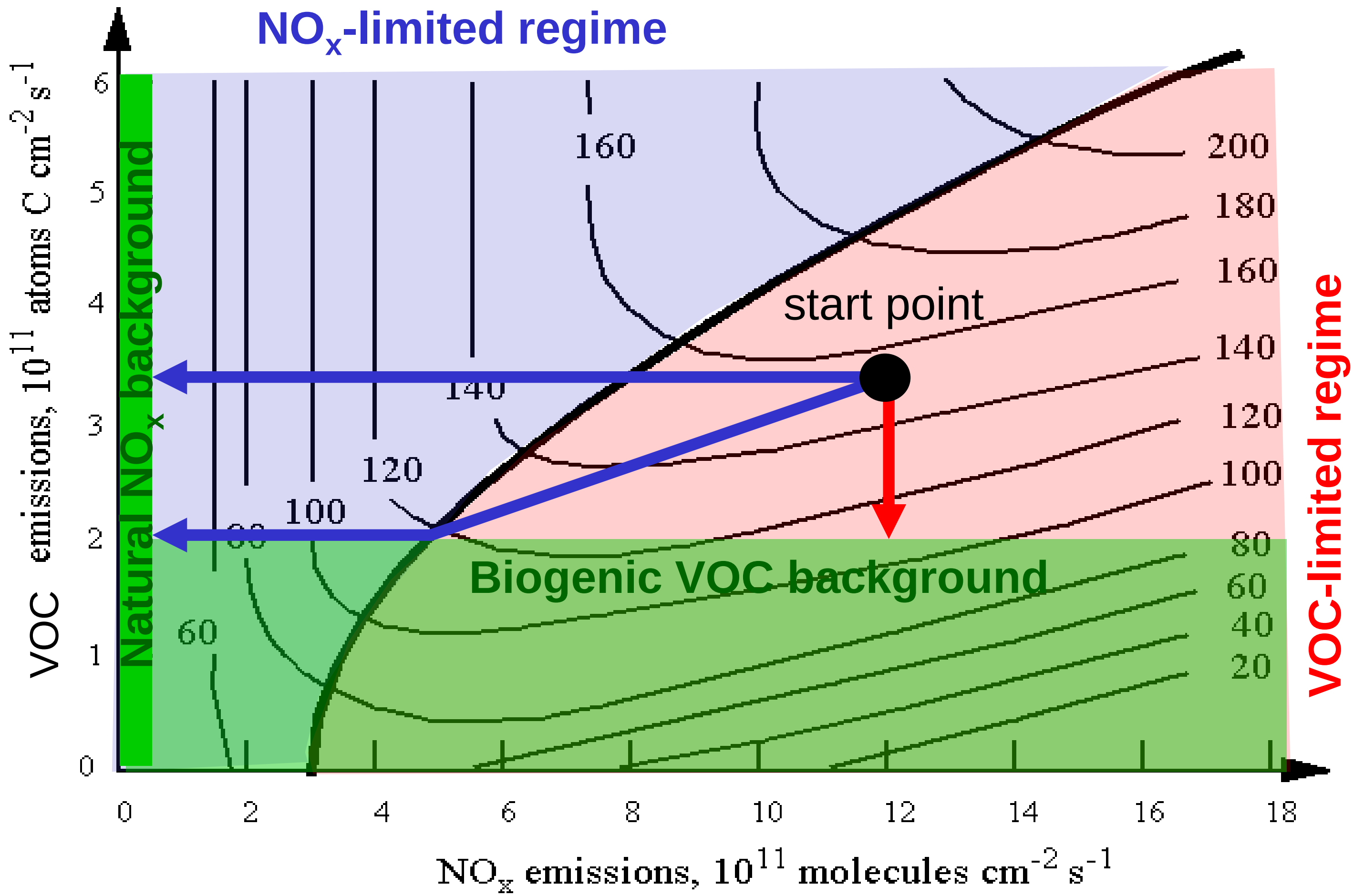
OMI annual mean tropospheric column data, 2006-2007



- VOC emissions collocated with NO_x emissions (combustion) though there is also a large biogenic component
- Glyoxal hotspot over Pearl River Delta from large aromatic emissions

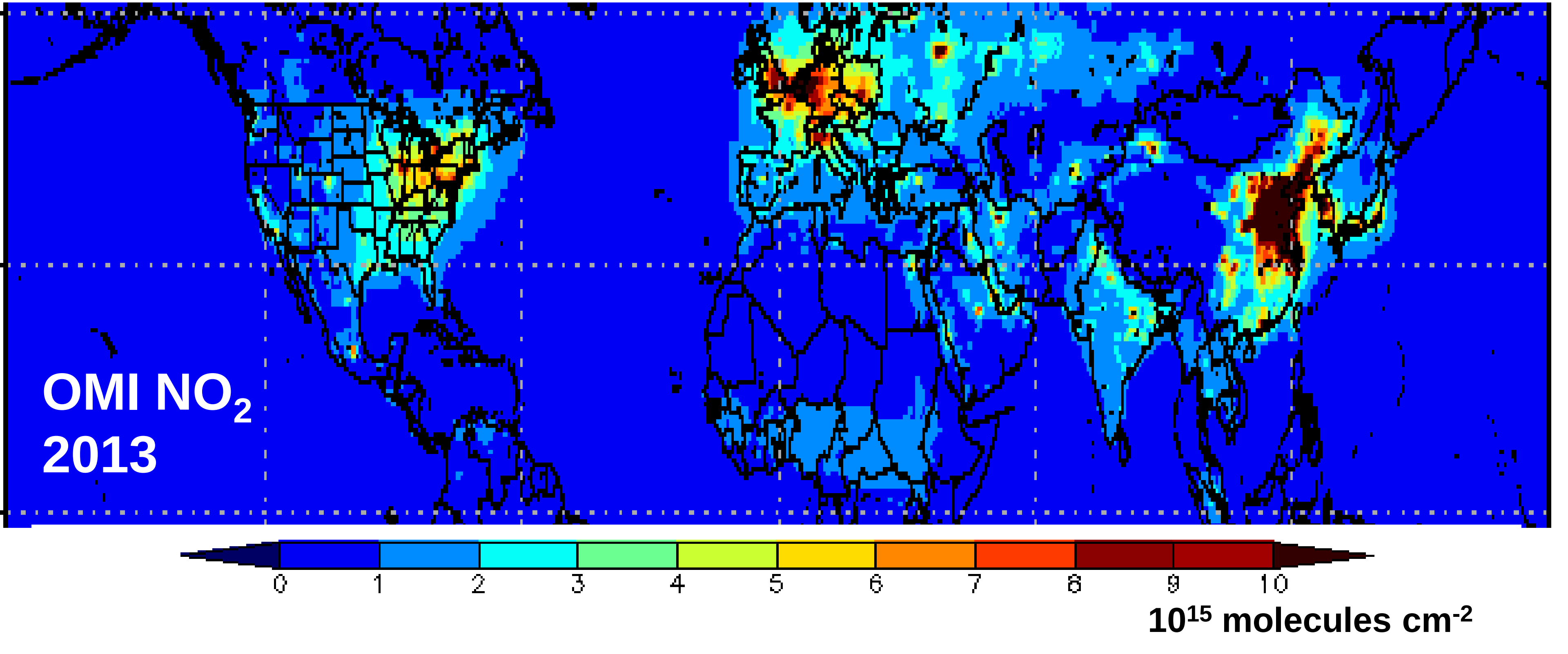
Chan Miller et al. [2016]

NO_x controls are needed to meet current ozone standards … even if production is locally VOC-limited



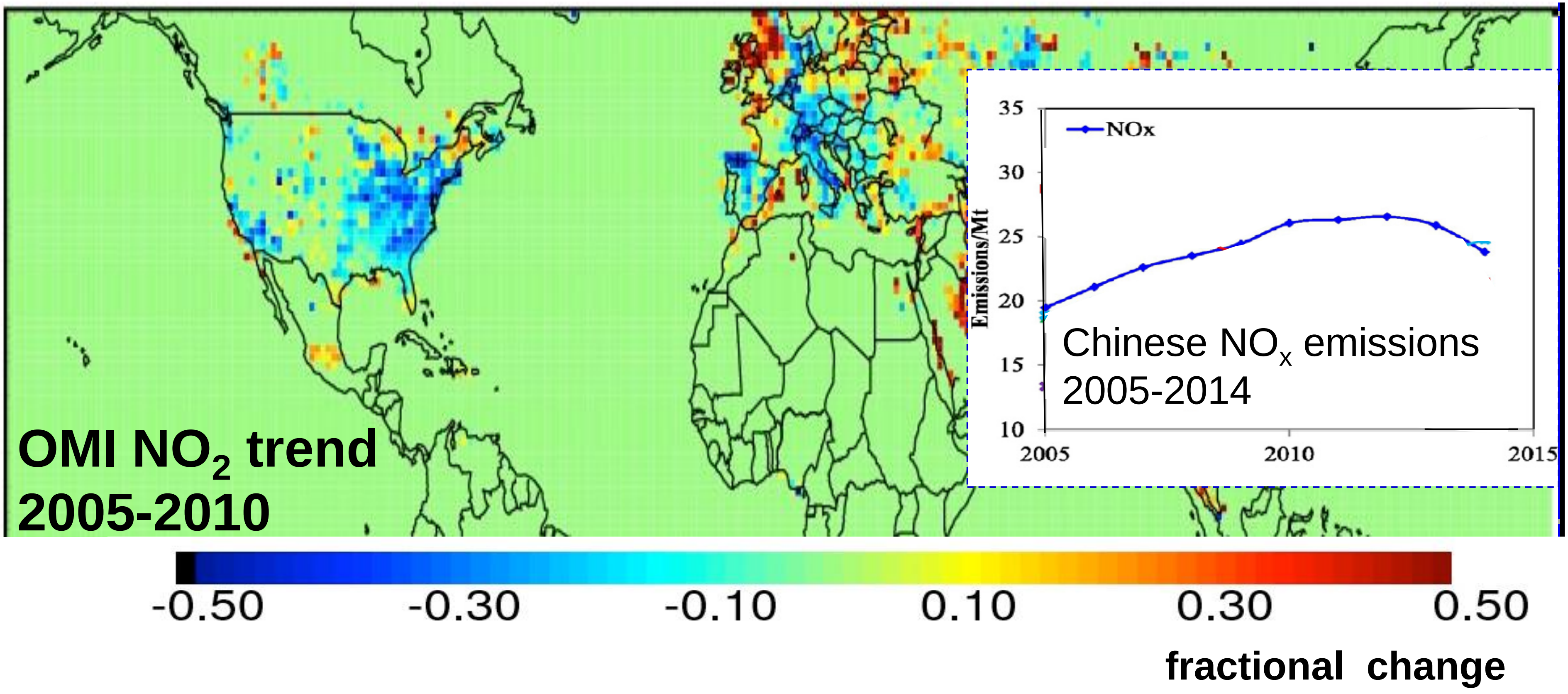
- VOC controls will only get you so far until you are limited by biogenic background
- NO_x controls are only way to get to current ozone standards and have side benefits (NO_2 air quality, nitrogen deposition)

NO_x emissions observed from space



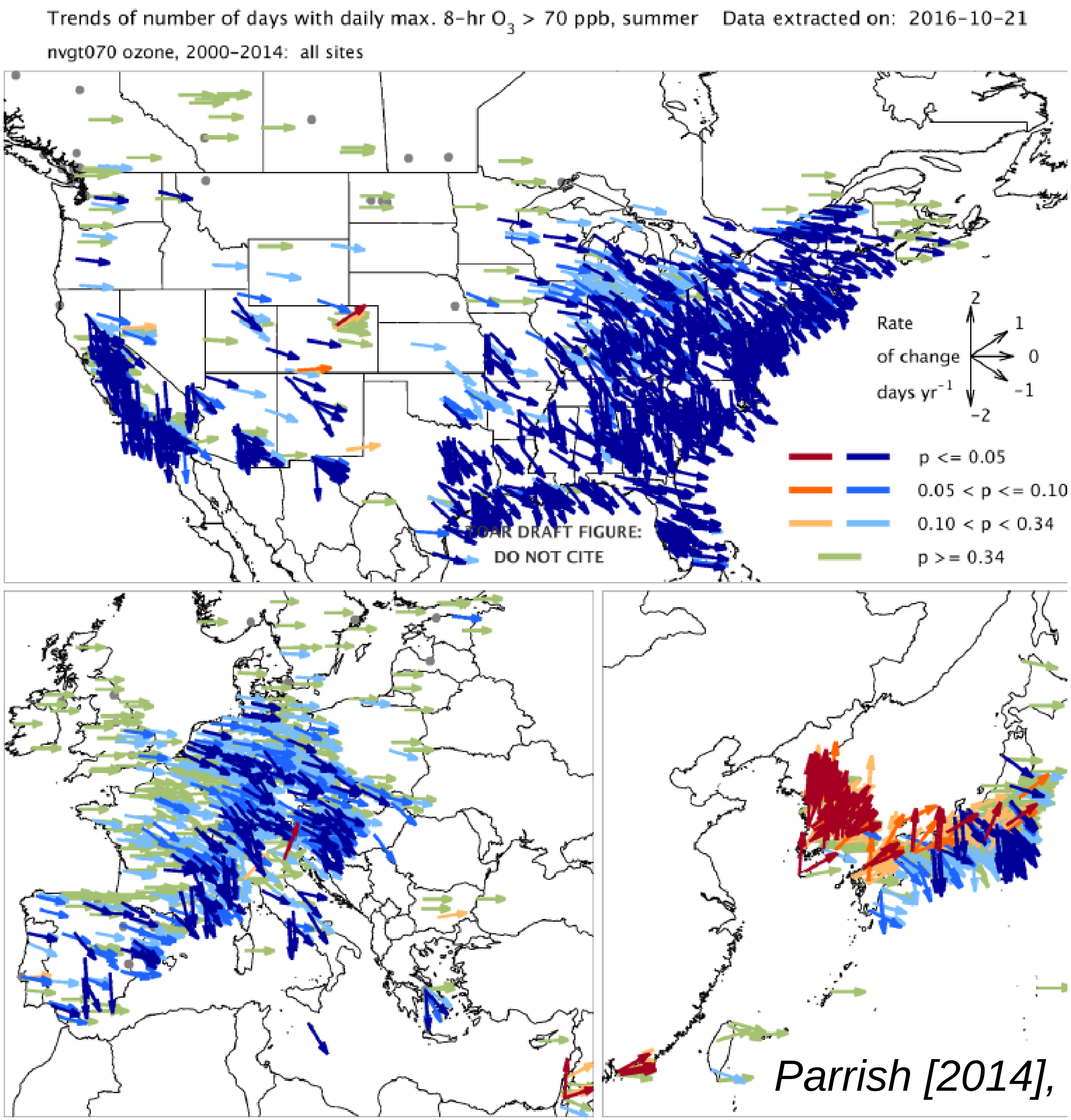
http://disc.sci.gsfc.nasa.gov/giovanni

NO_x emission trends observed from space

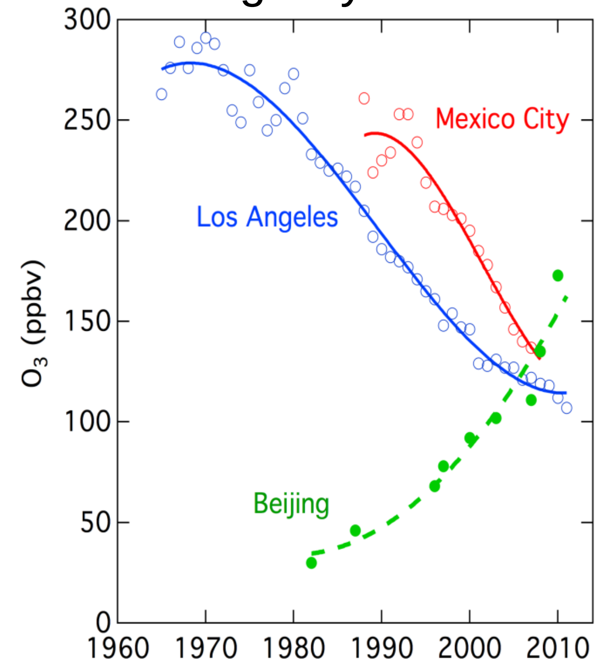


Verstraeten et al. [2014]

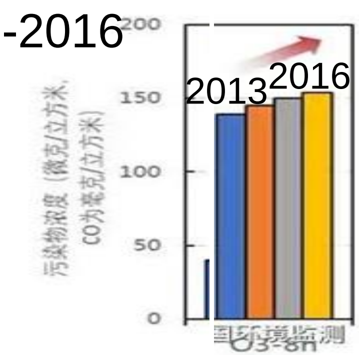
Trend in #days/year with ozone > 70 ppb, summer 2000-2014



Megacity trends

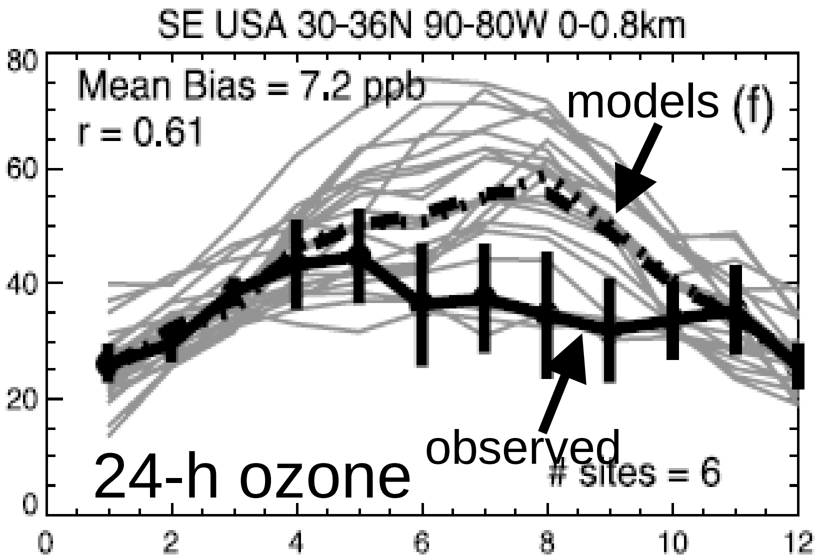


Ozone at Chinese sites, 2013-2016



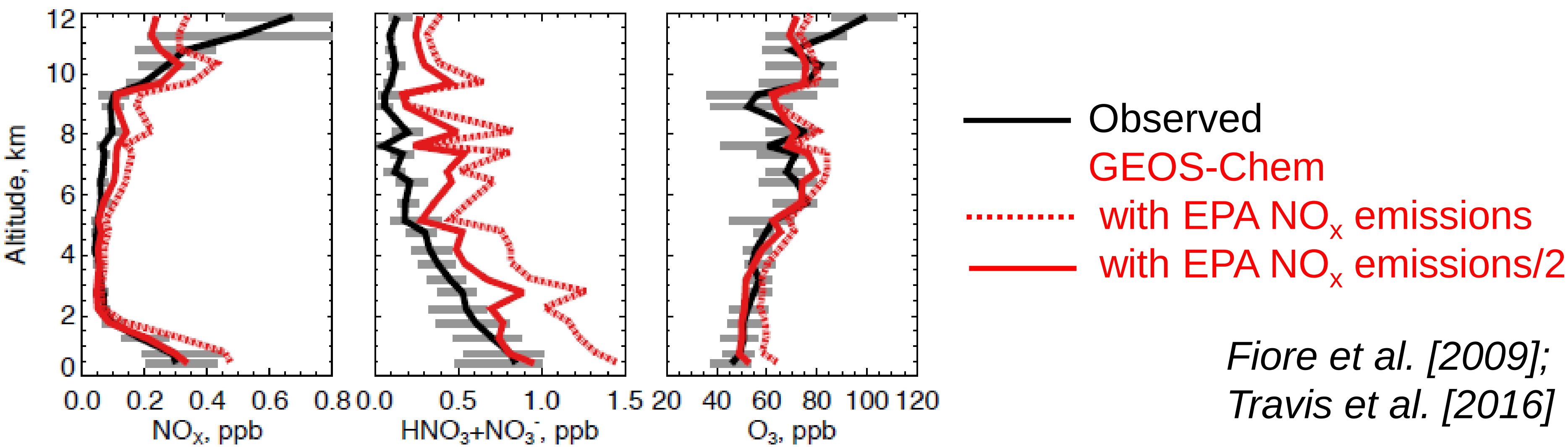
Parrish [2014], TOAR [2017], Wang et al. [2017]

Models still overestimate surface ozone in Southeast US



A major reason is that the EPA NO_x emission inventory is a factor of 2 too high:

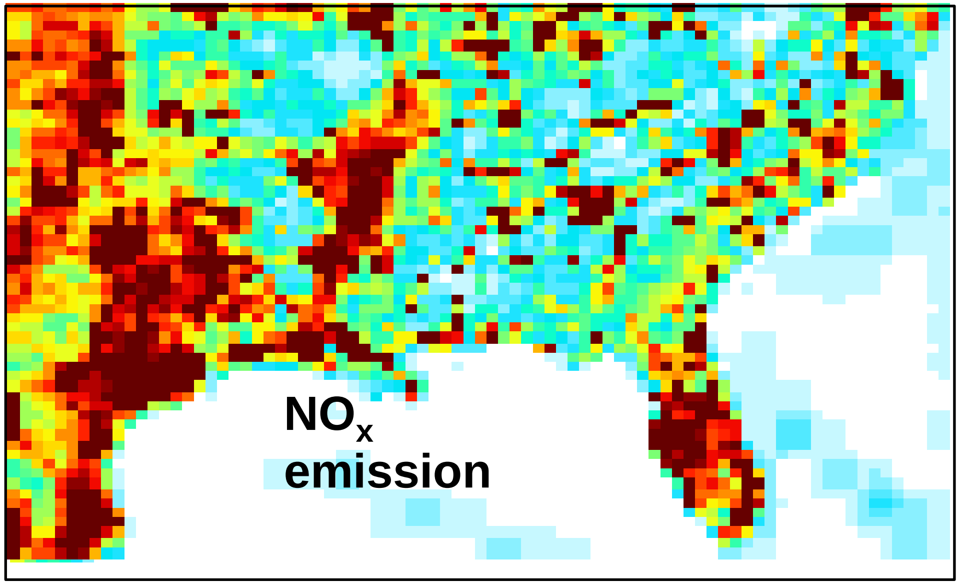
NASA SEAC[4]RS aircraft campaign, Aug Sep 2013



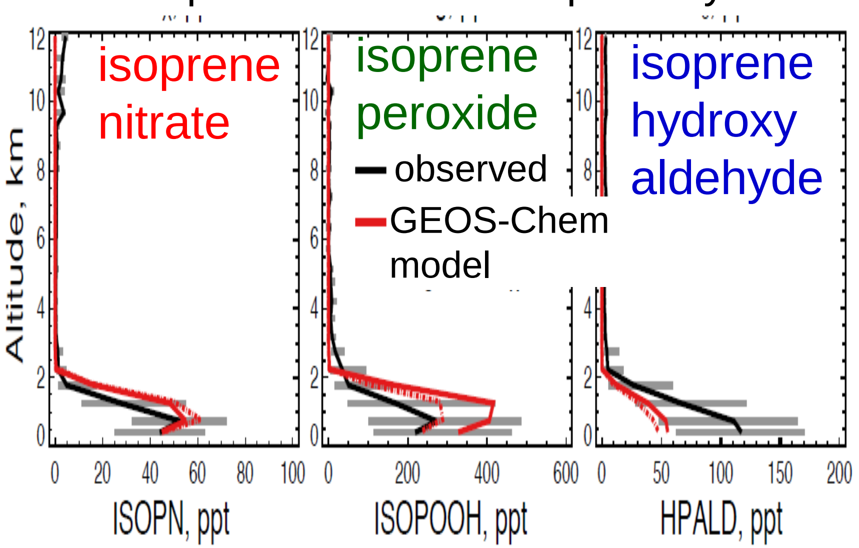
Fiore et al. [2009]; Travis et al. [2016]

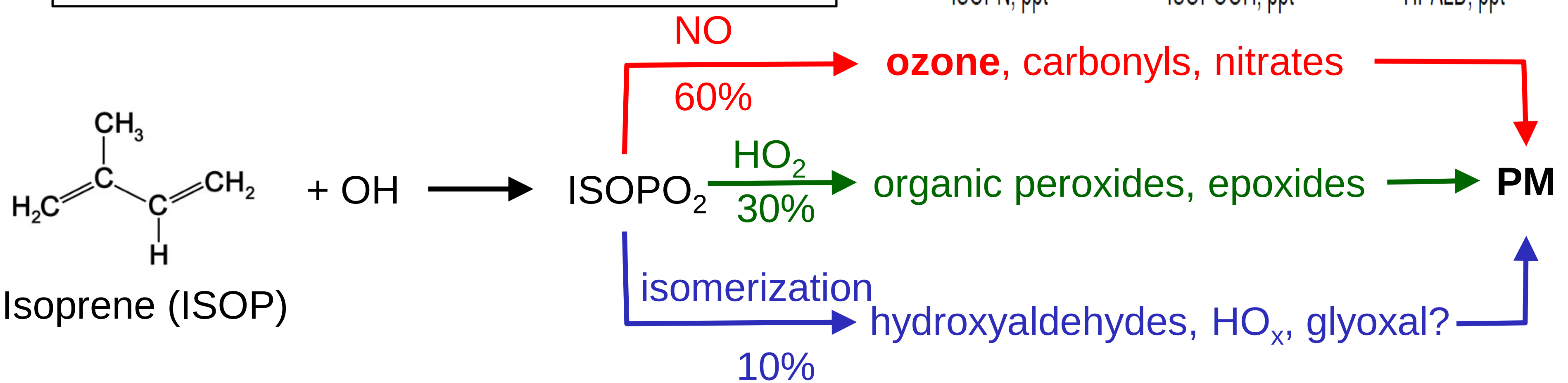
NO_x emissions in US are sufficiently low that VOC oxidation by low-NO_x pathways (poorly understood!) becomes important

Segregation between isoprene and NO_x emissions increases importance of low-NO_x pathways



SEAC[4]RS aircraft campaign, Aug-Sep 2013: oxidation products from the 3 pathways

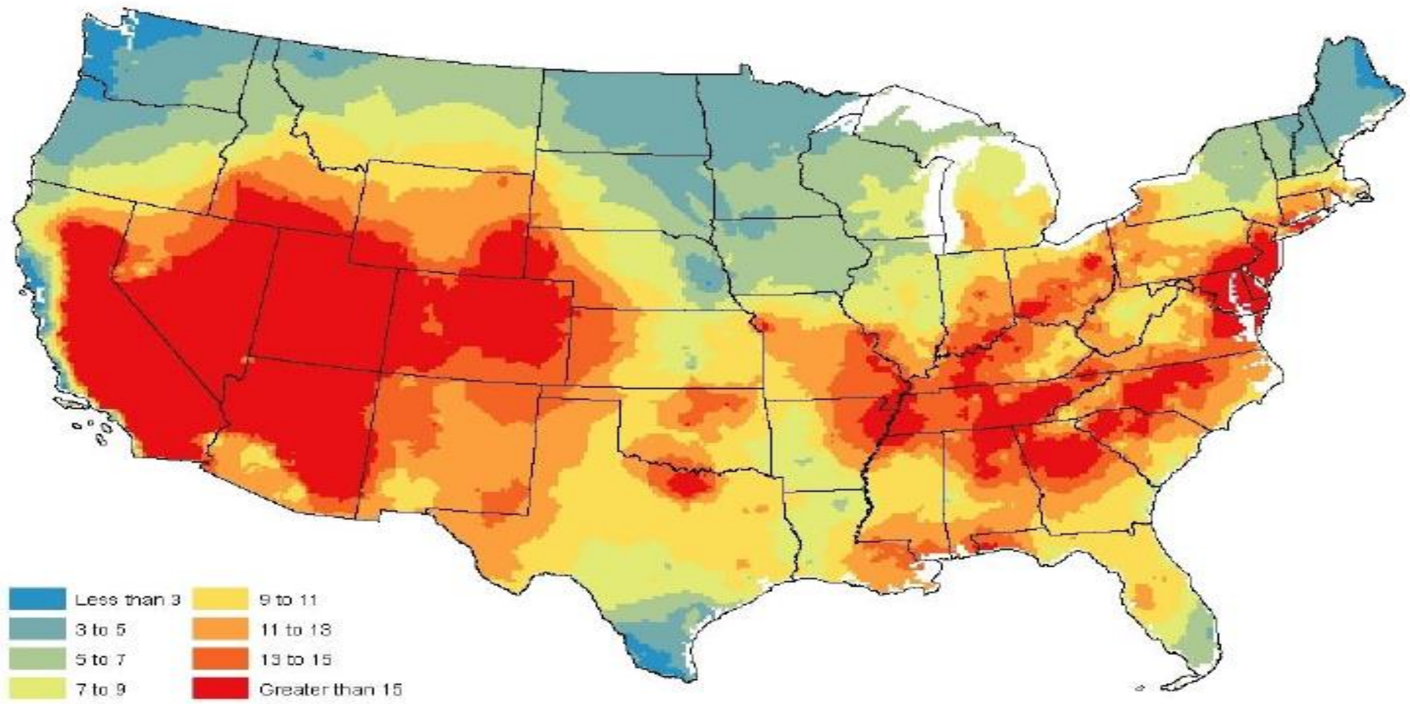




Travis et al. [2016], Yu et al. [2016]

As ozone standard tightens, the nature of the problem changes

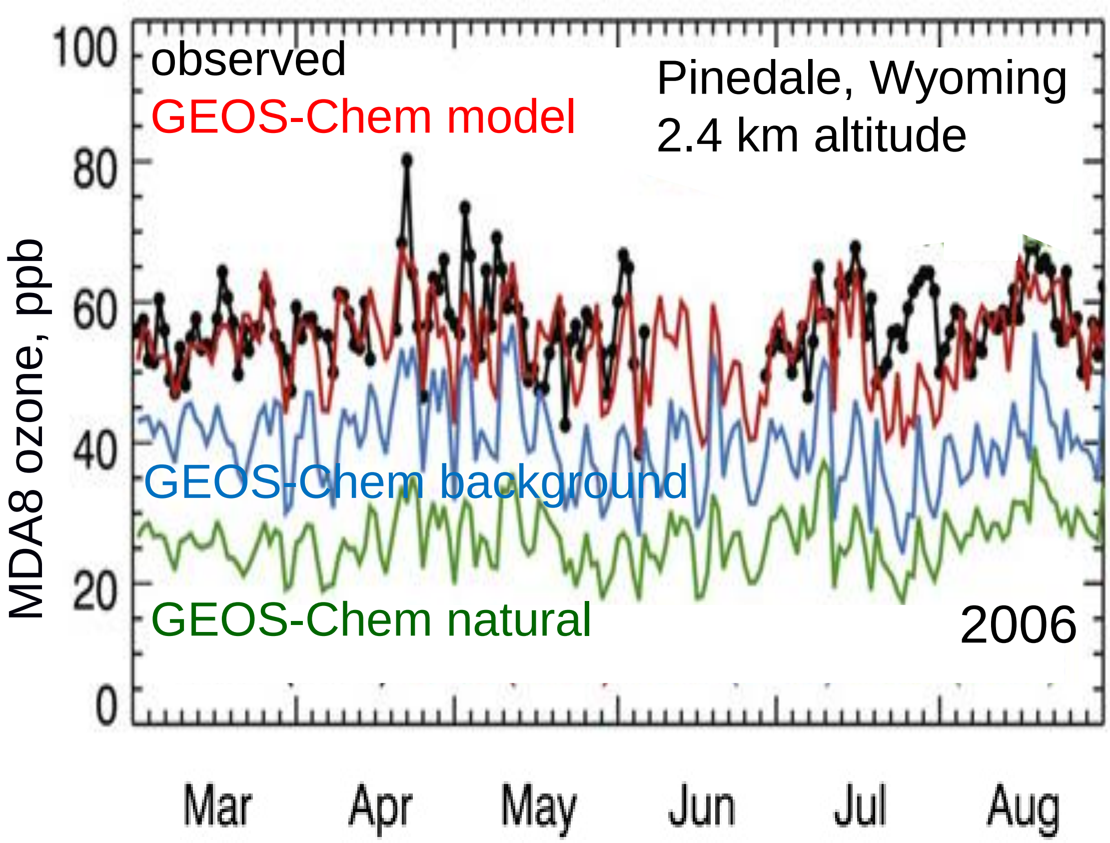
Seasonal dose in excess of 60 ppb [EPA, 2014]

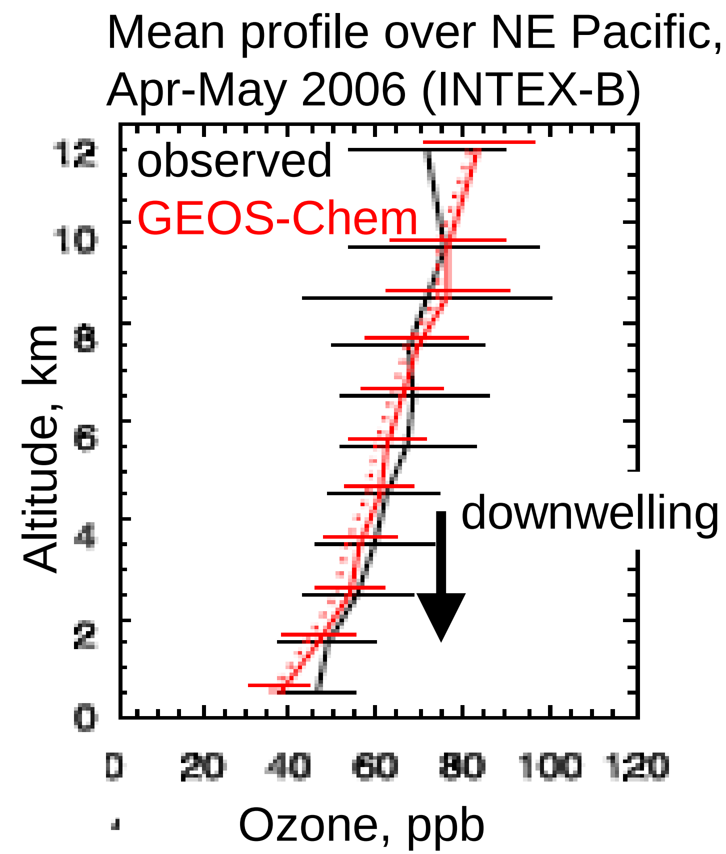


60 ppb exceedances are largest in Intermountain West

Ozone in Intermountain West originates out of N America

Background = ozone present in absence of anthropogenic sources in North America



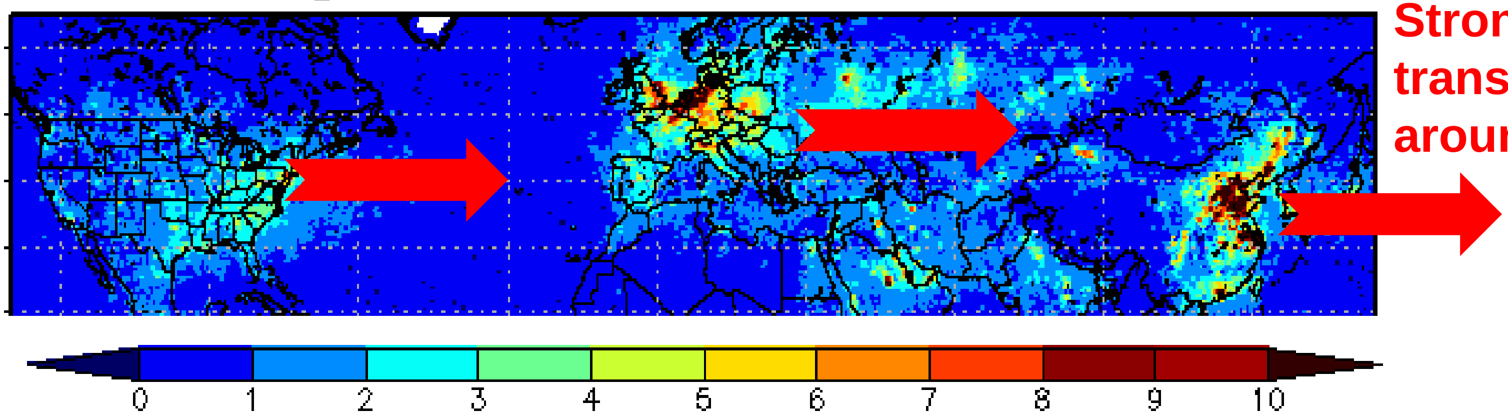


- Domestic emissions have little influence on intermountain west
- Anthropogenic background contributes ~15 ppb with little day-to-day variability

Zhang et al. [2014]

Intercontinental transport of ozone pollution

2012 OMI NO_2 column, 10^{15} molecules cm^{-2}



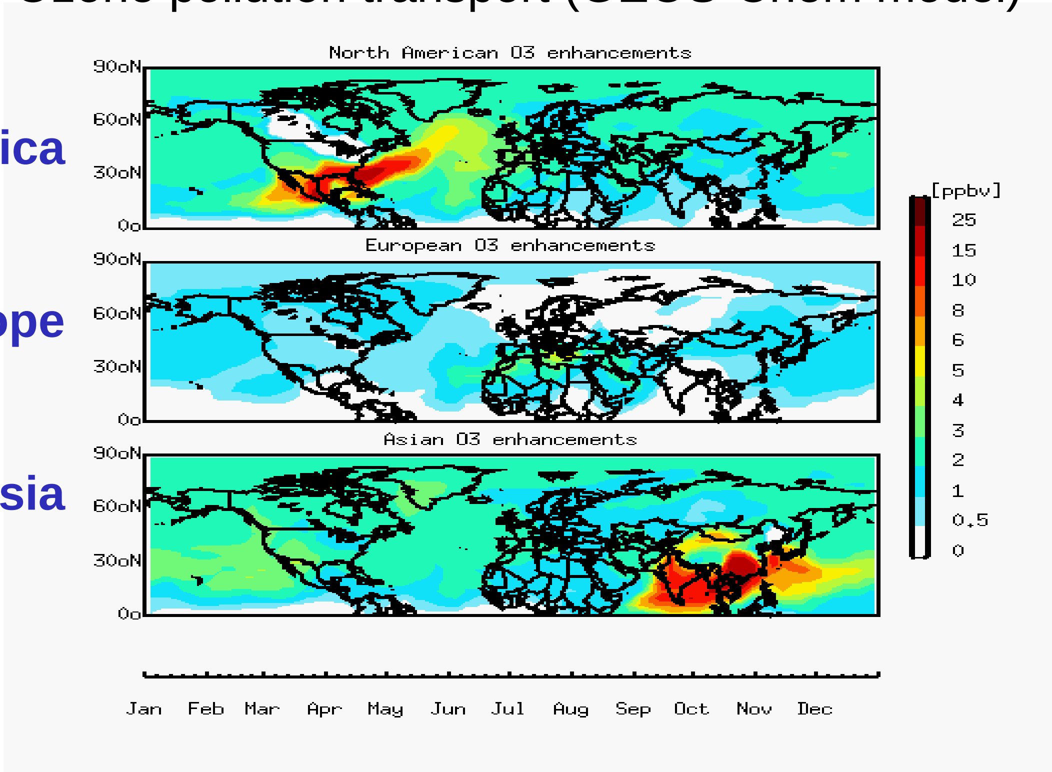
Strong westerlies transport ozone around mid-latitudes

Ozone pollution transport (GEOS-Chem model)

N America

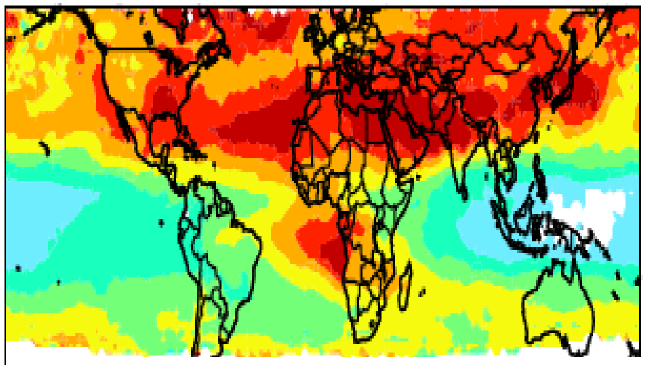
Europe

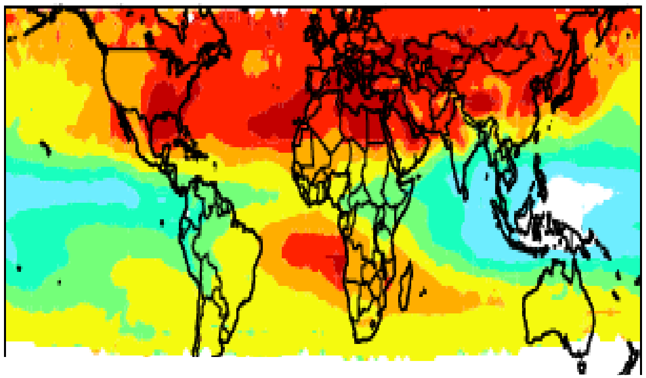
Asia



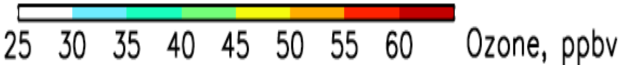
Global tropospheric ozone is rising…and we don't know why

Mean 500 hPa ozone in JJA 2013





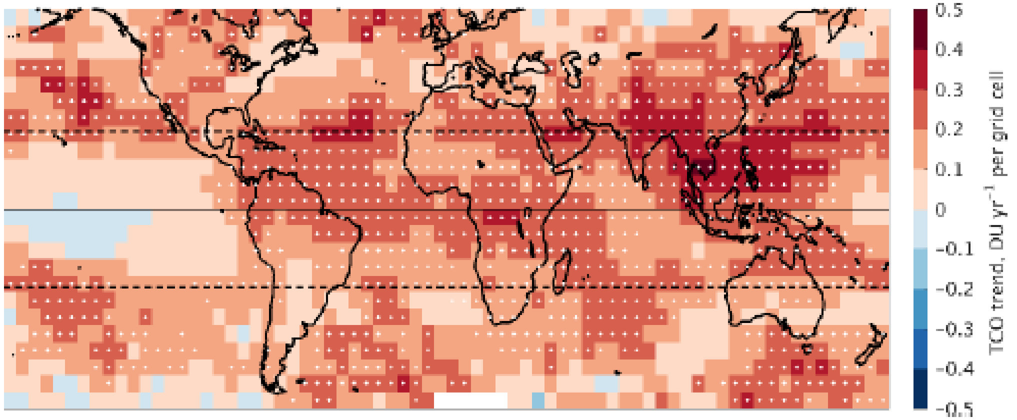
OMI satellite data



GEOS-Chem model

- **Partly natural:** stratospheric influence, lightning, wildfires
- **Partly anthropogenic:** methane, intercontinental pollution, fires, ships, aircraft…

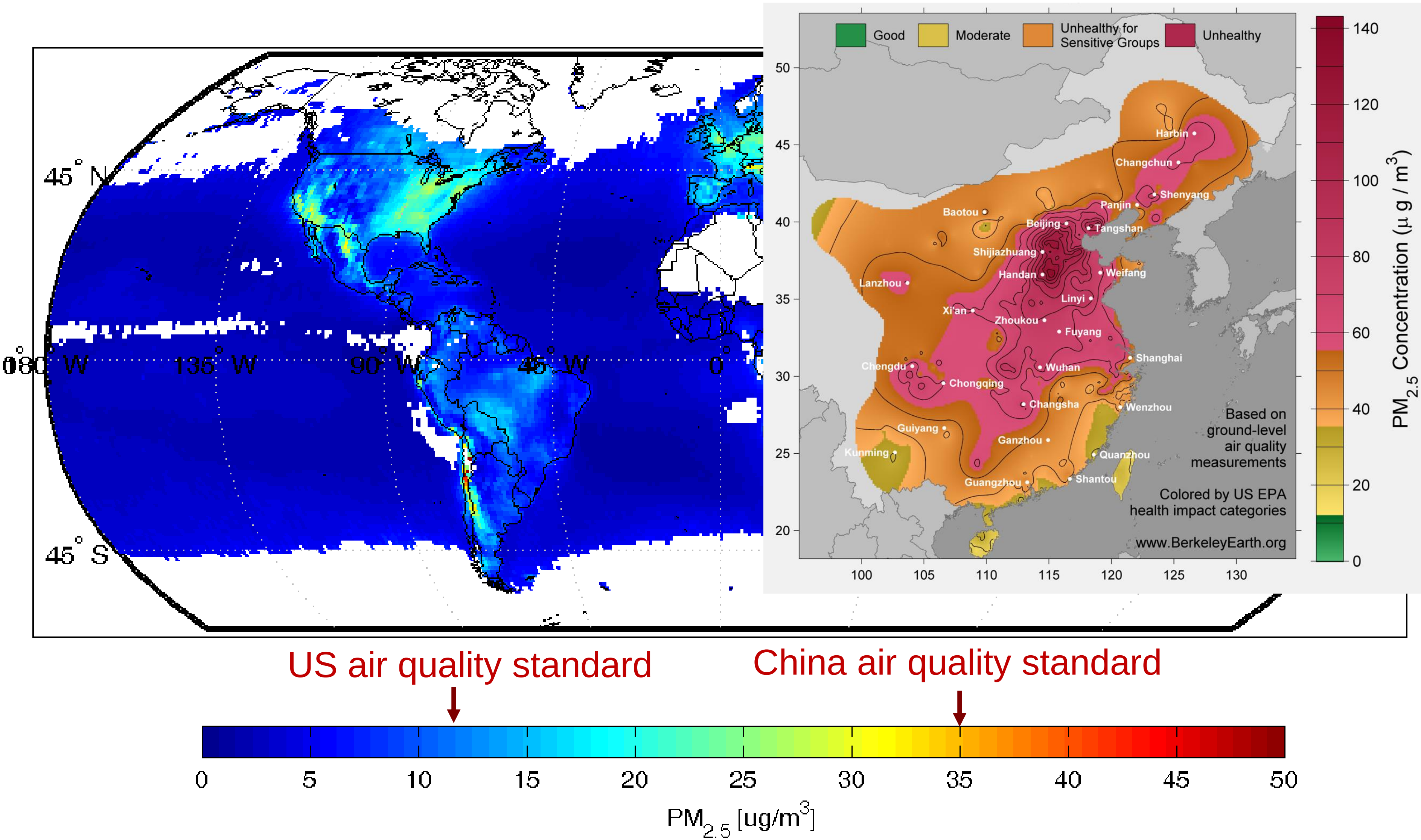
OMI tropospheric ozone column trend, 2005-2016:
increasing almost everywhere



Models can reproduce present-day levels but not long-term trends

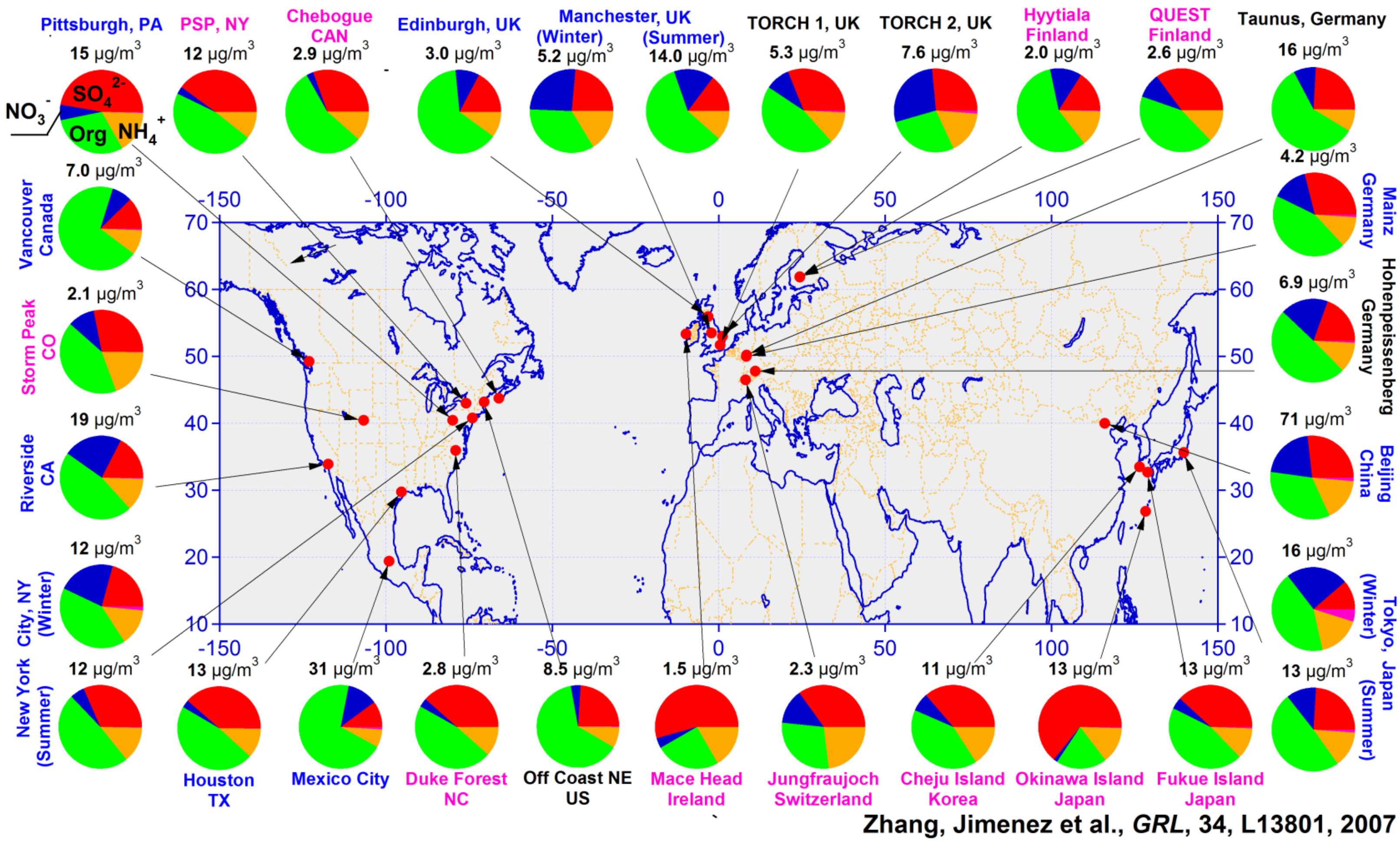
Hu et al. [2017], TOAR [2017]

Annual mean concentrations of fine particulate matter ($PM_{2.5}$) inferred from satellite data



van Donkelaar et al. [2010]; Rhode and Muller [2015]

$PM_{2.5}$ composition

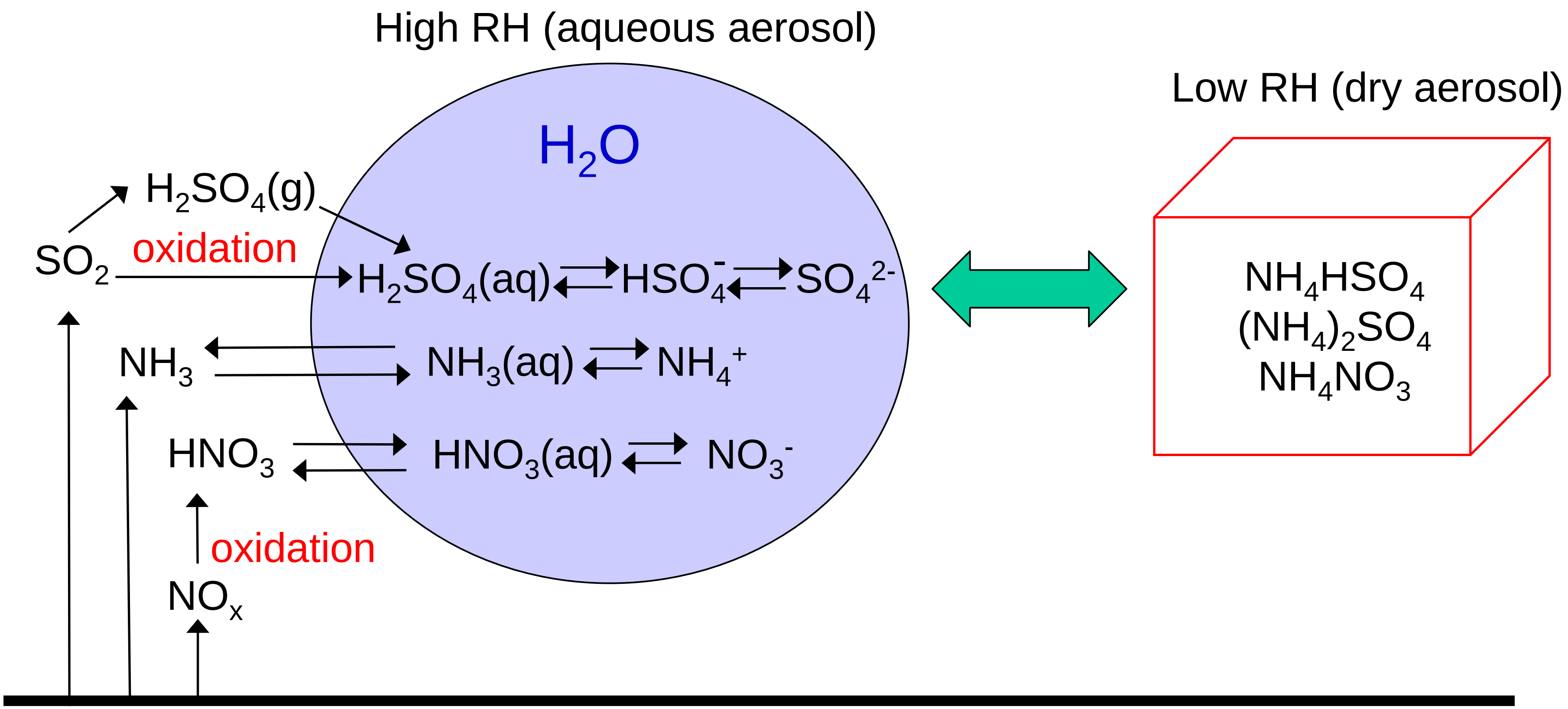


Wang et al. [2014]

Two components dominate $PM_{2.5}$ mass under almost all conditions:

- Sulfate-nitrate-ammonium (SNA)
- Organic carbon (OC)

Formation of sulfate-nitrate-ammonium aerosol



EMISSION

SO_2: coal combustion

NH_3: agriculture

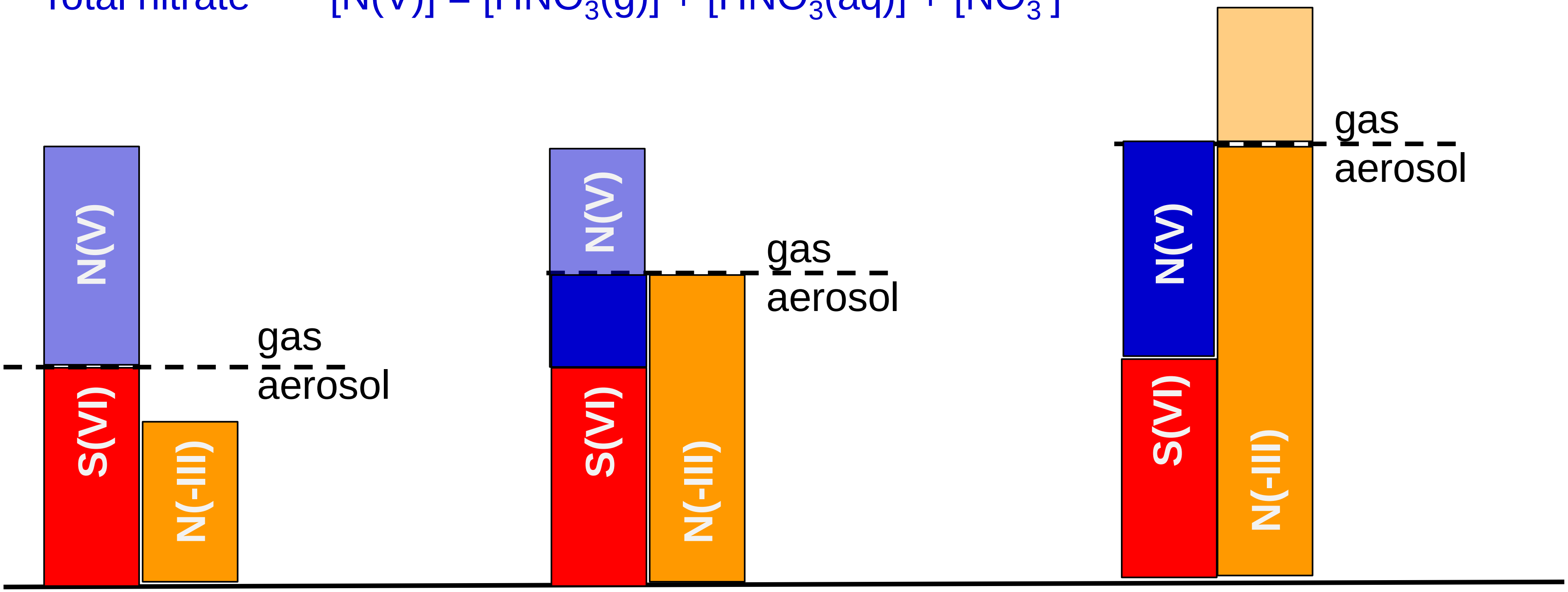
NO_x: fuel combustion

- Sulfuric acid produced from SO_2 oxidation is ~100% incorporated into the aerosol
- Ammonium and nitrate are incorporated as determined by acid-base titration

Three different regimes for SNA aerosol formation

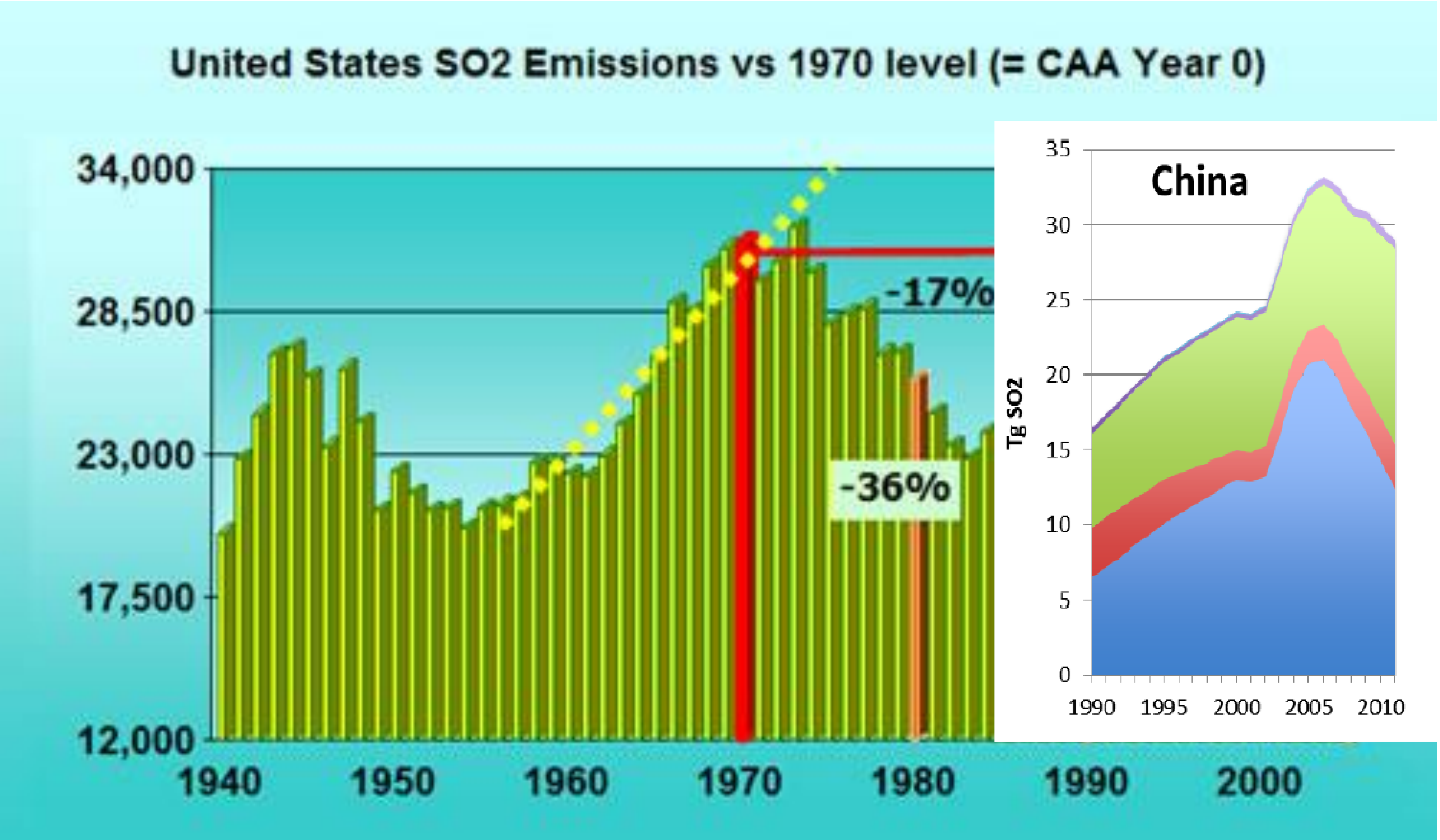
Total sulfate $[S(VI)] = [H_2SO_4(aq)] + [HSO_4^-] + [SO_4^{2-}]$
Total ammonia $[N(-III)] = [NH_3(g)] + [NH_3(aq)] + [NH_4^+]$
Total nitrate $[N(V)] = [HNO_3(g)] + [HNO_3(aq)] + [NO_3^-]$

Equivalents per m^3 of air



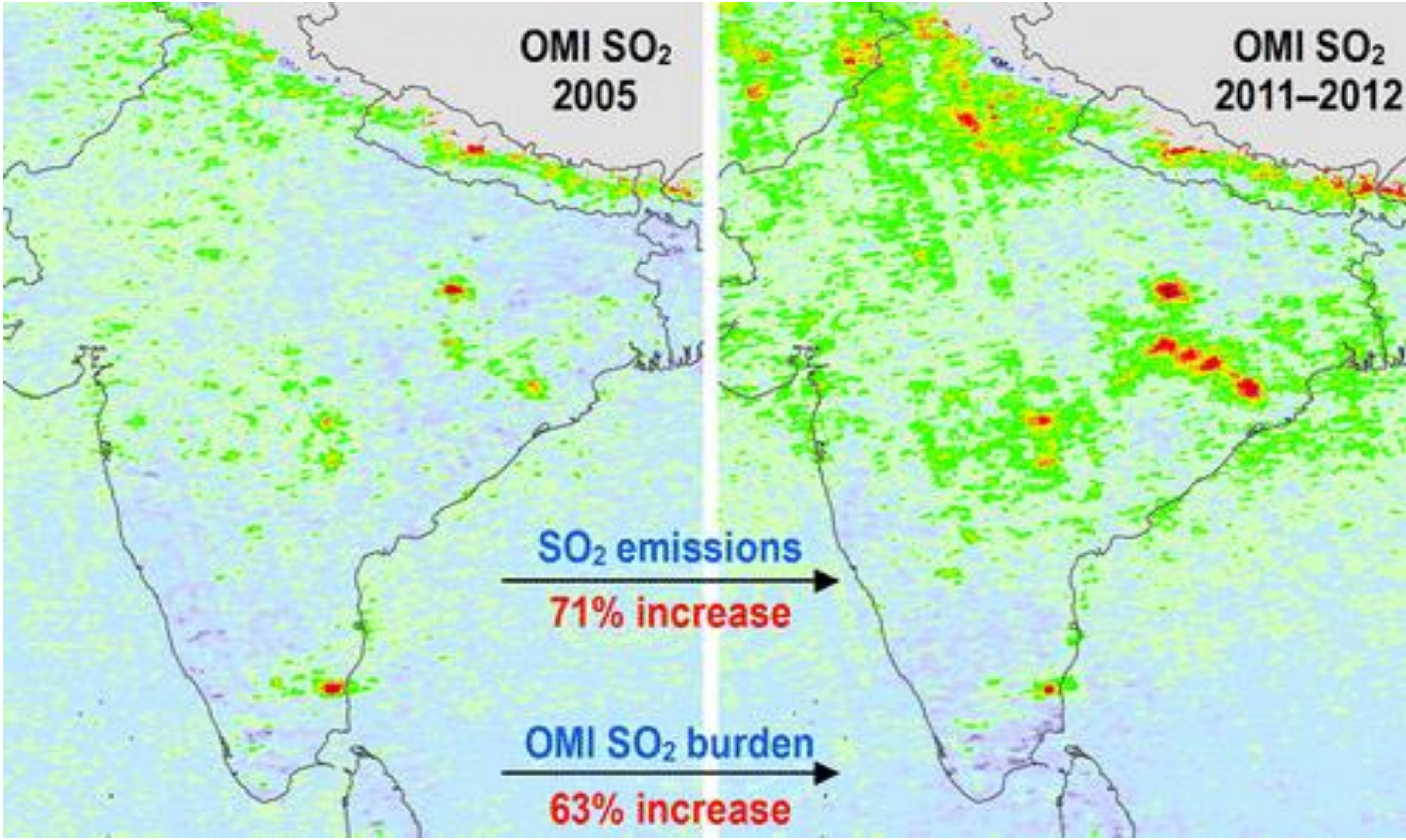
$[S(VI)] > [N(-III)]$	$[S(VI)]+[N(V)] > [N(-III)] > [S(VI)]$	$[S(VI)]+[N(V)] < [N(-III)]$
• all ammonia in aerosol • no nitrate in aerosol	• almost all ammonia in aerosol • nitrate partly in aerosol	• ammonia partly in aerosol • almost all nitrate in aerosol
REGIME 1	**REGIME 2**	**REGIME 3**

Long-term trends in SO_2 emissions



New SO_2 pollution frontier: India

OMI satellite instrument shows rapid growth in SO_2 emissions from coal use

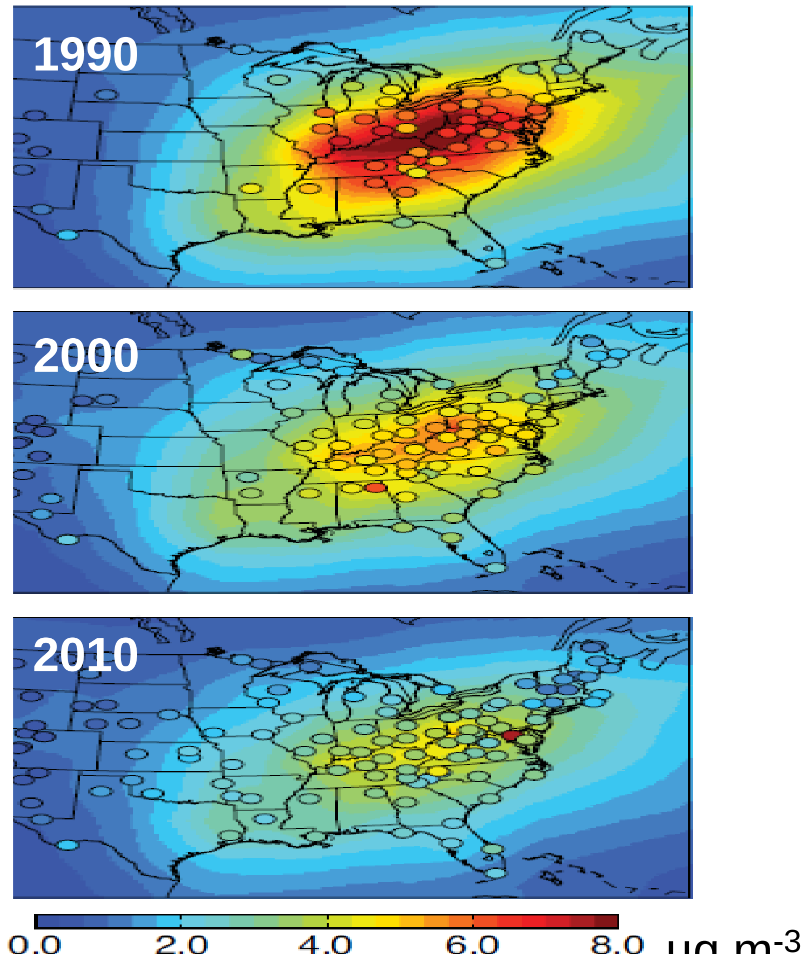


Lu et al. [2013]

Sulfate in US has shown linear response to SO_2 emissions

$$SO_2 \xrightarrow[\text{atmospheric oxidation}]{\text{OH, } H_2O_2 \text{ (in cloud), ozone (in cloud)}} \text{sulfate}$$

observed (circles), model (background)

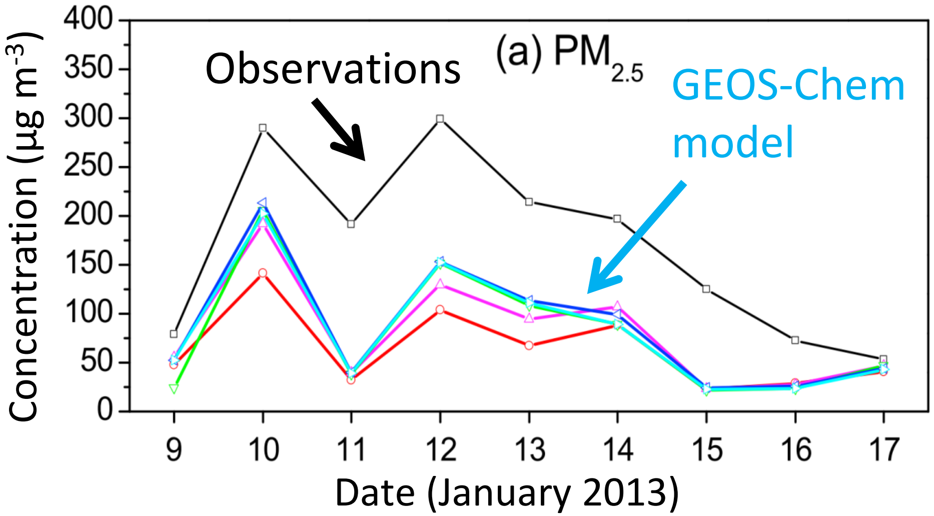


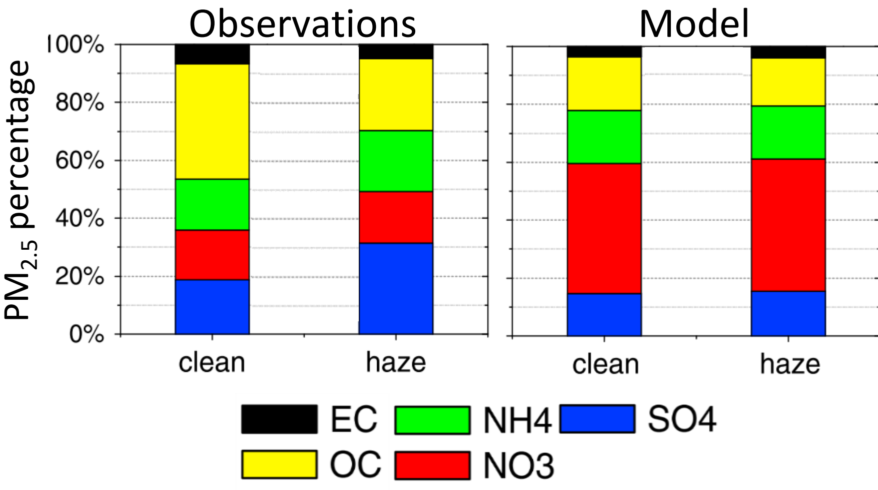
SO_2 emissions decreased by 3% per year from 1990 to 2010

➡ Sulfate decreased by 3% per year

Leibensperger et al. [2012]

Problem with explaining winter sulfate haze in Beijing

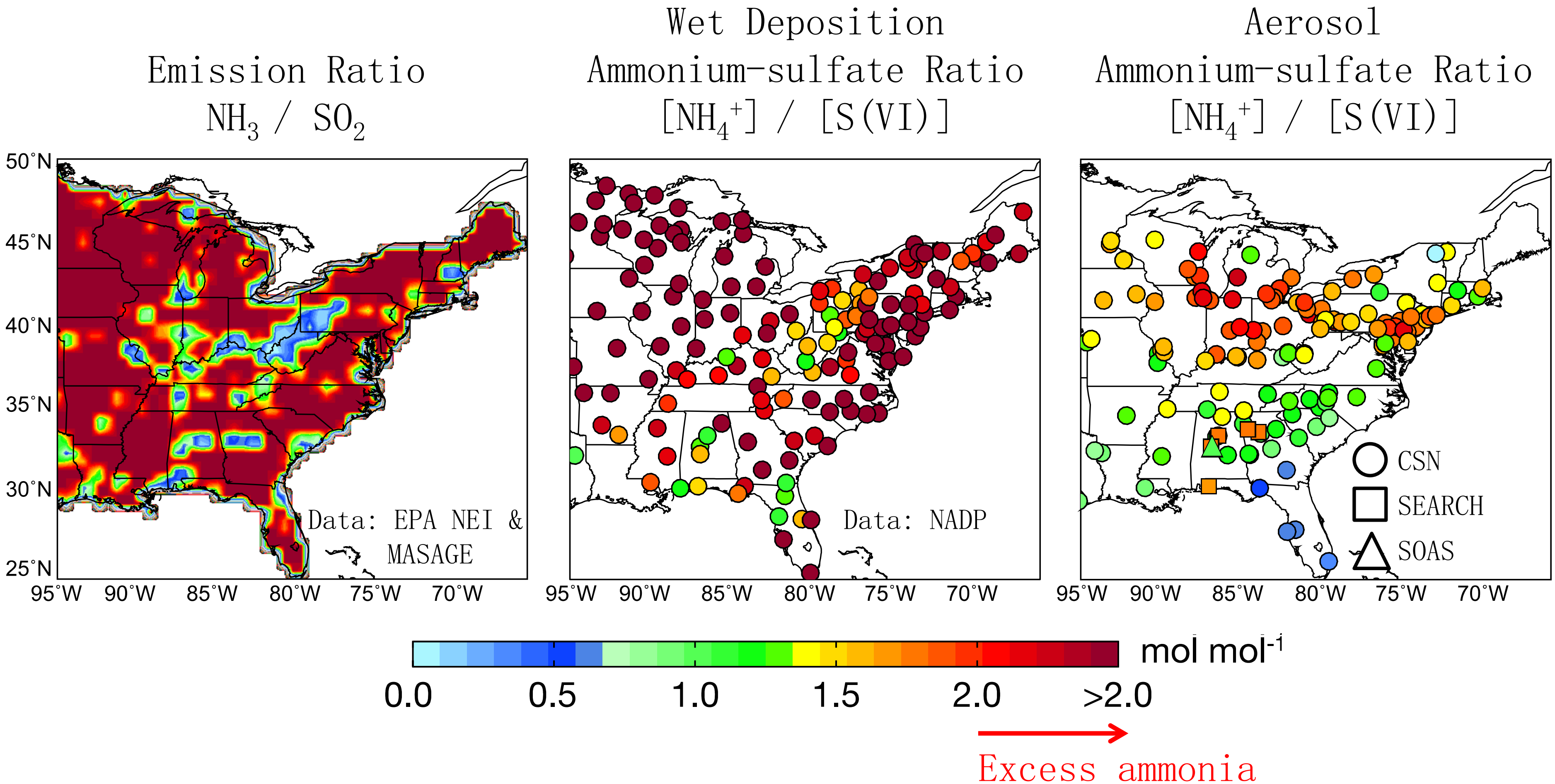




- Sulfate production in models is limited by supply of photochemical oxidants
- Possible solutions: transition-metal-catalyzed oxidation by O_2, formation of SO_2-formaldehyde complexes; strongly dependent on aerosol/cloud pH

Wang et al. [2014]; Jonathan Moch, Harvard

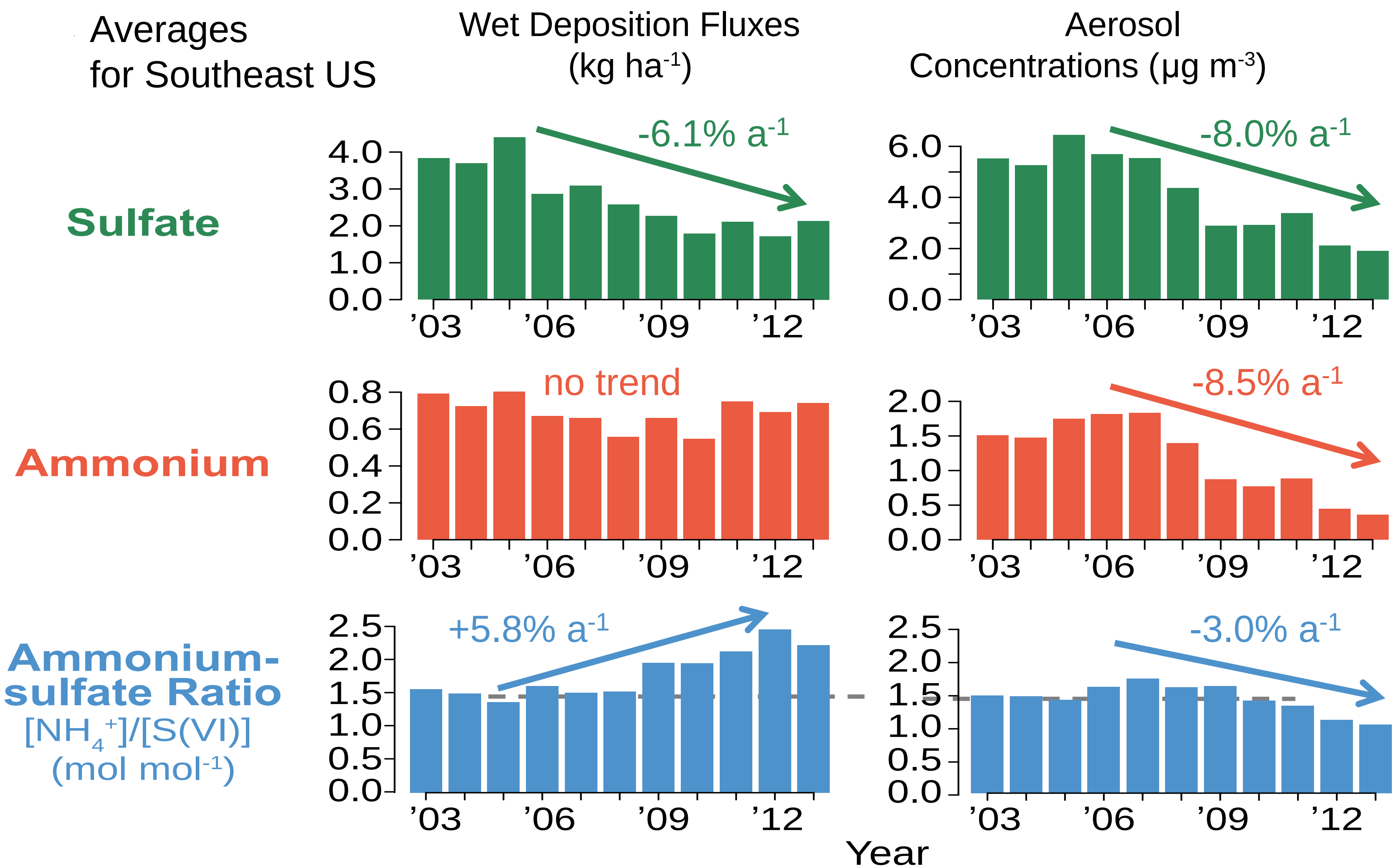
Sulfate aerosol should now be titrated by ammonia in eastern US… but it isn't



Major departure from standard sulfate-ammonium aerosol thermodynamics

Silvern et al. [2017]

Long-term trends in Southeast US also depart from thermodynamics

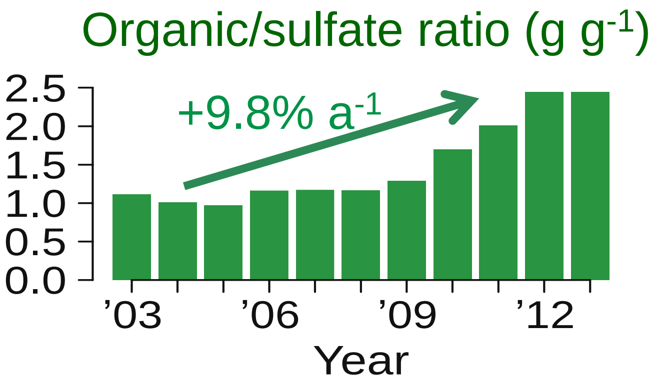


Ammonium-sulfate aerosol ratio decreases as sulfate decreases!

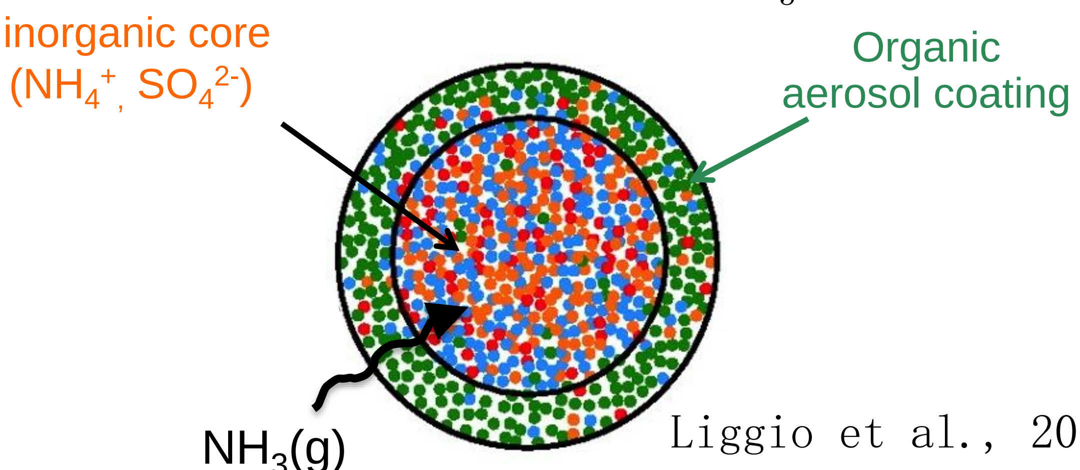
Silvern et al. [2017]

Possible retardation of thermodynamic equilibrium by organic aerosol

US aerosol has changed over past decade
from sulfate-rich to organic-rich



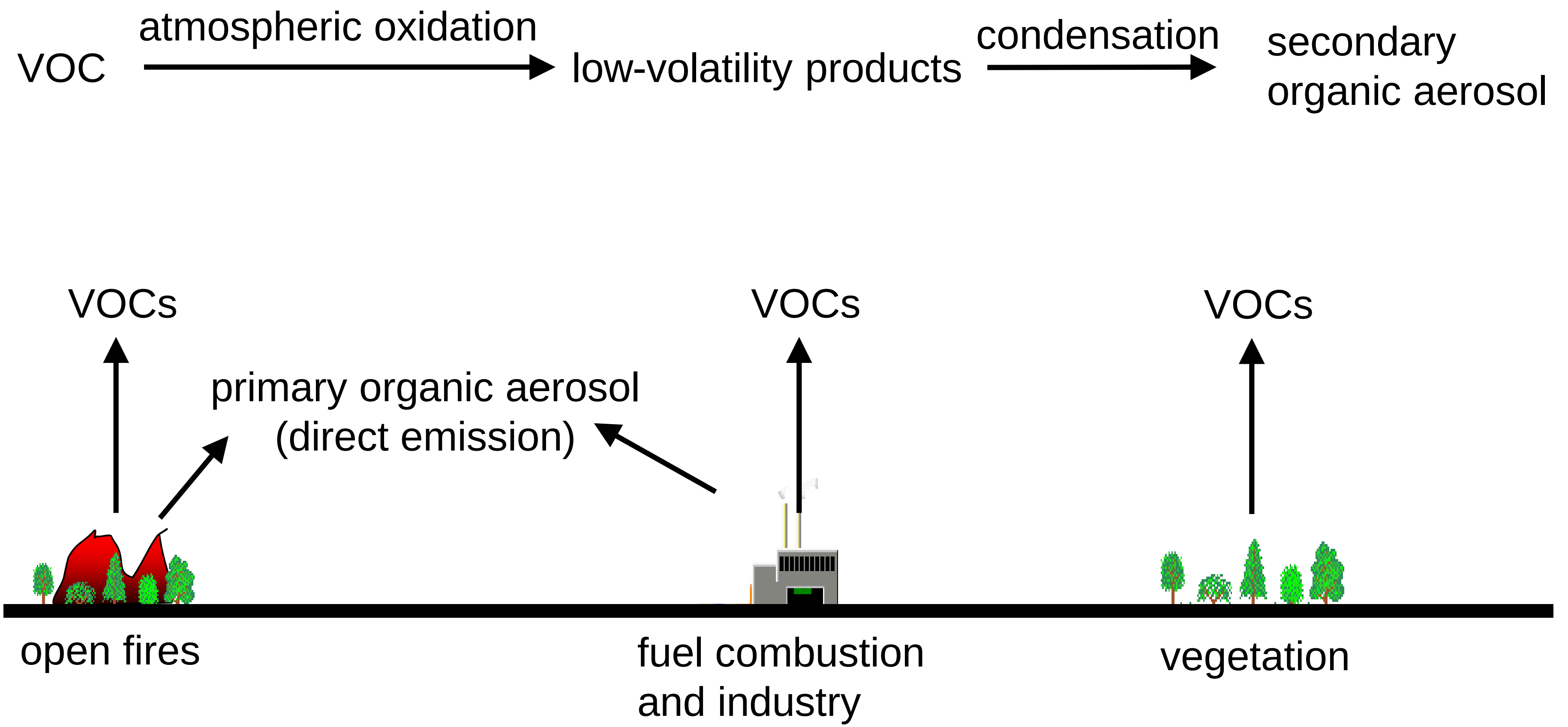
Evidence of phase separation,
kinetic limitation to NH_3 uptake



Liggio et al., 201
You et al., 2012

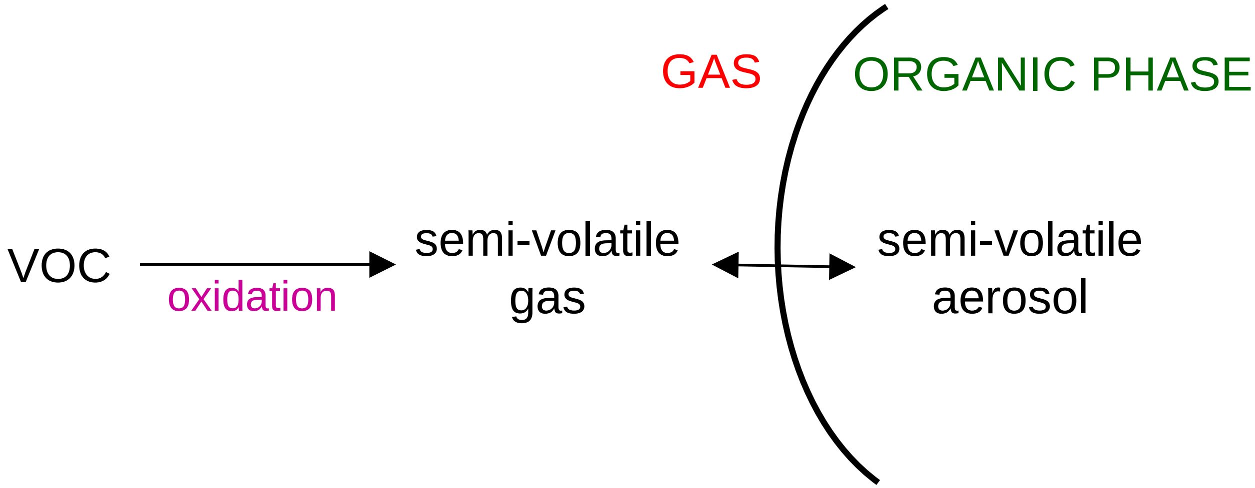
Retardation/modification of equilibrium by organics
could affect uptake of other gases, including water

Primary and secondary organic aerosol

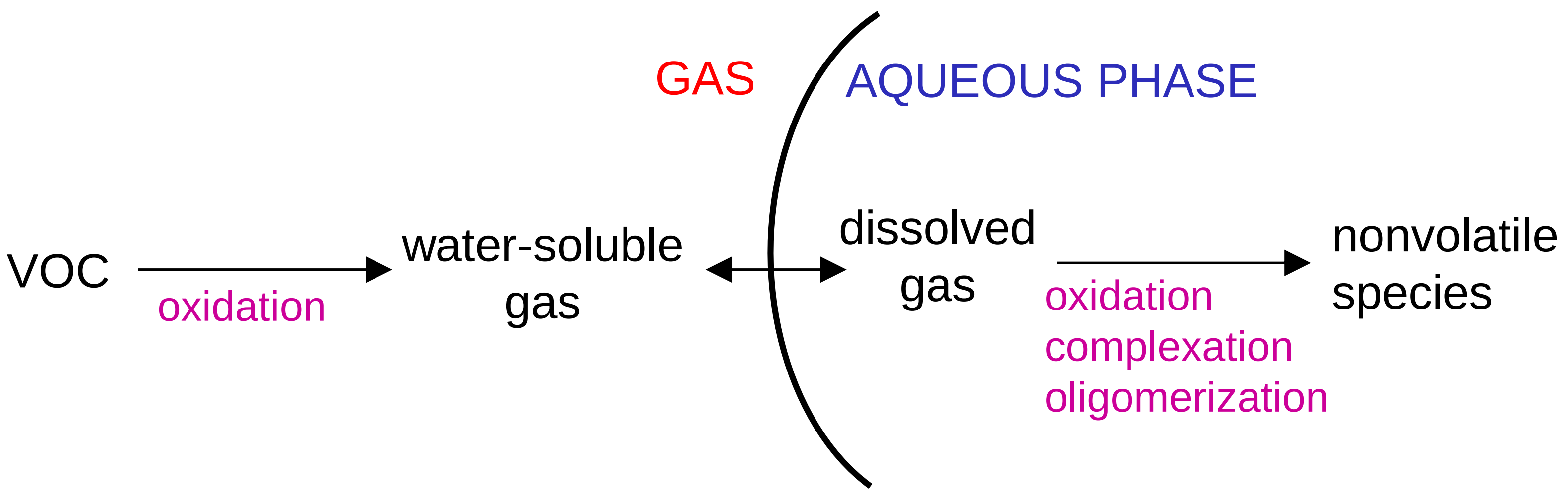


Two models for formation of secondary organic aerosol

Classical model for reversible uptake by pre-existing organic aerosol

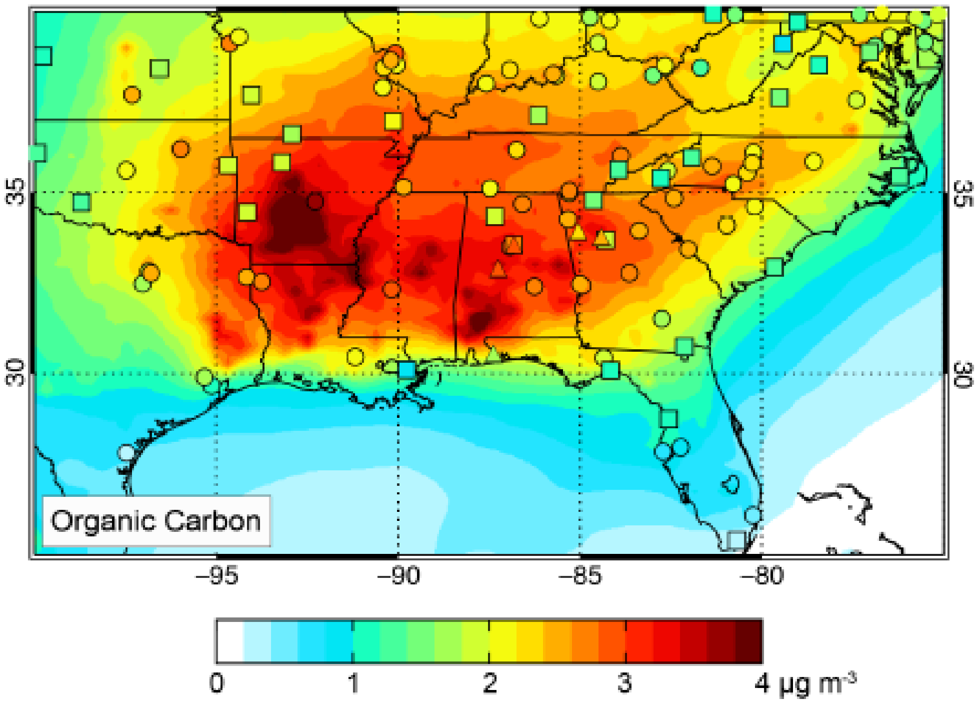


Alternate model for irreversible uptake by aqueous aerosol

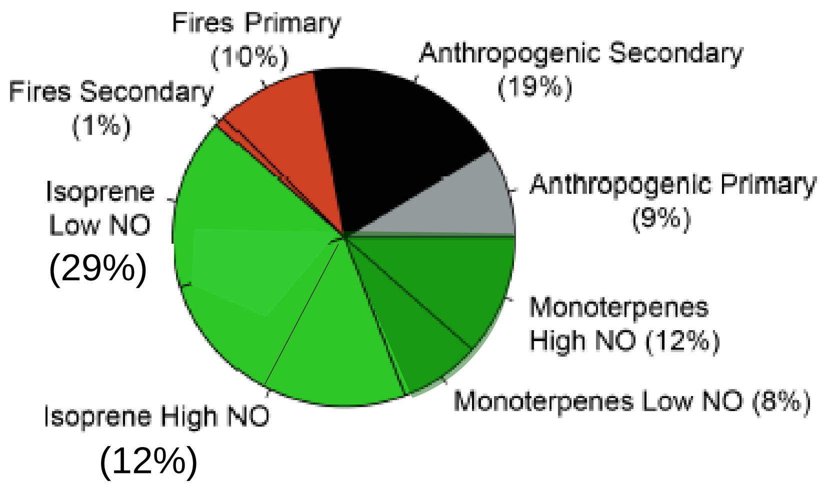


Sources of organic aerosol in the Southeast US in summer

Observed (circles), GEOS-Chem (background)
Aug-Sep 2013



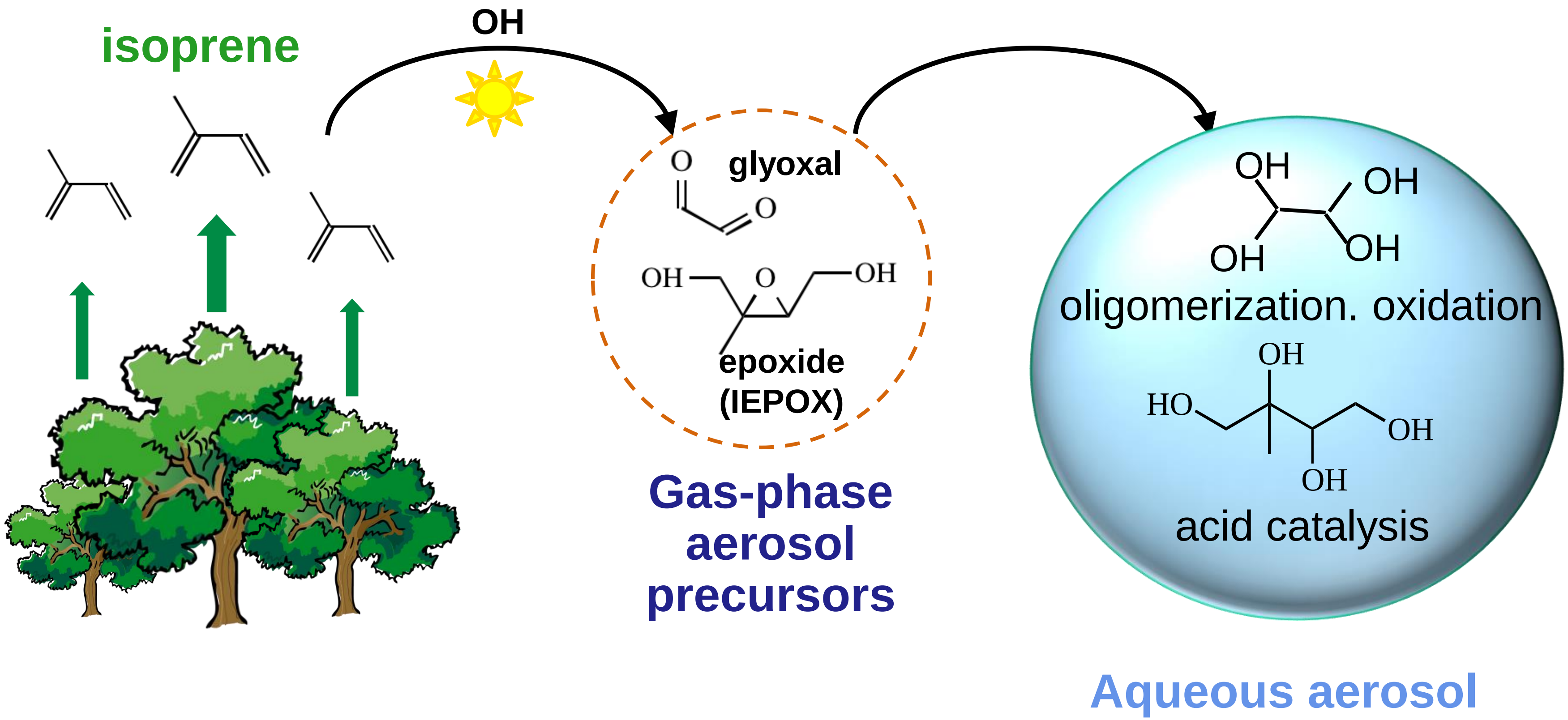
GEOS-Chem source attribution



Most organic aerosol in summer is biogenic;
isoprene accounts for ~50%, most by low-NO_x channel

Kim et al. [2015]

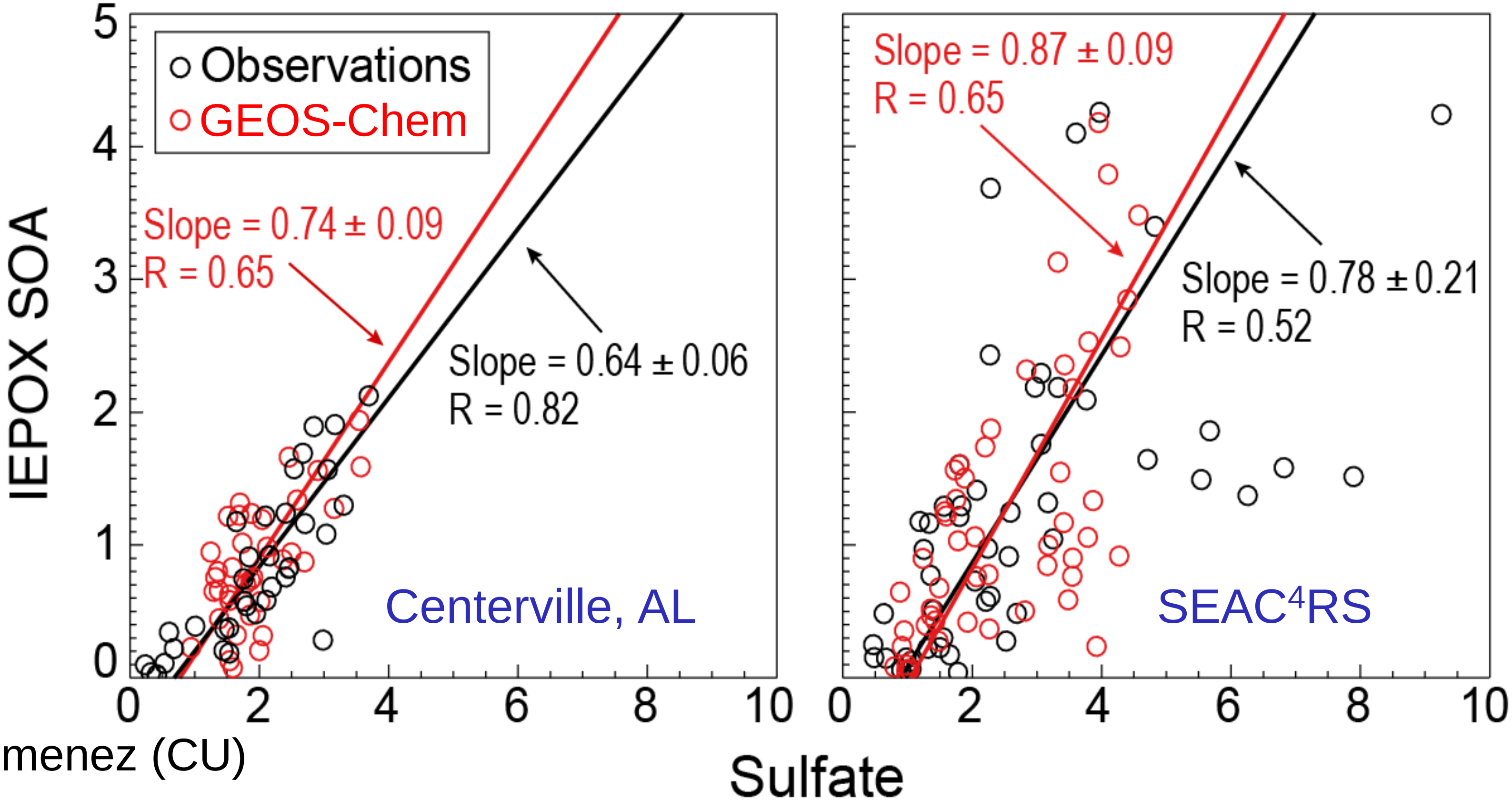
Aqueous-phase mechanism for secondary organic aerosol from isoprene: the short version



Marais et al. [2016]

Association of IEPOX secondary organic aerosol with sulfate

Correlation with sulfate in $SEAC^4RS$ and at Centerville, Alabama research site



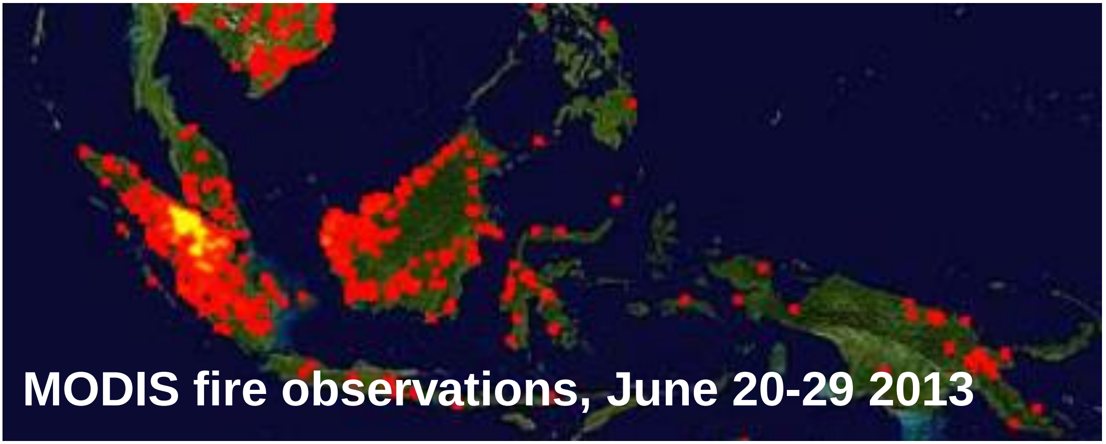
J. Jimenez (CU)

Sulfate ↓ → Aerosol volume ↓ Aerosol acidity ↓ → IEPOX SOA ↓

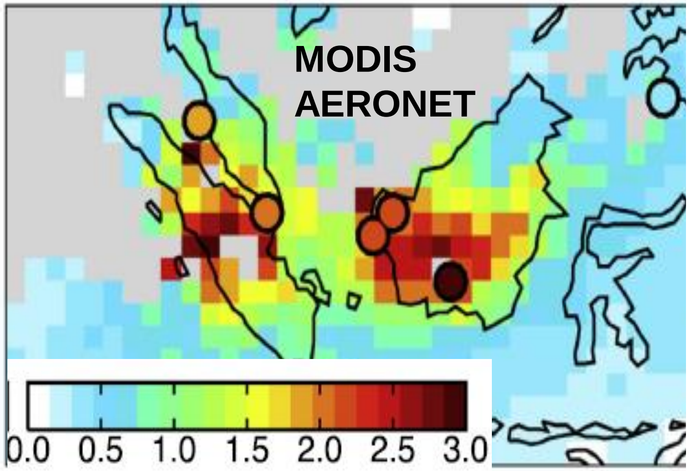
Marais et al. [2016]

Equatorial Asia: new frontier for air pollution

Massive agricultural fires in one of the most densely populated regions of Earth



2015 agricultural fires caused 100,000 excess deaths



Mean aerosol optical depths,
Sept-Oct 20015

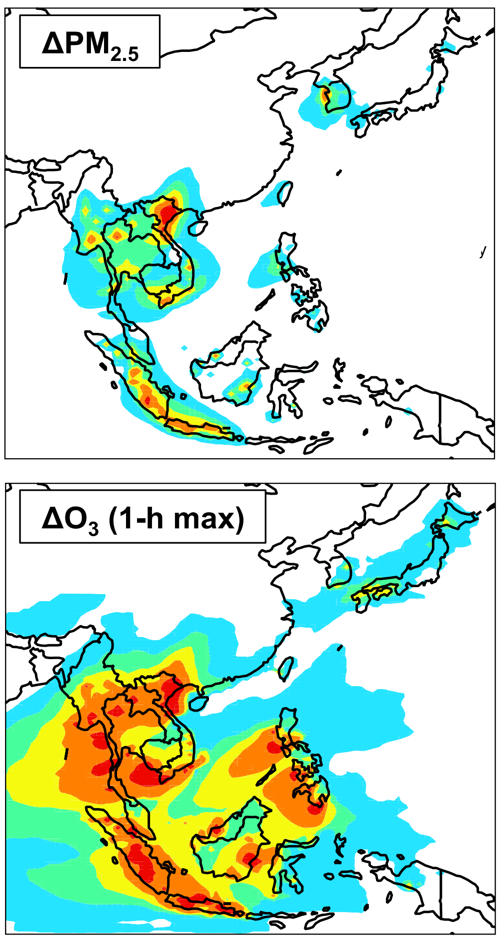
Koplitz et al. [2017]

Large planned increases of coal emissions in Equatorial Asia

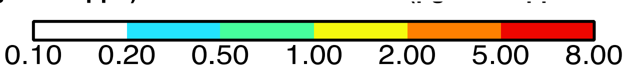
Planned 2030 coal power plants

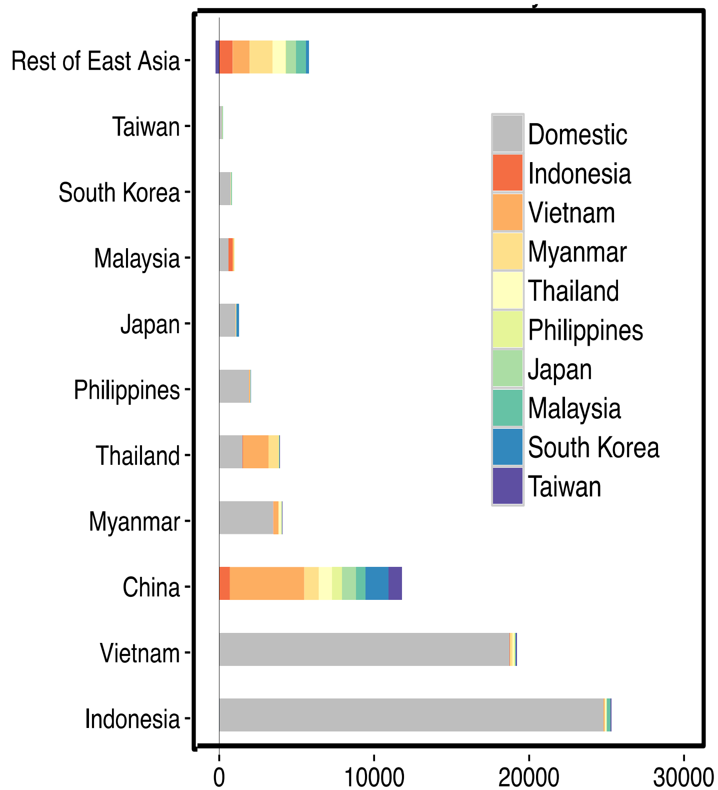
GEOS-Chem simulations with vs. without 2030 coal emissions

Coal Air Pollution in 2030



(μg m^{-3} or ppb)



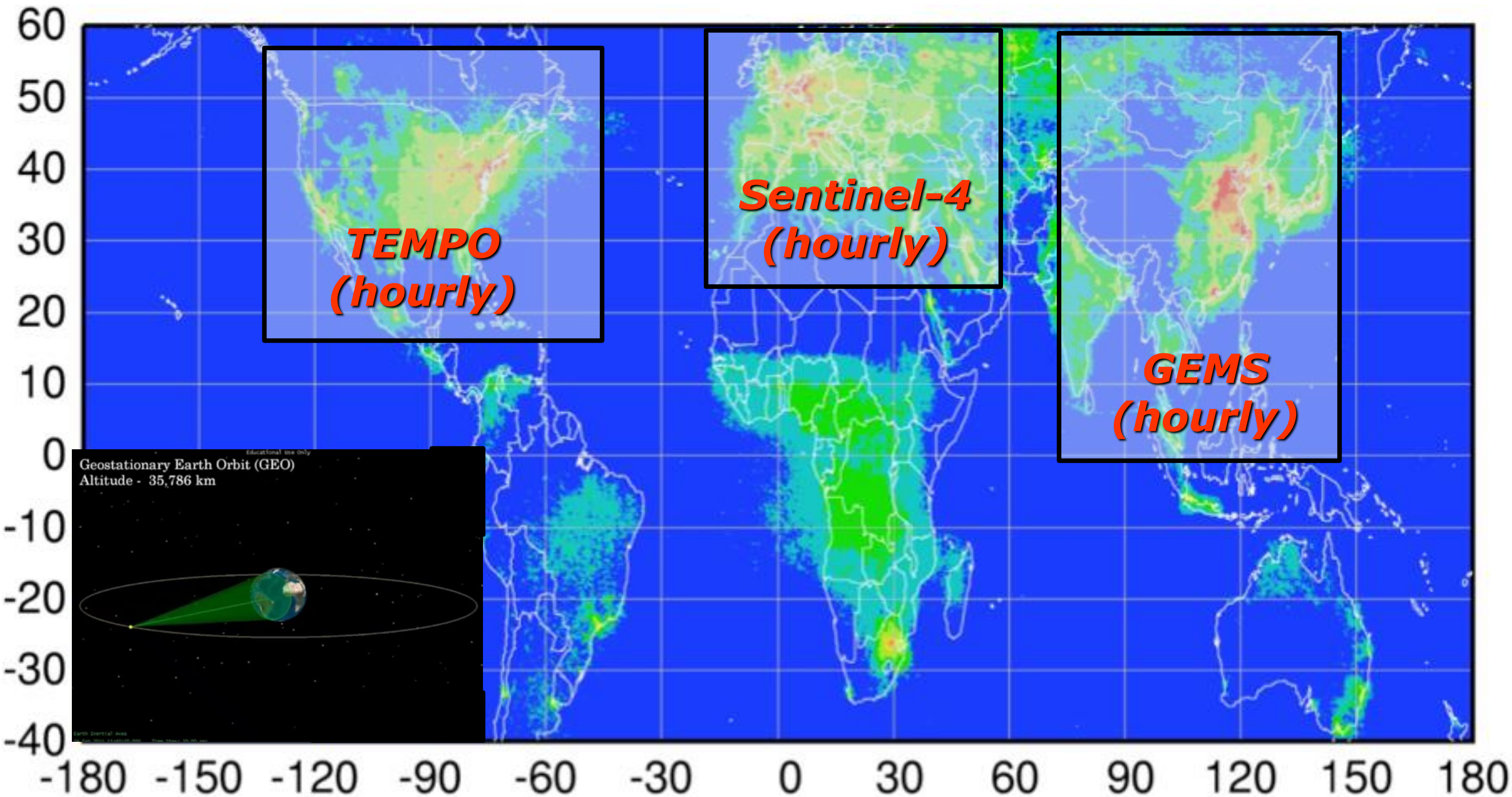


excess deaths per year from coal emissions

Transboundary transport of Southeast Asia pollution to cause 10000 excess deaths in China by 2030

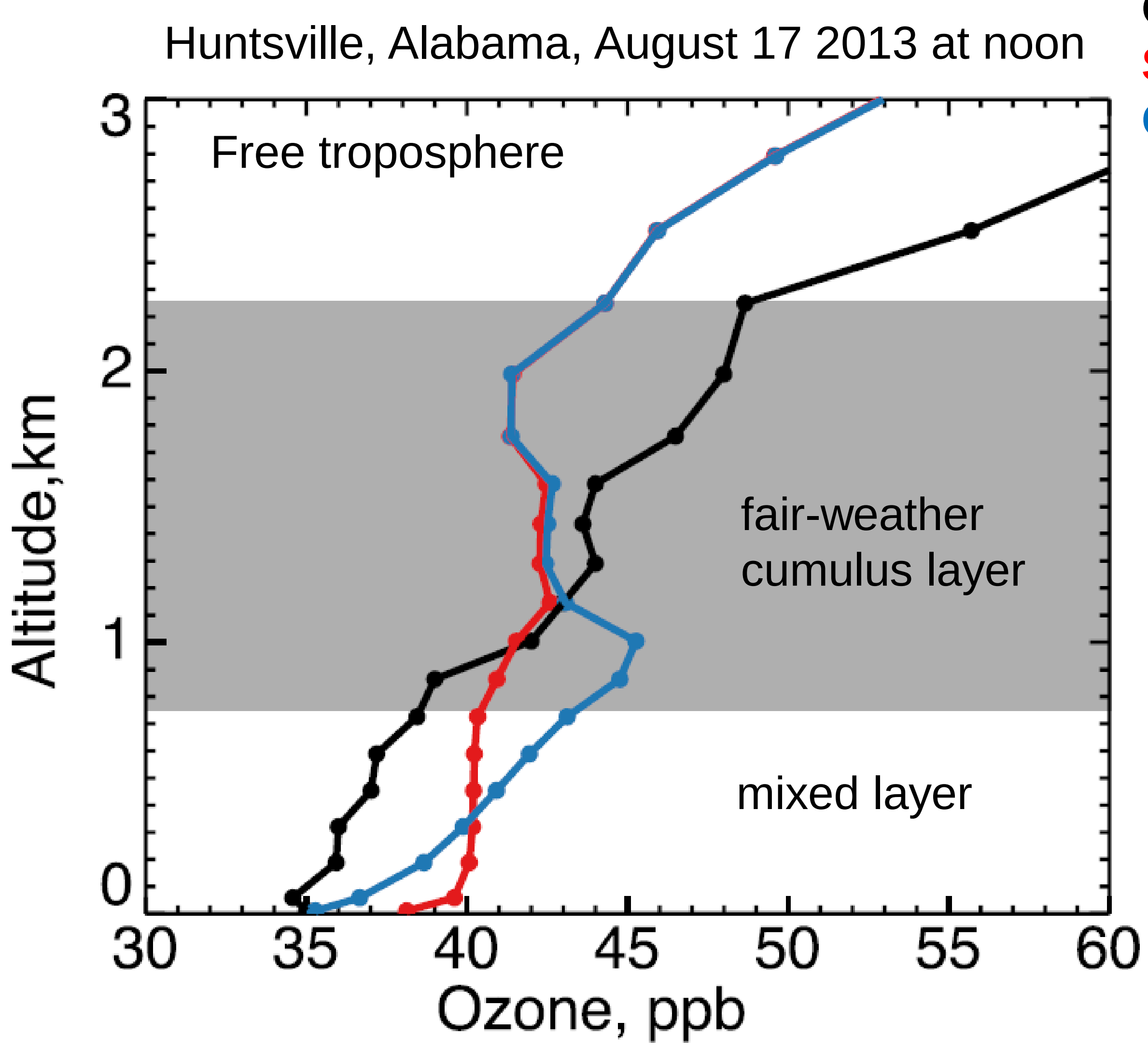
Koplitz et al. [2017]

Geostationary satellite constellation for air quality (2019-2020 launch)

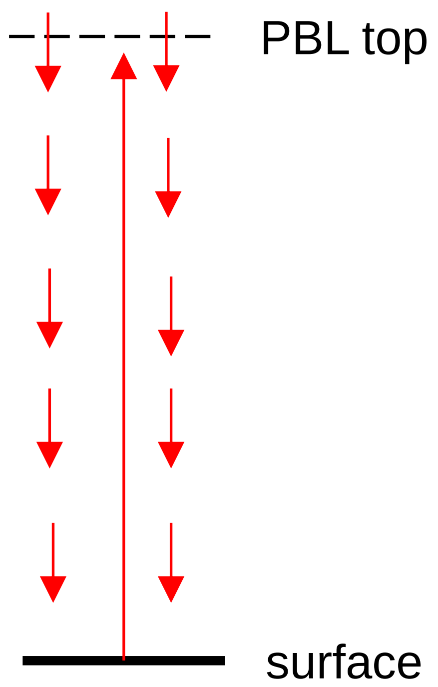


- GEMS to be launched by Korean Aerospace Research Institute (KARI)
  - UV/Vis solar backscatter: aerosol, NO_2, SO_2, HCHO, O_3 (free troposphere)
  - 7x8 km^2 pixels, hourly data
- TEMPO will also detect O_3 in boundary layer (weak 500-600 nm Chappuis bands)

Excessive top-down PBL mixing in models also causes overestimate in surface ozone



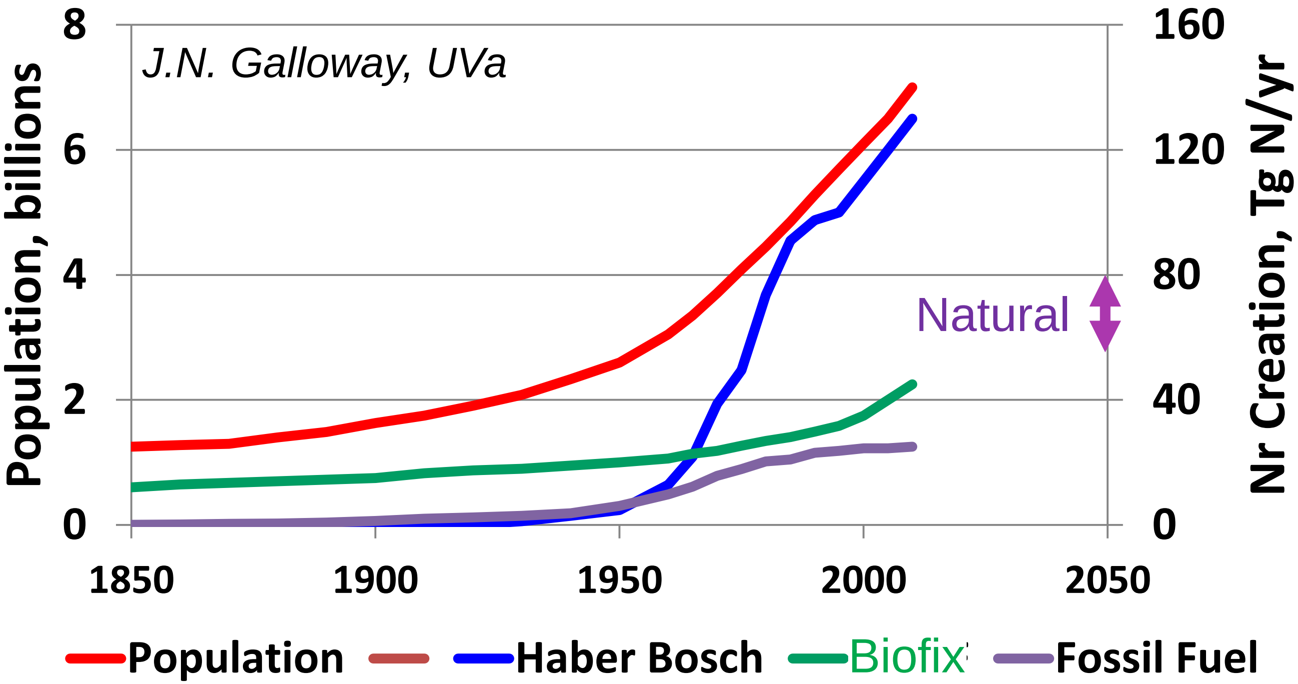
Observations
Standard GEOS-Chem
GEOS-Chem with reduced top-down mixing

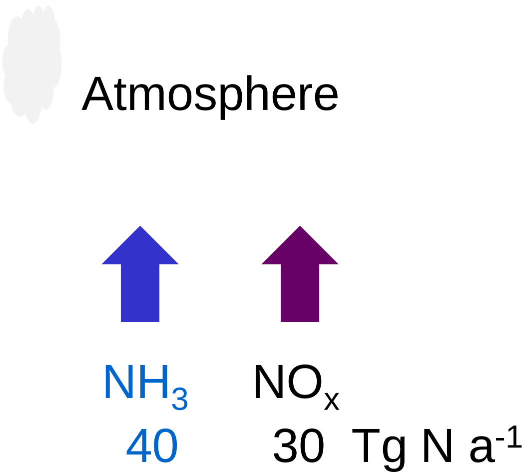


Travis et al. [2017]

Global human perturbation of nitrogen cycle

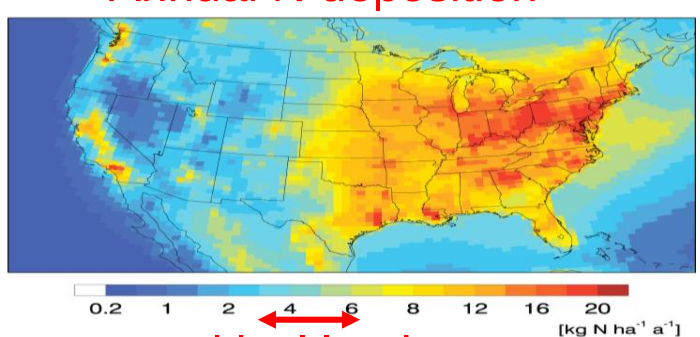
Global anthropogenic N fixation now greatly exceeds natural:





Resulting N deposition (NH_4^+, NO_3^-) modifies ecosystem function, C storage

Annual N deposition

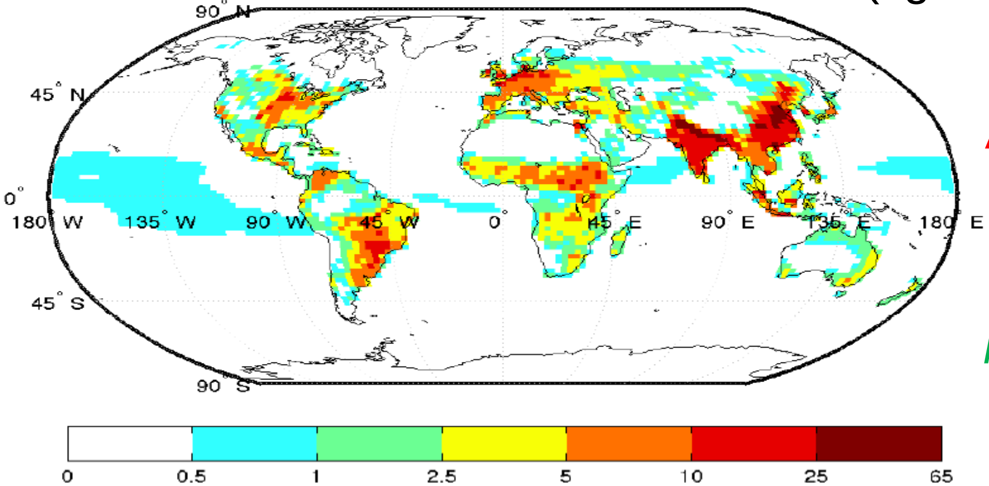


critical load

Zhang et al. [2012]

Need better understanding of ammonia emissions

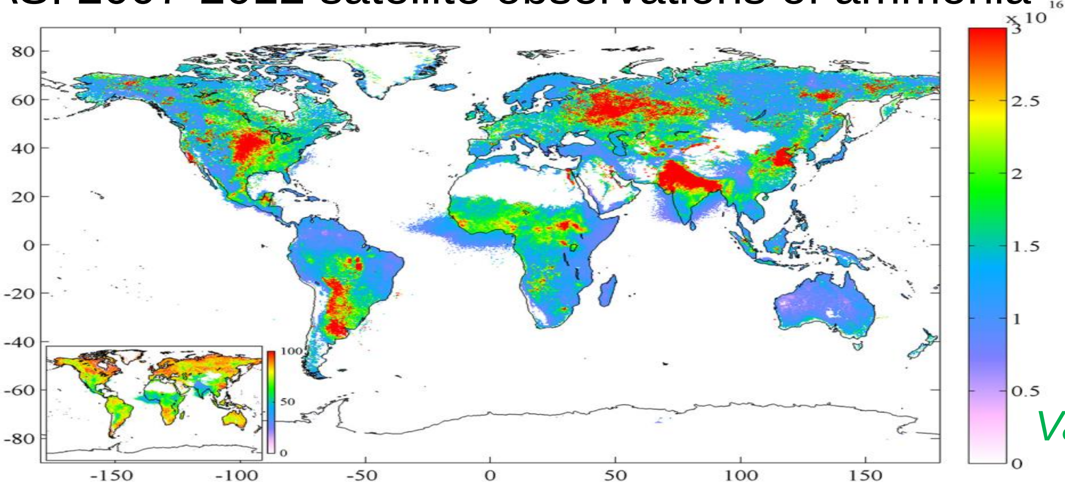
Global ammonia emissions 2005-2008 (kg N ha^{-1} a^{-1})



Agriculture is 75% of global source

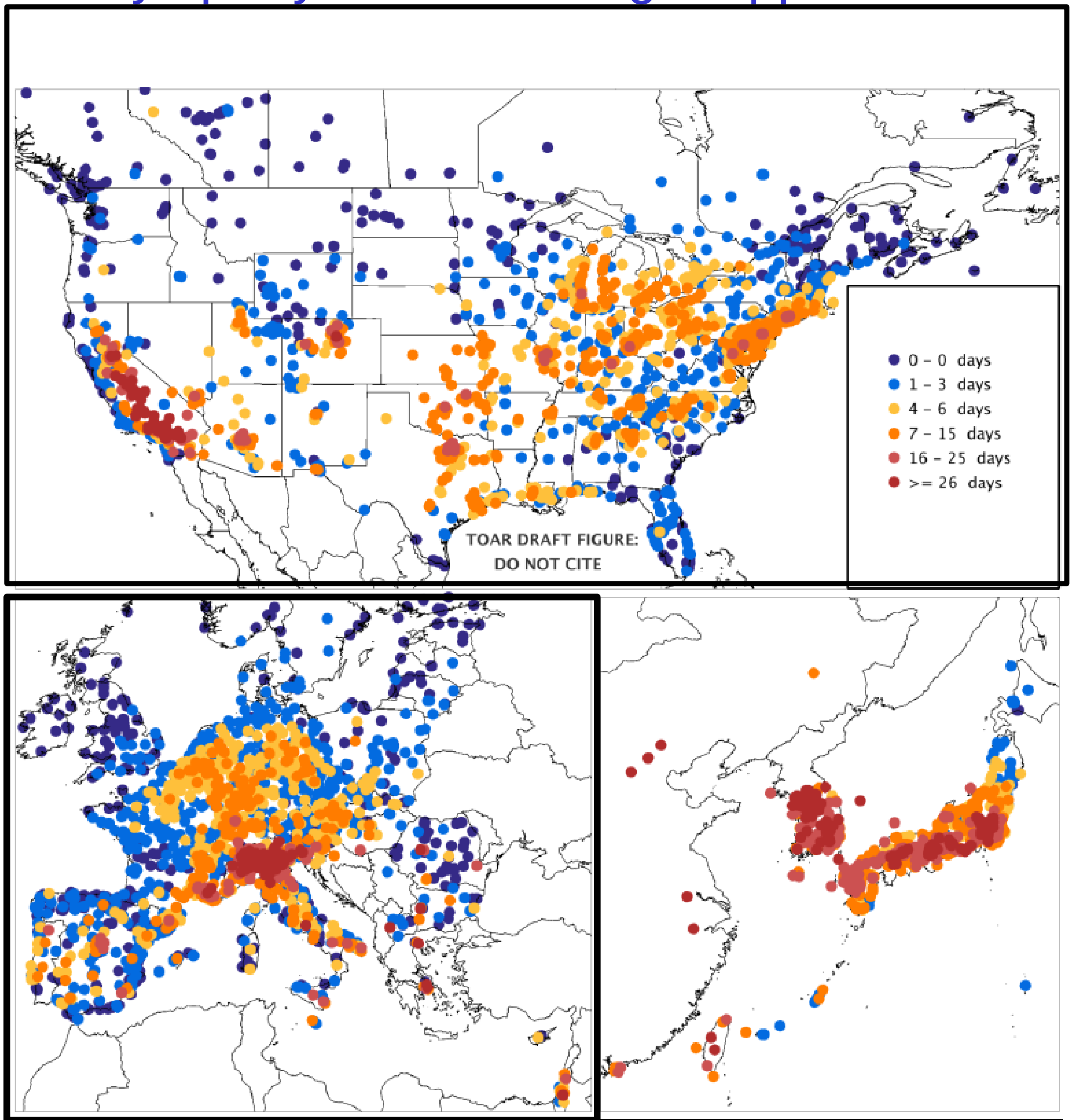
Paulot et al. [2014]

IASI 2007-2012 satellite observations of ammonia



Van Damme et al. [2014]

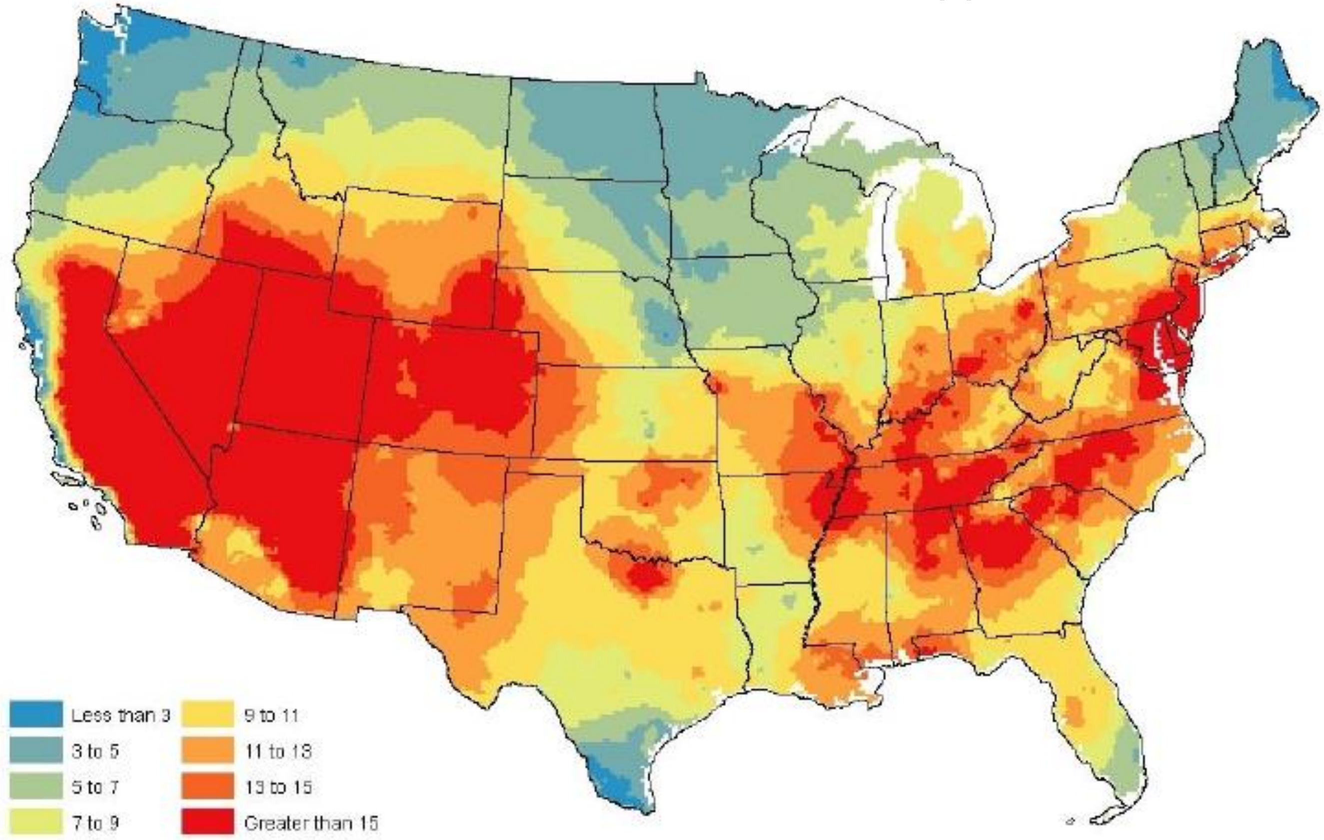
Days per year exceeding 70 ppb ozone standard, 2010-2014



TOAR [2017]

Seasonal ozone (affecting vegetation) shows different picture

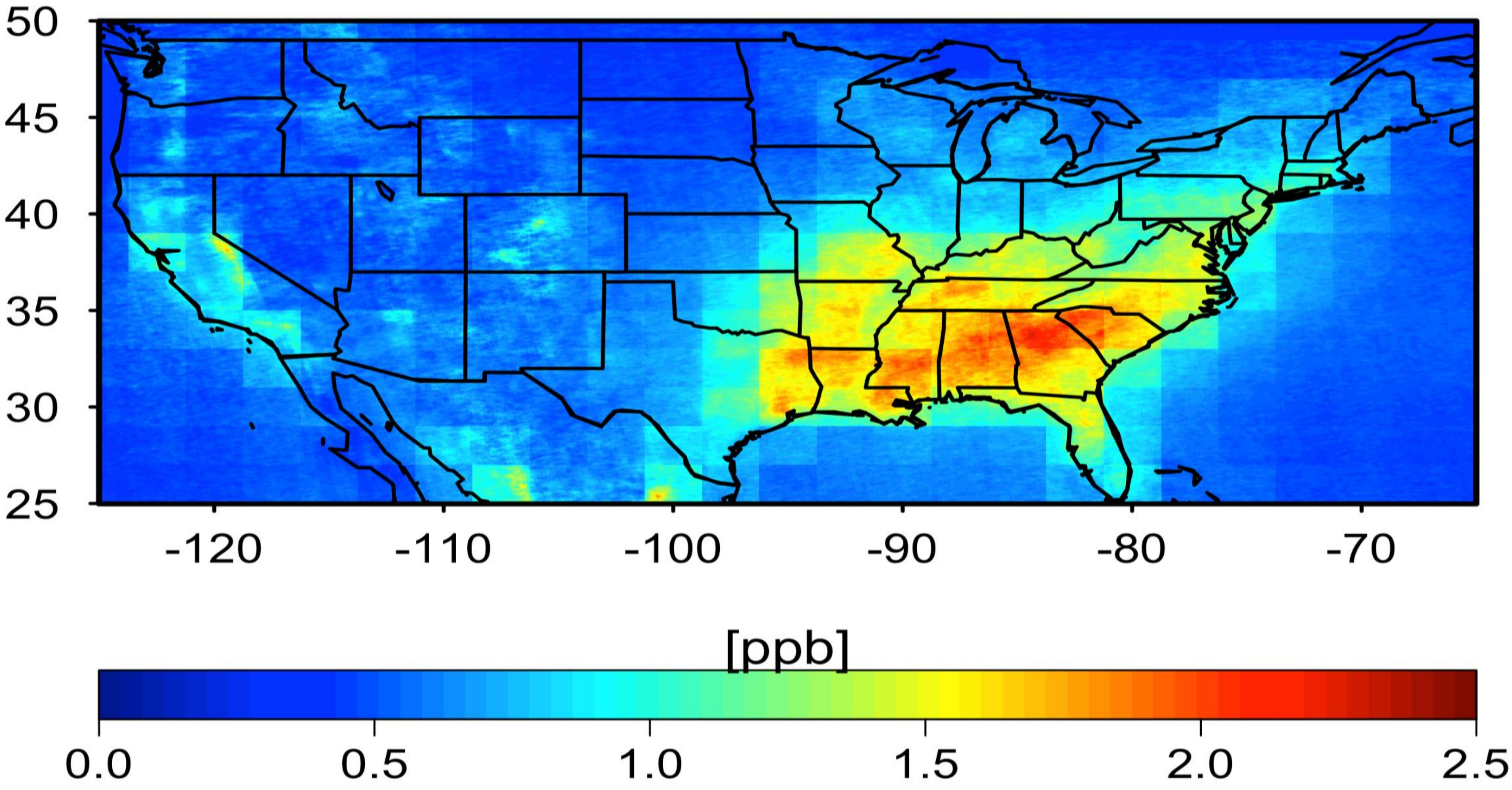
Seasonal dose in excess of 60 ppb



Maximum over western US (“Intermountain West”)
where ozone constantly hovers around 60 ppb

EPA [2014]

Formaldehyde as EPA Hazardous Air Pollutant (EPA): OMI-derived annual concentration in surface air, 2005-2014



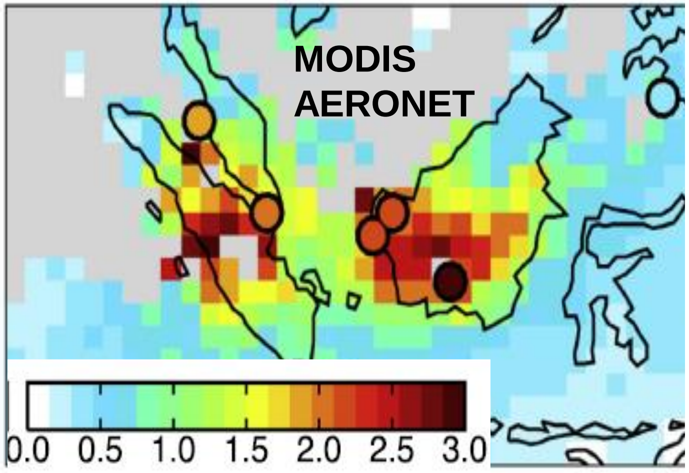
1 ppb HCHO = 16 cancer risks per million people;
6,043 US cancer risks due to ambient HCHO

Zhu et al., 2017

Equatorial Asia: new frontier for air poll

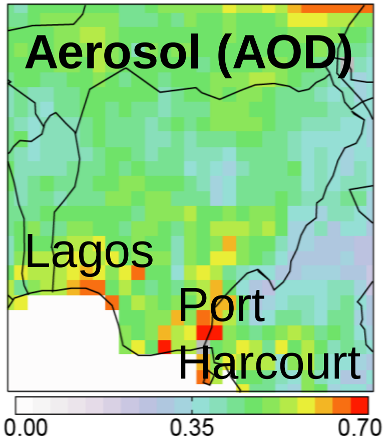
- Equatorial Asia: 2015 agricultural fires caused 100,000 excess deaths

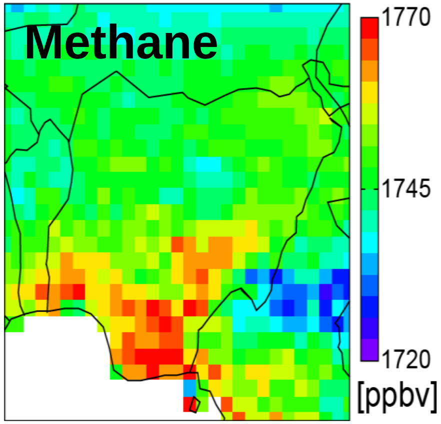
Mean aerosol optical depths,
Sept-Oct 20015

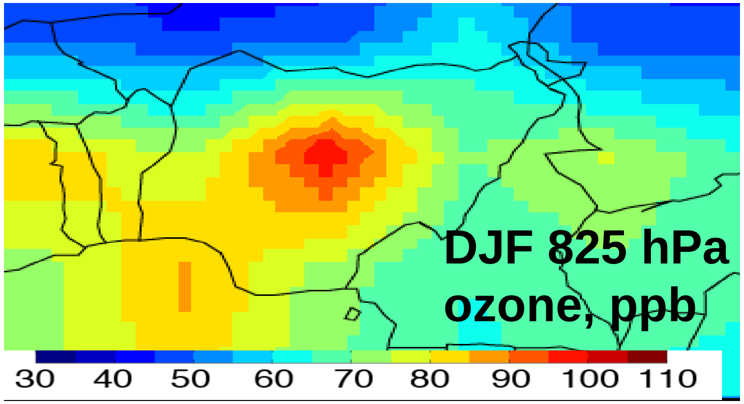


Planned coal power plants (T. Nace, 2014)

- Nigeria: dysfunctional populous country sitting on huge oil/coal reserves



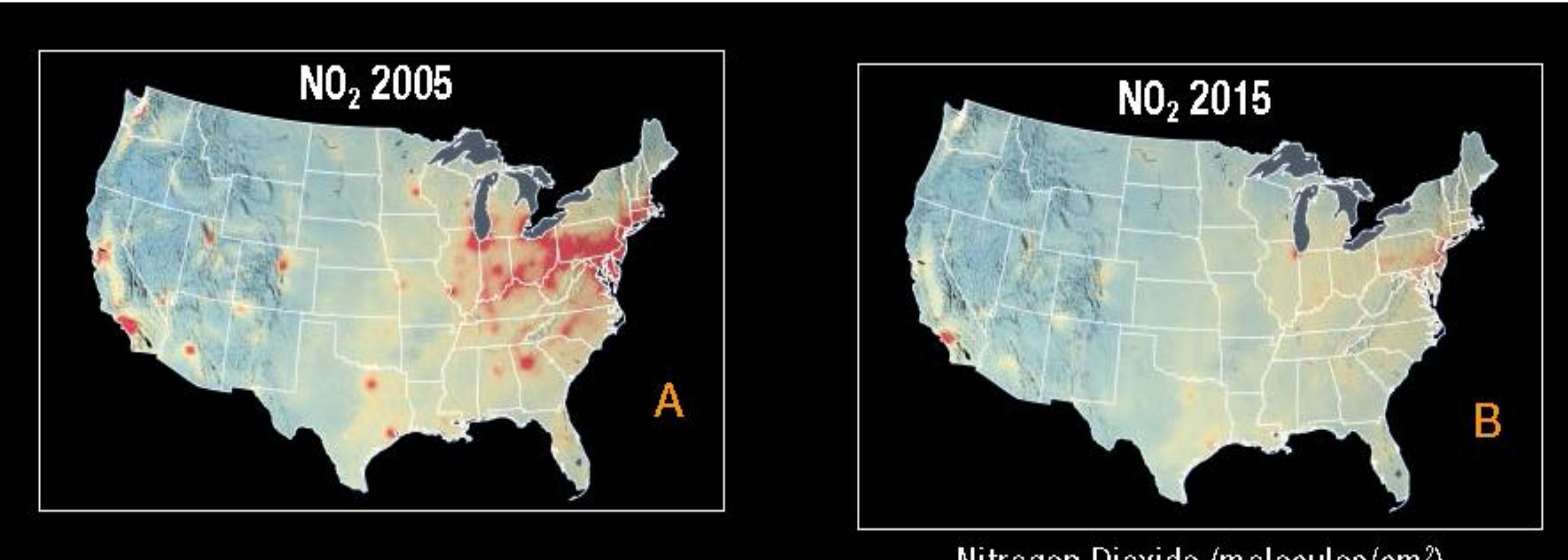




Marais et al. [2014]; Koplitz et al. [2016]

Post-2000 decline in US emissions of NO_x ($\equiv NO + NO_2$)

as seen by OMI satellite observations of NO_2



Sources:

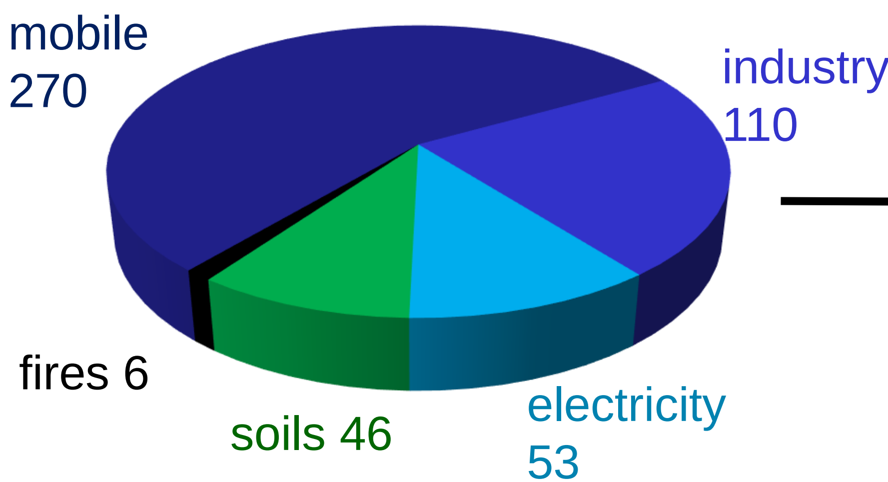
power plants

motor vehicles

UA EPA NO_x emissions are 2x too high

Aug 2013 Southeast US NO_x emissions including EPA National Emission Inventory [Mg]

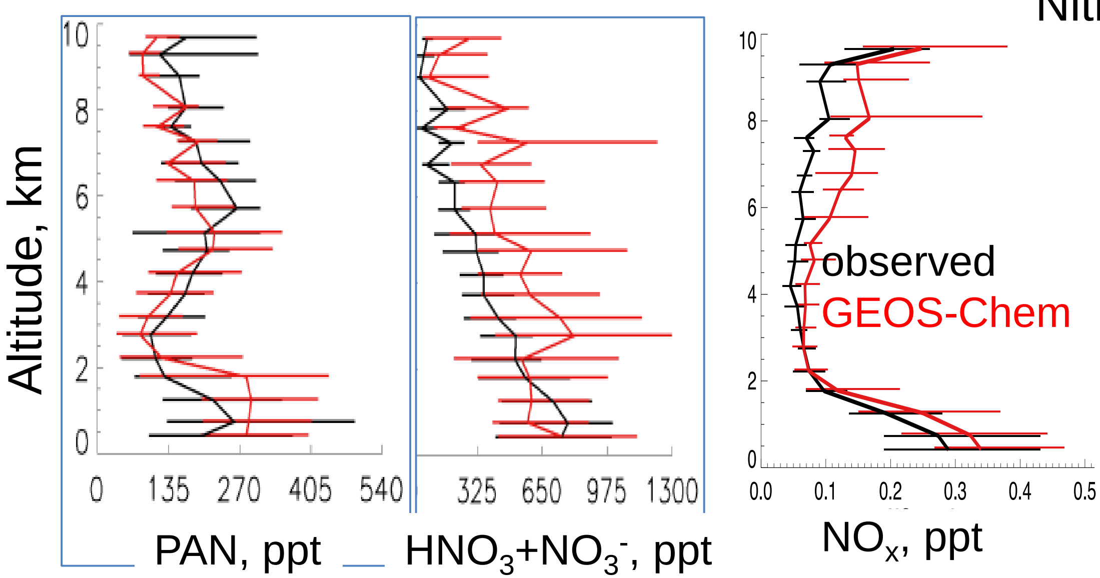
Travis et al., in prep



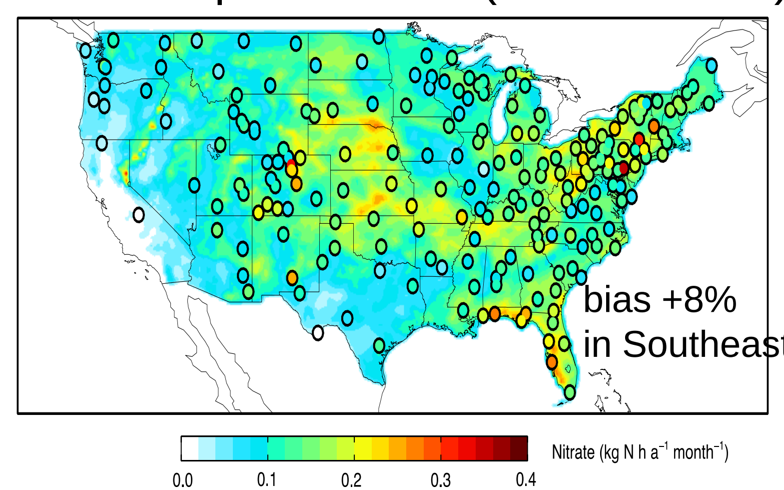
Reduce emissions by 50%

Observations by G. Huey, J. Dibb, T. Ryerson

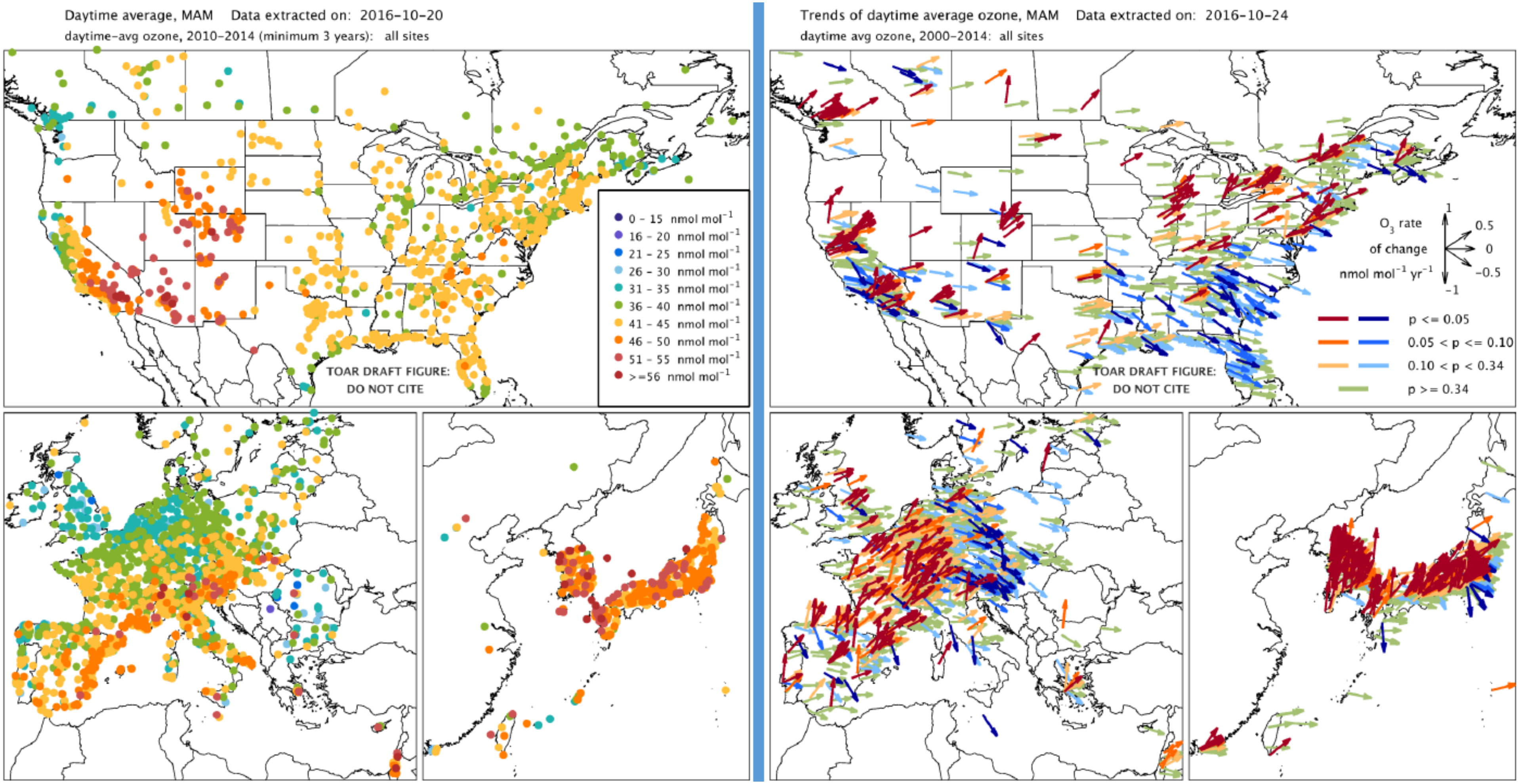
Median vertical profiles



Nitrate wet deposition flux (obs in circles)

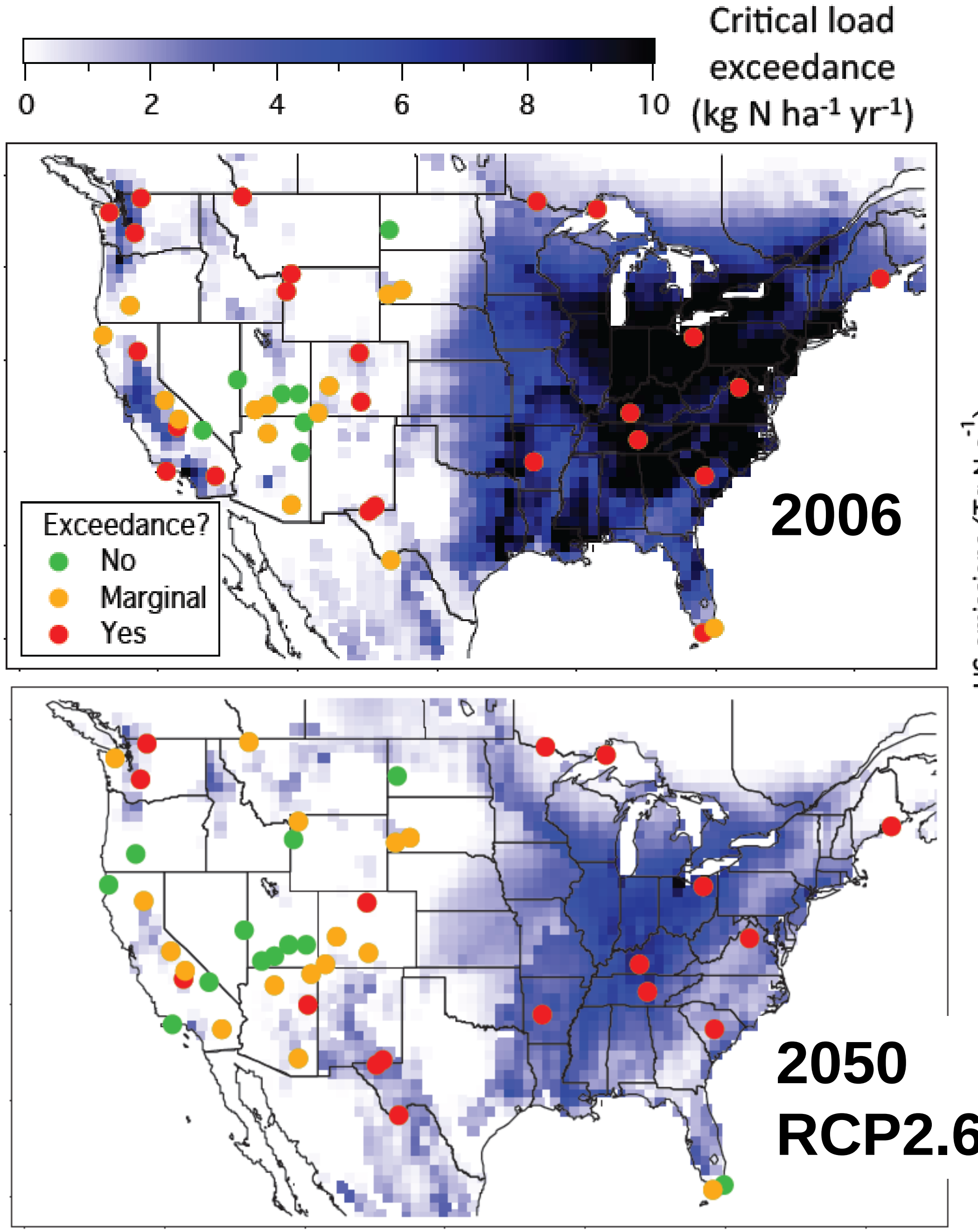


Trend in #days/year with ozone > 70 ppb, spring 2000-2014

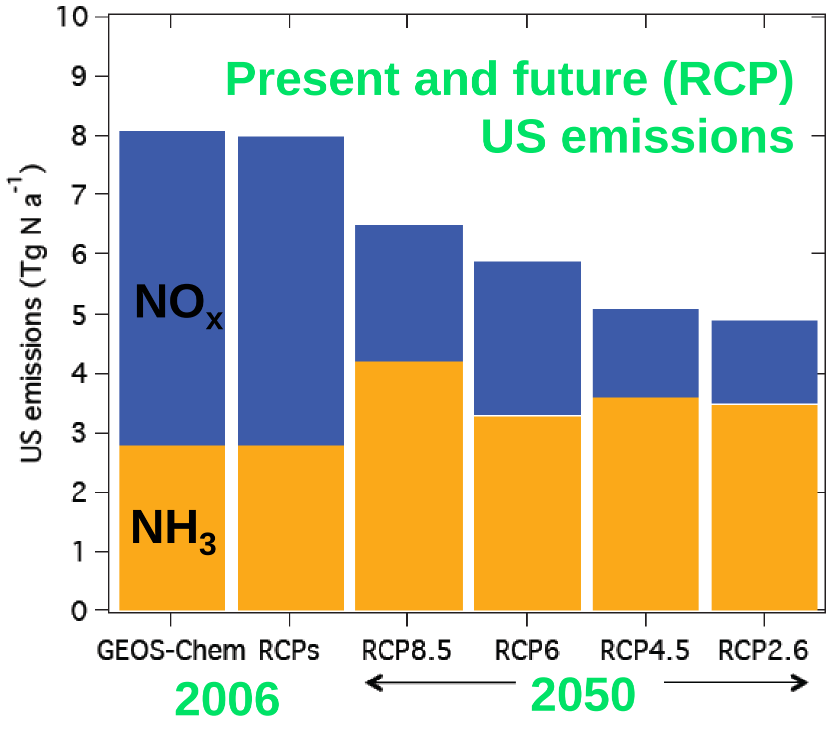


TOAR [2017]

N deposition at US national parks: critical load exceedances



Critical loads are 3-5 kg N ha^{-1} a^{-1} depending on ecosystem

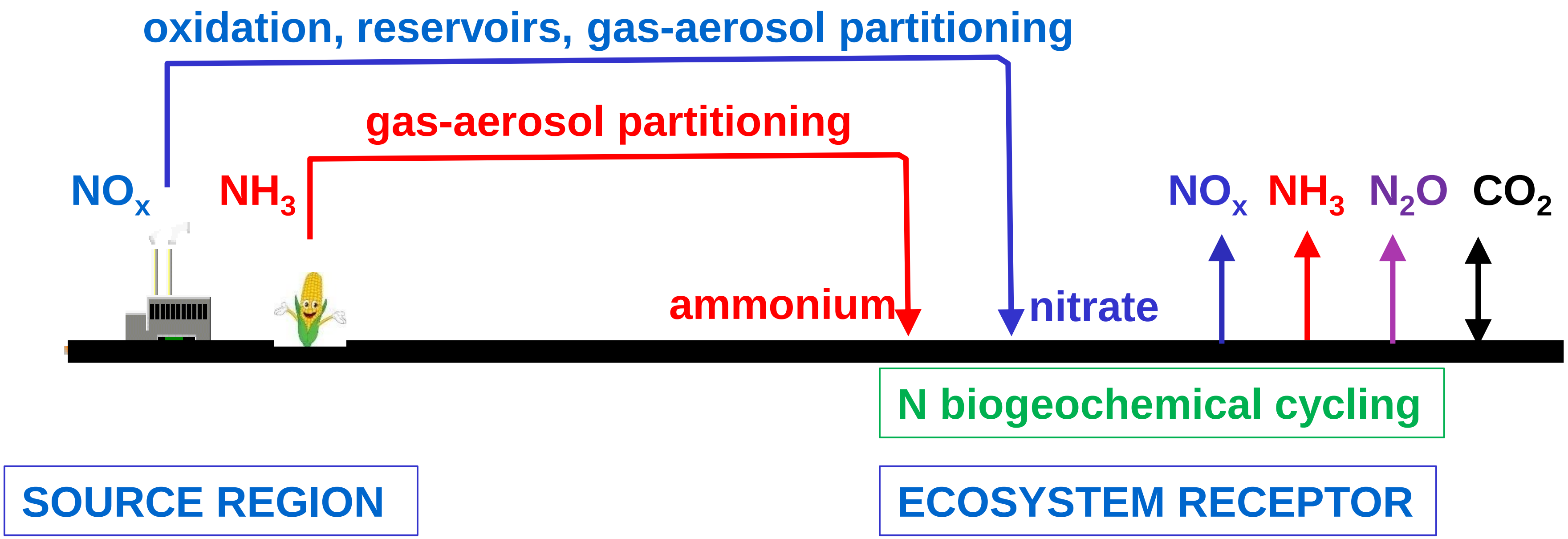


Future exceedances driven by ammonia emissions

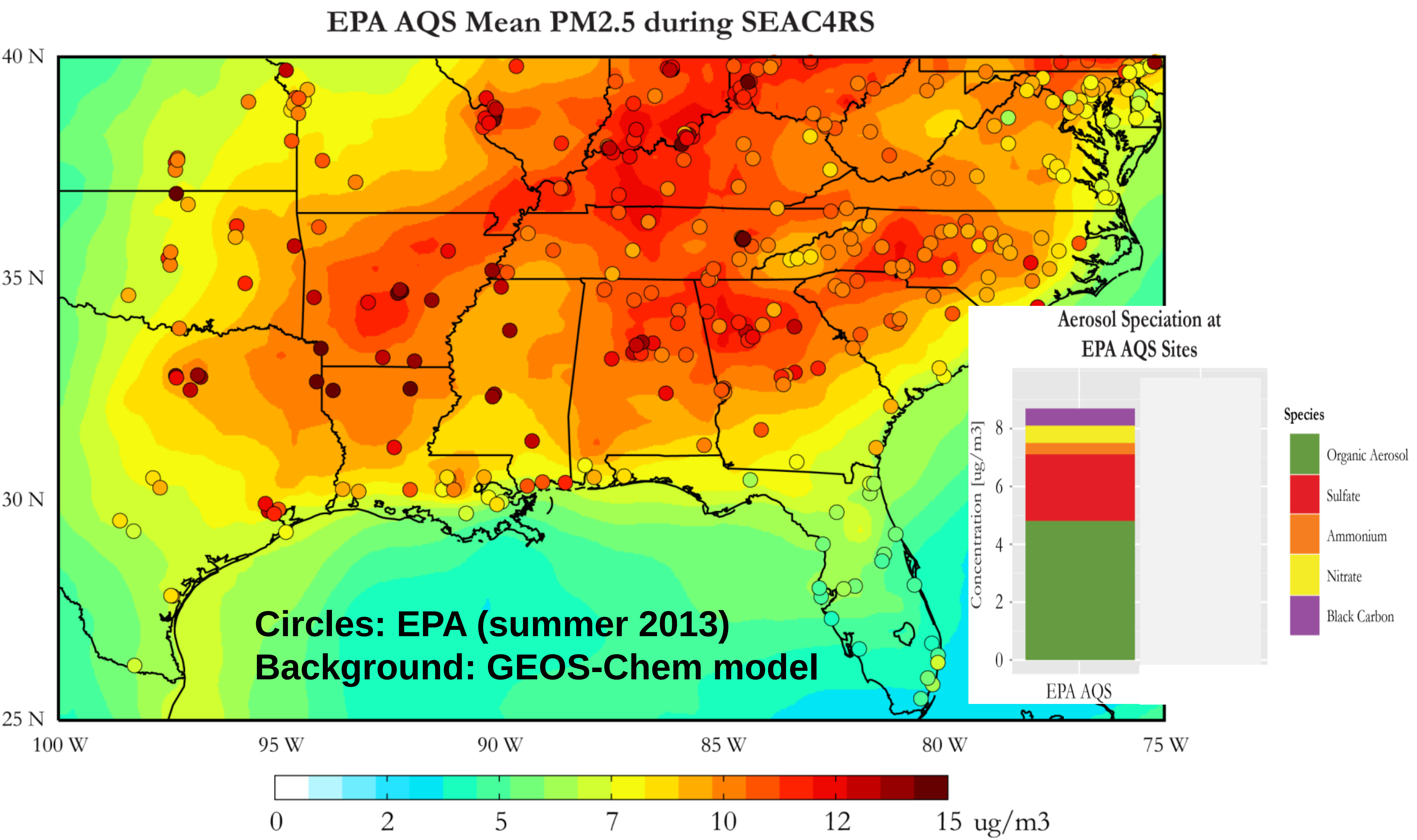
Ellis et al. [2013]
Ellis et al. [2013]

Coupling atmospheric chemistry to N biogeochemical cycle

- **Grasshopper effect of nitrogen mediated by atmosphere, coupling to carbon**



Biogenic organics contribute about half to all organic $PM_{2.5}$ over US

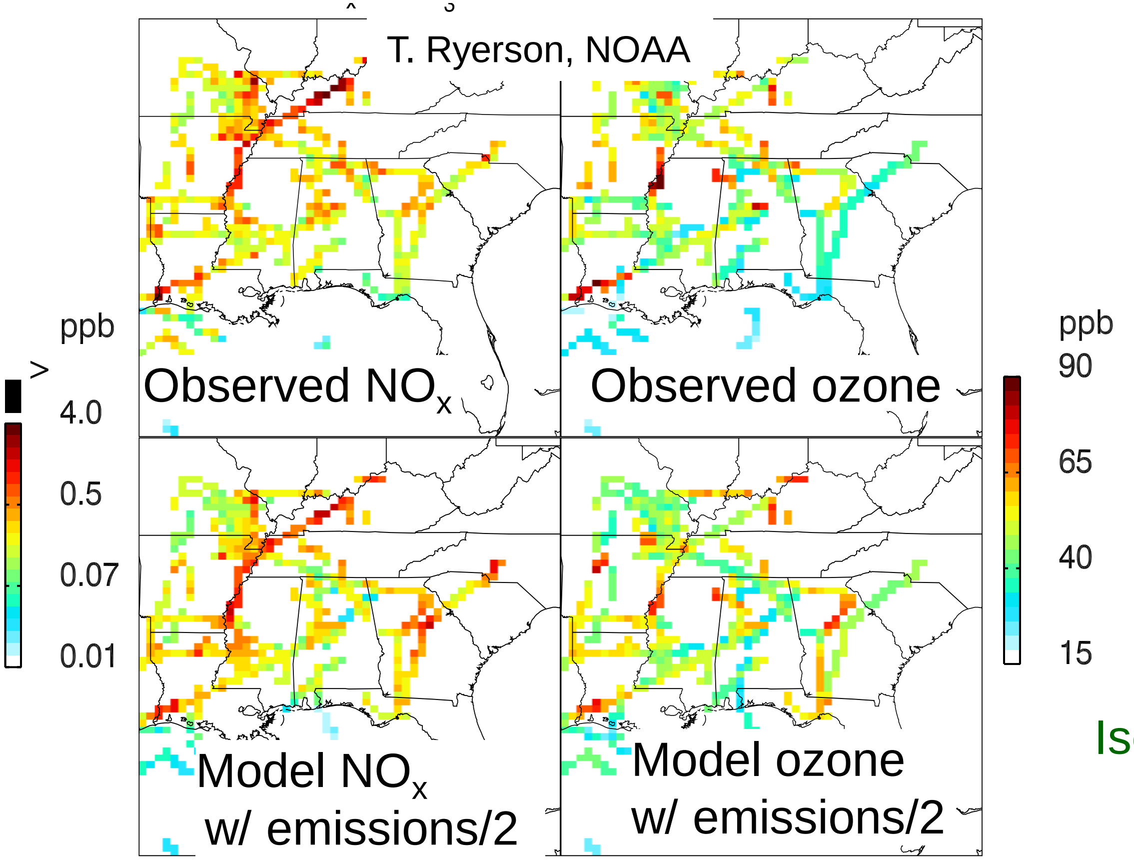


Patrick Kim, Harvard

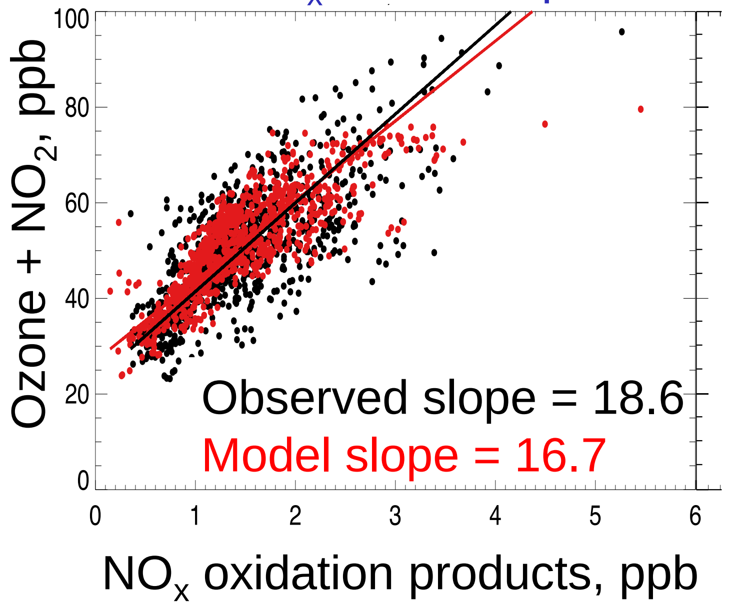
Recent eastern US data show large overestimate in EPA NO_x inventory

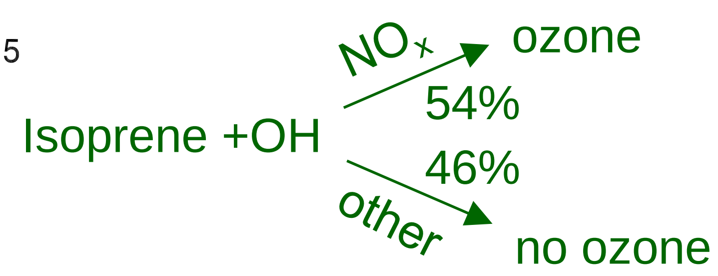
Fitting 2013 campaign data with GEOS-Chem requires halving of US NO_x emissions

Aircraft SEAC4RS data below 1.5 km



Ozone vs. NO_x oxidation products





- Model bias for ozone with original EPA emissions was +16 ppb
- Understanding isoprene chemistry, ozone background becoming more critical

Travis et al. [2016], A21C-044 (this morning!)

Composition of fine particulate matter ($PM_{2.5}$)

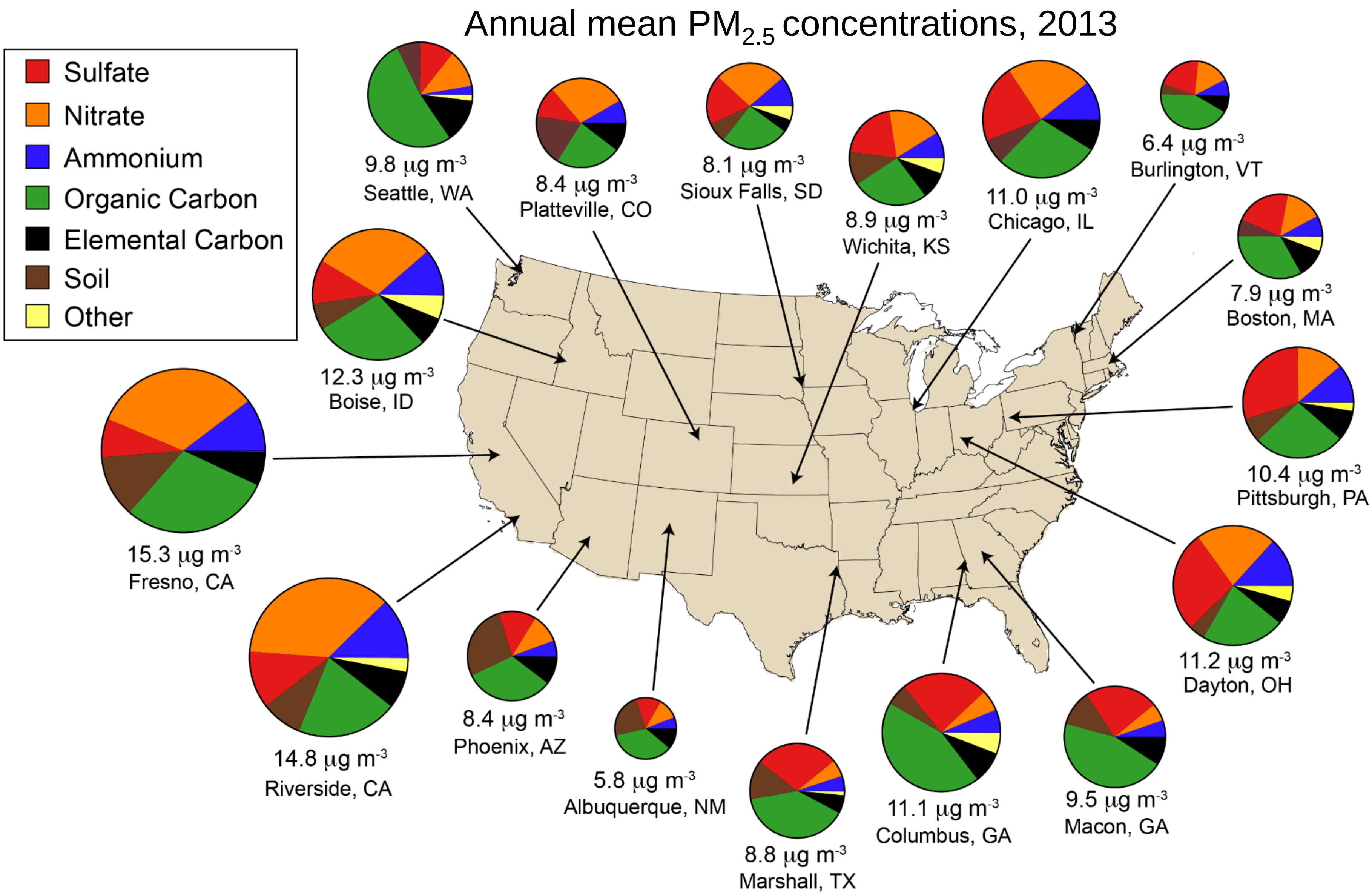
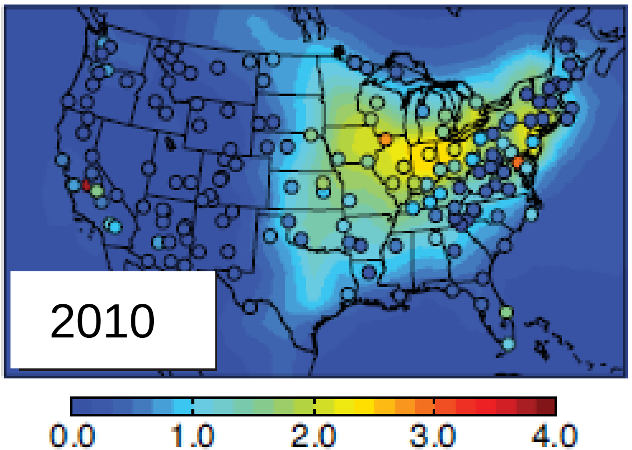


Figure produced by Eloise Marais, Harvard

Ammonia emissions and air pollution

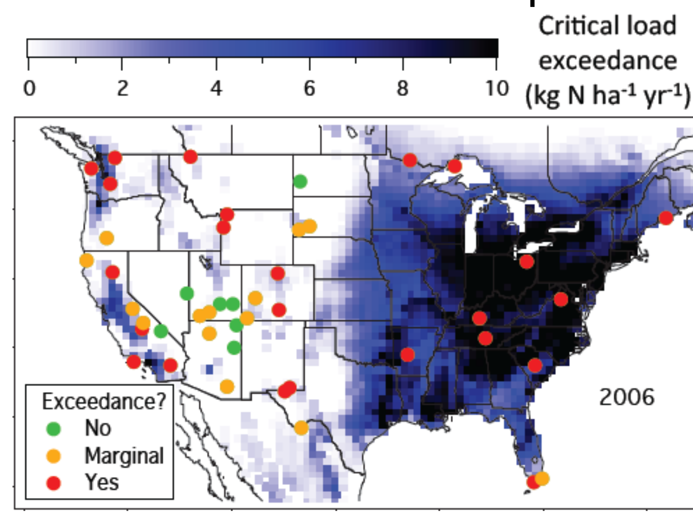
Nitrate PM
(mainly ammonium nitrate)

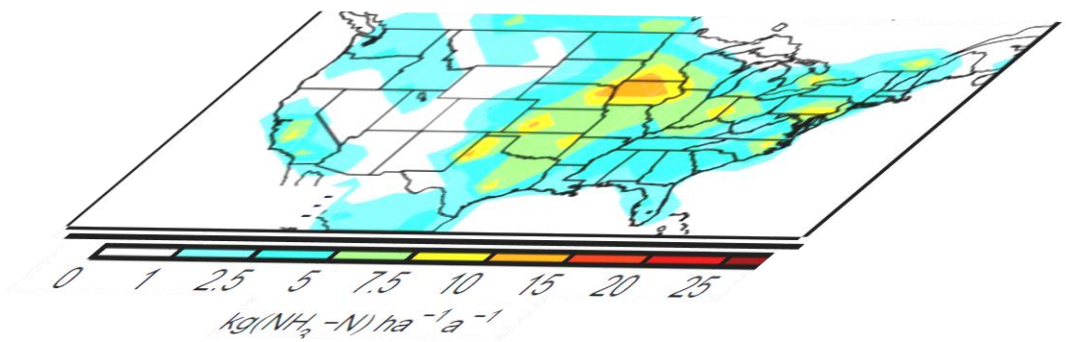


PM formation

Nitrogen deposition

Critical nitrogen load exceedance in national parks



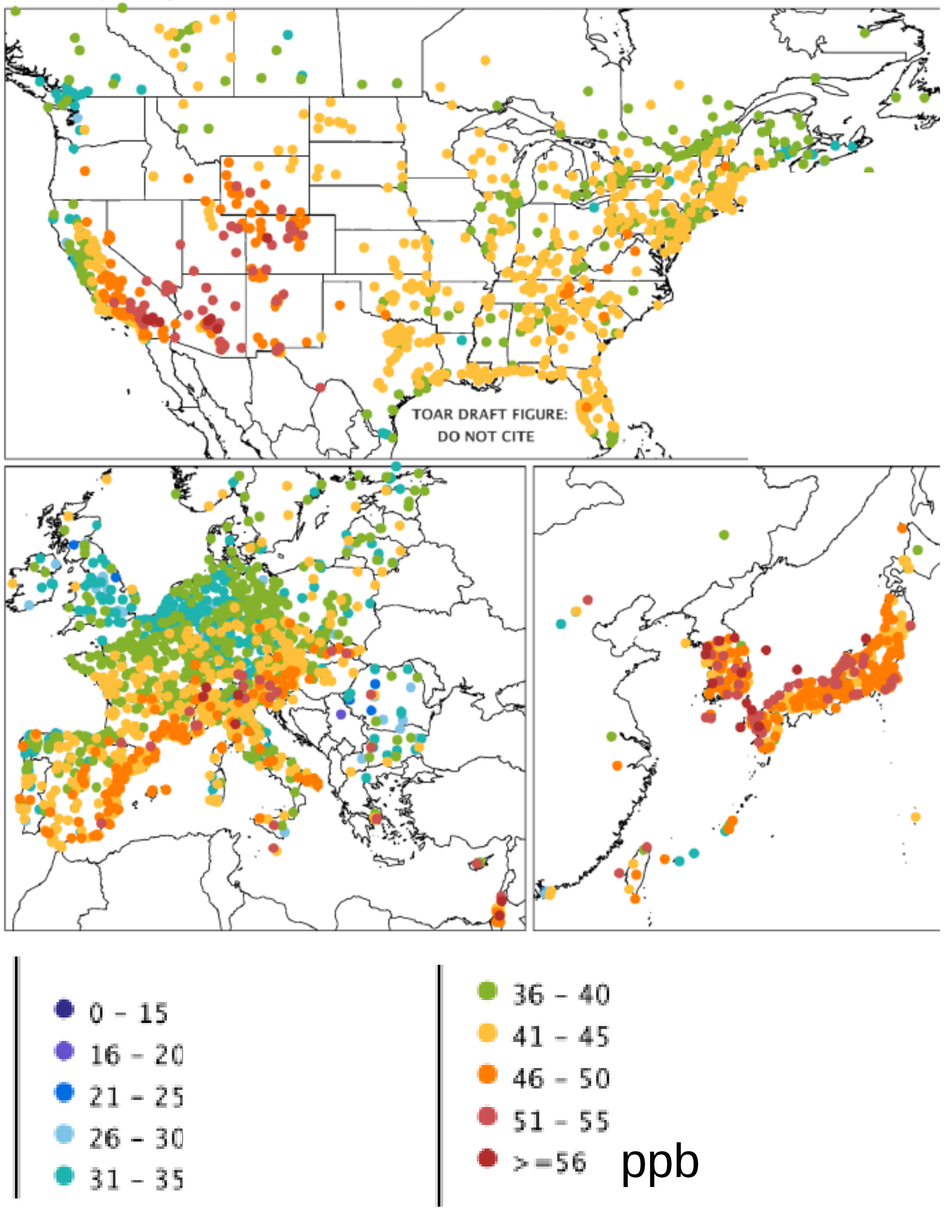


US ammonia emissions:
60% manure, 20% fertilizer

Leibensperger et al., 2012;
Ellis et al., 2013;
Paulot et al., 2014

Seasonal ozone (affecting vegetation) shows different picture

Spring (MAM) daytime average ozone, 2010-2014



Seasonal dose in excess of 60 ppb

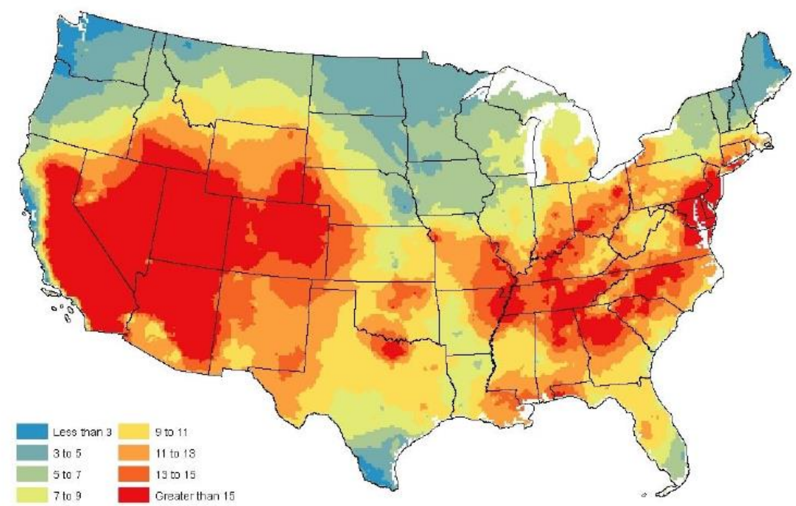
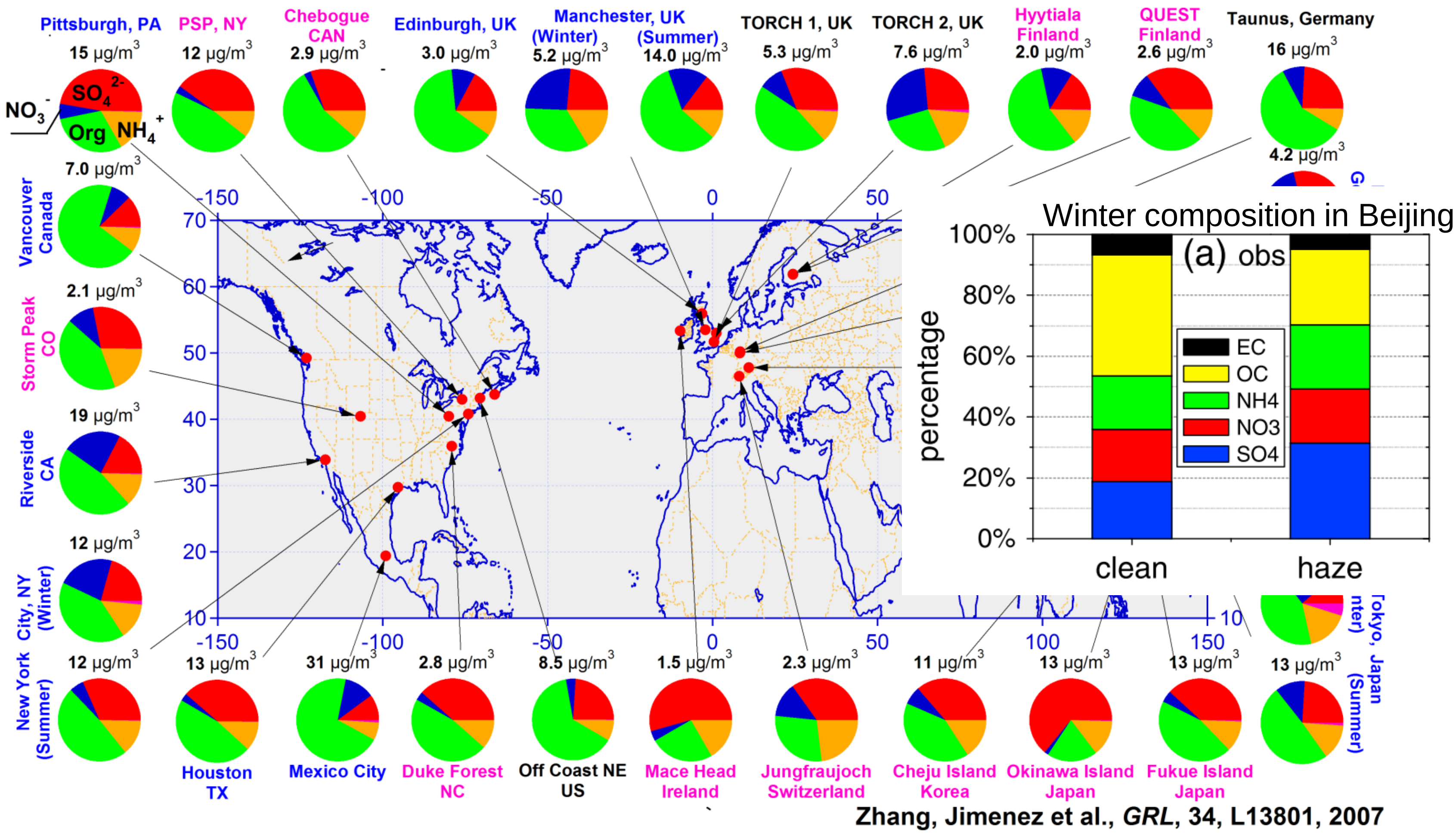


Figure 4-5 **National surface of observed 2006-2008 average W126 concentrations, in ppm-hrs**

EPA [2014]; TOAR [2017]

PM$_{2.5}$ composition

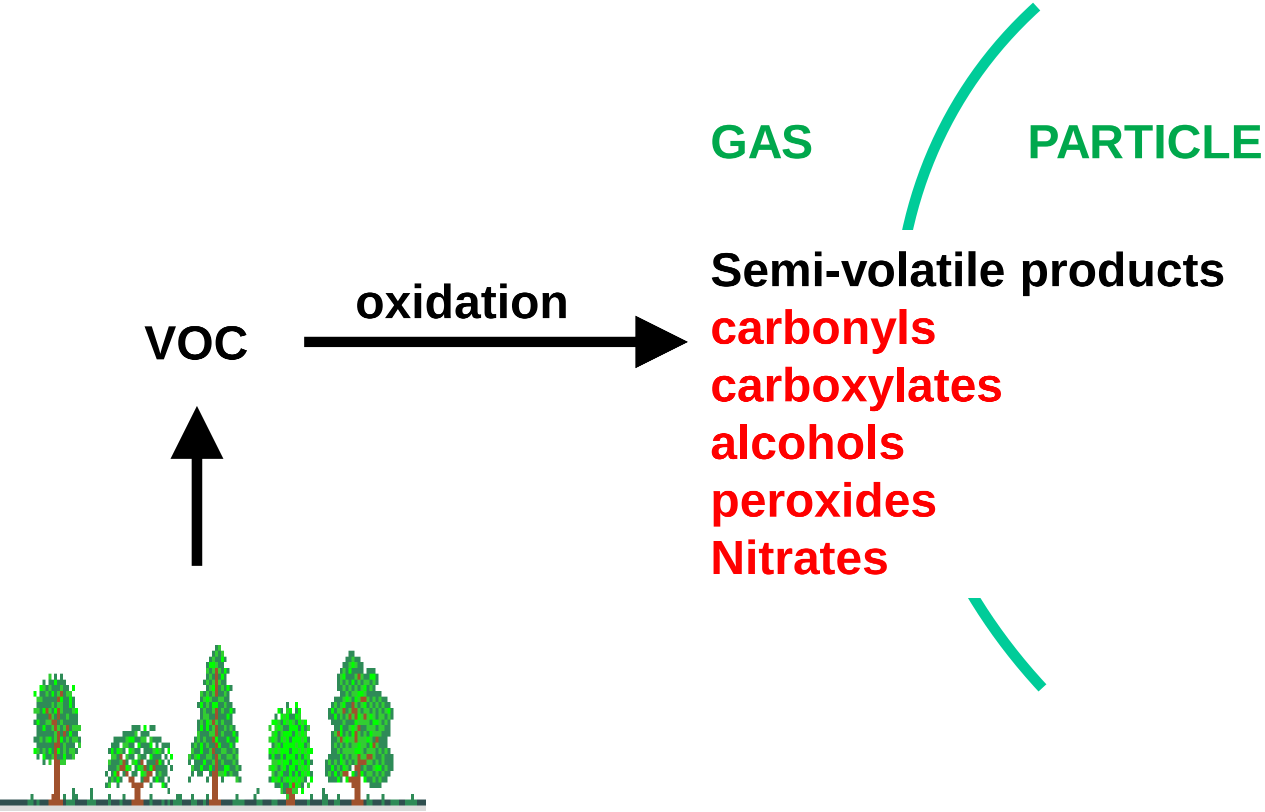


Wang et al. [2014]

Two components dominate PM$_{2.5}$ mass under almost all conditions:

- Sulfate-nitrate-ammonium (SNA)
- Organic carbon (OC)

To what extent is “biogenic” particulate matter controllable?



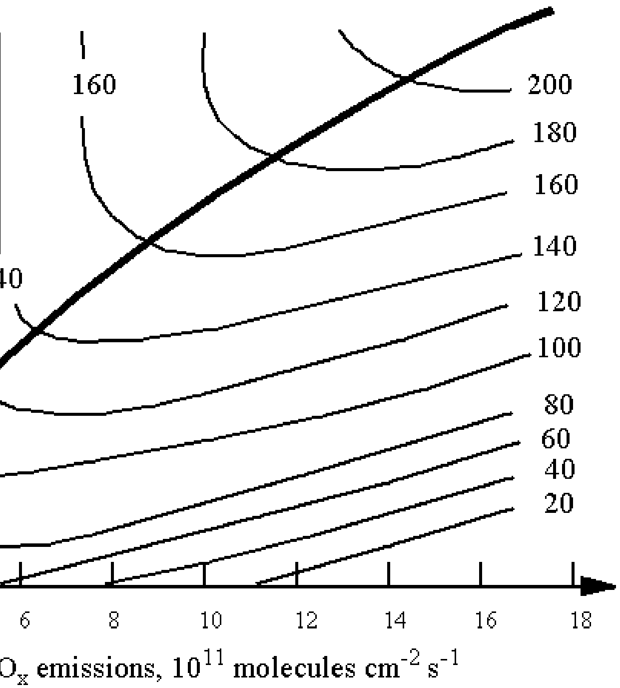
Can anthropogenic particles increase biogenic particle yield by providing a pre-existing condensed phase for partitioning of semi-volatile products?

How to control ozone pollution?

Decrease emissions of nitrogen oxides ($NO_x \equiv NO + NO_2$)
and/or volatile organic compounds (VOCs)

NO_x: efficient combustion (power plants, vehicles)
VOCs: inefficient combustion (vehicles, fires), industry, vegetation

but complicated by non-linear dependence



ism:

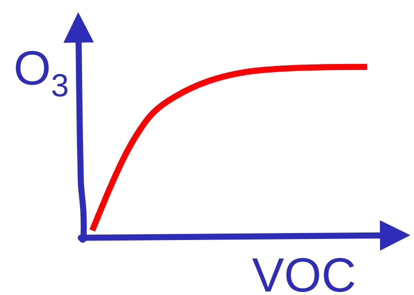
on RH)

H_2O (1)

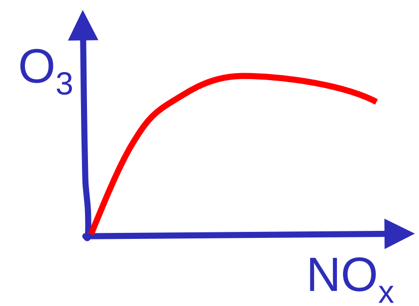
O_2 (2)

$_3$ (3)

Production can be VOC- or NO_x-limited:

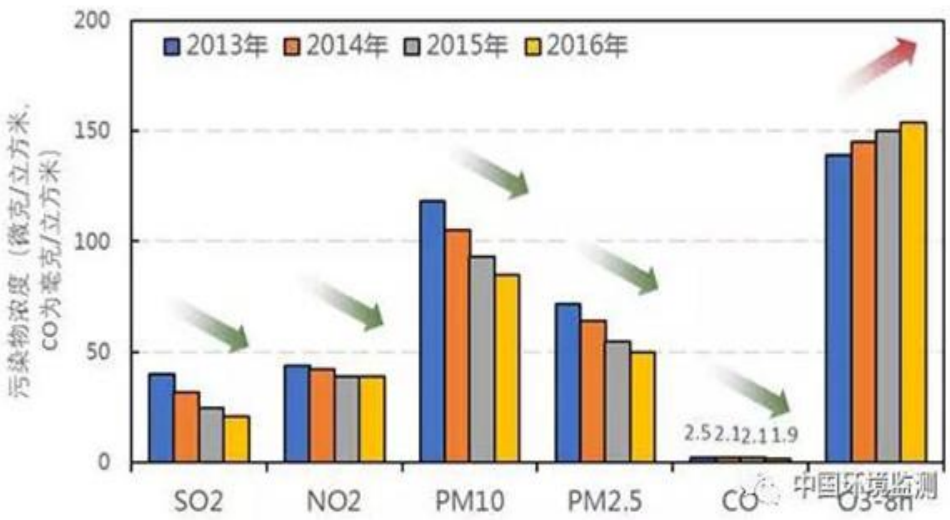


limited by
reaction (1)

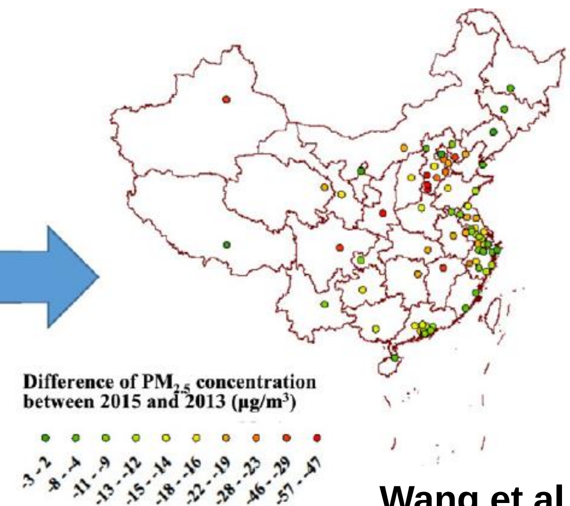


limited by
reaction (2)

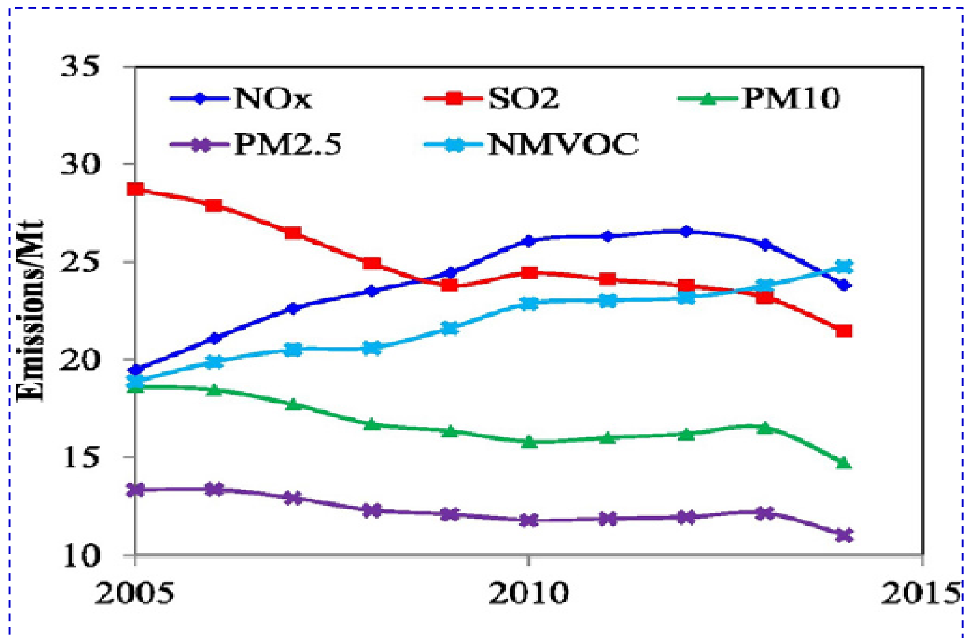
Latest trends in China: decreasing NO_x but rising ozone



Source: CNEMC, 2017

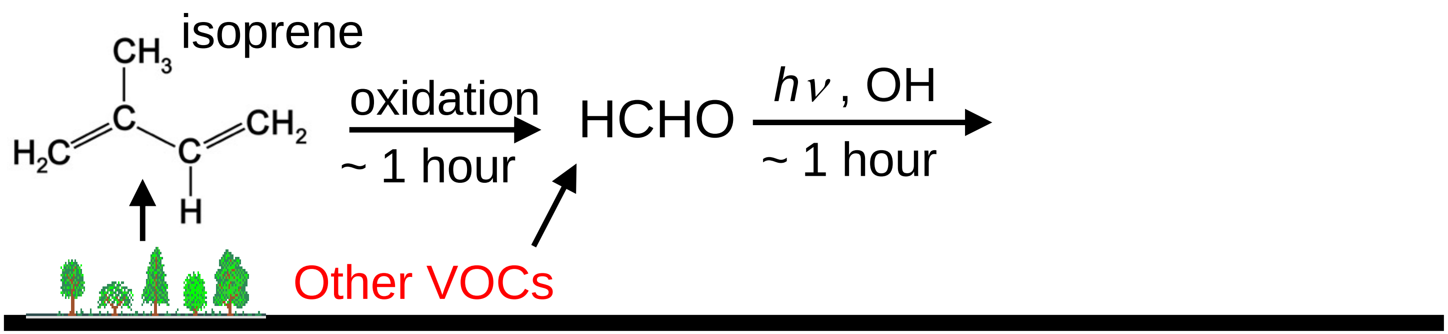


Wang et al., Sci. Tot. Env., 2017

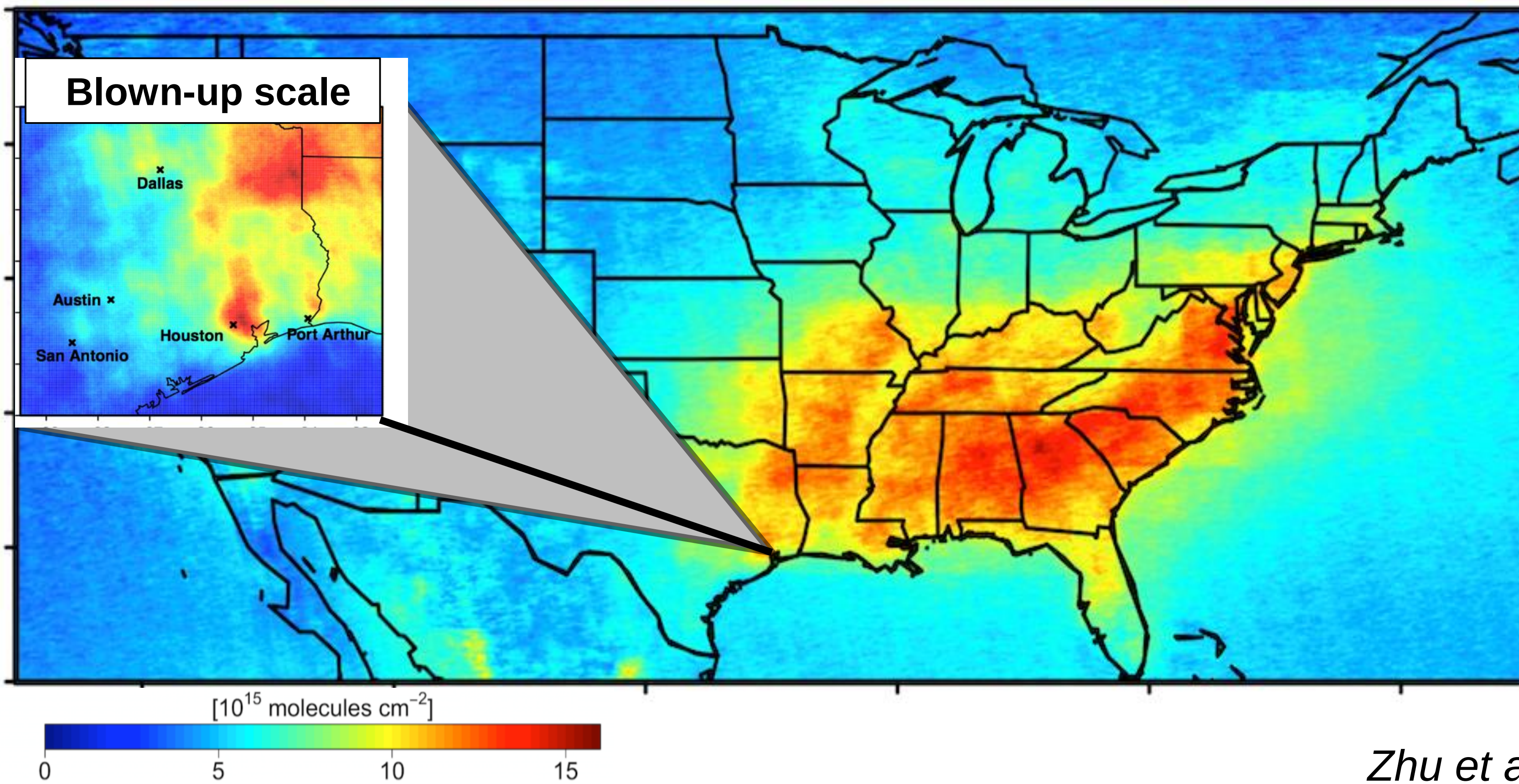


from H Liao, NUIST

US is NO_x-limited due to high emissions of biogenic isoprene

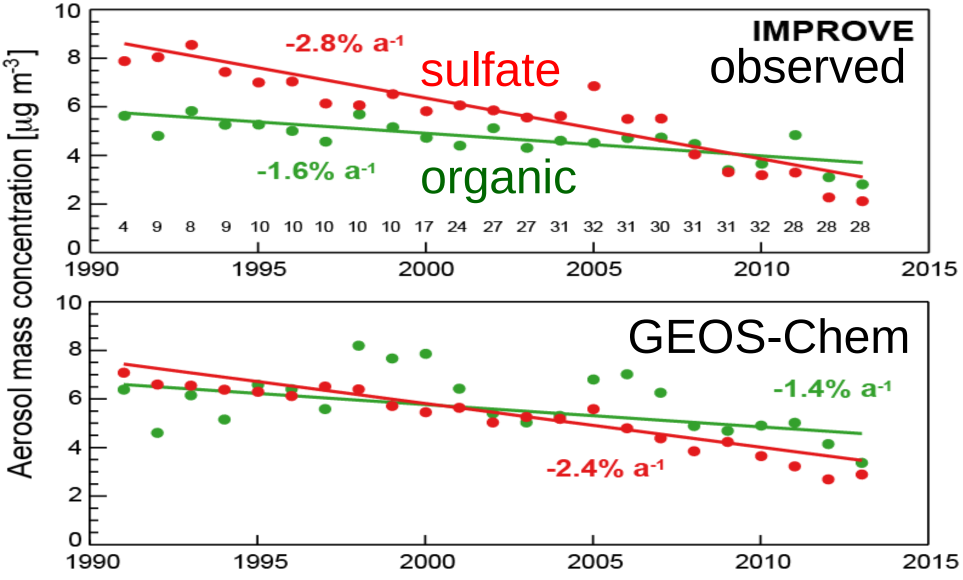


OMI satellite observations of formaldehyde (HCHO) columns, May-Aug 2005-2014



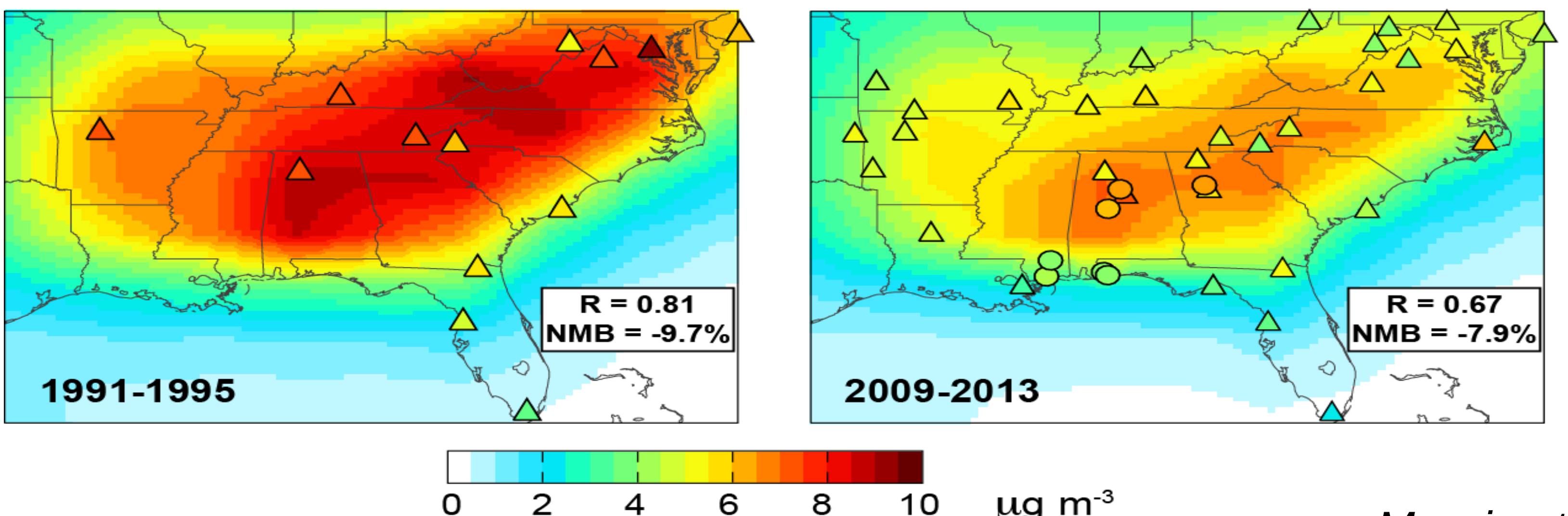
Zhu et al. [2017]

2003-2013 summer trends of sulfate and organic aerosol



Observed organic aerosol decrease can be explained by isoprene SOA dependence on sulfate

Organic aerosol concentrations: observed (symbols) and model (background)



Marais et al. [2017]