Evolving understanding of particulate matter (PM) air pollution: lessons from East Asia

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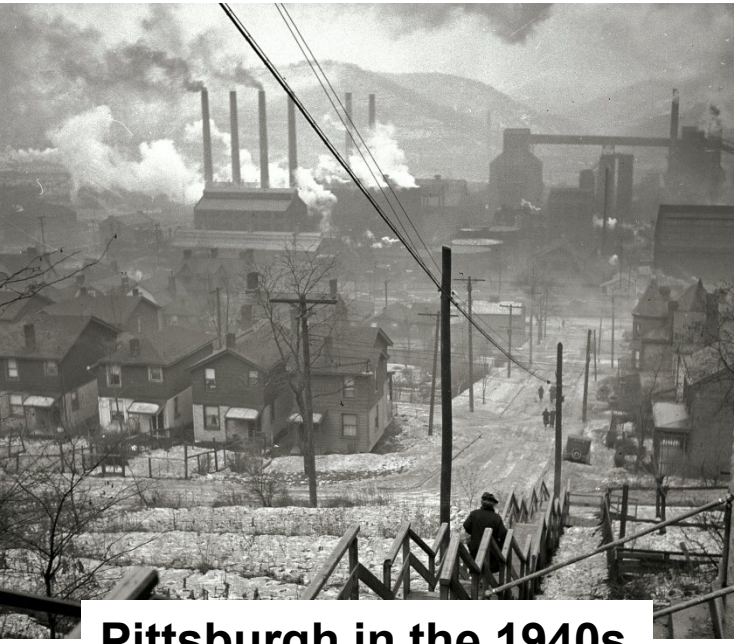
The industrial revolution and air pollution



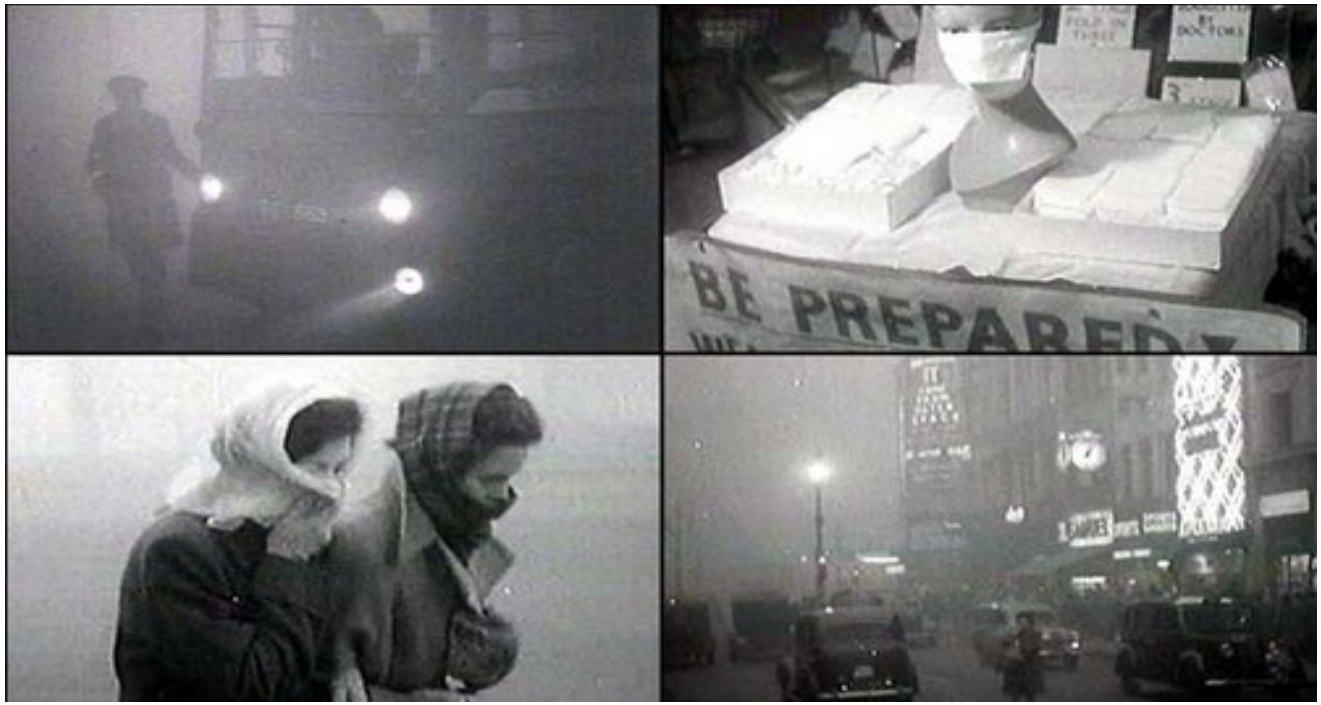
Pittsburgh in the 1940s

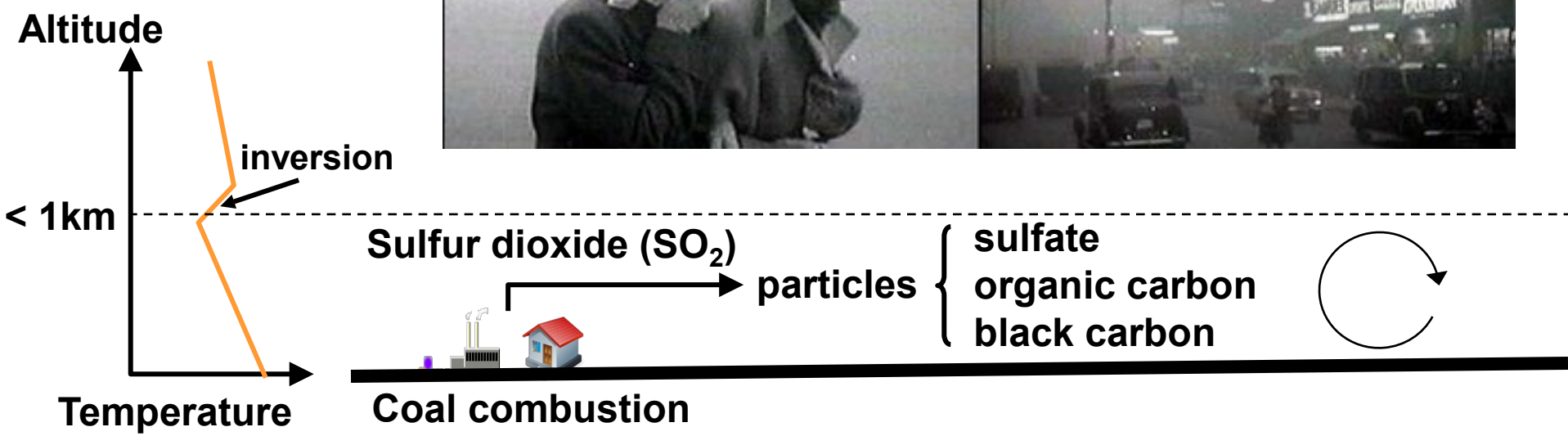
“Make great efforts to build China into a strong and prosperous industrialized country under the leadership of the Party and chairman Mao!”

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



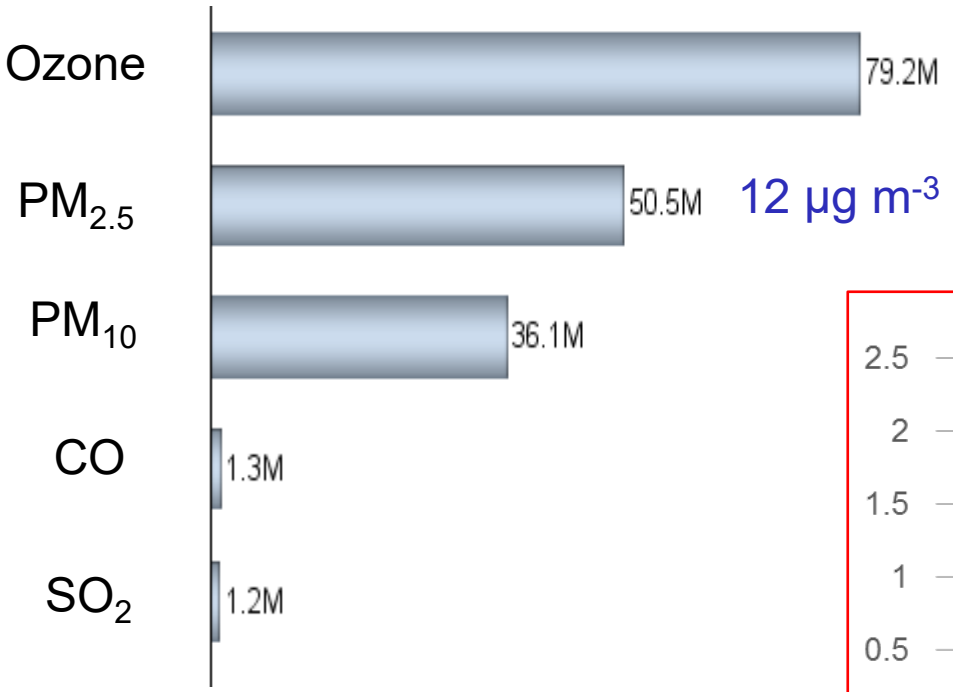


AIR POLLUTION TODAY:

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

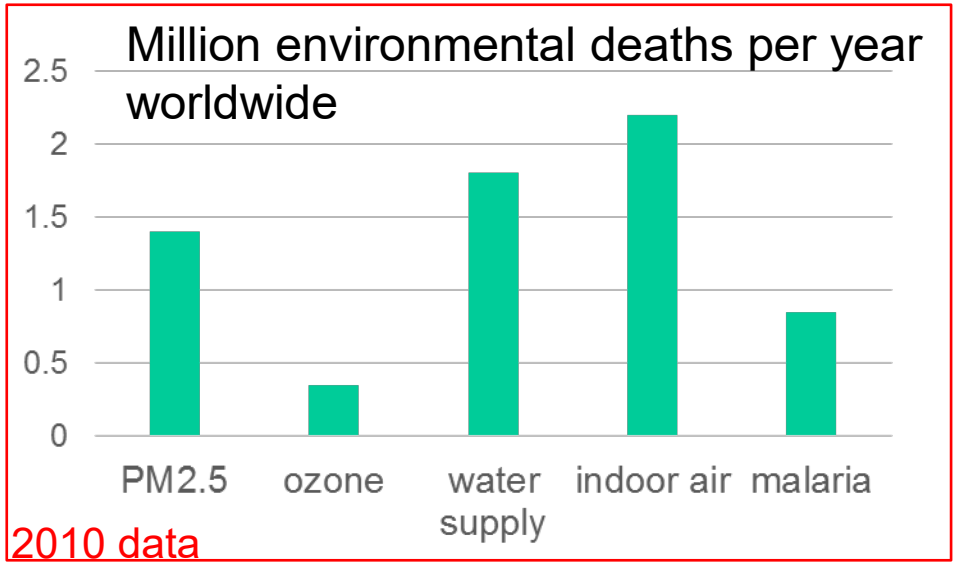
$PM_{2.5}$ ≡ particulate matter smaller than 2.5 μm in diameter

US population exposed to air pollutants
in excess of national ambient air quality standards (NAAQS), 2020



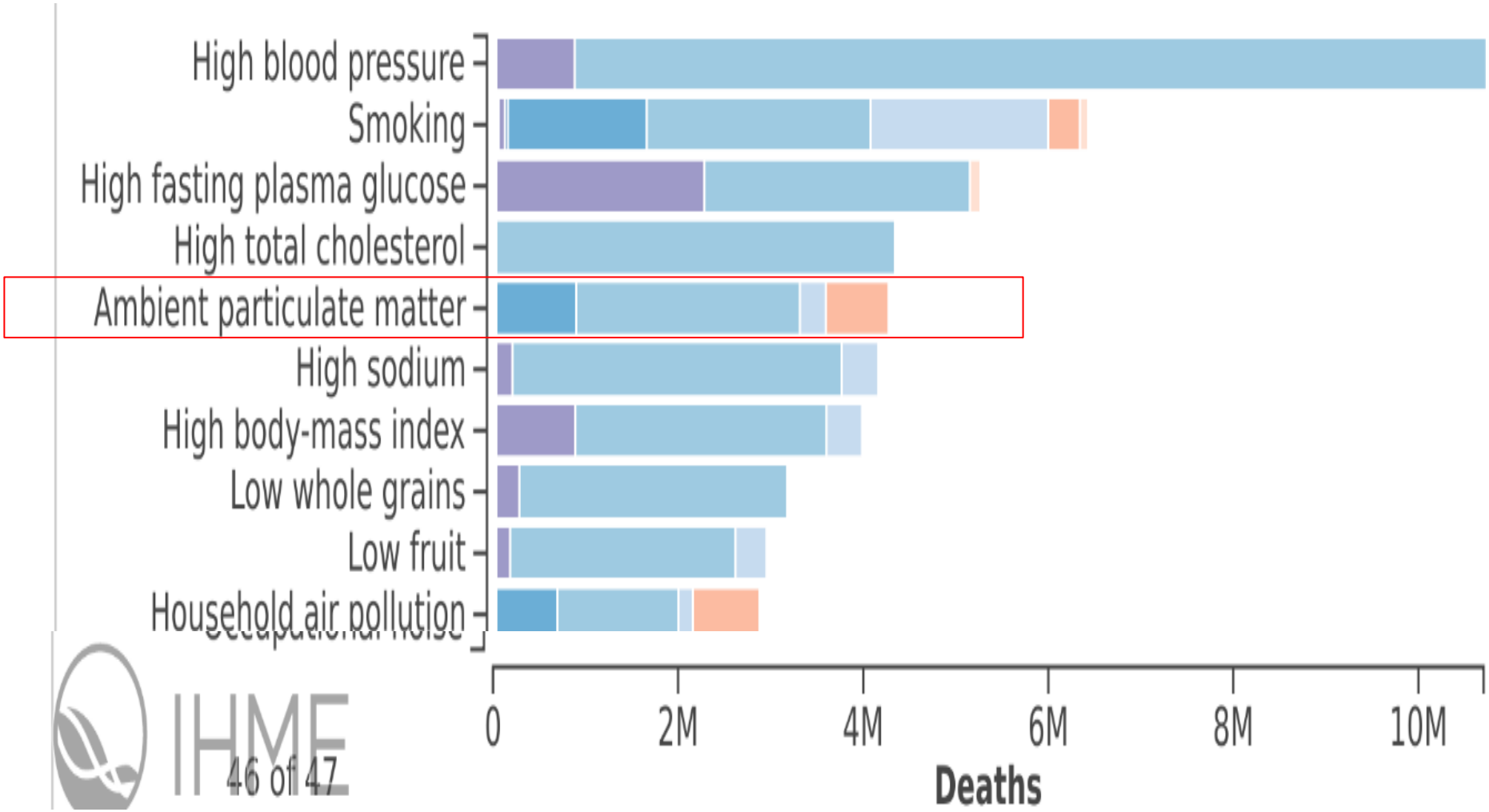
70 ppb (8-h average)

12 μg m^{-3} (annual), 35 μg m^{-3} (24-h)



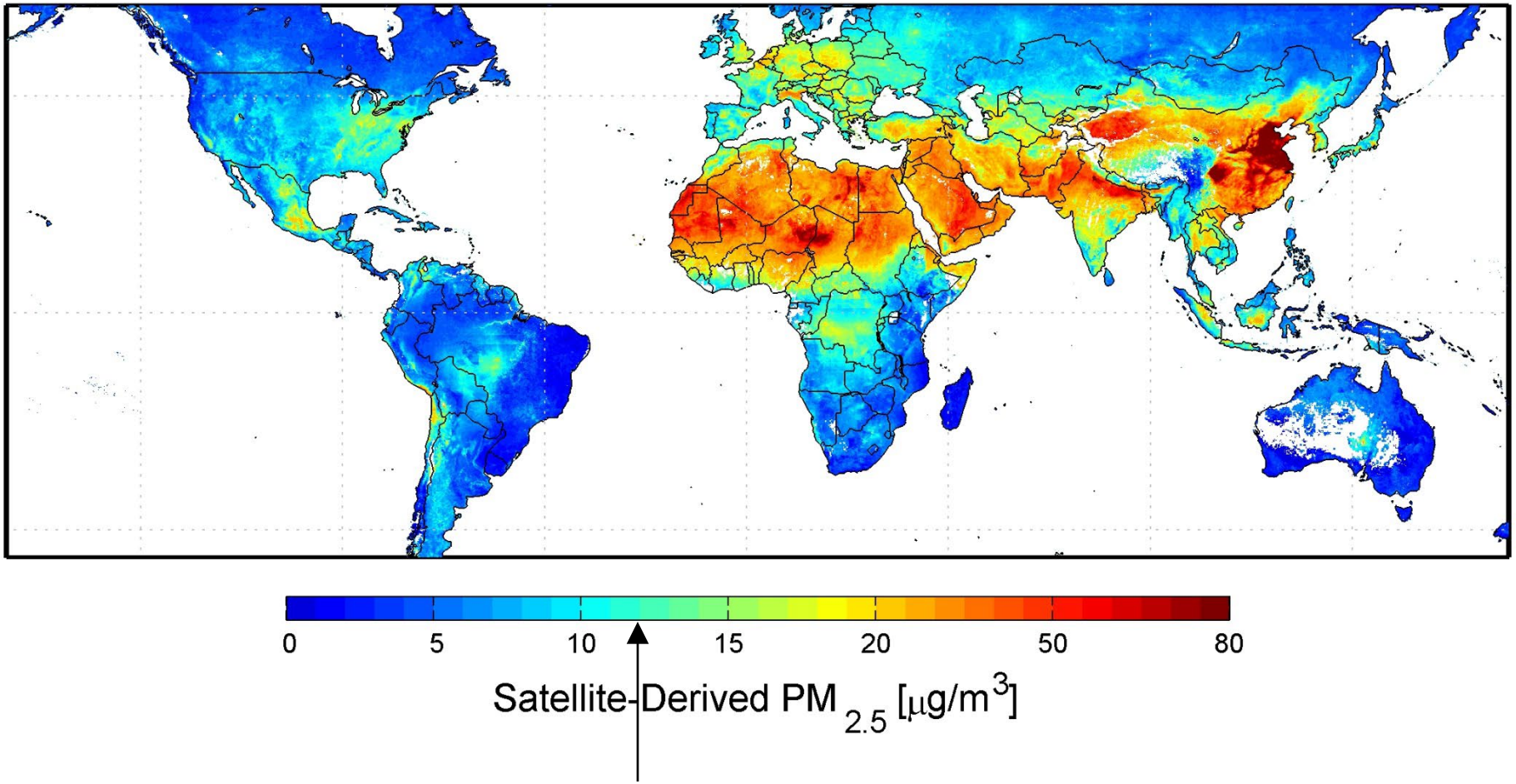
US EPA [2022], OECD [2012]

$PM_{2.5}$ is a major cause of mortality worldwide



Institute for Health Metrics and Evaluation, 2020

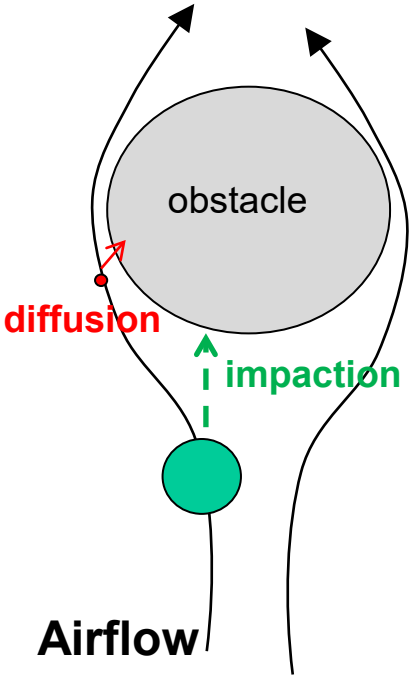
Annual mean $PM_{2.5}$ inferred from satellite observations of aerosol optical depth

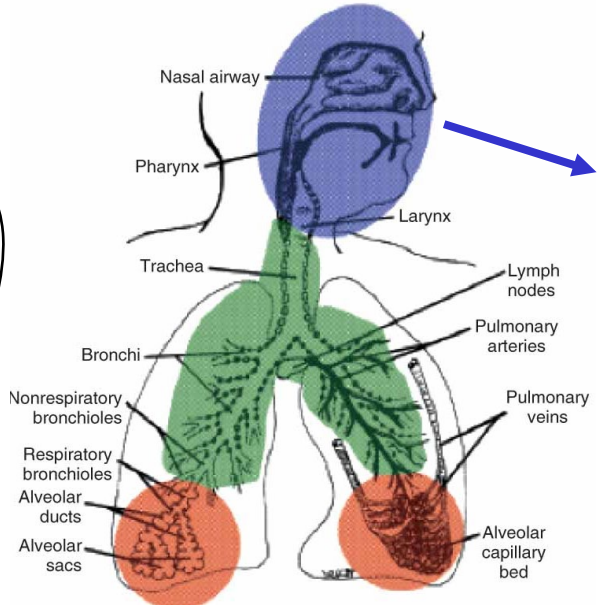


US air quality standard (12 μg m^{-3})

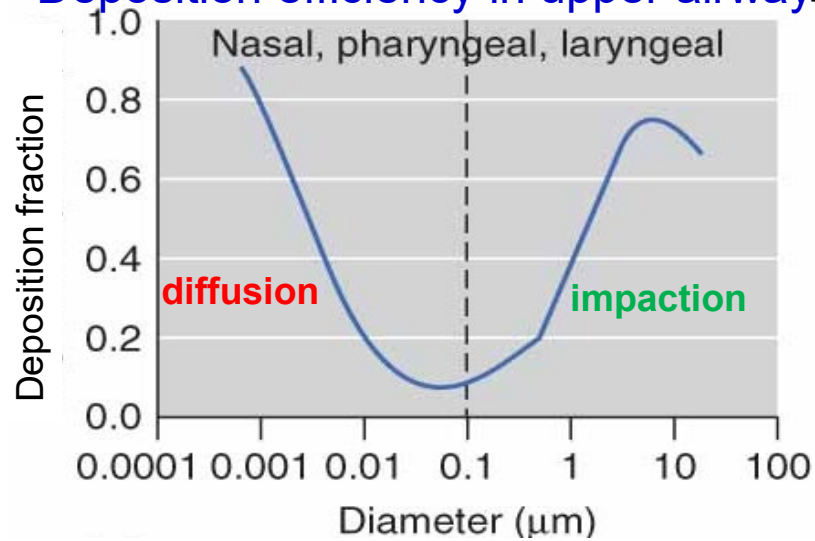
http://www.nasa.gov/topics/earth

Why fine particulate matter? Because it penetrates deep in lung

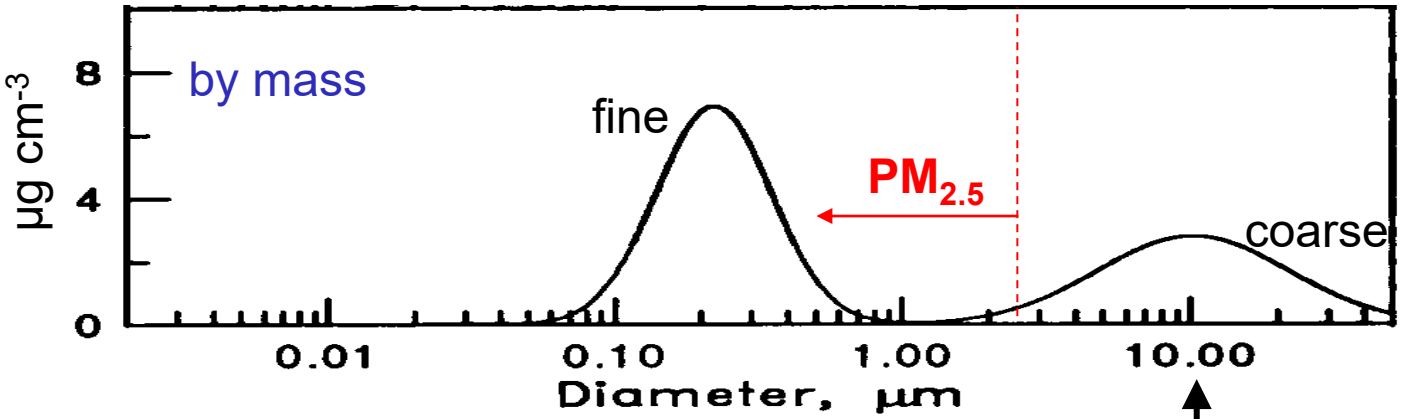




Deposition efficiency in upper airways



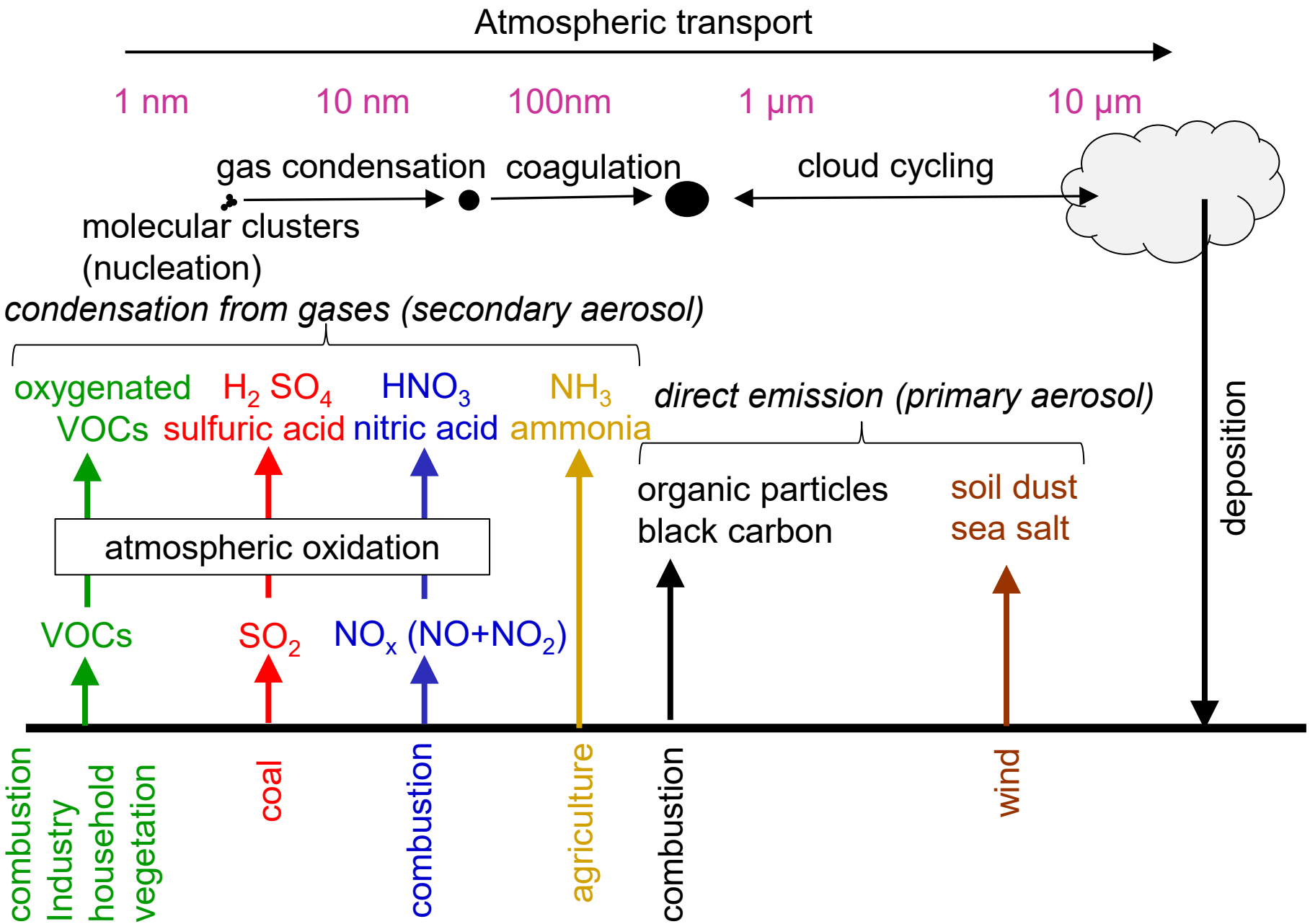
Typical PM size distribution



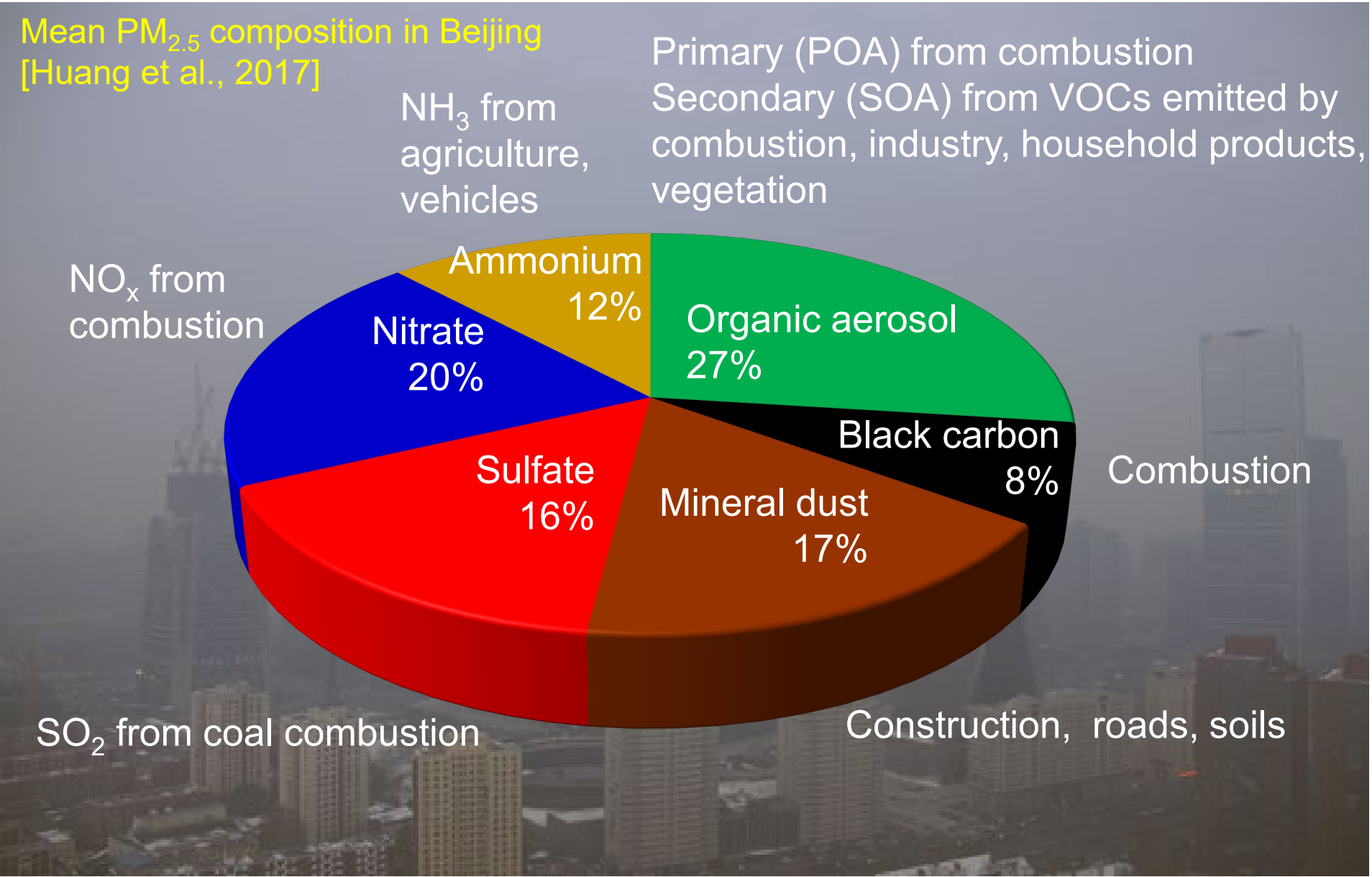
Condensation from gas phase (*secondary* particles):

Direct emission (*primary* particles)

Sources and life cycle of particulate matter



$PM_{2.5}$ composition in Beijing



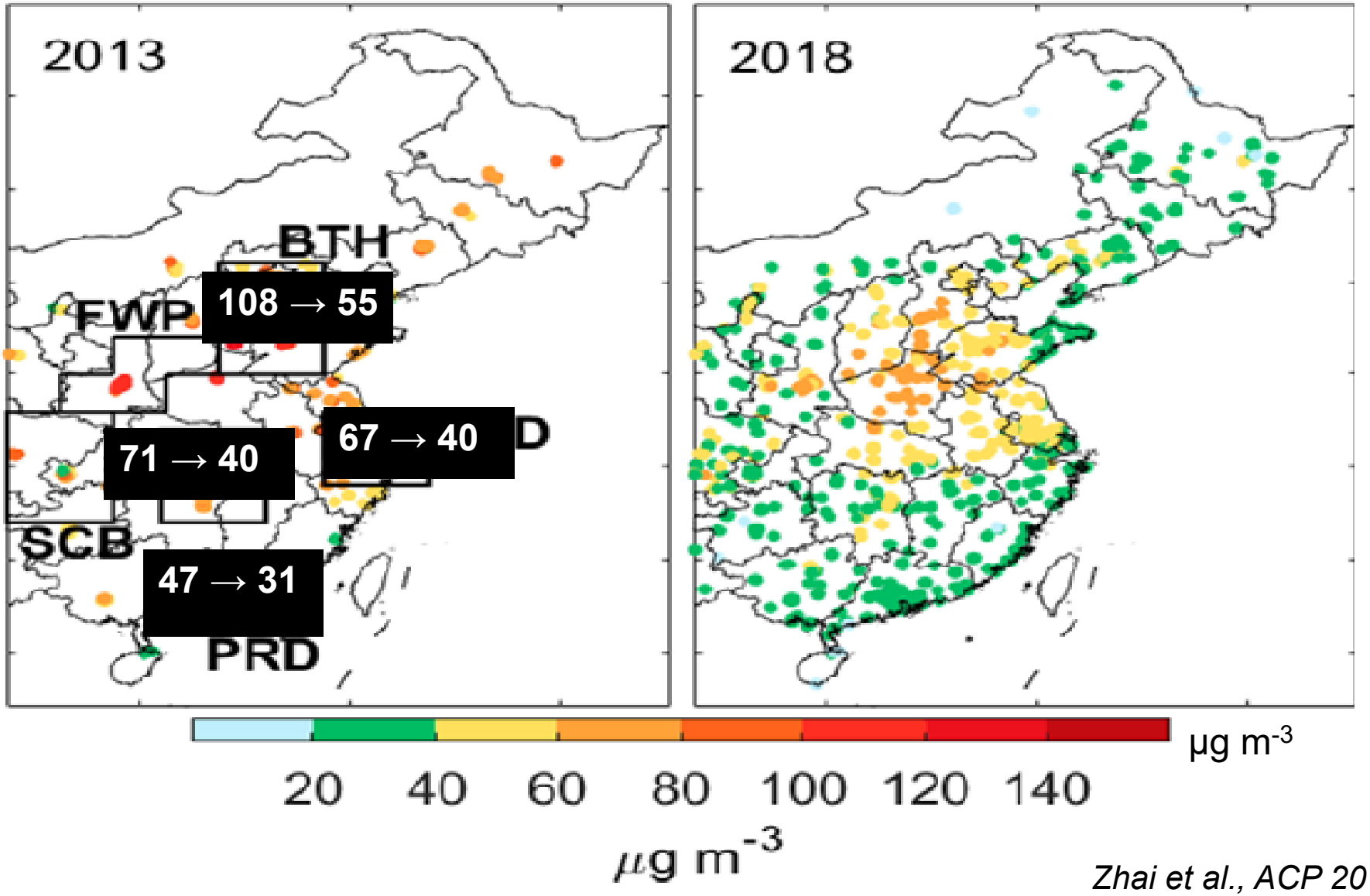
In 2013, the Chinese government initiated the “Clean Air Action”

- **Scrubbing of SO_2 emissions from coal combustion**
- **Ban on residential coal combustion**
- **Closing of polluting industries**
- **Emission standards for vehicles**
- **Ban on agricultural fires**
- **Encouragement of renewable energy sources**

Winter haze episode

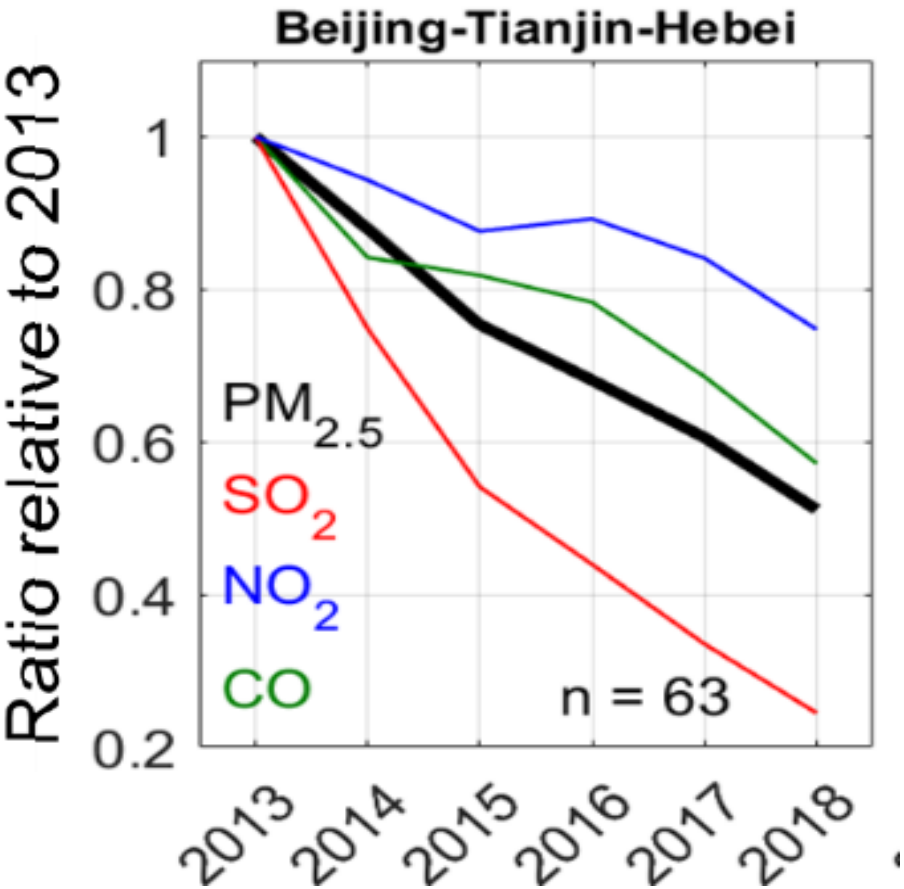
Clean Air Action has led to great improvement in $PM_{2.5}$ air quality

Annual mean $PM_{2.5}$ at China Ministry of Ecology and Environment (MEE) sites:
$PM_{2.5}$ decreased by 30-50% across urban China over 2013-2018

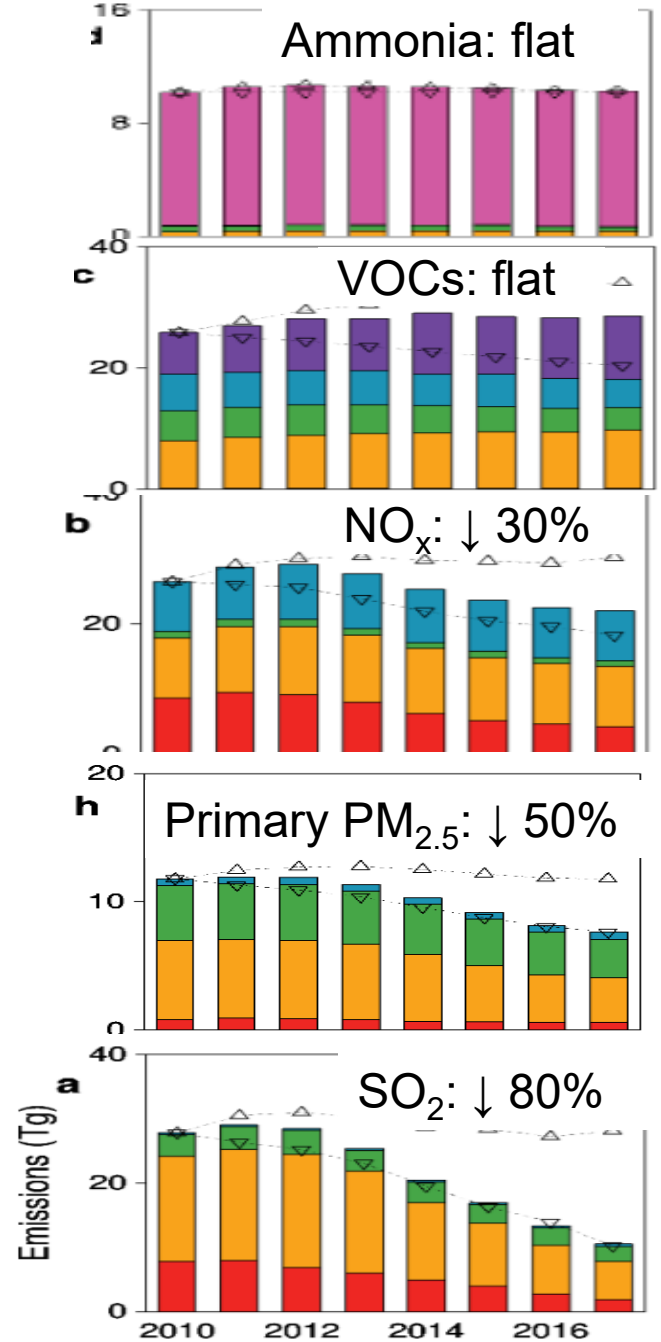


Zhai et al., ACP 2019

$PM_{2.5}$ trends have been driven by controls on SO_2 and primary emissions



Chinese emission trends (MEIC)

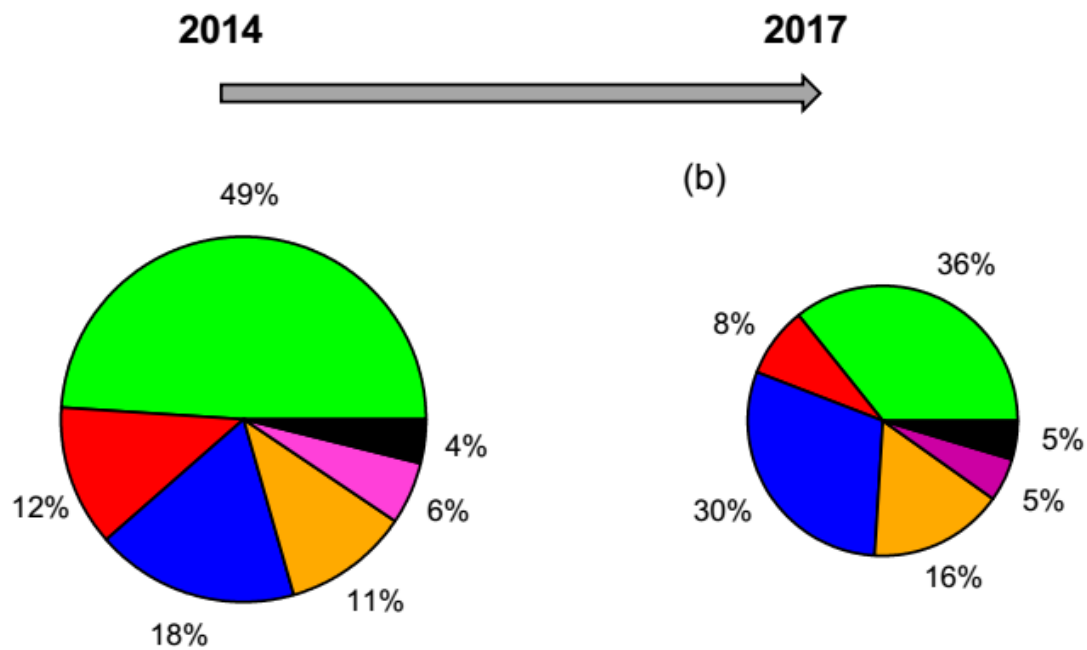


Agriculture
Solvents
Transportation
Residential
Industry
Electricity

Zhai et al., ACP 2019; Zheng et al., ACP 2018

Evolution of $PM_{2.5}$ composition in Beijing: transition from sulfate-organic dominated to nitrate-organic dominated

Organic
Sulfate
Nitrate
Ammonium
Chloride
Elemental carbon

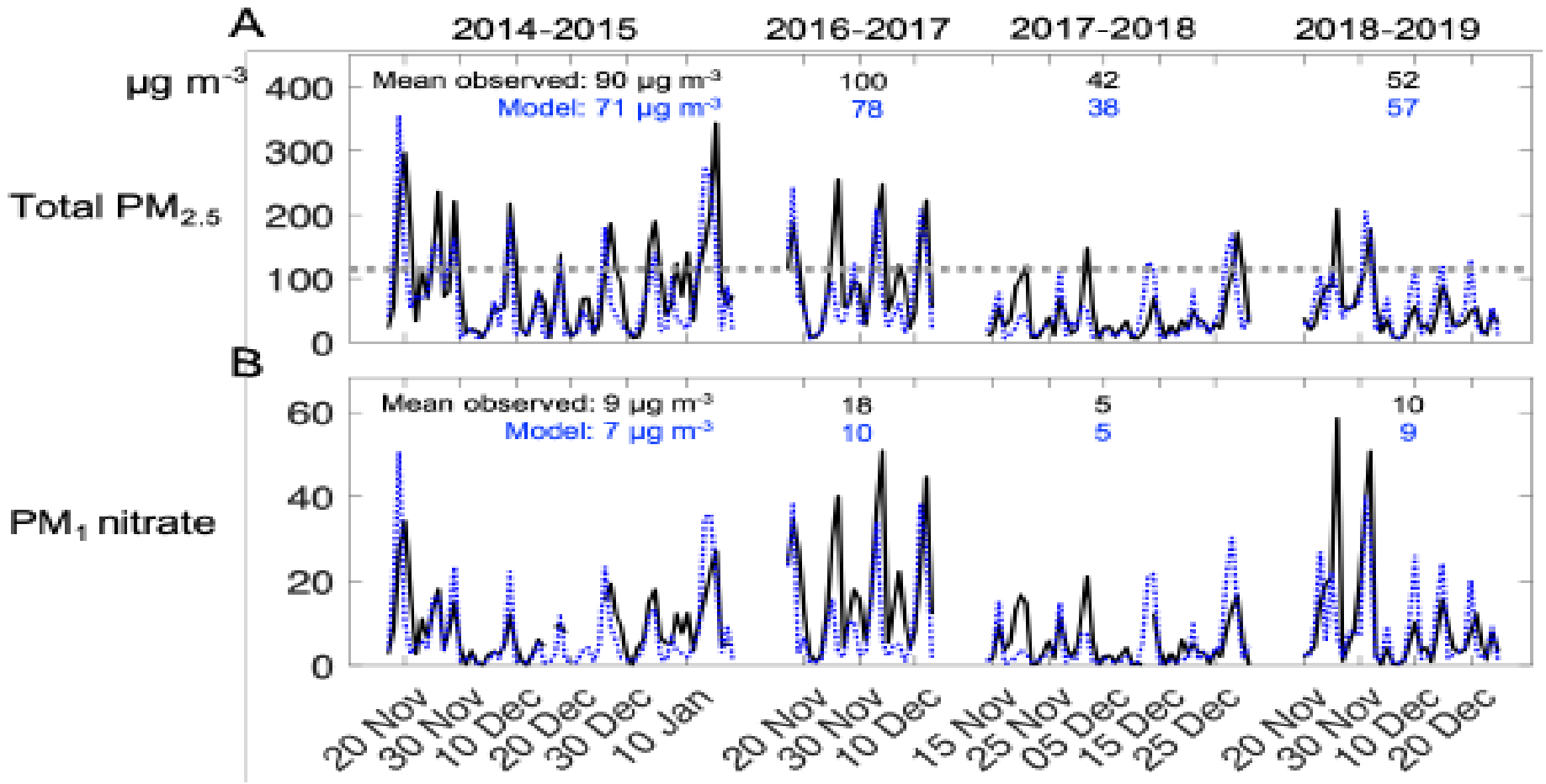


- Sulfate and organic components have been most effectively controlled
- Nitrate is of increasing relative importance

H. Li et al., 2019

NO_x emissions have decreased by 30% since 2013 - but PM nitrate has not decreased, and is up in winter haze events

Beijing wintertime data: nitrate is now the most important component of $PM_{2.5}$



Zhai et al., 2021a

Decreasing NO_x emission can increase nitrate production through nighttime chemistry

$$NO \xrightarrow{O_3} NO_2 \xrightarrow{O_3} NO_3 \xrightarrow{NO_2} N_2O_5 \xrightarrow[H_2O]{aerosol} HNO_3$$

Combustion

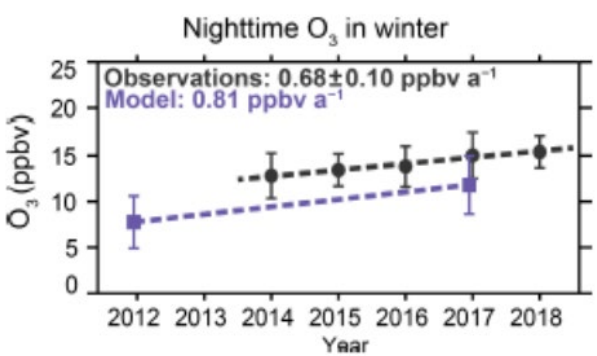
$$O_2 \xrightarrow{heat} O + O$$

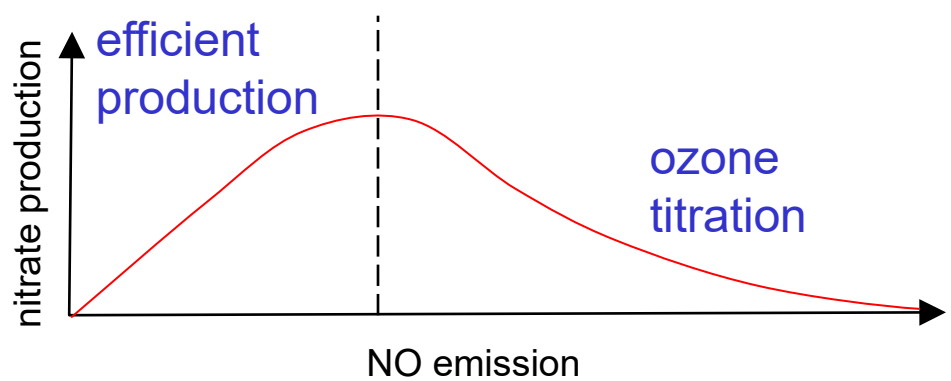
$$O + N_2 \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

$$net: N_2 + O_2 \rightarrow 2NO$$

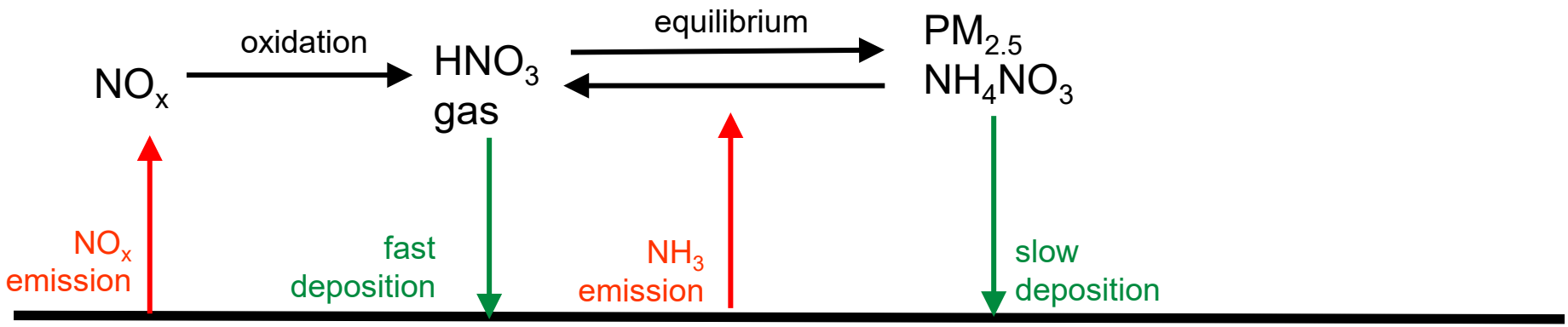
- NO_x is mainly emitted as NO
- NO and ozone titrate each other at night
- In ozone titration regime, decreasing NO emission allows more ozone to react with NO_2 and produce nitrate



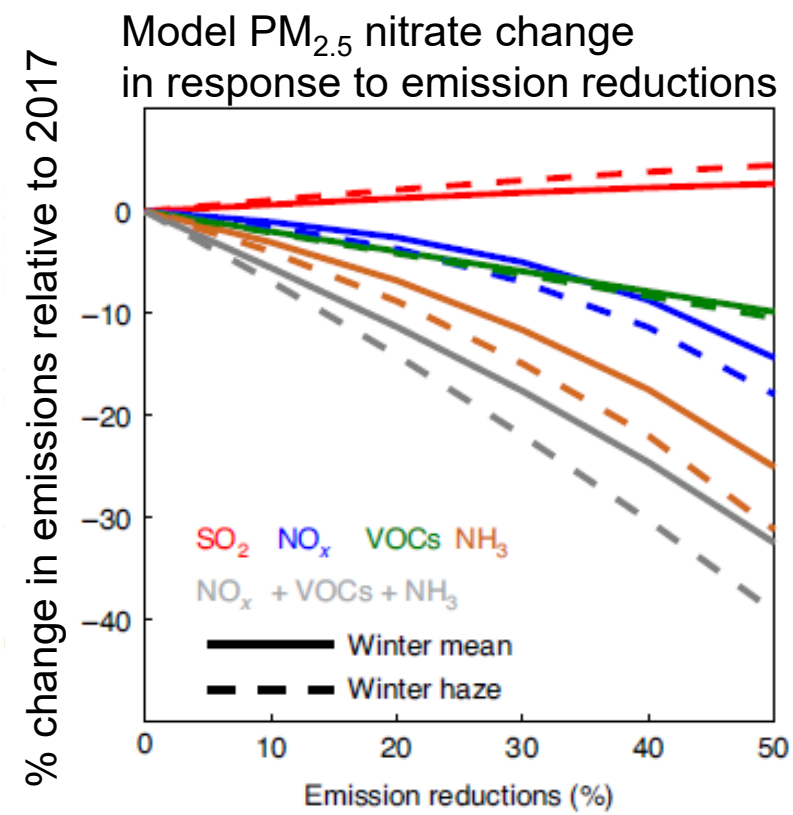


Shah et al., 2020

Decreasing NO_x emission can increase nitrate lifetime by shifting fast-depositing nitric acid to slow-depositing $PM_{2.5}$ nitrate

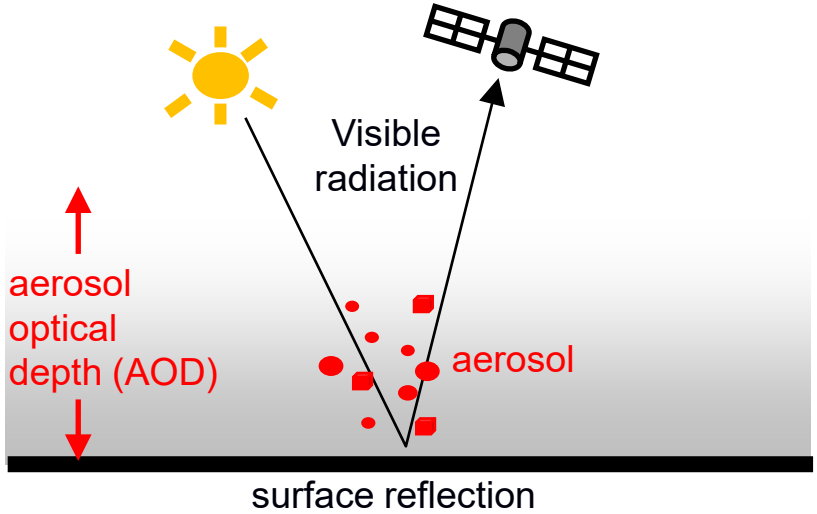


- Decreasing source of total nitrate shifts partitioning from HNO_3 to $PM_{2.5}$ nitrate, slowing down deposition
- Decreasing ammonia emissions is the most effective strategy for decreasing $PM_{2.5}$ nitrate

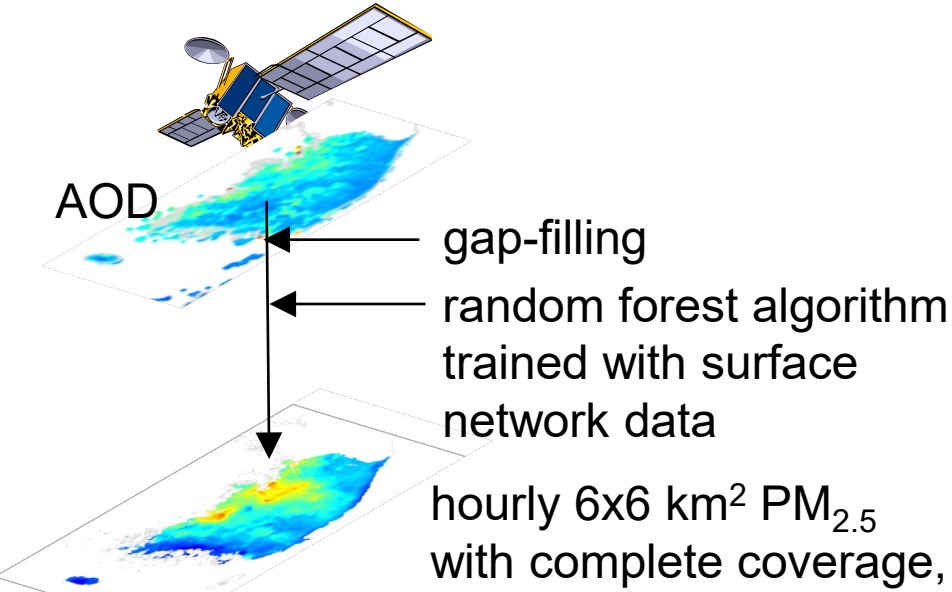


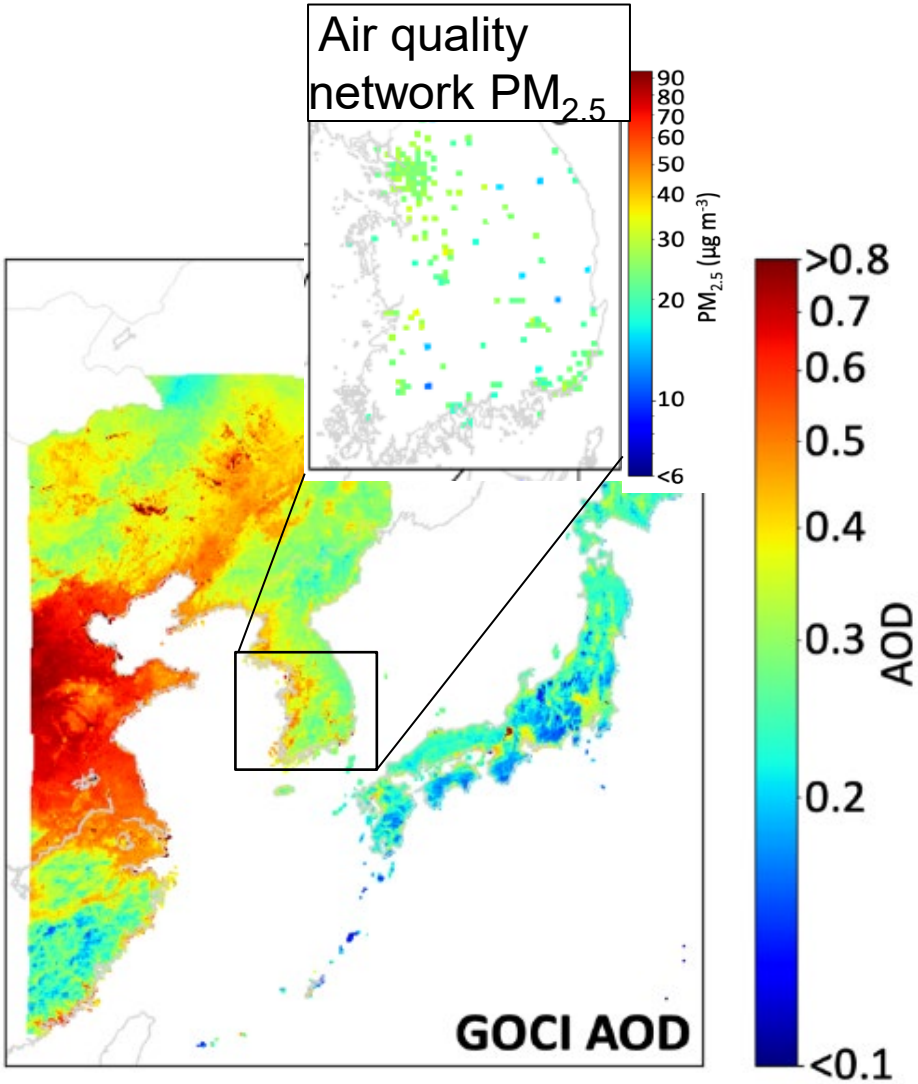
Zhai et al. [2021a]

Mapping of $PM_{2.5}$ over East Asia with GOCI geostationary satellite data (2010-)



hourly 6x6 km^2 GOCI AOD product
from 0.5x0.5 km^2 native data



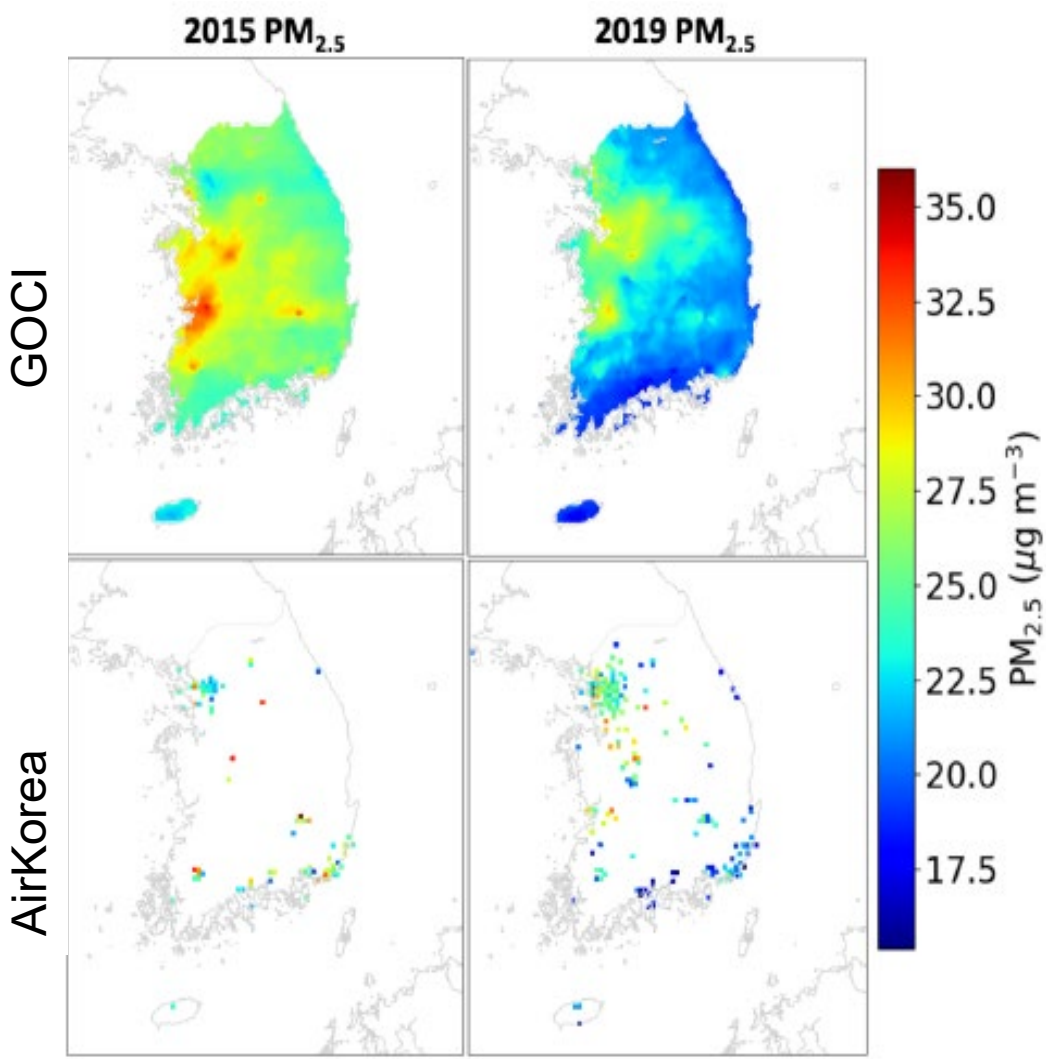


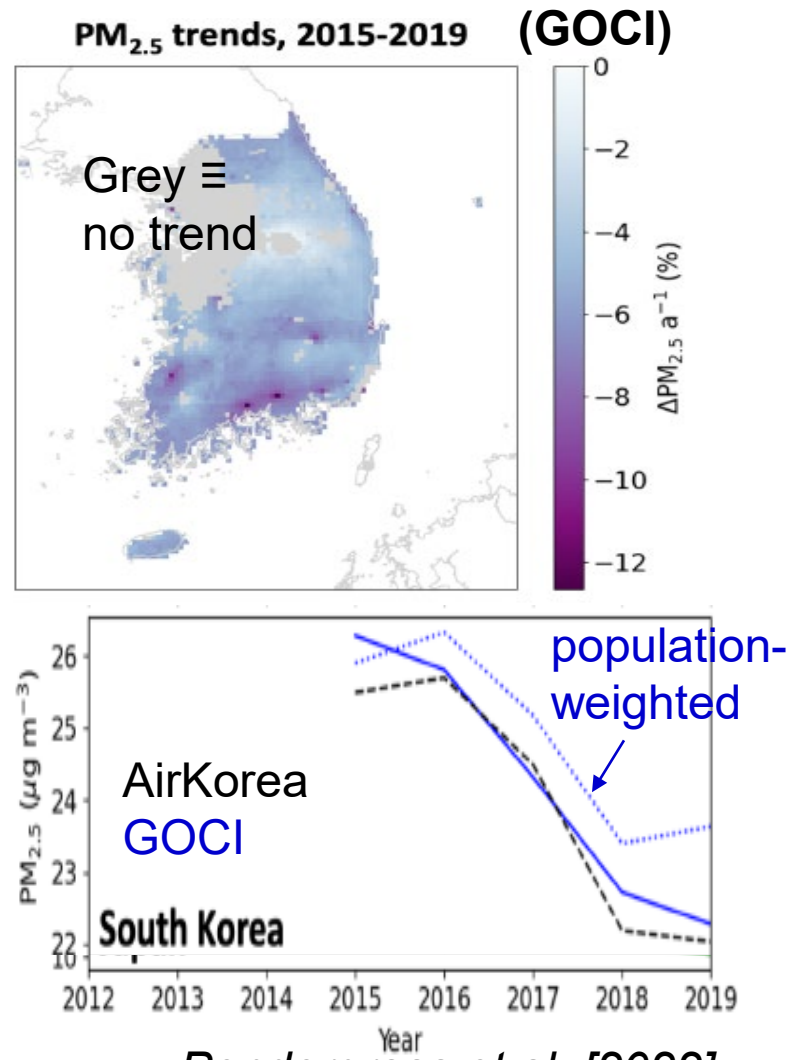
Pendergrass et al. [2022]

Application to $PM_{2.5}$ distribution and long-term trends

GOCI provides

- observations in hotspots missing from AirKorea regulatory network;
- complete coverage of trends and population exposure

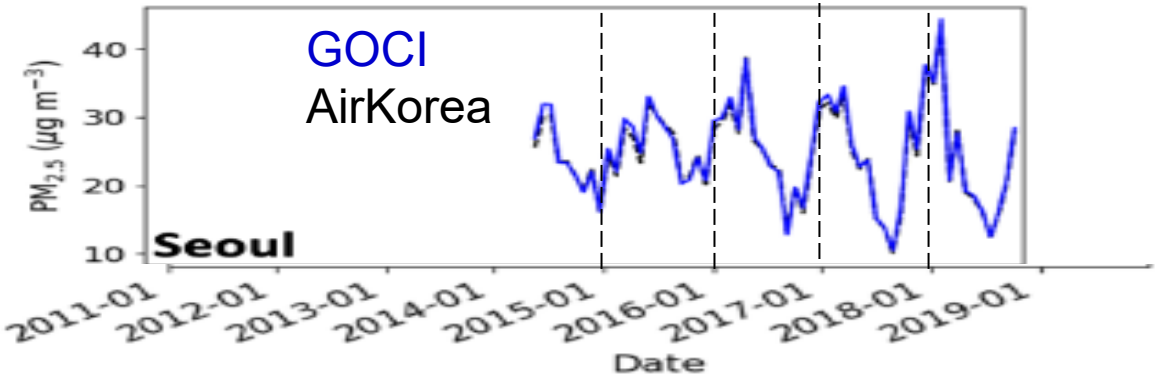




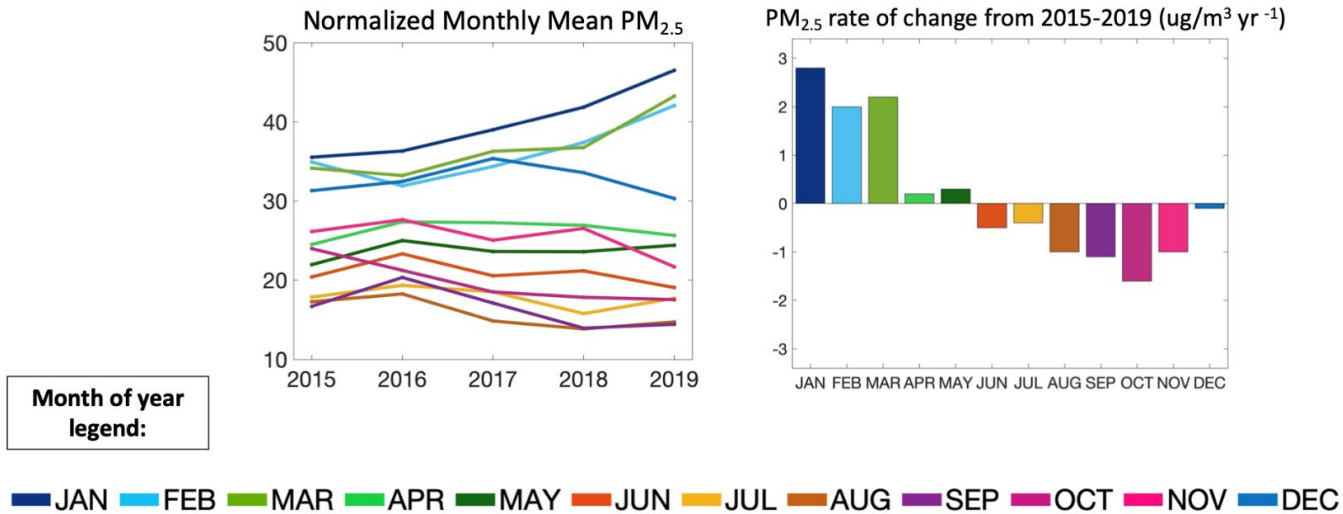
Pendergrass et al. [2022]

What is happening in Seoul?

No $PM_{2.5}$ trend over 2015-2019…while the rest of South Korea has decreased



Meteorologically corrected trend for AirKorea sites shows 3% increase driven by winter:



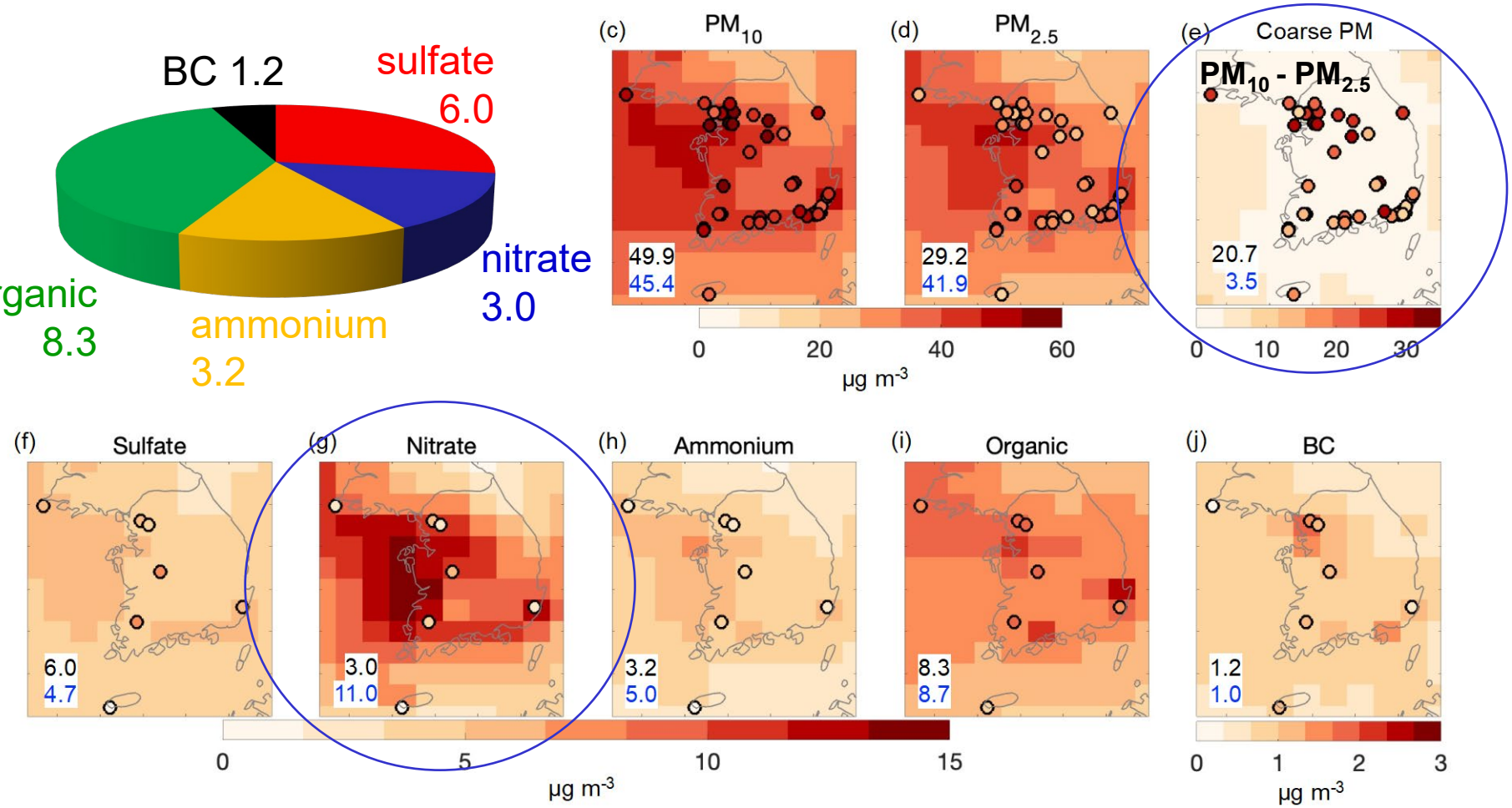
Could winter increase be driven by nitrate? We have seen that previously in Beijing

Pendergrass et all. [2022]; Nadia Colombi, in prep.

PM composition over Korea during KORUS-AQ campaign (May-June 2016)

Median observed
$PM_{2.5}$ composition (μg m^{-3})

Surface site data (circles)
GEOS-Chem model (background)

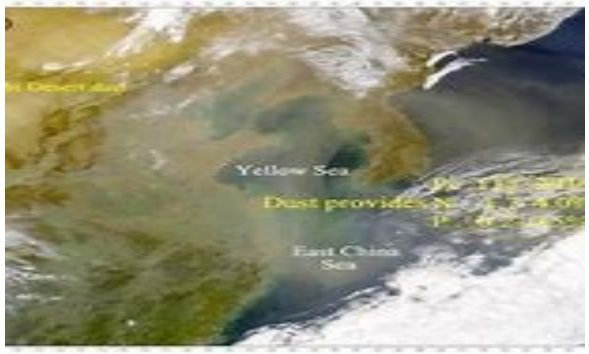


GEOS-Chem model overestimates nitrate (mainly from nighttime) and does not account for coarse PM ≡ $PM_{10} – PM_{2.5}$

Zhai et al. [2021b]

Coarse PM is generally assumed to be mainly from natural desert dust, but we find over East Asia that it is mainly of urban origin

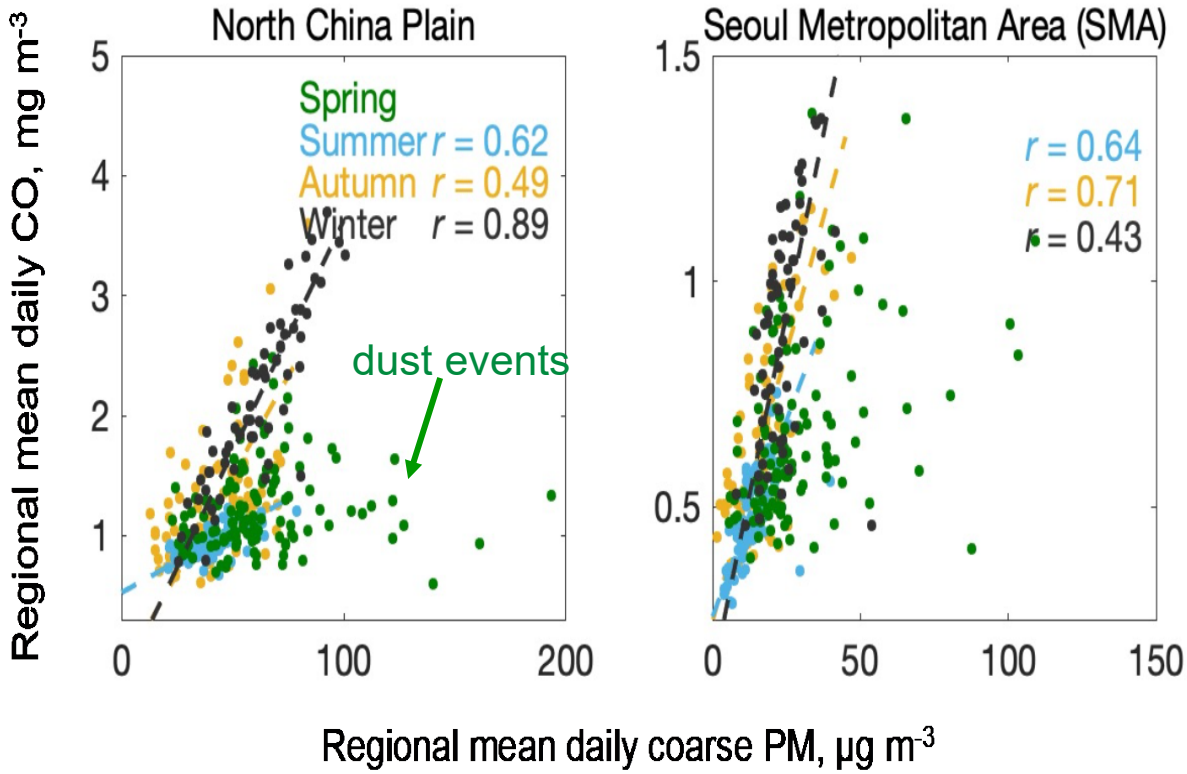
Gobi desert dust events (spring)



Vehicles

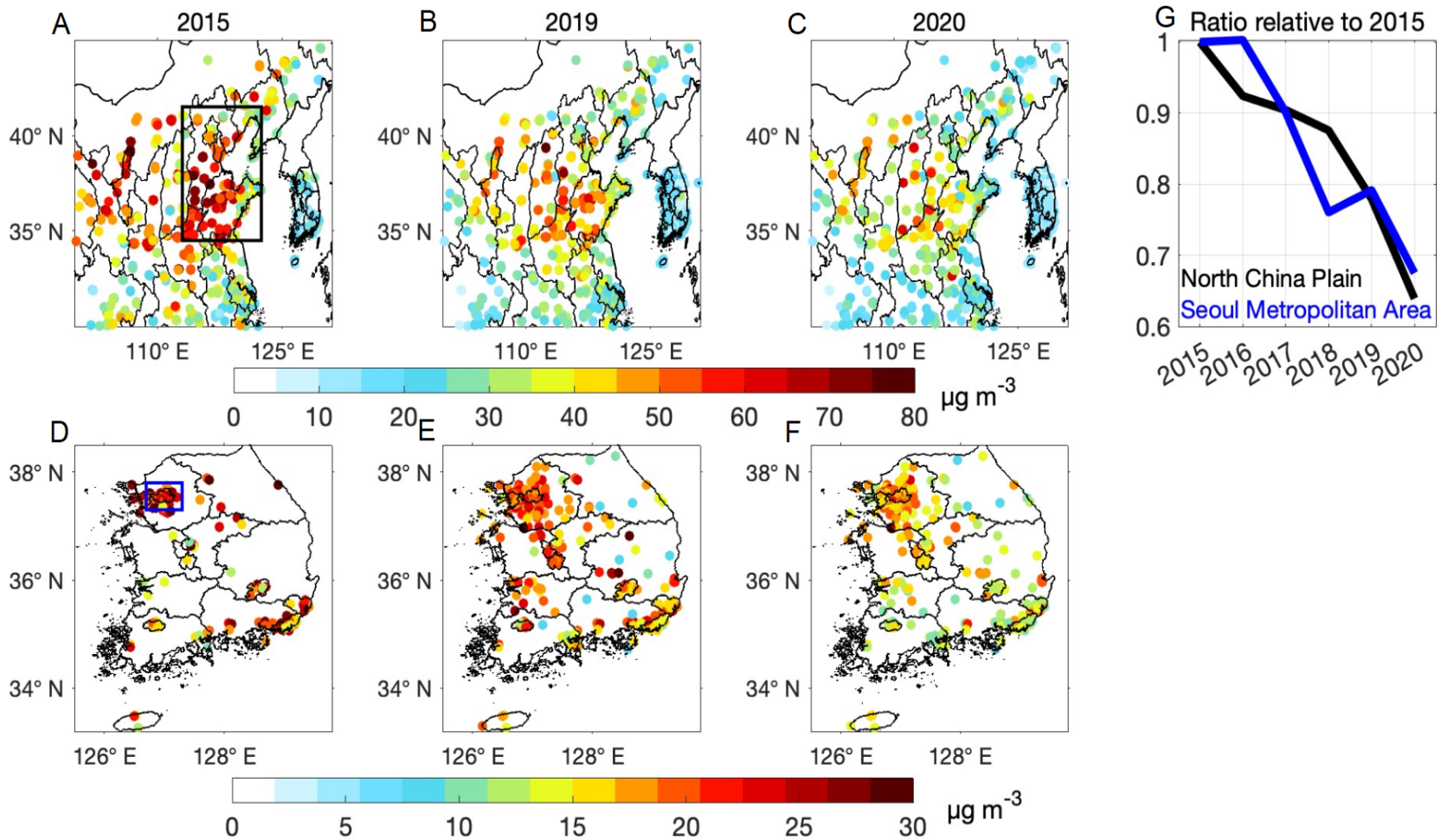
Construction

Air quality network data show strong correlation with CO



Shixian Zhai, in prep.

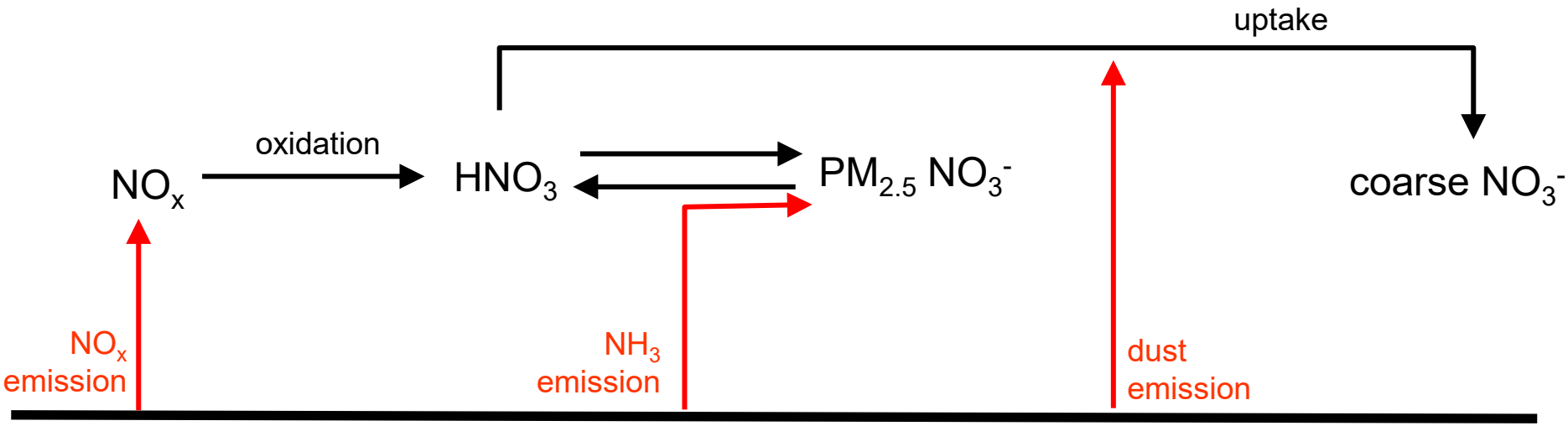
Coarse PM trends from air quality networks, 2015-2020

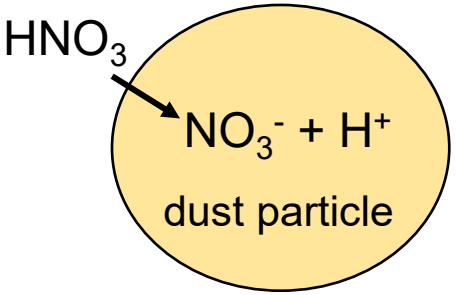


- Decreased emissions from construction sites and road dust
- COVID-19 shutdown led to abrupt decrease

Shixian Zhai, in prep.

Coarse anthropogenic dust suppresses $PM_{2.5}$ nitrate formation





- Emitted dust particles are alkaline, take up HNO_3 efficiently
- The resulting coarse NO_3^- is eventually deposited

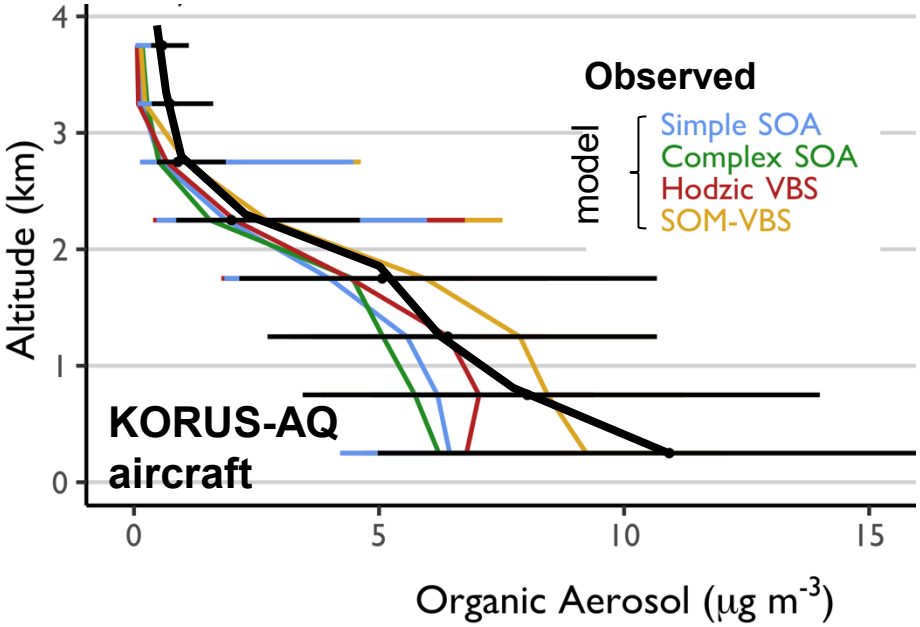
We find in GEOS-Chem model that

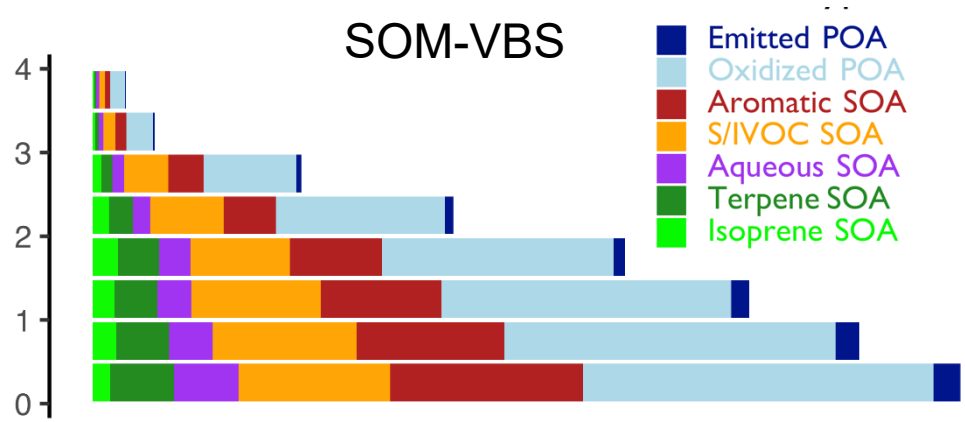
- Dust emission controls drive an increase in $PM_{2.5}$ nitrate
- HNO_3 uptake by dust particles doubles sensitivity of $PM_{2.5}$ nitrate to NH_3 emission

Shixian Zhai, in prep.

Sources of organic aerosol over Korea

- Primary (POA) from combustion, secondary (SOA) from oxidation of VOCs
- New SOM-VBS mechanism in GEOS-Chem including improved aromatic SOA yields





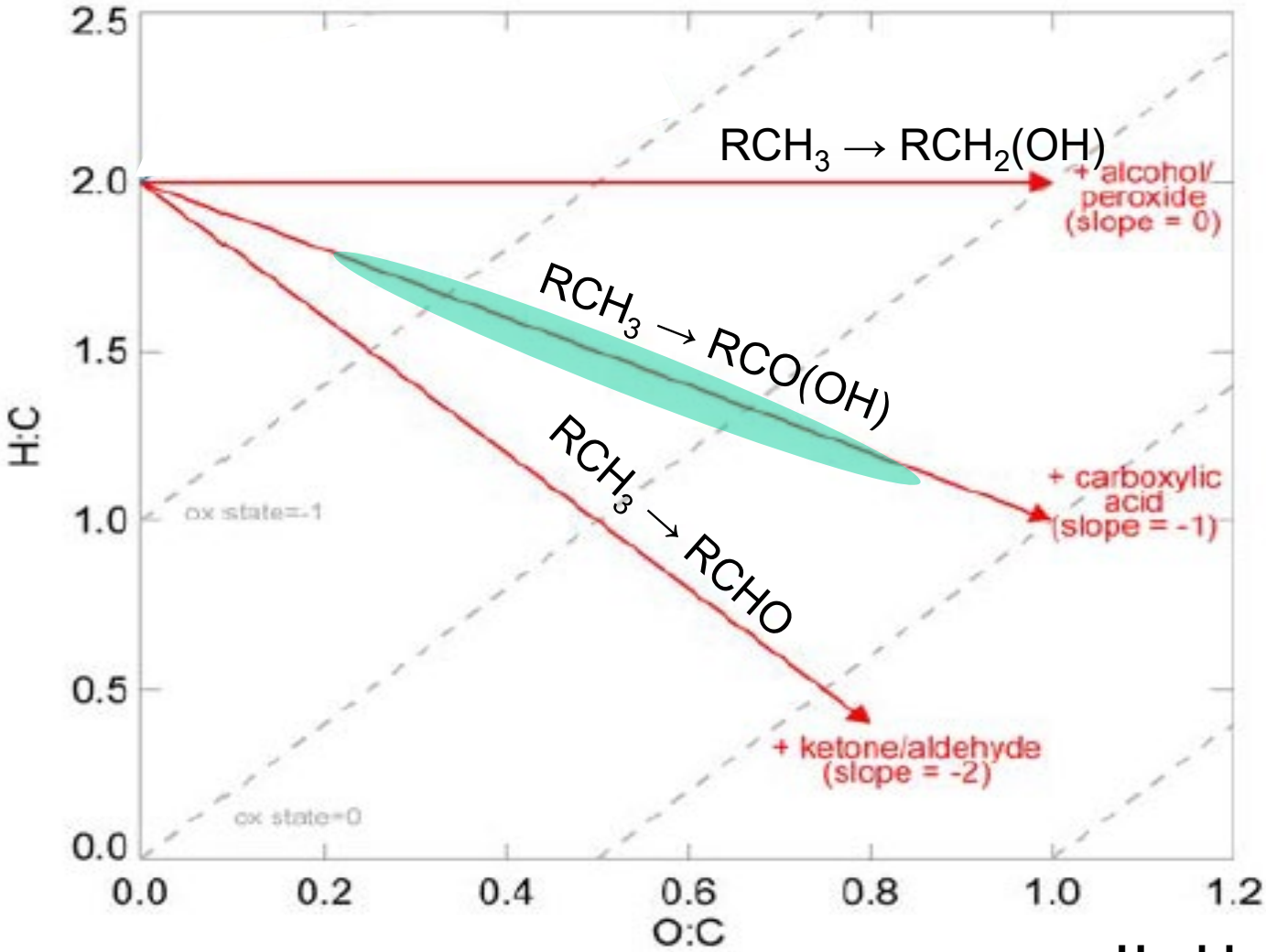
- Organic aerosol over S. Korea is mainly from fuel combustion

- 40% is oxidized primary organic aerosol (POA), 25% is aromatic secondary organic aerosol (SOA)

Brewer et al., submitted

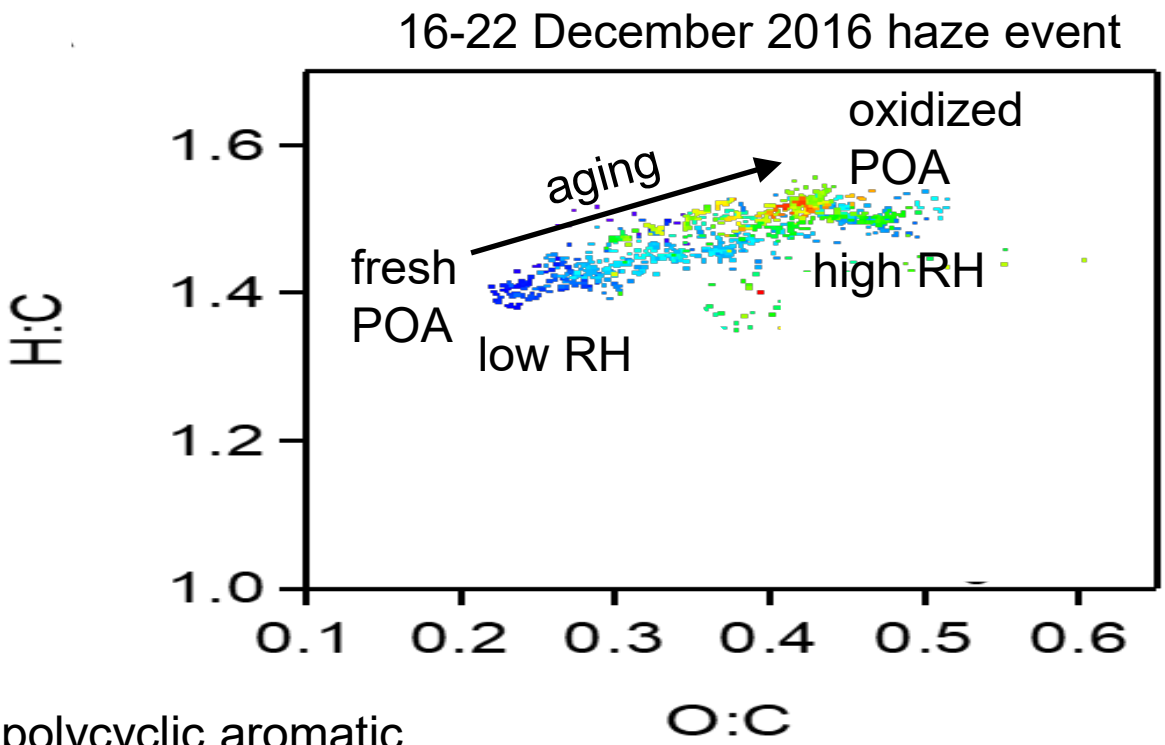
Van Krevelen diagram to interpret chemical evolution of organic aerosol

- Measured H:C and O:C molar ratios gives insight into functionalization
- Observations in the US usually suggest carboxylic acid functionalization



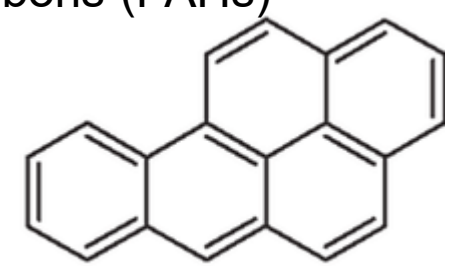
Heald et al. [2010]

Van Krevelen diagram for Beijing haze organic aerosol



- Both H:C and O:C ratios increase during rapid aging observed at high relative humidity
- But how do you get an increase in the H:C ratio?

polycyclic aromatic hydrocarbons (PAHs)



Benzo[a]pyrene

Fresh fossil fuel POA

aqueous-phase oxidation

ring opening, hydration, functionalization

Oxidized POA

oxidized POA is consistent with a PAH source

Wang et al. [2021]

Some take-aways

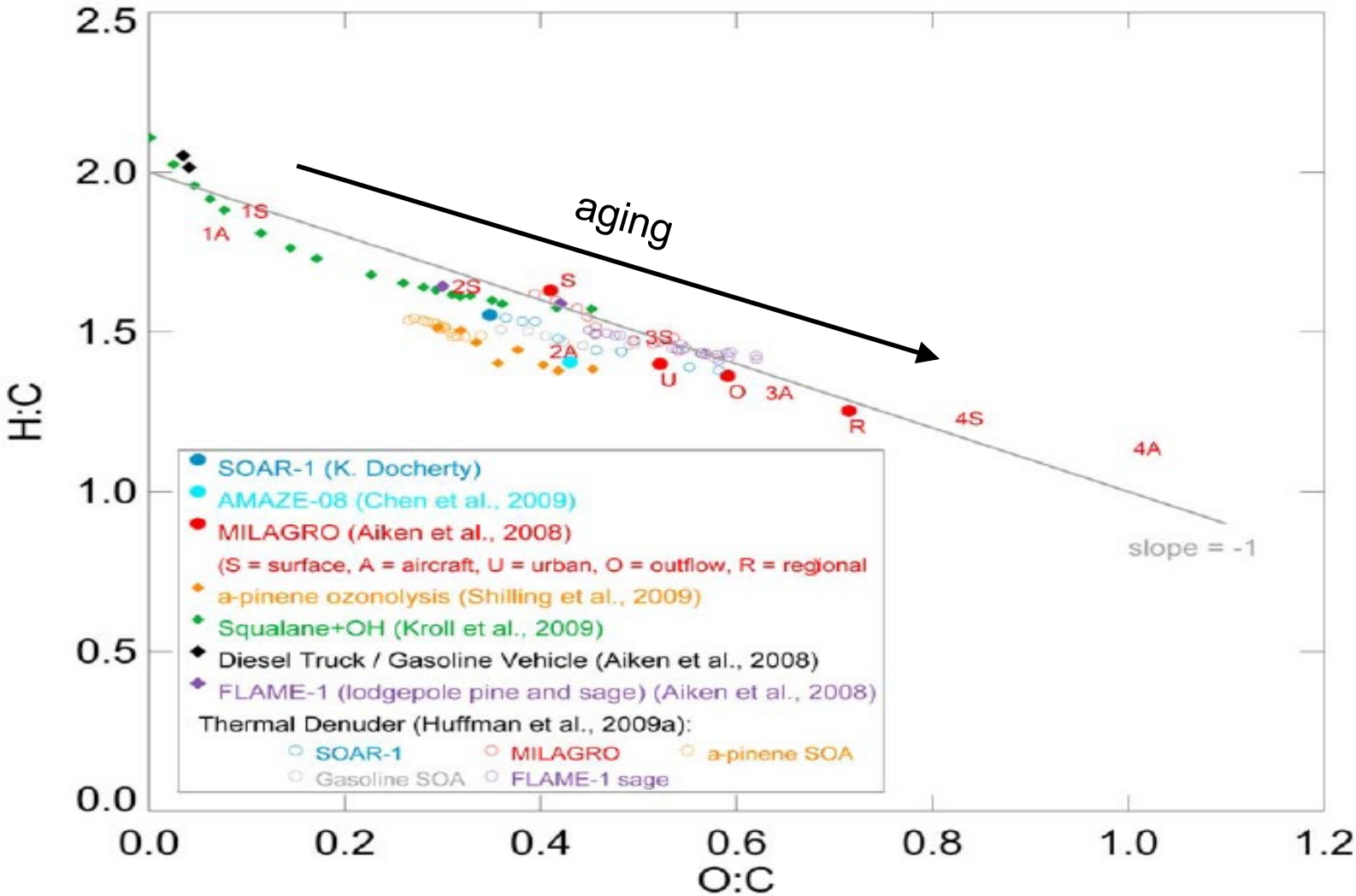
- Nitrate is an increasingly important component of $PM_{2.5}$ in East Asia (and elsewhere) as sulfate rapidly decreases
  - Formation of nitrate from NO_x emissions is highly non-linear, and NO_x emission decreases can actually cause nitrate increases
  - Decreasing NH_3 emissions from agriculture is more effective for controlling nitrate than decreasing NO_x emissions

- Coarse PM in East Asia is very high and mainly of urban dust origin
  - Emission controls targeting urban dust may be causing increase in $PM_{2.5}$ nitrate and increased sensitivity to NH_3 emissions

- Organic aerosol over East Asia is mostly anthropogenic with a large contribution from oxidized primary organic aerosol (POA) and aromatic VOCs
  - Observed aging of POA is consistent with a combustion source from polycyclic aromatic hydrocarbons (PAHs)
  - Observation of high O:C ratios in organic aerosol does not necessarily imply a secondary origin

Van Krevelen diagram: application to organic aerosol

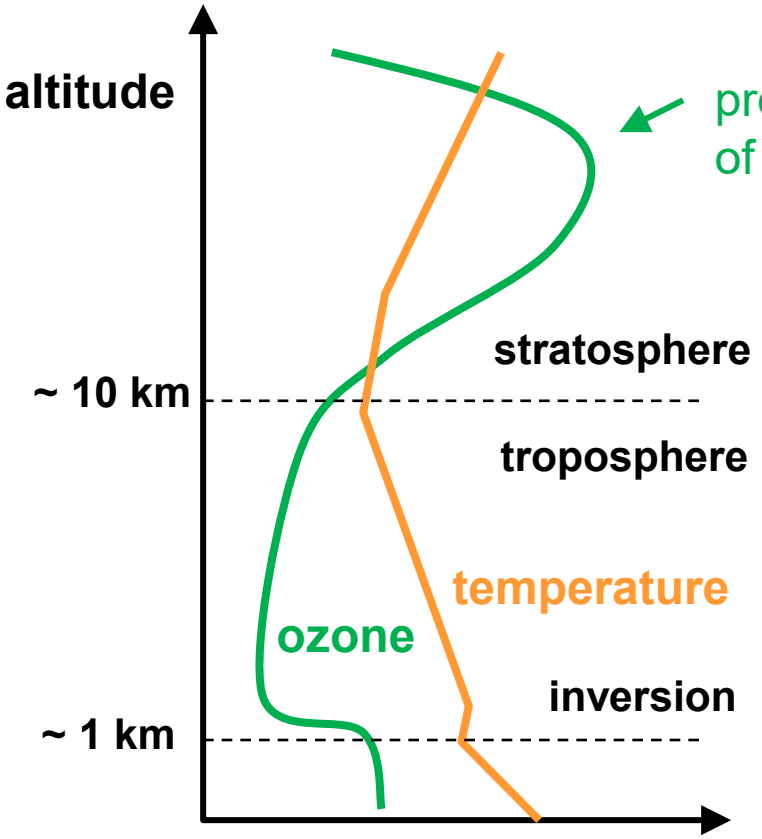
-1 slope suggests that aging is by adding of carboxylic functionalities, consistent with aqueous mechanism

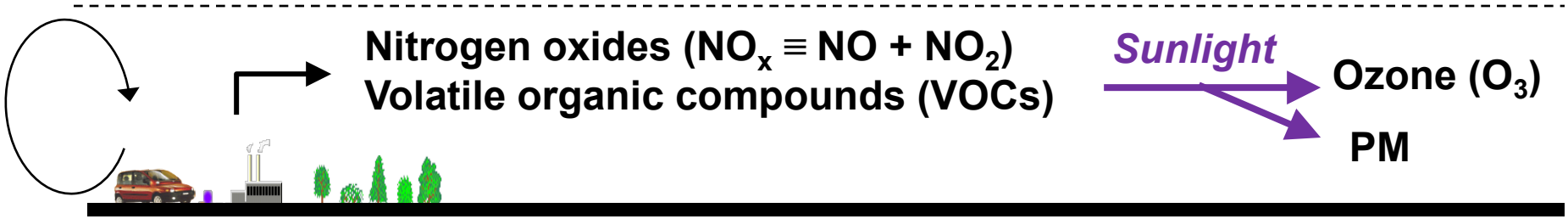


Heald et al. [2010]

Los Angeles smog

Respiratory problems, vegetation damage due to high surface ozone

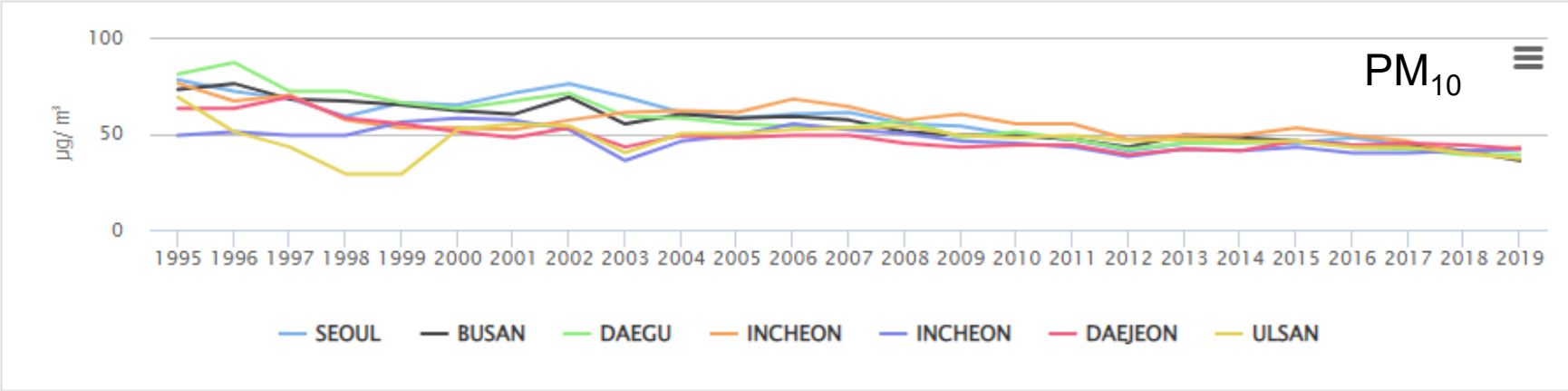


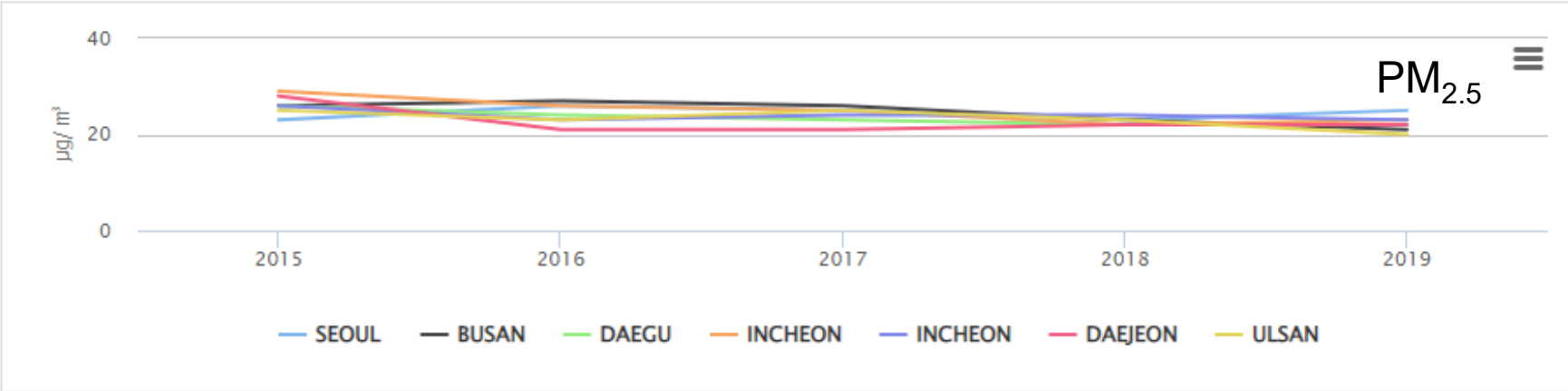


vehicles, industry, vegetation

Coarse PM as ‘forgotten’ component of PM air pollution

Annual mean PM_{10} and $PM_{2.5}$ at AirKorea sites (https://www.airkorea.or.kr)

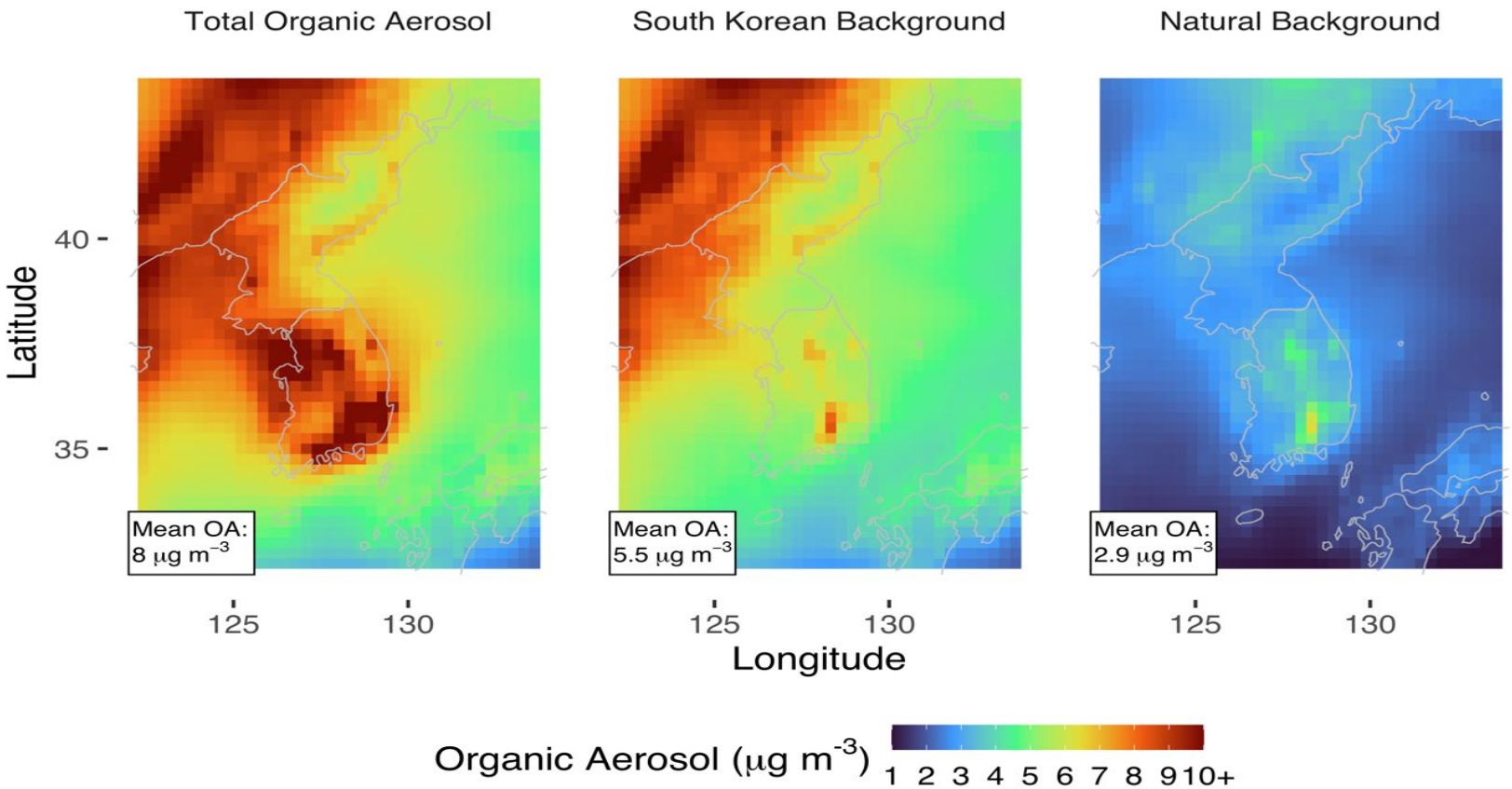




- PM_{10} has been steadily decreasing since 1995, is close to NAAQS of 50 µg m^{-3}
- Coarse PM is about 50% of PM_{10}

Background contributions to organic aerosol in Korea

from GEOS-Chem simulations for KORUS-AQ period (May-June 2016)



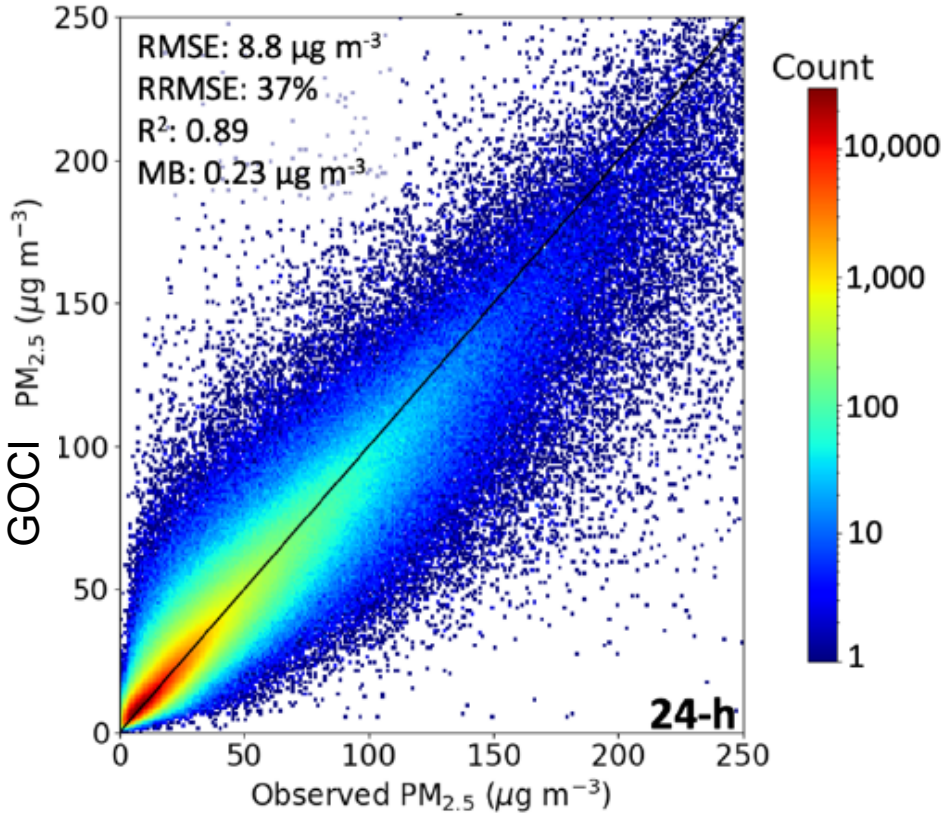
South Korean background ≡ simulation with zero domestic anthropogenic emissions

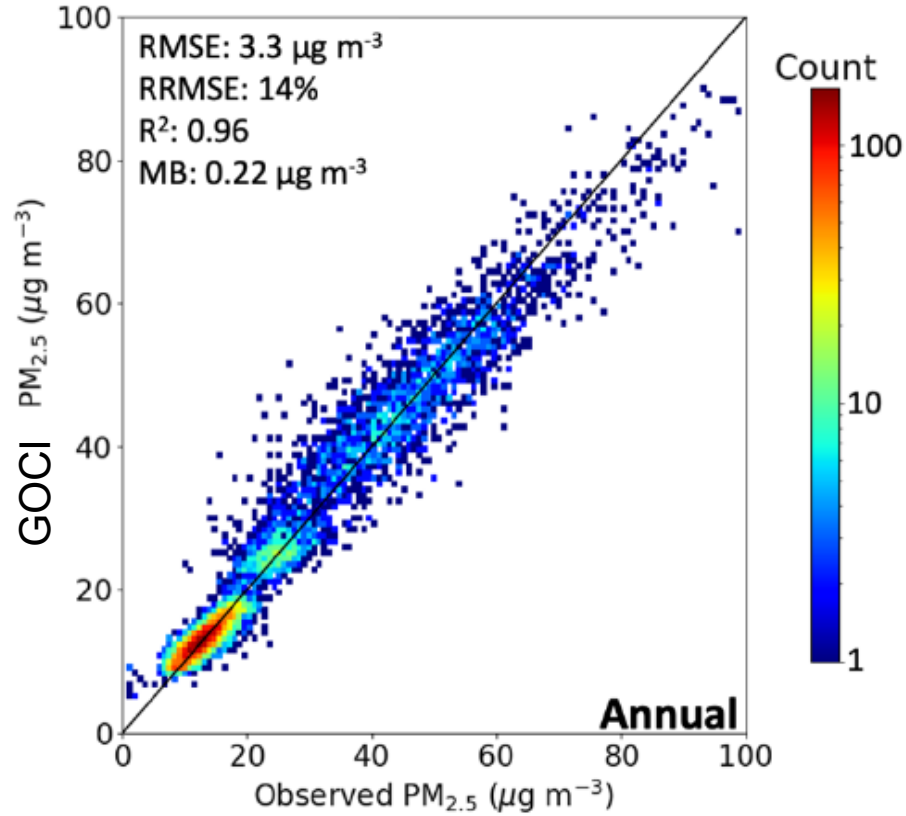
- 1/3 of OA over South Korea in May-June is from external anthropogenic sources, 1/3 is from domestic anthropogenic sources, 1/3 is from biogenic sources
- About half of domestic anthropogenic OA is from aromatics

Brewer et al., submitted.

Ability of random-forest algorithm to infer $PM_{2.5}$ from GOCI satellite data

Statistics over East Asia for independent (withheld) surface network sites

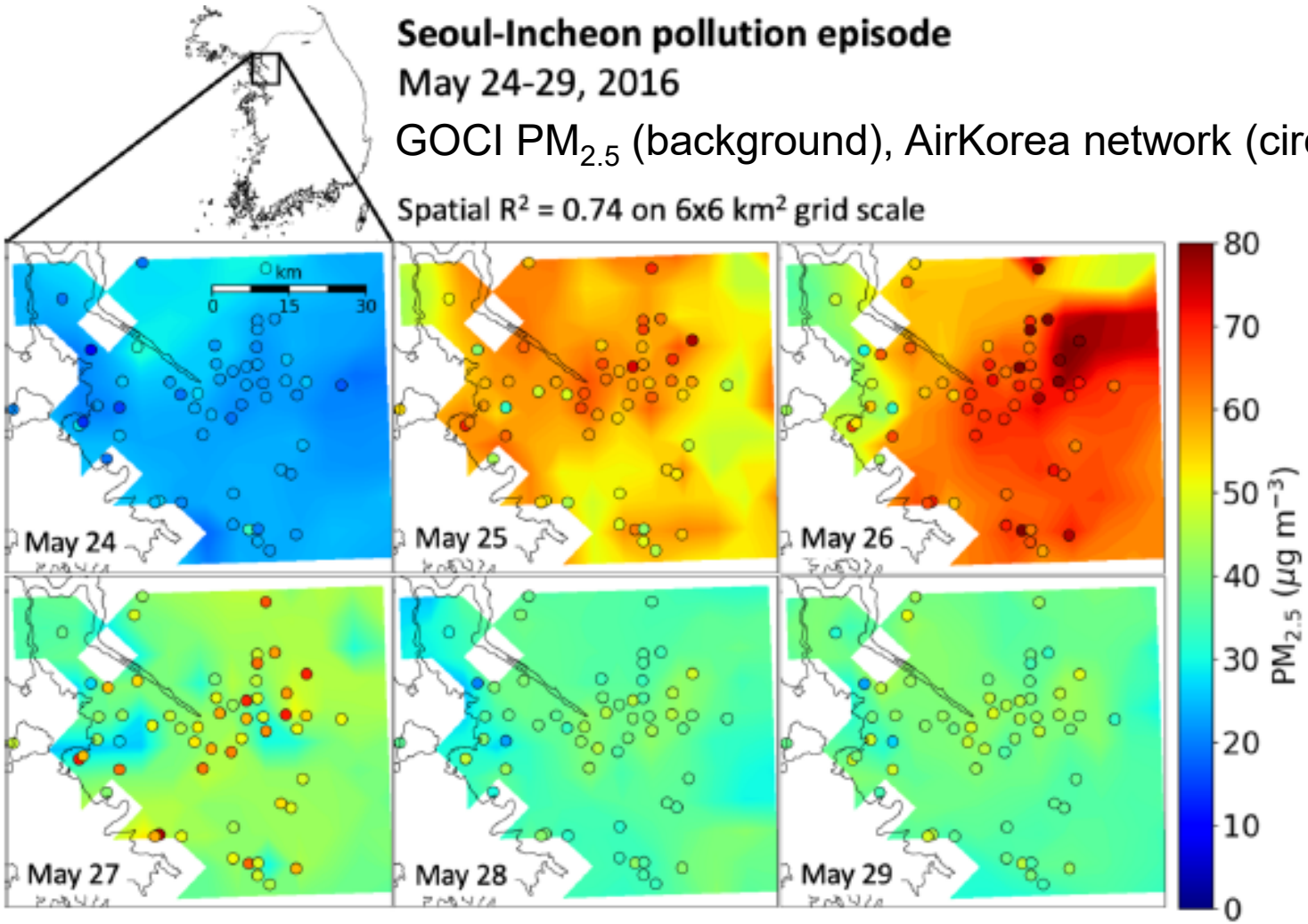




Precision of 37% or 8.8 μg m^{-3} (24-h), 14% or 3.3 μg m^{-3} (annual), negligible bias

Pendergrass et al. [2022]

Application to tracking of $PM_{2.5}$ pollution episodes



Complete mapping serves need for air quality warnings, public health assessments

Pendergrass et al. [2022]