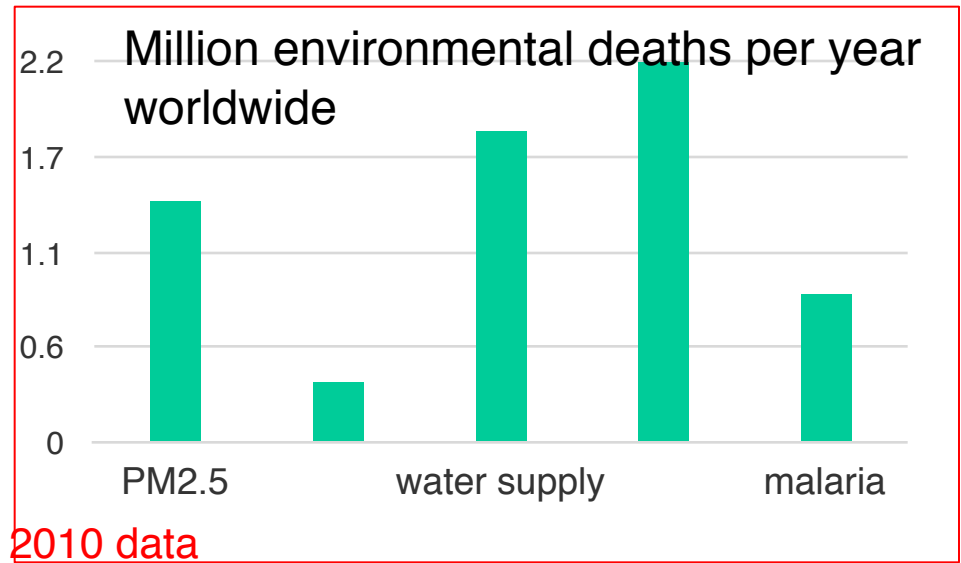
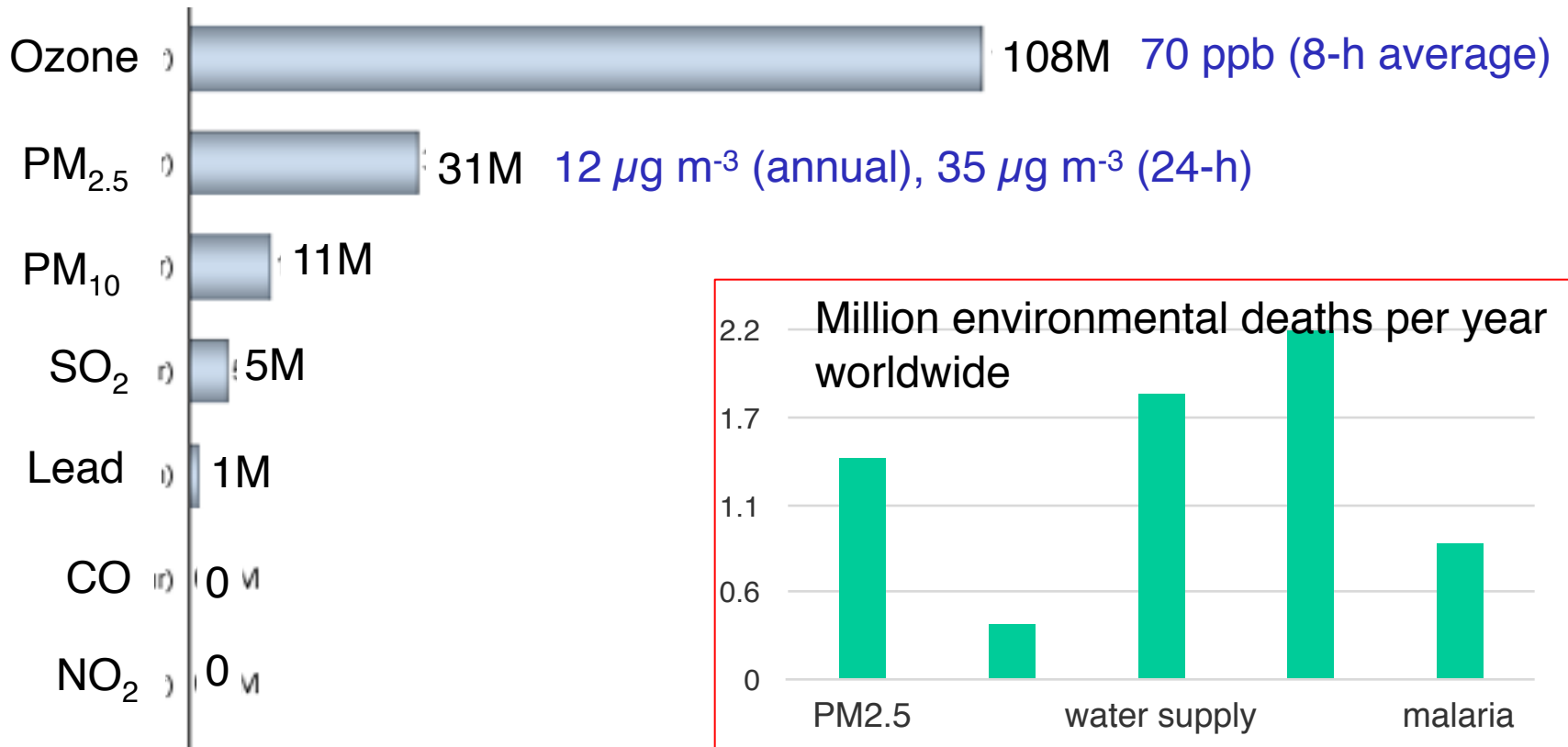
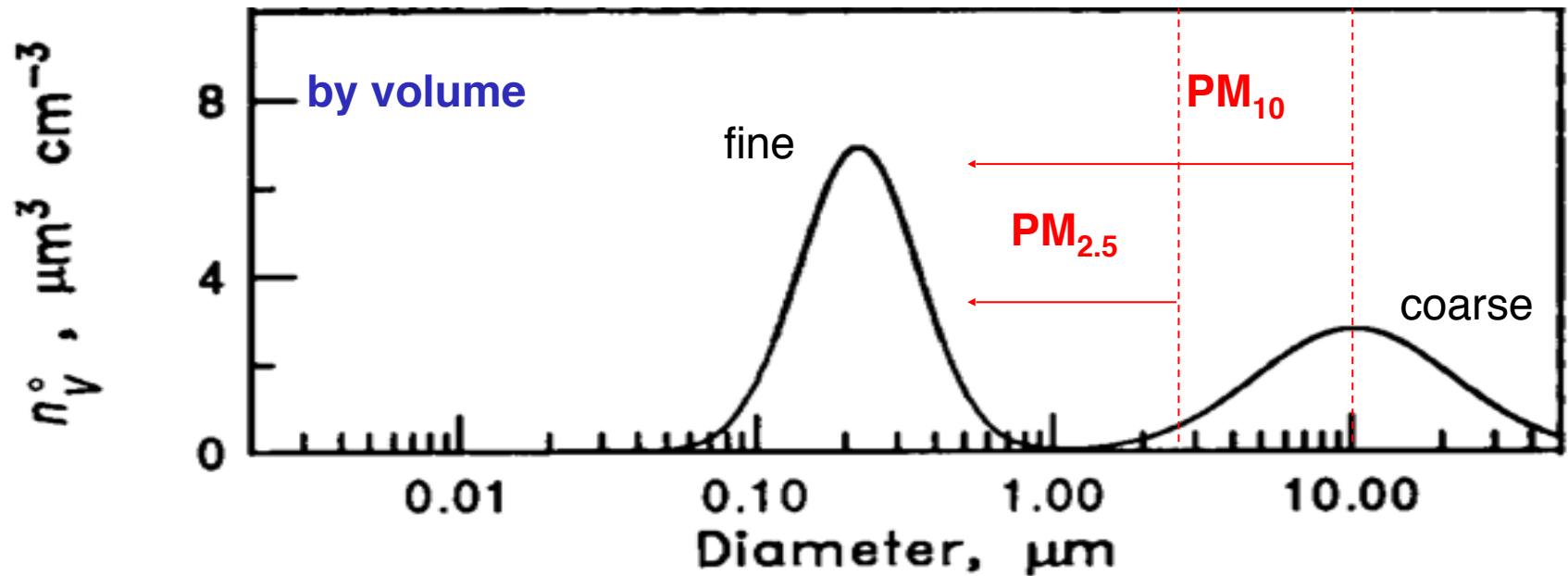


- “Particulate matter” (PM) is the same thing as “particles” or “aerosols”
- “PM<sub>x</sub>” refers to the mass concentration of particles smaller than x μm diameter

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



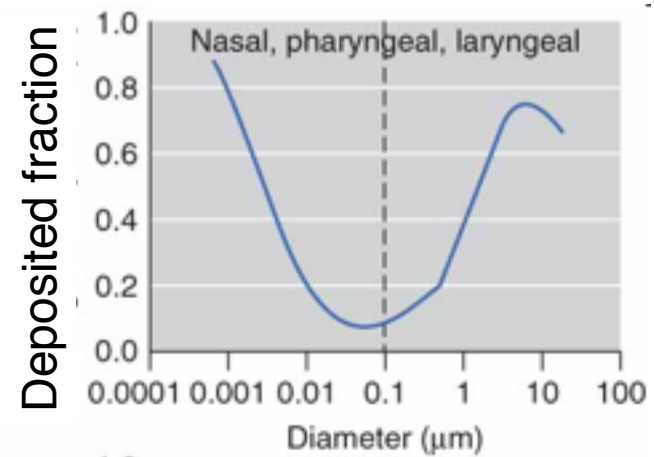
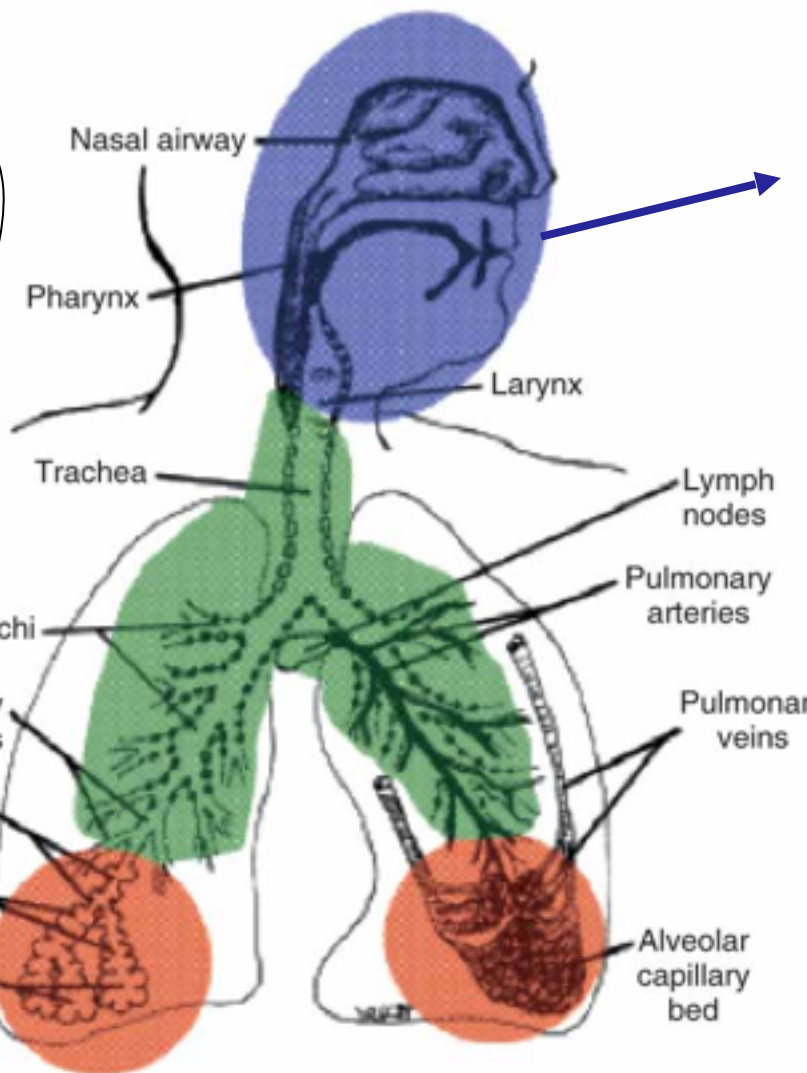
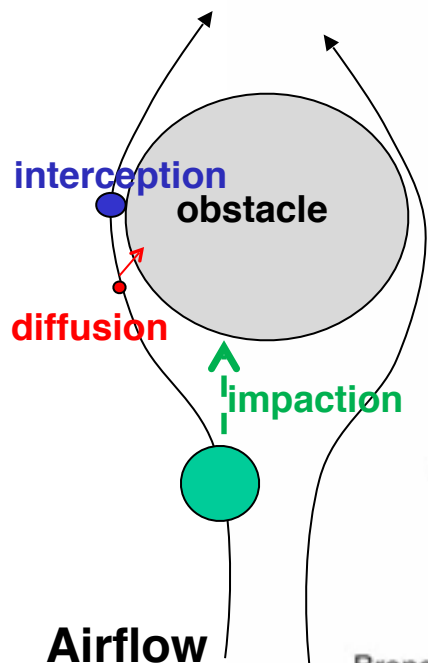
# TYPICAL AEROSOL SIZE DISTRIBUTION



coagulation  
cloud cycling

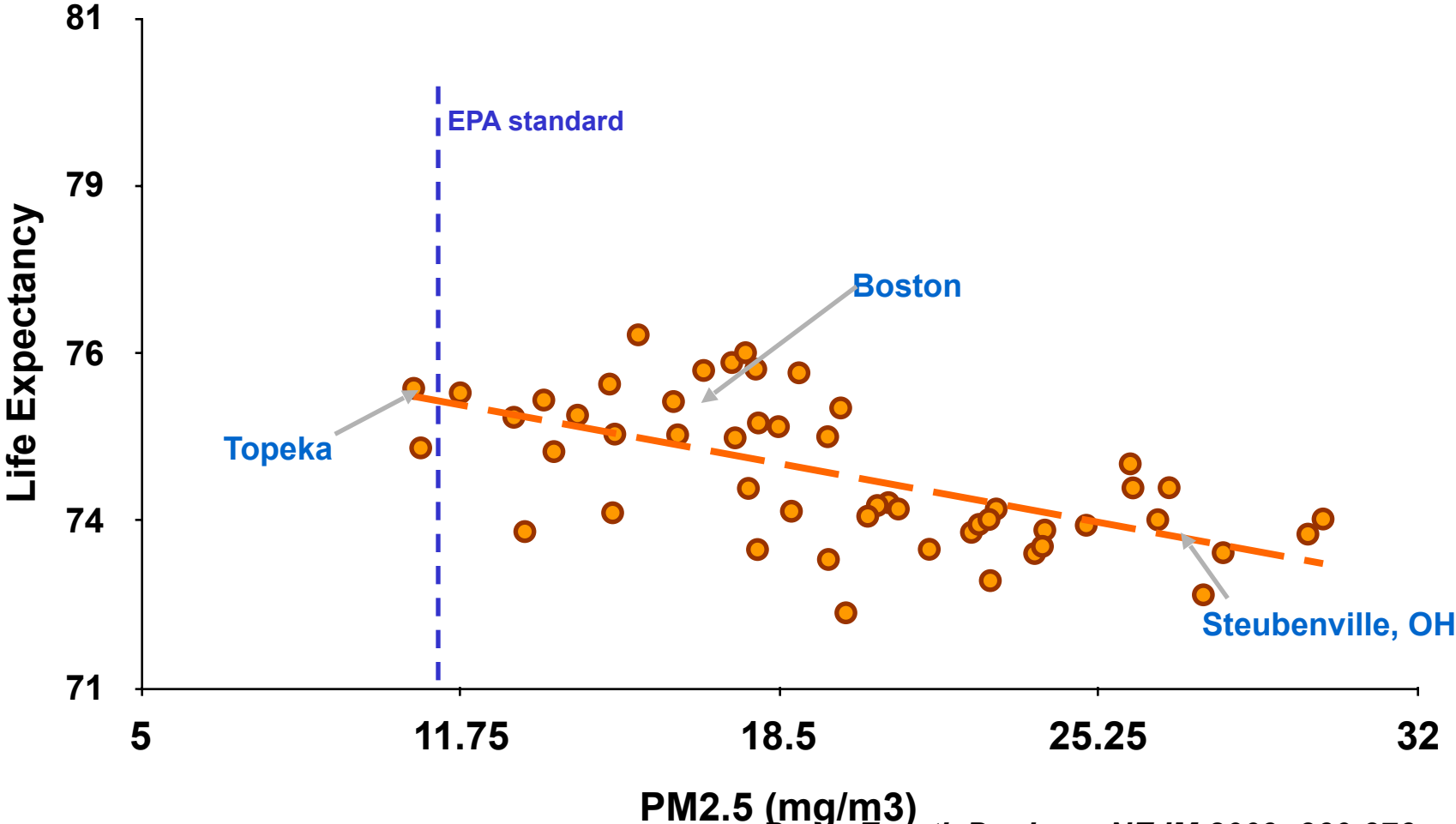
Condensation from gas phase  
(*secondary particles*):  
sulfate, nitrate, ammonium, organics

Direct emission (*primary particles*):  
dust, sea salt, pollen



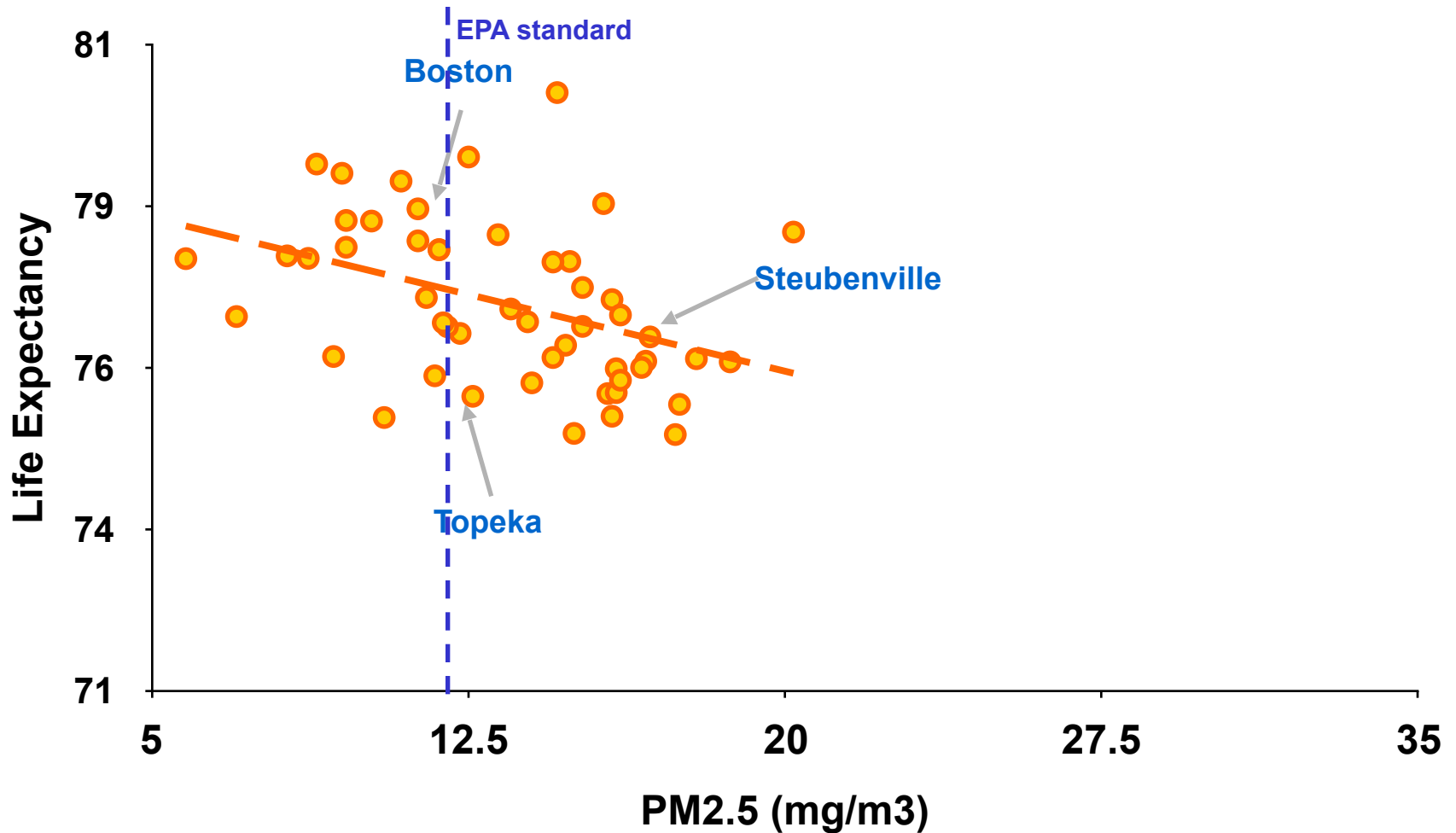
$\text{PM}_{2.5}$  penetrates deep into the lungs – larger particles do not

# Life Expectancy vs annual PM<sub>2.5</sub> 1978-82



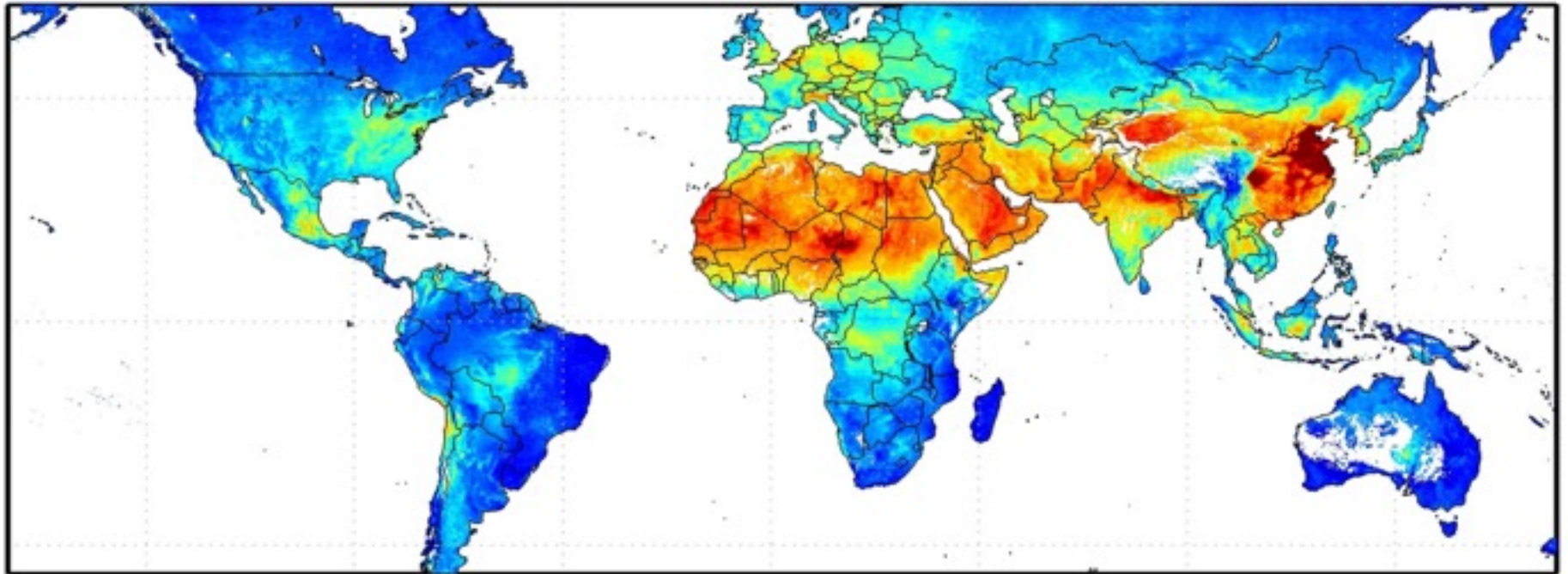
Pope, Ezzati, Dockery. NEJM 2009; 360:376

# Life Expectancy vs annual PM<sub>2.5</sub> 1997-2001



*Pope, Ezzati, Dockery. NEJM 2009; 360:376*

# Annual mean PM<sub>2.5</sub> observed from satellite



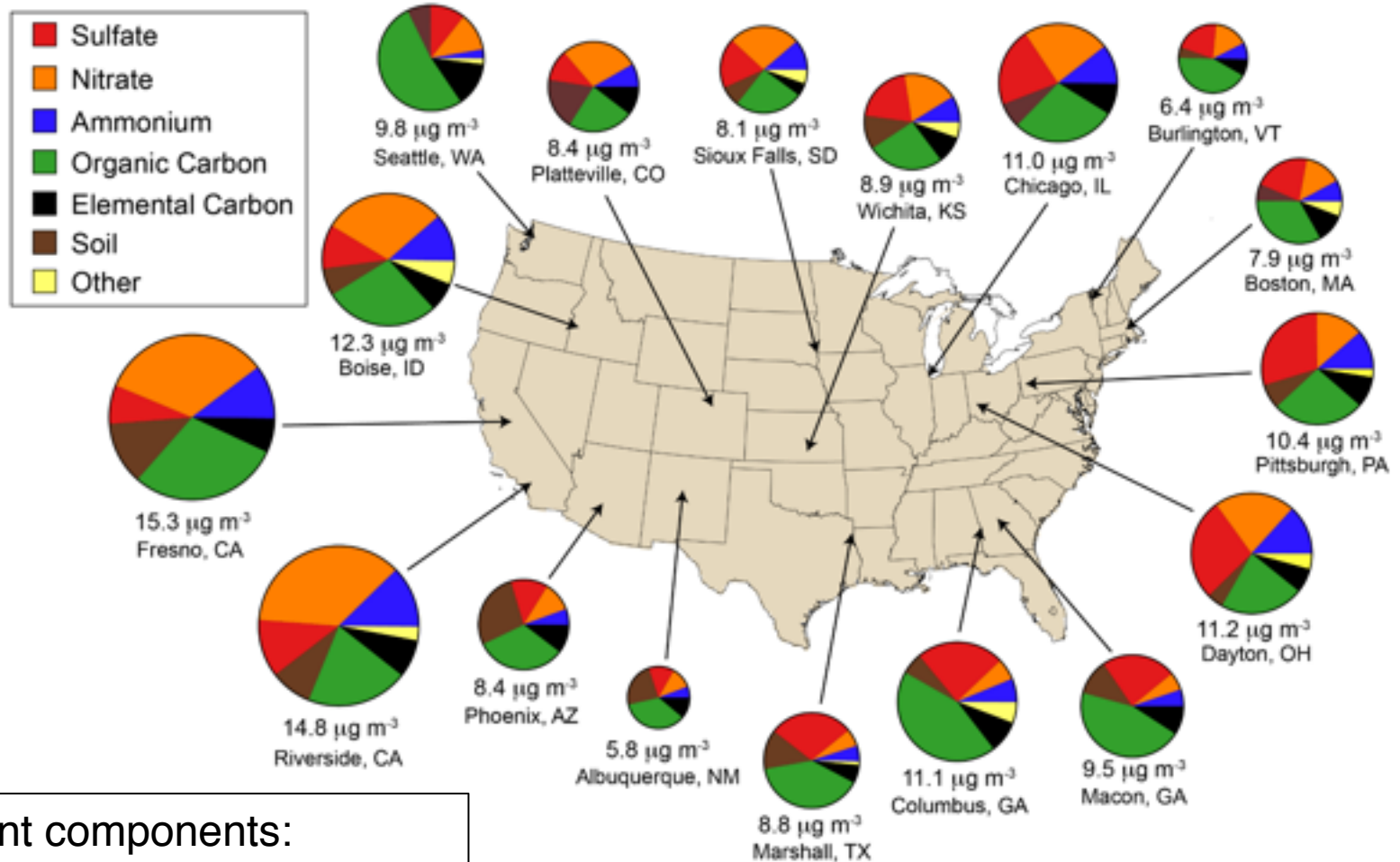
Satellite-Derived PM<sub>2.5</sub> [μg/m<sup>3</sup>]

US air quality standard

# FINE AEROSOL COMPOSITION IN NORTH AMERICA

Annual mean PM<sub>2.5</sub> concentrations (2013)

Current air quality standard is 12  $\mu\text{g m}^{-3}$

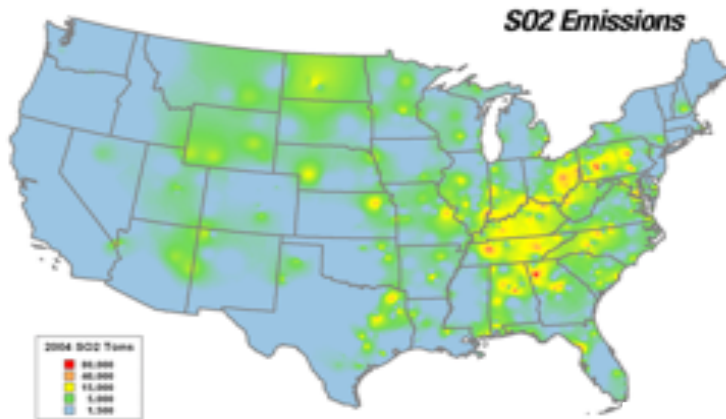


Two dominant components:

- Sulfate-nitrate-ammonium (SNA)
- Organic



# Coincidence of SO<sub>2</sub> emissions, sulfate aerosol concentrations, sulfate wet deposition

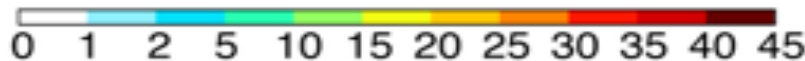
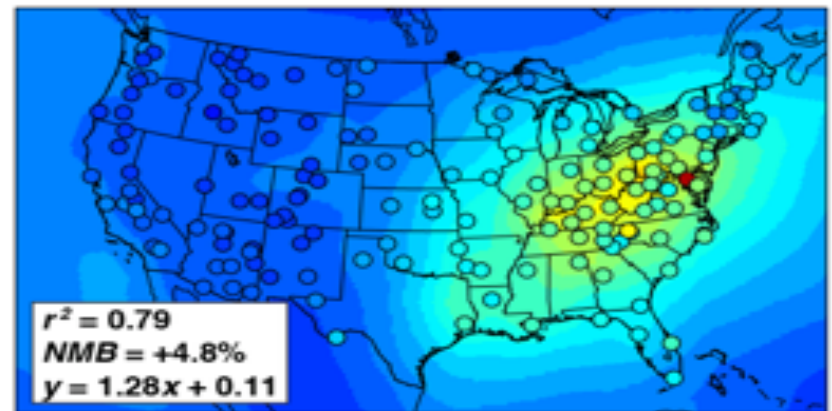
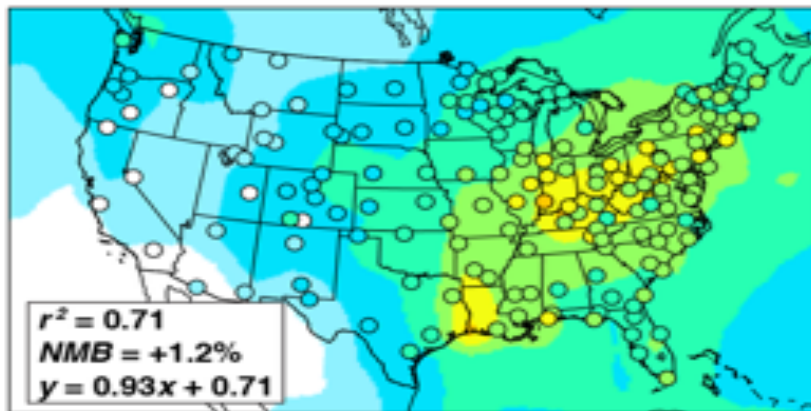


SO<sub>2</sub> in US is mainly from coal combustion and is rapidly oxidized to sulfate... but oxidation by OH is too slow

Sulfate Wet Deposition (kg ha<sup>-1</sup> a<sup>-1</sup>)

Sulfate Concentration (μg m<sup>-3</sup>)

2010

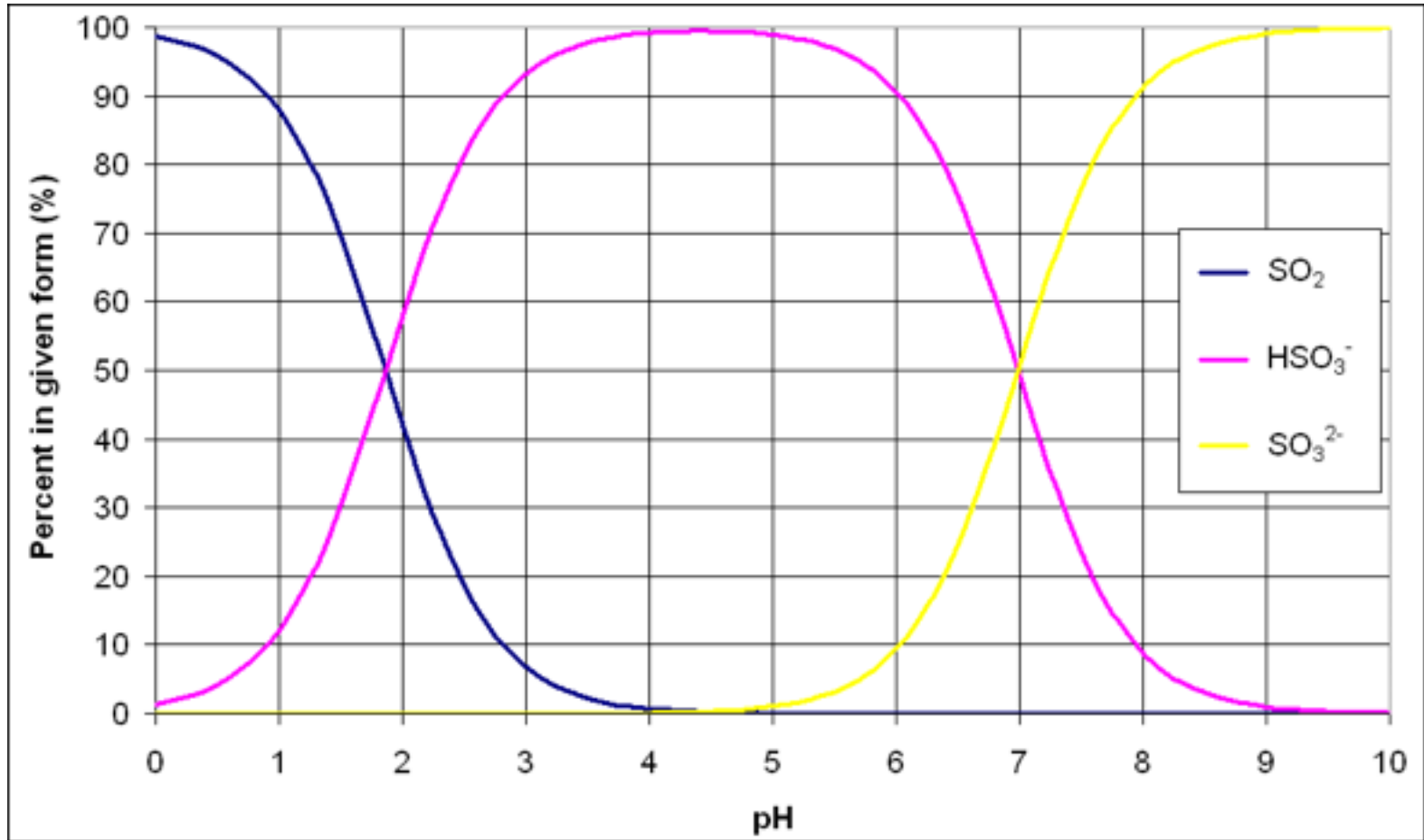




## Questions

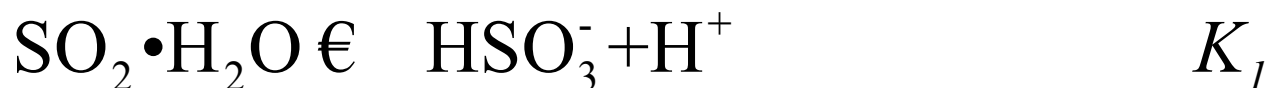
1. . It has been proposed to inject  $\text{SO}_2$  into the stratosphere so that the resulting sulfate particles reflect solar radiation to space and offset greenhouse warming. Injecting  $\text{SO}_2$  into the stratosphere seems like a lot of trouble, why not just inject it into the troposphere?
2. Volcanoes are a natural source of  $\text{SO}_2$ . In the early Earth, the emitted  $\text{SO}_2$  was not oxidized to sulfate. Why not?

# $\text{SO}_2(\text{aq})/\text{HSO}_3^-/\text{SO}_3^{2-}$ partitioning vs. pH in clouds



typical cloud pH range

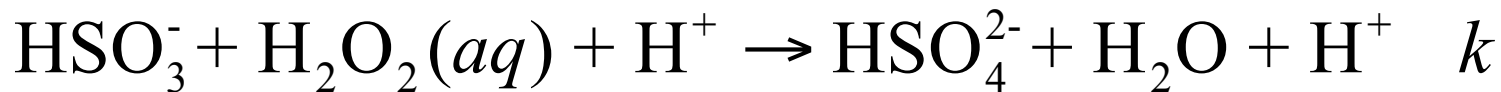
## Aqueous-phase oxidation of SO<sub>2</sub> by ozone



$$\frac{d[\text{SO}_4^{2-}]}{dt} = kK_1K_{H,\text{SO}_2}K_{H,\text{O}_3}p_{\text{SO}_2}p_{\text{O}_3} / [\text{H}^+]$$

Reaction shuts itself down as H<sup>+</sup> increases

## Acid-catalyzed aqueous-phase oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>



$$\frac{d[\text{SO}_4^{2-}]}{dt} = kK_1K_{H,\text{SO}_2}K_{H,\text{H}_2\text{O}_2}P_{\text{SO}_2}P_{\text{H}_2\text{O}_2}$$

Rate does not slow down as H<sup>+</sup> increases

# OBSERVED TITRATION OF SO<sub>2</sub> BY H<sub>2</sub>O<sub>2</sub> IN CLOUD

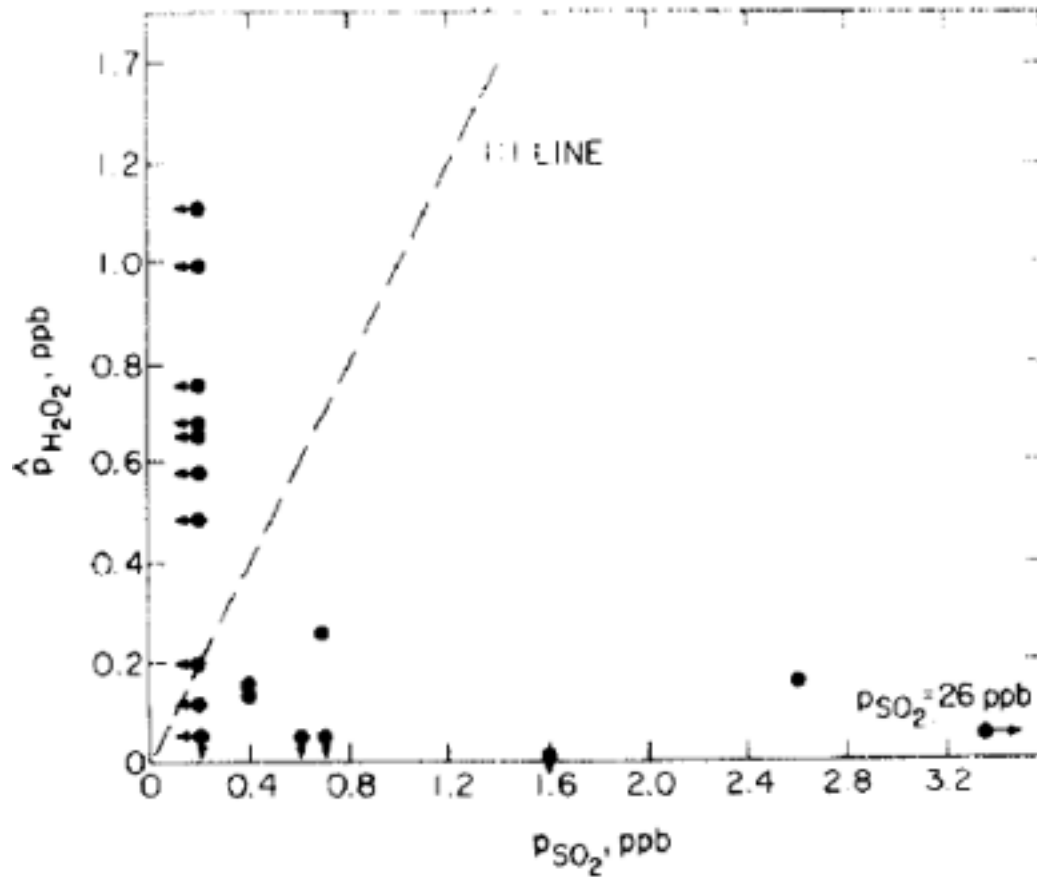


Fig. 7. Cloudwater peroxide potential partial pressure vs interstitial SO<sub>2</sub> partial pressure.

First aircraft observations by Daum et al. [1984]

# A Dynamic Model for the Production of $H^+$ , $NO_3^-$ , and $SO_4^{2-}$ in Urban Fog

DANIEL J. JACOB AND MICHAEL R. HOFFMANN

*Environmental Engineering Science, W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125*

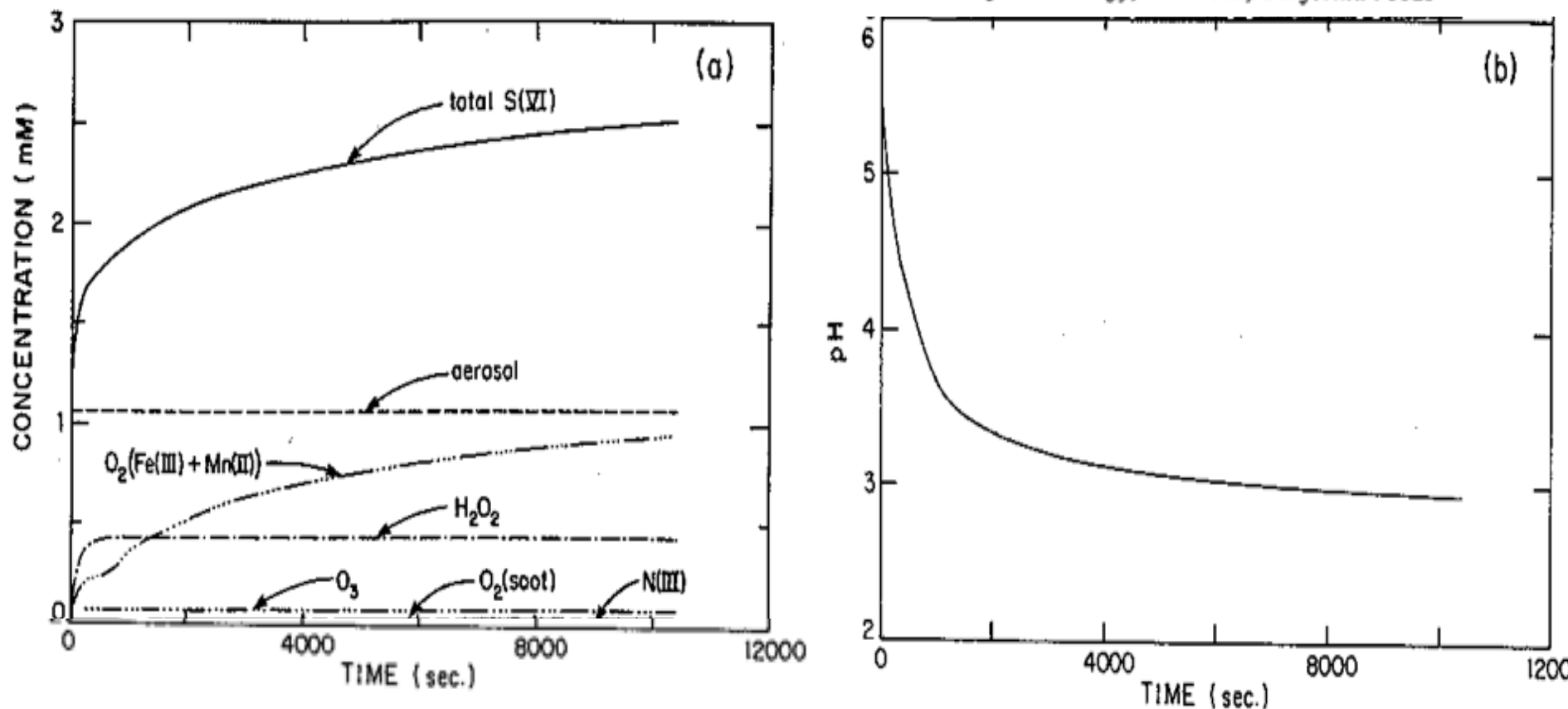
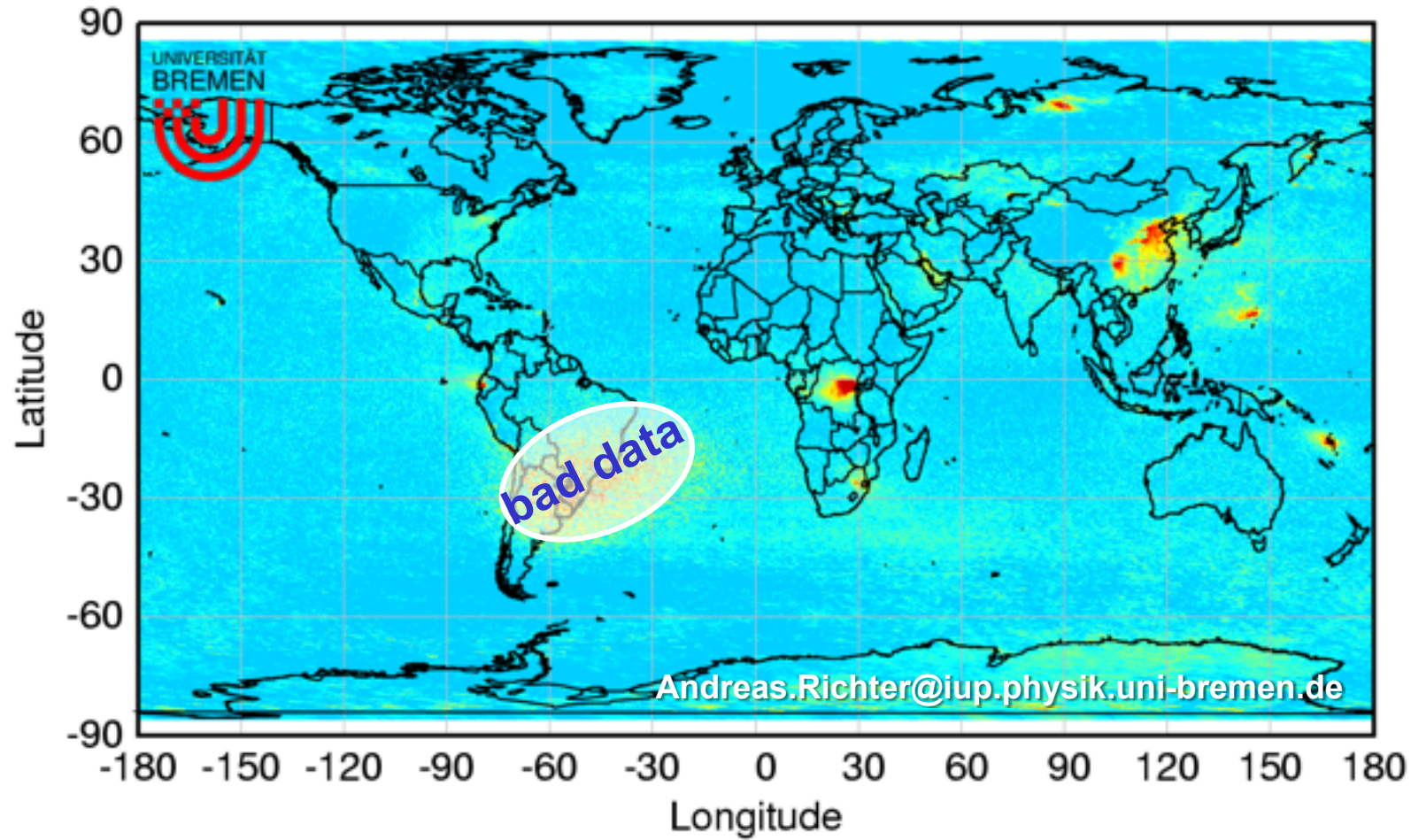
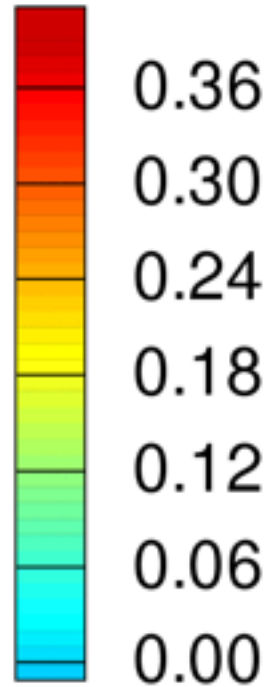


Fig. 1. (a) Profile versus time of total sulfate in the fogwater and of the individual contributions to the total sulfate of sulfate aerosol and different S(IV) oxidants. (b) Profile of pH versus time. The fog formed under the conditions of Table 3, with liquid water content =  $0.1 \text{ g m}^{-3}$ , temperature =  $10^\circ\text{C}$ .

# Global SO<sub>2</sub> columns observed from space

## SCIAMACHY SO<sub>2</sub>: 01.2003 - 08.2005

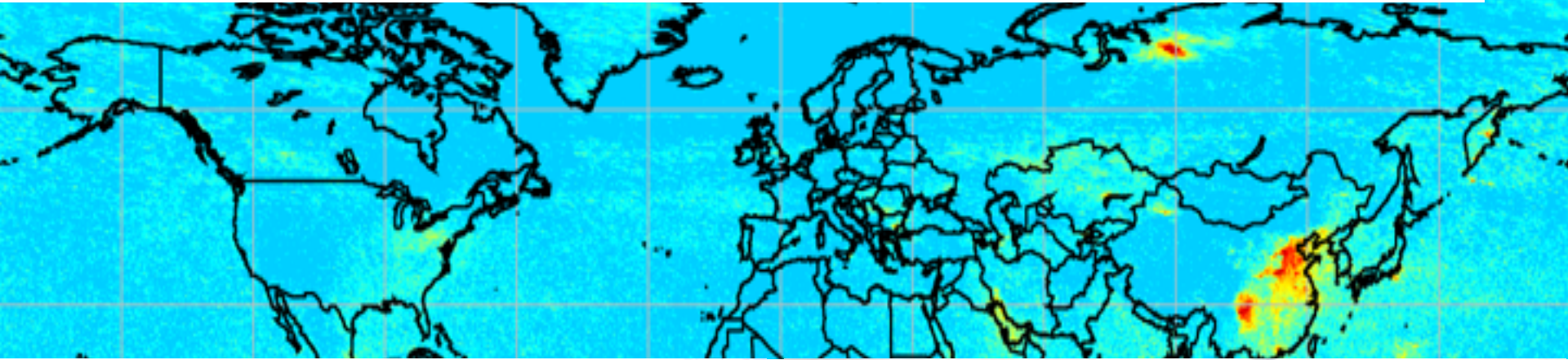
VC SO<sub>2</sub>  
[DU]





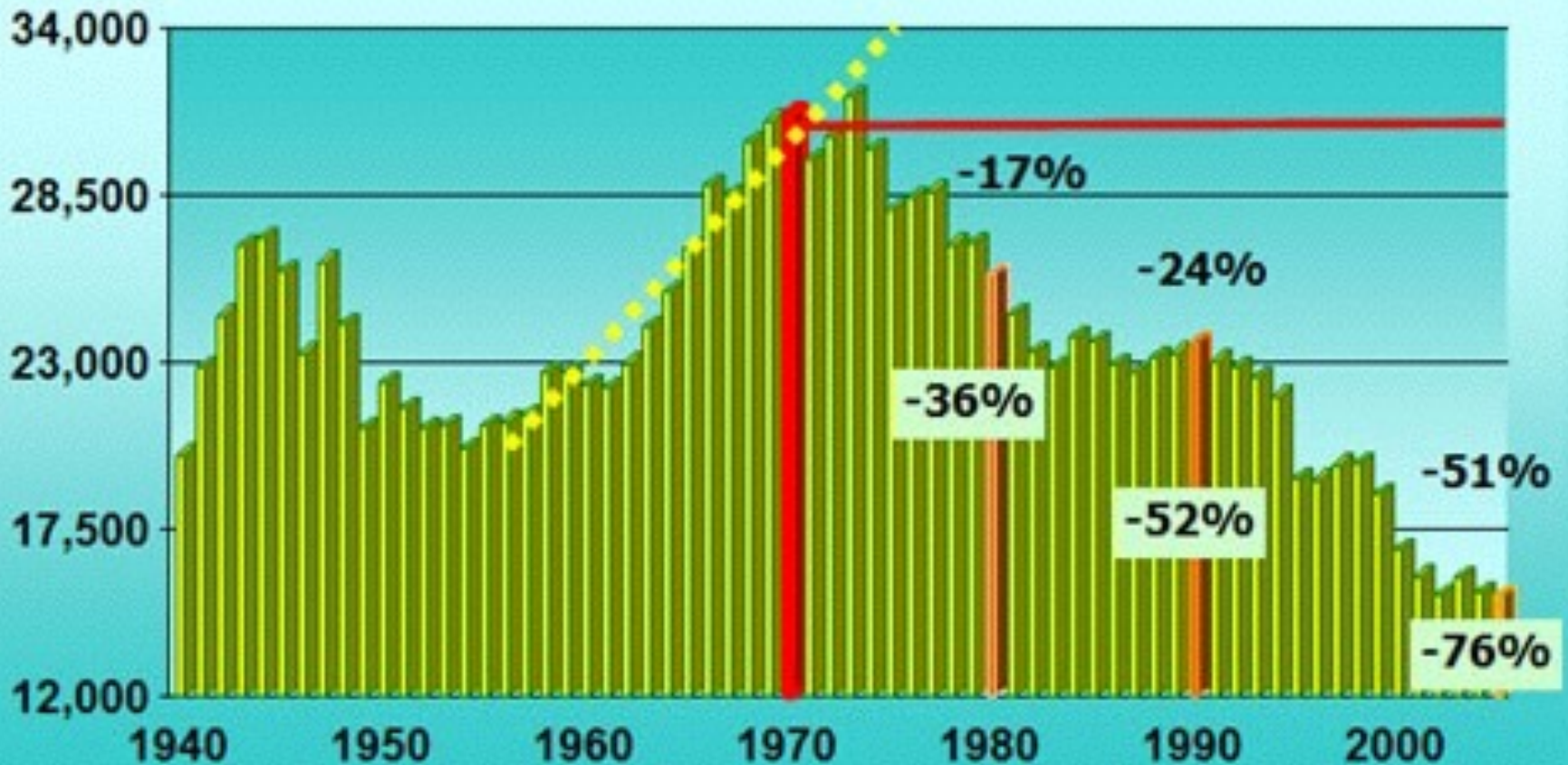
# Norilsk, Siberia: the most polluted city in Russia

Sulfur dioxide observed from space: emissions from coal combustion, metal smelters



## Long-term trends in US SO<sub>2</sub> emissions

United States SO<sub>2</sub> Emissions vs 1970 level (= CAA Year 0)



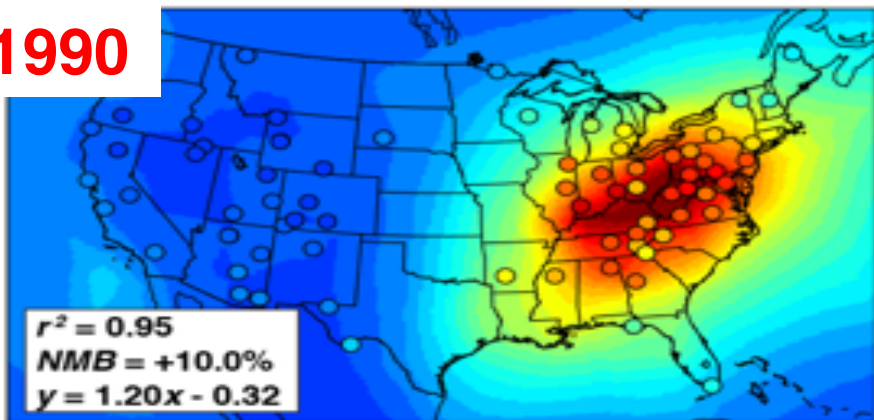


# Decline of sulfate aerosol in the US

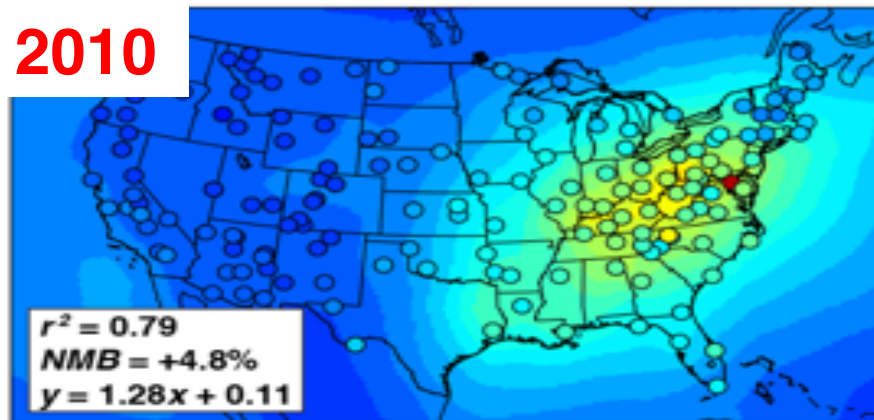
Scrubbers on coal power plants, transition to natural gas

Observed sulfate concentrations (circles), GEOS-Chem (background)

1990



2010



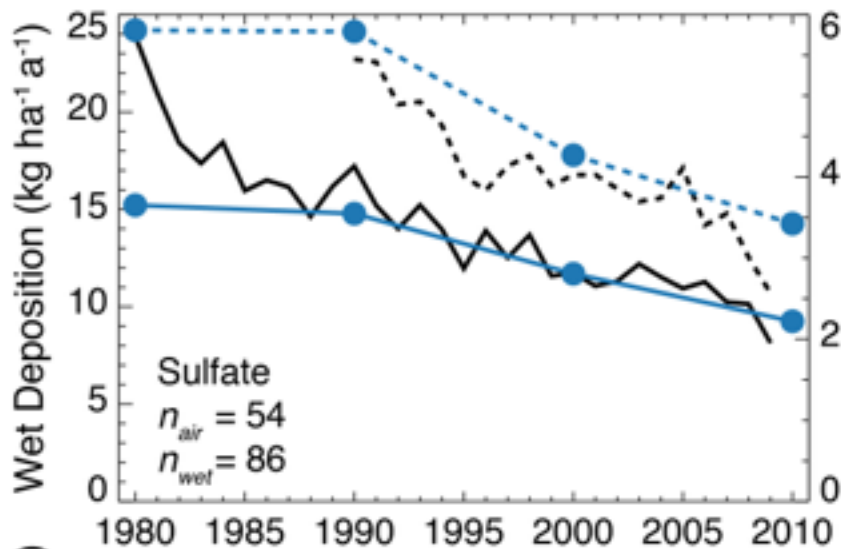
0.0 2.0 4.0 6.0 8.0  $\mu\text{g m}^{-3}$

## Observations

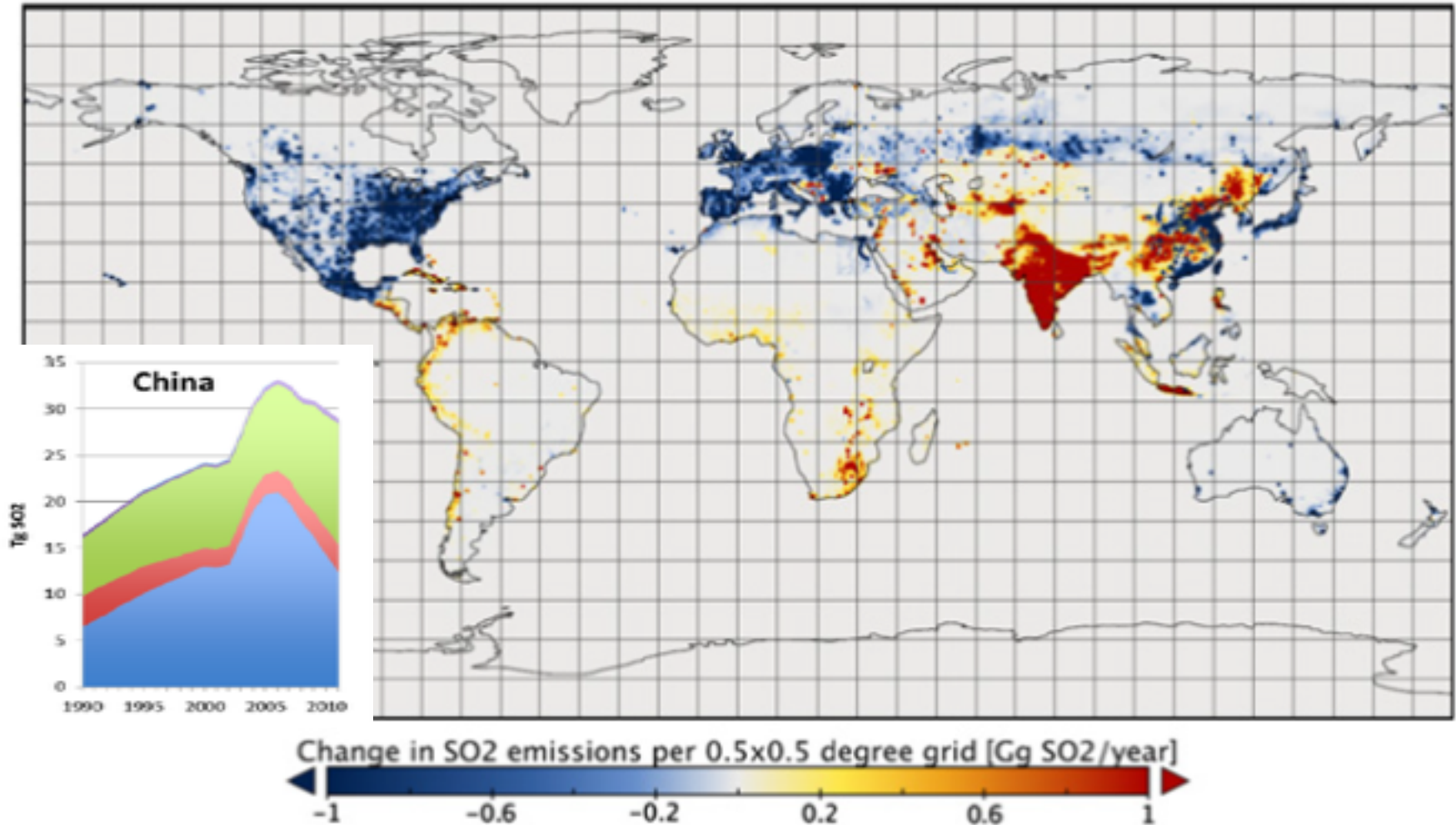
- ..... Surface Concentrations
- Wet Deposition

## Model

- ..... Surface Concentrations
- Model Wet Deposition



# Global SO<sub>2</sub> emission trends

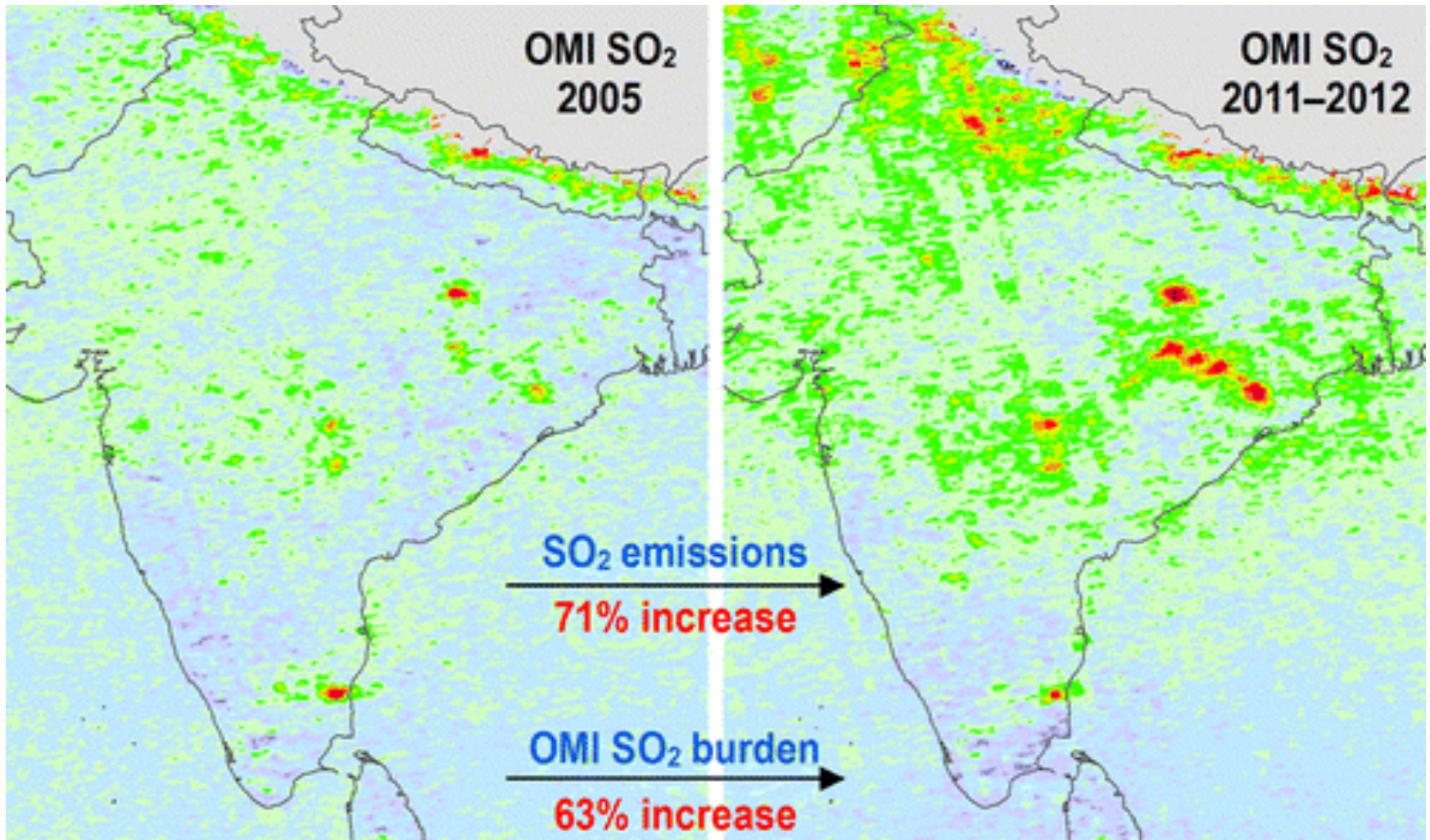


**Figure 3.** Change in regional distribution of anthropogenic land based SO<sub>2</sub> emissions. Changes indicated as a difference between 2010 and 2005 emissions in  $0.5^\circ \times 0.5^\circ$  grids.



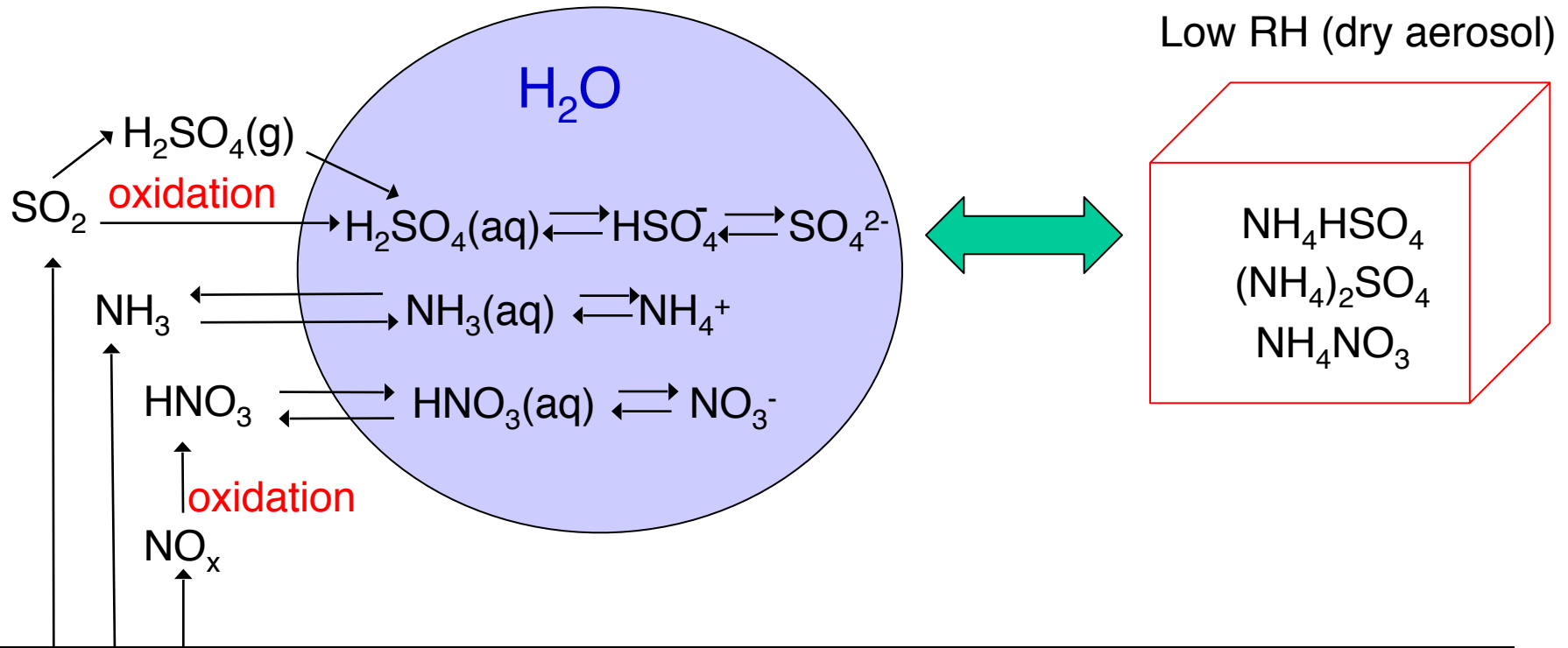
# New SO<sub>2</sub> pollution frontier: India

OMI satellite reveal rapid growth in SO<sub>2</sub> emissions from coal use



# Formation of sulfate-nitrate-ammonium (SNA) aerosol

High RH (aqueous aerosol)



## EMISSION

$SO_2$ : coal combustion

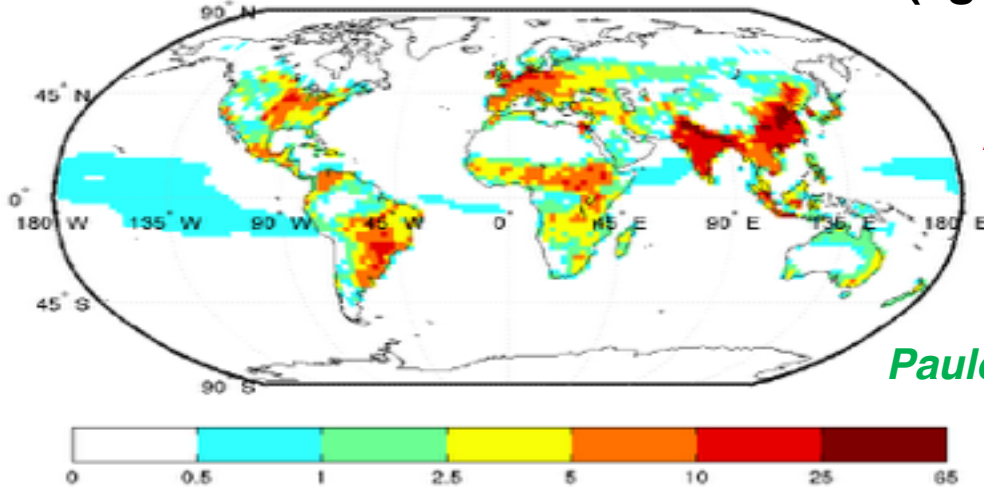
$NH_3$ : agriculture

$NO_x$ : fuel combustion

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

# Ammonia emissions

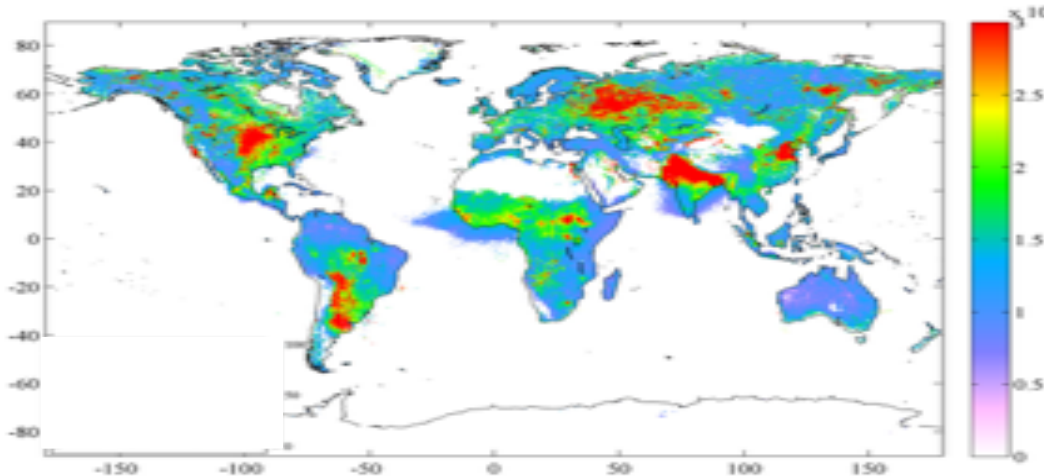
Global ammonia emissions 2005-2008 ( $\text{kg N ha}^{-1} \text{ a}^{-1}$ )



**Agriculture is 75% of global source**

*Paulot et al. [2014]*

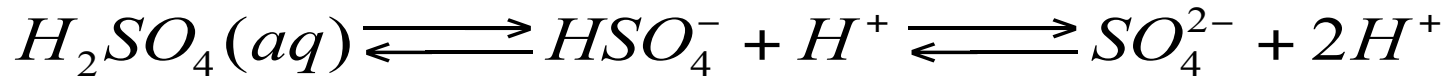
IASI 2007-2012 satellite observations of ammonia



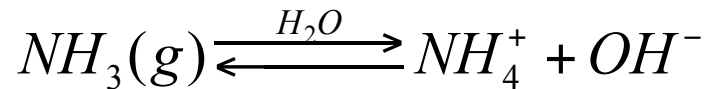
*Van Damme et al. [2014]*



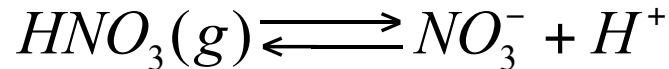
## Approximate thermodynamic rules for SNA aerosol formation



**H<sub>2</sub>SO<sub>4</sub> condenses to aqueous solution; dissociation to HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> governed by pH**



**NH<sub>3</sub> condenses into acid sulfate aerosol until titration; no further uptake**



**HNO<sub>3</sub> condenses only if excess NH<sub>3</sub> is available**

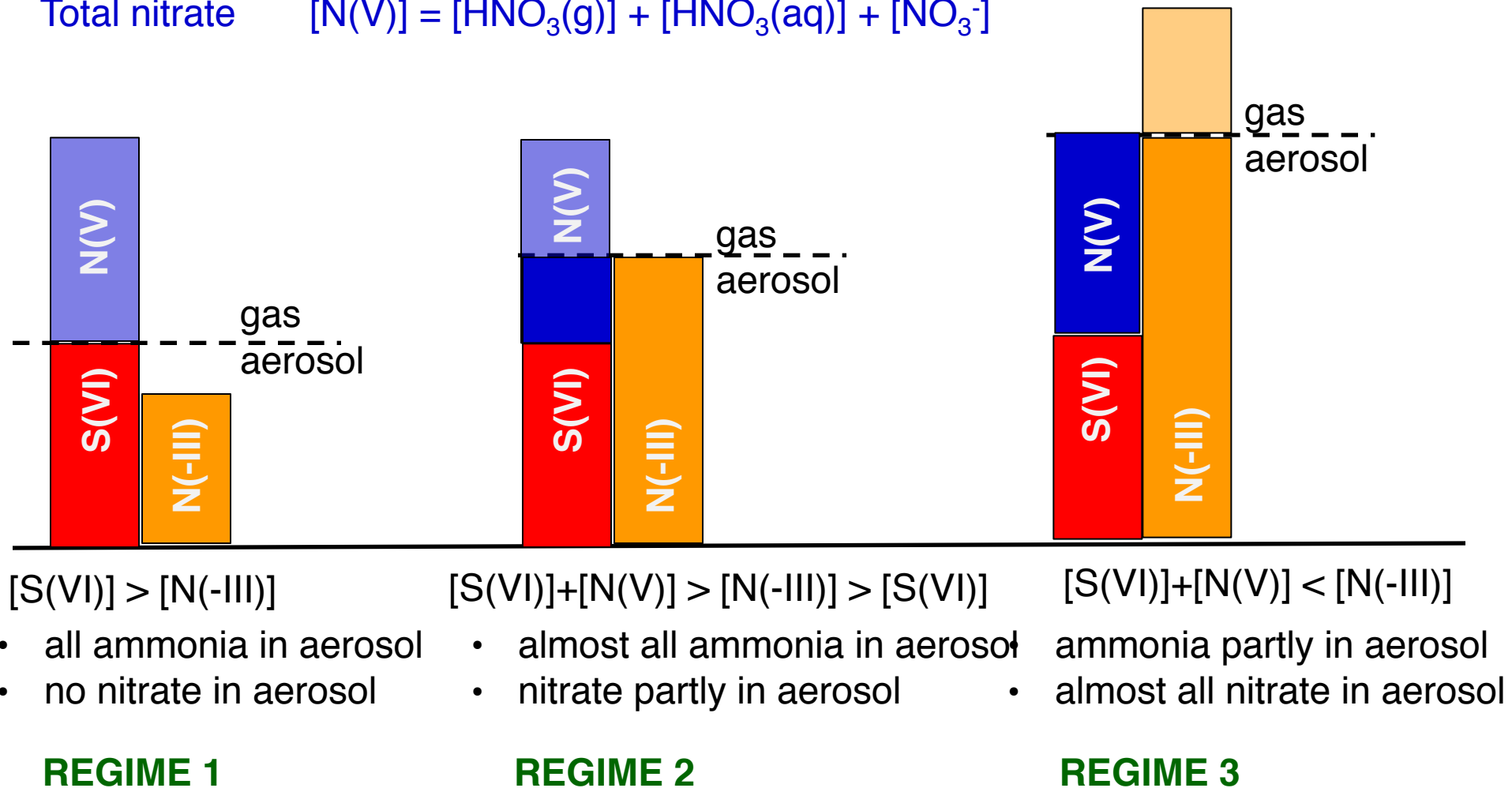
# Three different regimes for SNA aerosol formation

Total sulfate  $[S(VI)] = [H_2SO_4(aq)] + [HSO_4^-] + [SO_4^{2-}]$

Total ammonia  $[N(-III)] = [NH_3(g)] + [NH_3(aq)] + [NH_4^+]$

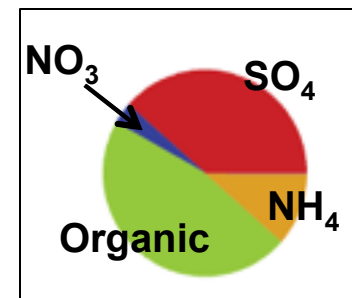
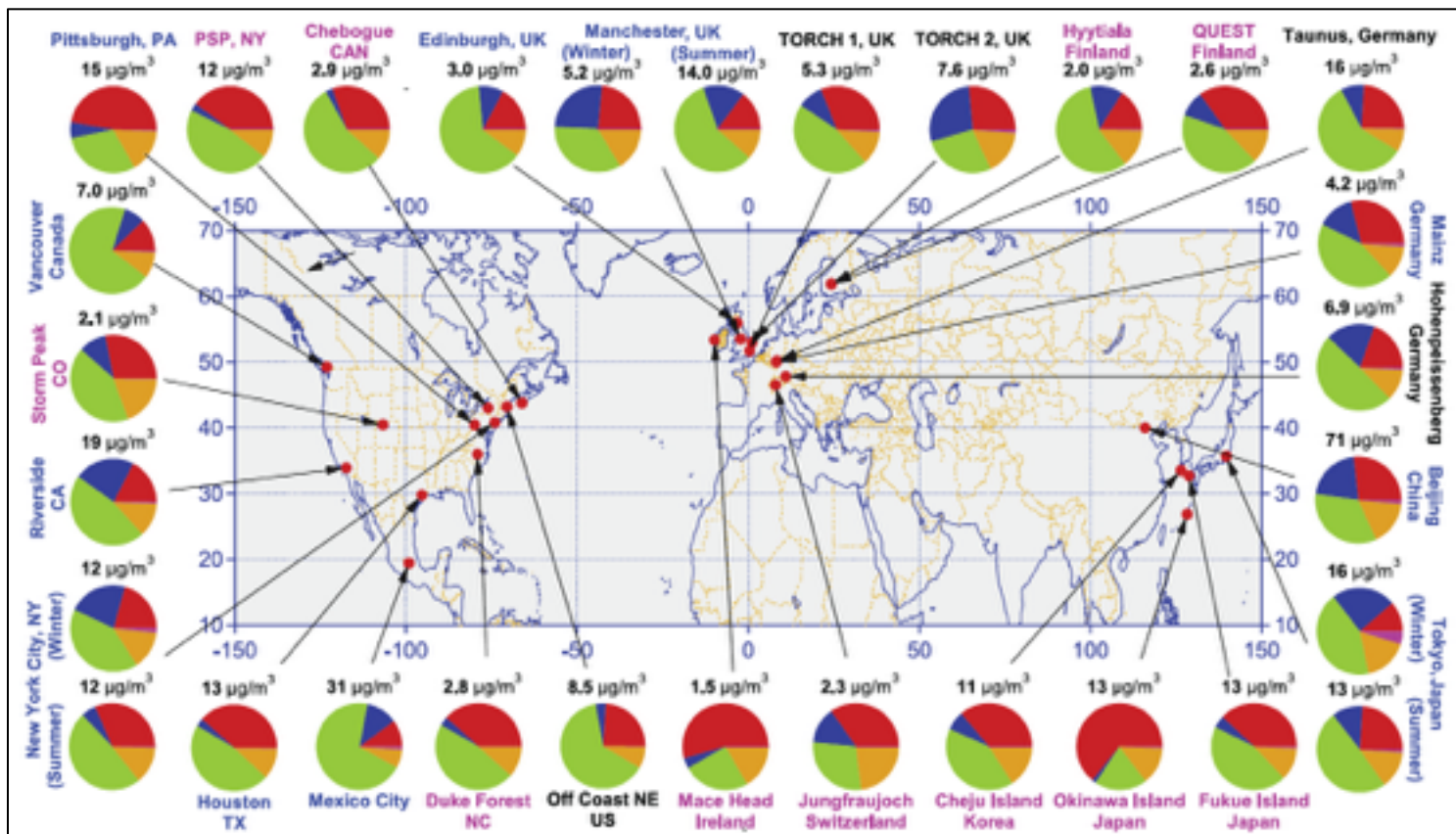
Total nitrate  $[N(V)] = [HNO_3(g)] + [HNO_3(aq)] + [NO_3^-]$

Equivalents per m<sup>3</sup> of air



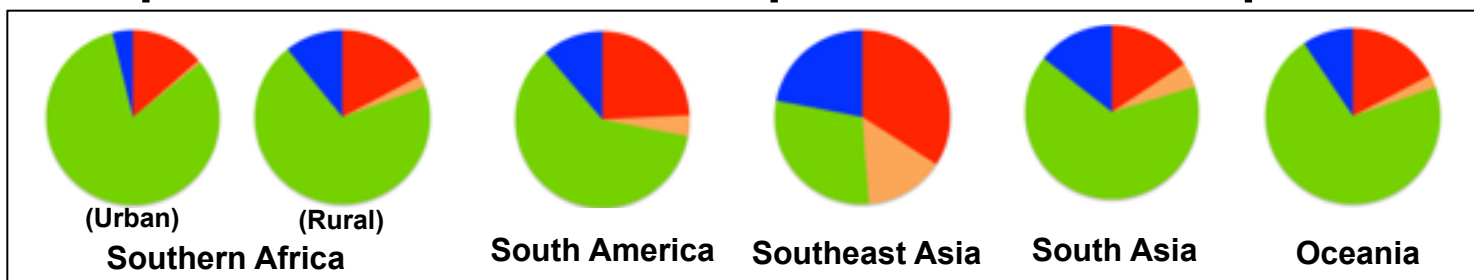
# Organic Aerosol is Ubiquitous in the Atmosphere

## Northern hemisphere aerosol components



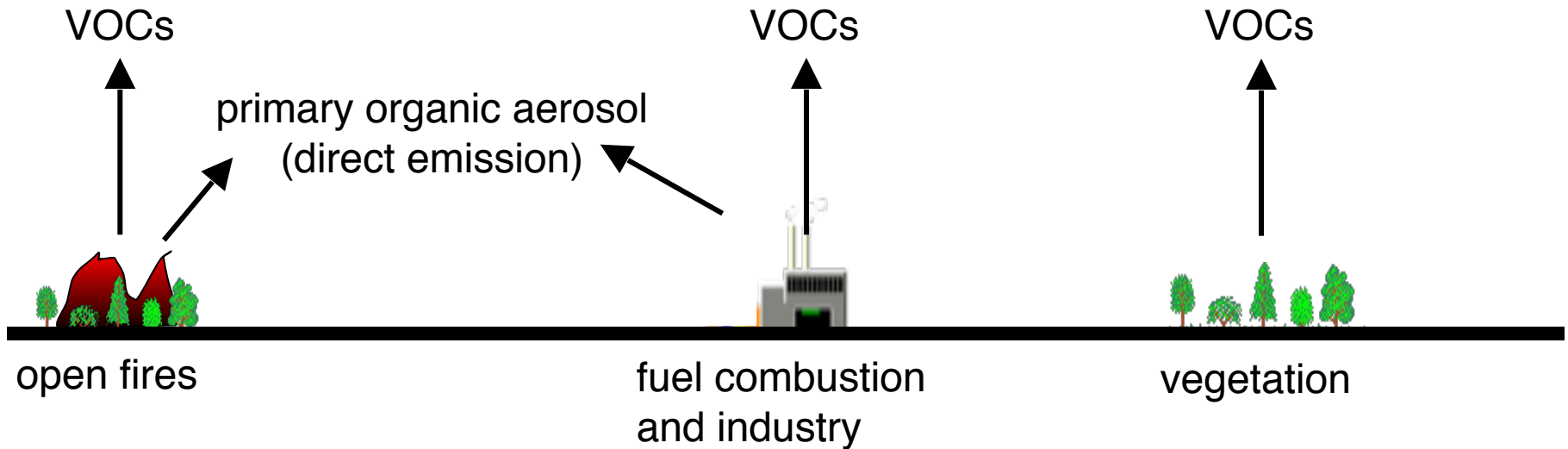
[Zhang et al., 2007]

## Tropics and southern hemisphere aerosol components



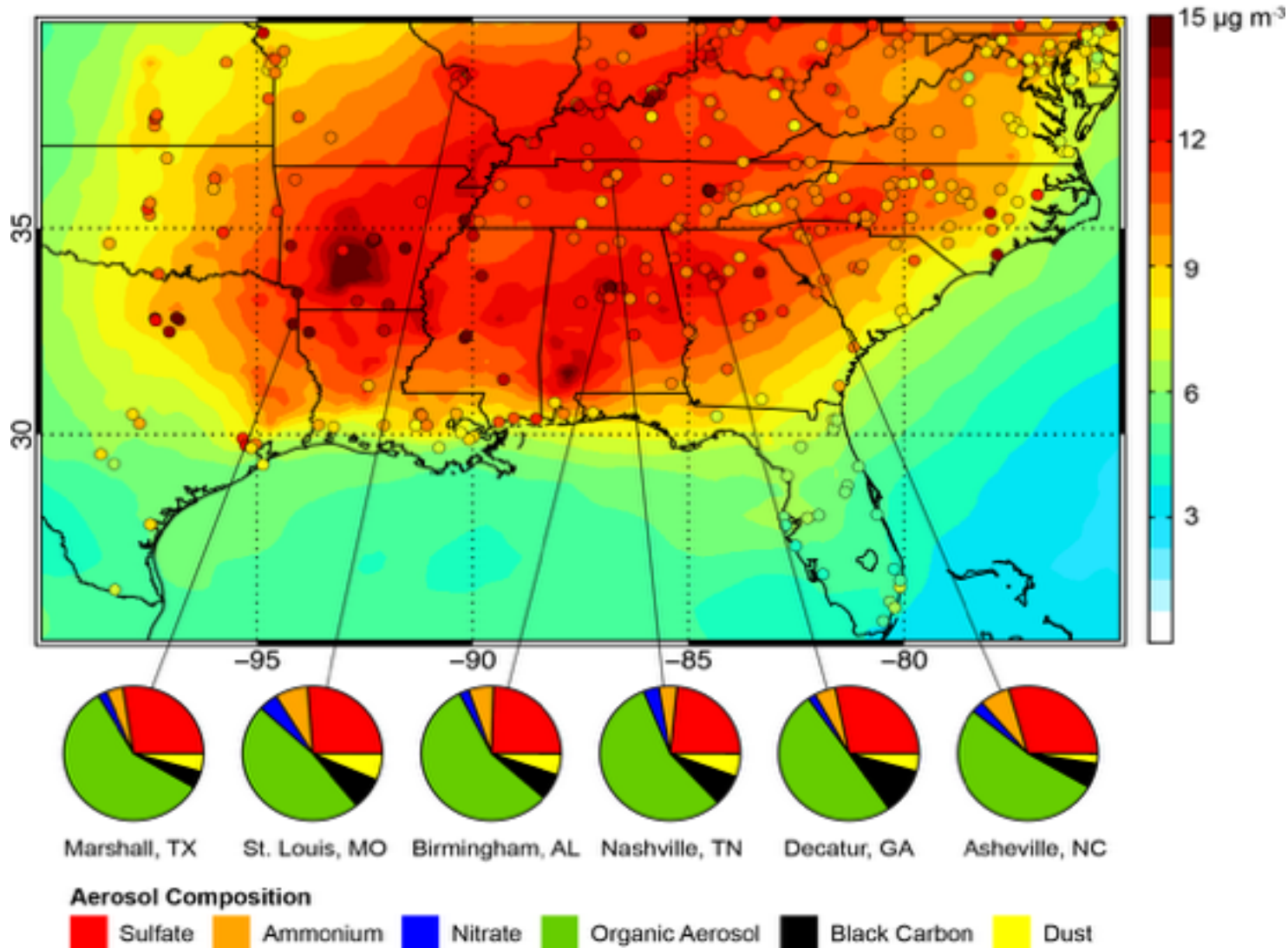
[IPCC, 2013]

# Primary and secondary organic aerosol (POA and SOA)



# Fine particulate matter (PM<sub>2.5</sub>) in the Southeast US

PM<sub>2.5</sub> in Aug-Sep 2013: observed (circles), GEOS-Chem model (background)

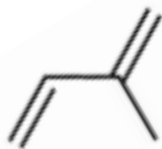


*Kim et al. [2015]*

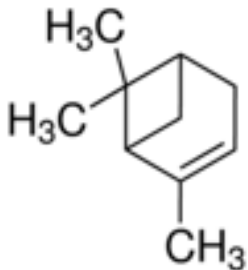
The organic aerosol is mostly biogenic SOA

# Biogenic VOCs as secondary organic aerosol (SOA) precursors

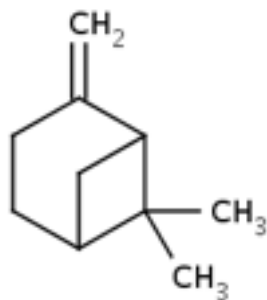
**Isoprene** (C<sub>5</sub>H<sub>8</sub>): mostly from deciduous trees, ~3% SOA yield per C atom



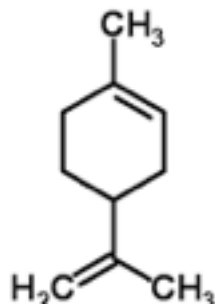
**Terpenes** (C<sub>10</sub>H<sub>16</sub>): mostly from evergreen trees, ~10% SOA yields



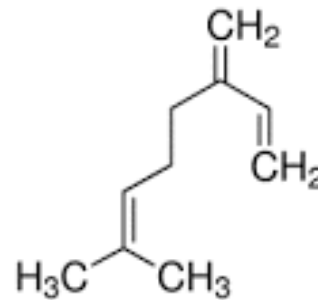
α-pinene



β-pinene

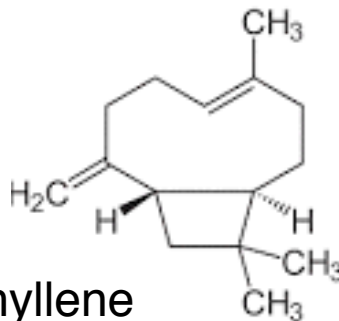


Limonene



Myrcene

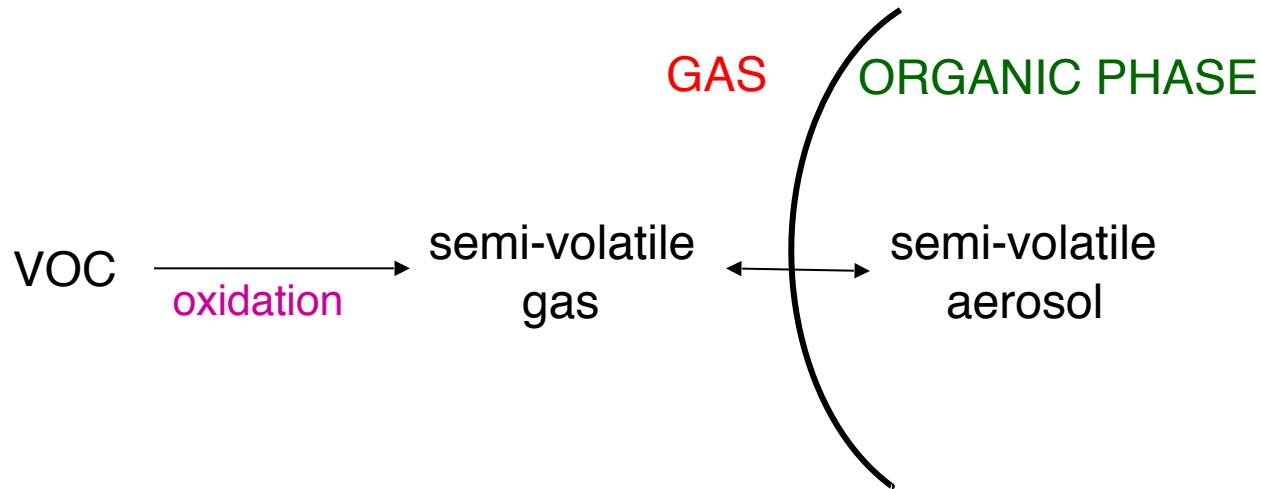
**Sesquiterpenes** (C<sub>15</sub>H<sub>24</sub>): little understood, highly reactive, high SOA yields



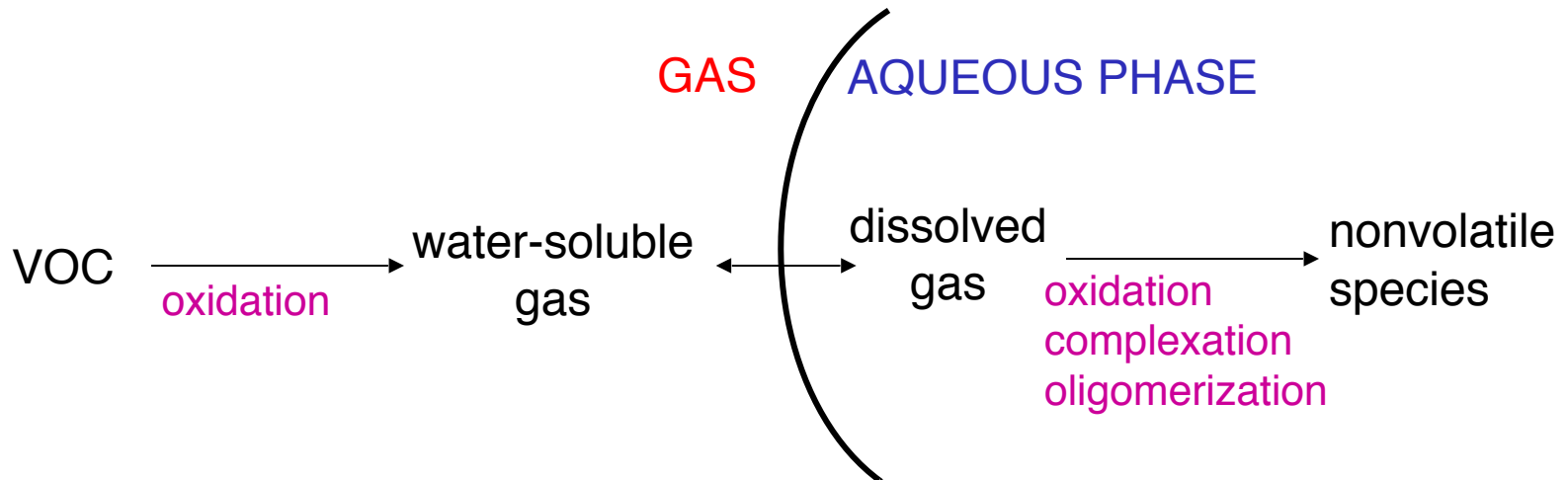
Caryophyllene

# Two models for formation of secondary organic aerosol

## A. Classical model for reversible uptake by pre-existing organic aerosol

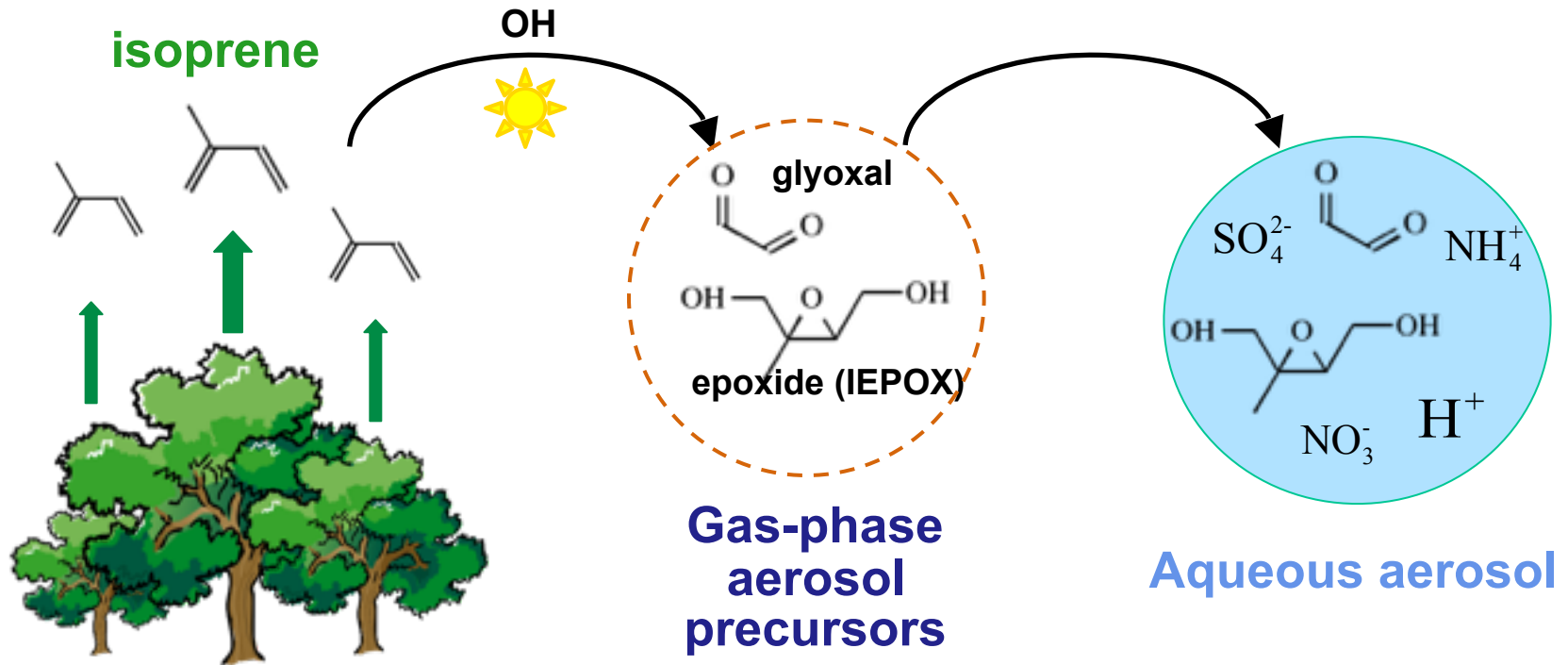


## B. Alternate model for irreversible uptake by aqueous aerosol





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



# Aqueous-phase formation of organic aerosol from glyoxal

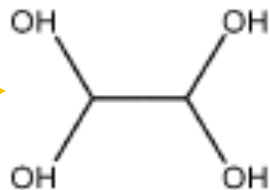
**GAS**

**AQUEOUS PHASE**

glyoxal



tetrol



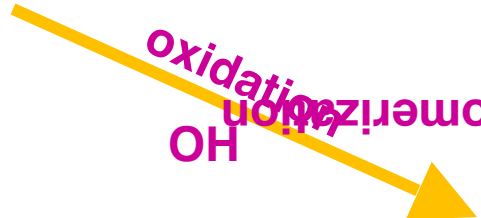
oligomerization



**Oligomers**



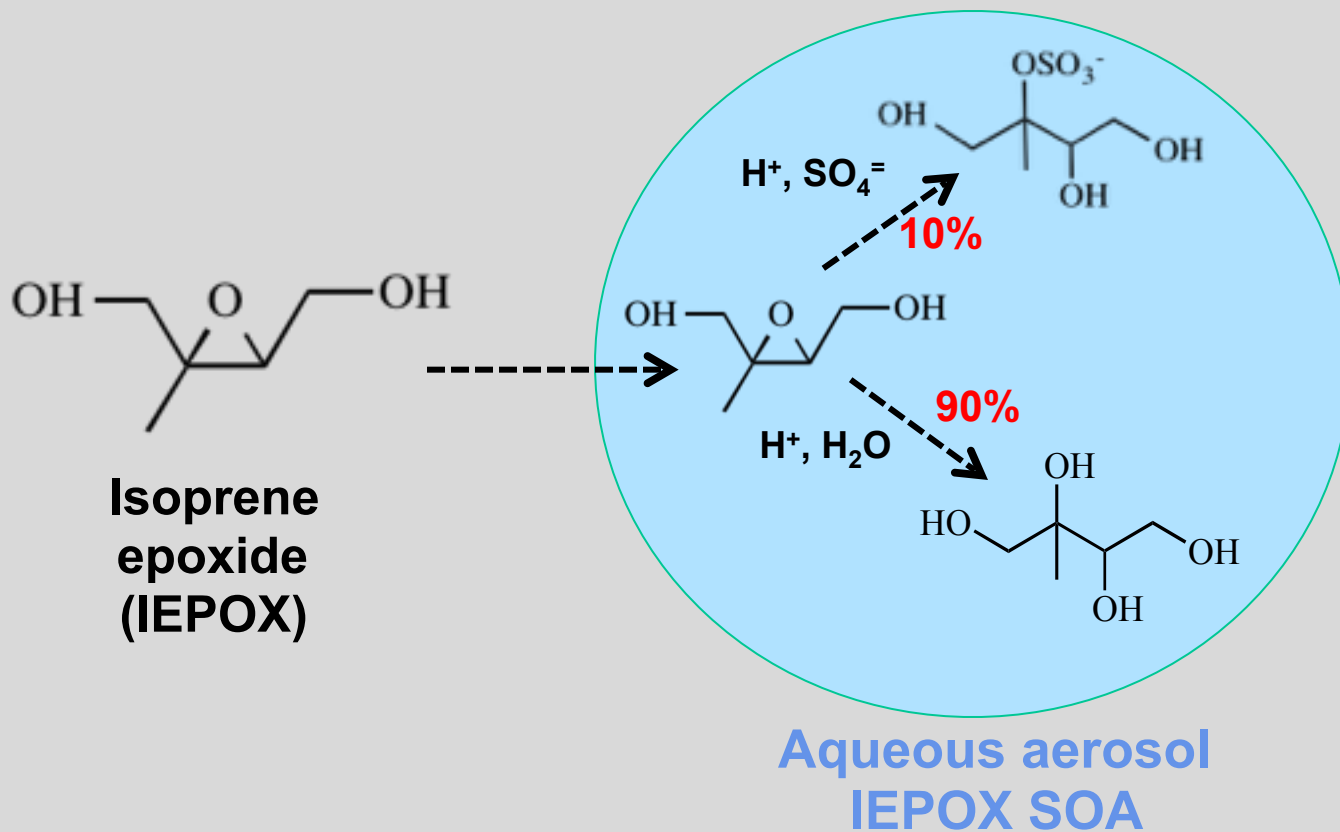
oxidation  
oligomerization  
OH



**Organic acids**

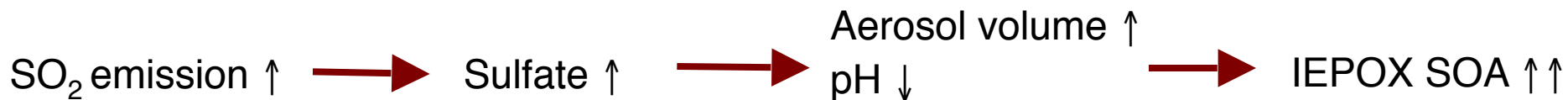
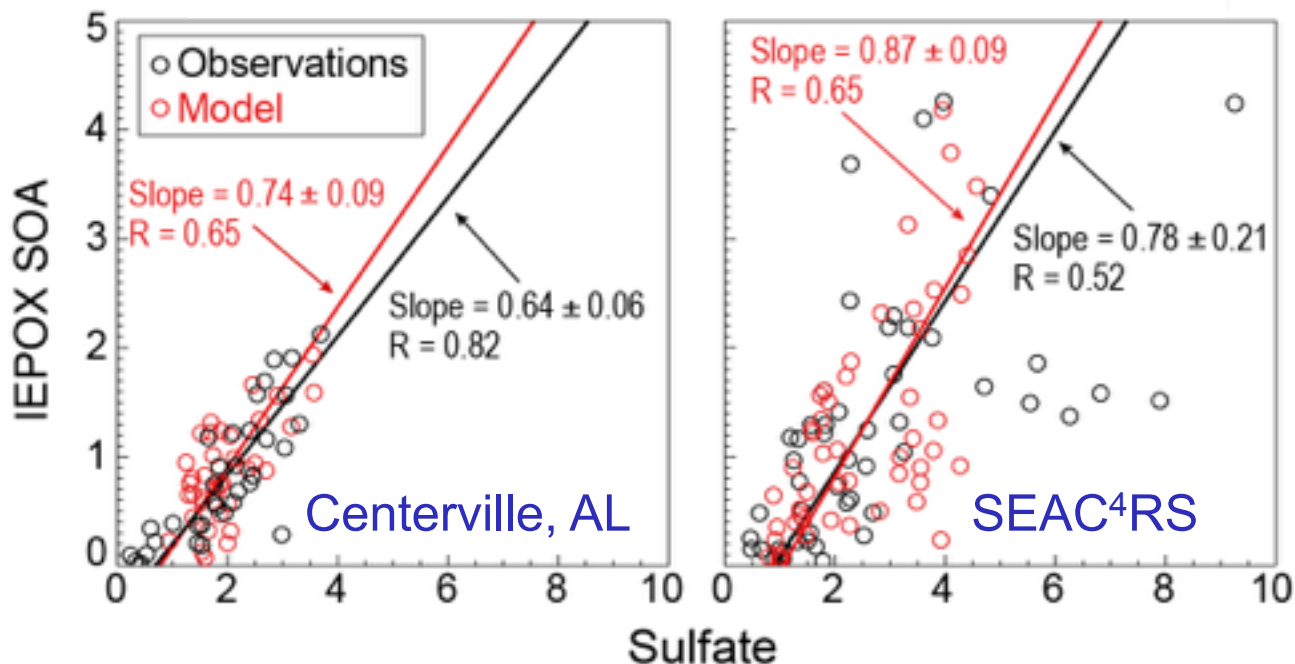
# Aqueous-phase formation of organic aerosol from epoxides

Acid-catalyzed ring cleavage to produce non-volatile species



# Observations show correlation of IEPOX SOA with sulfate

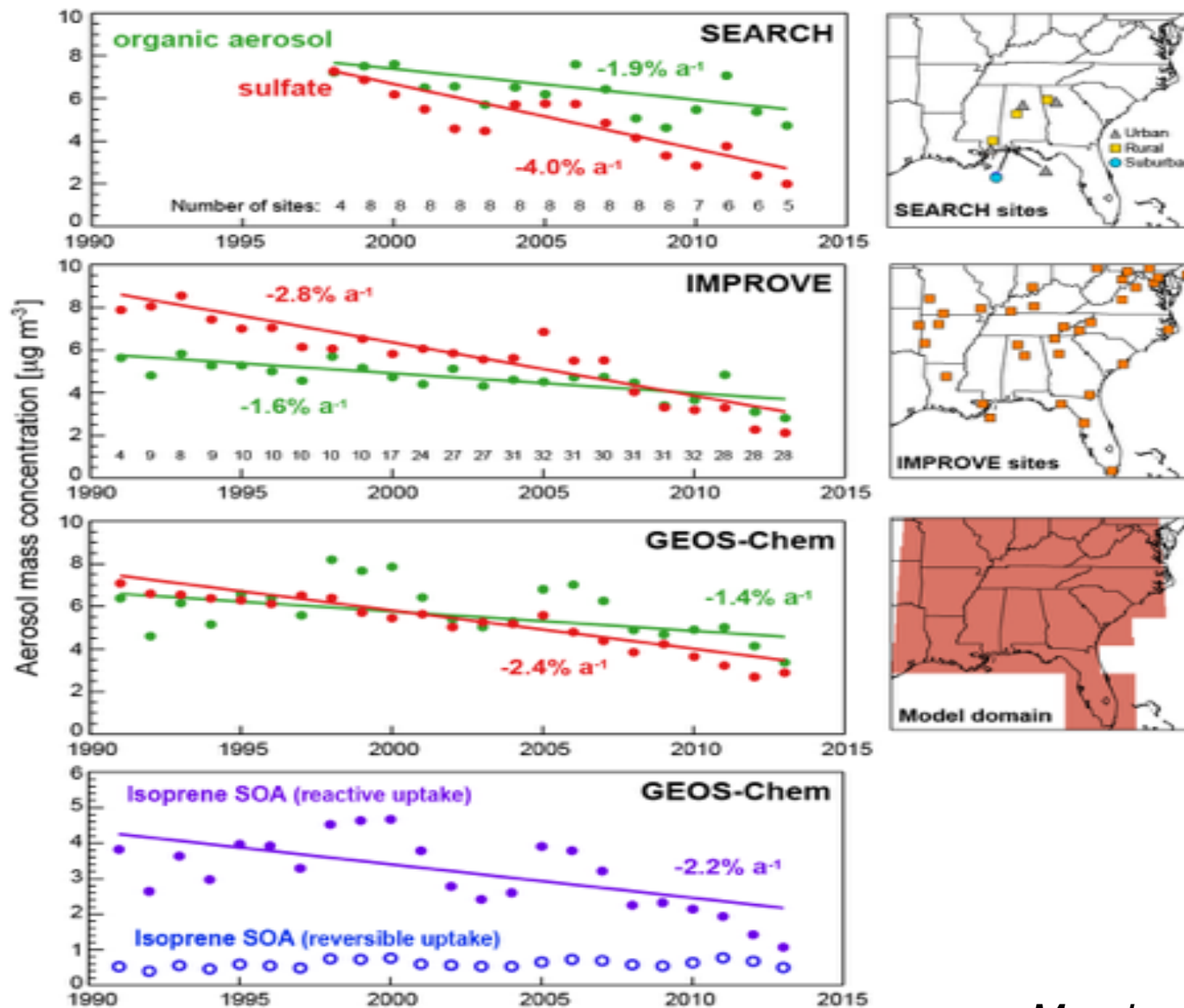
Correlations with sulfate in SEAC<sup>4</sup>RS and at Centerville, Alabama research site



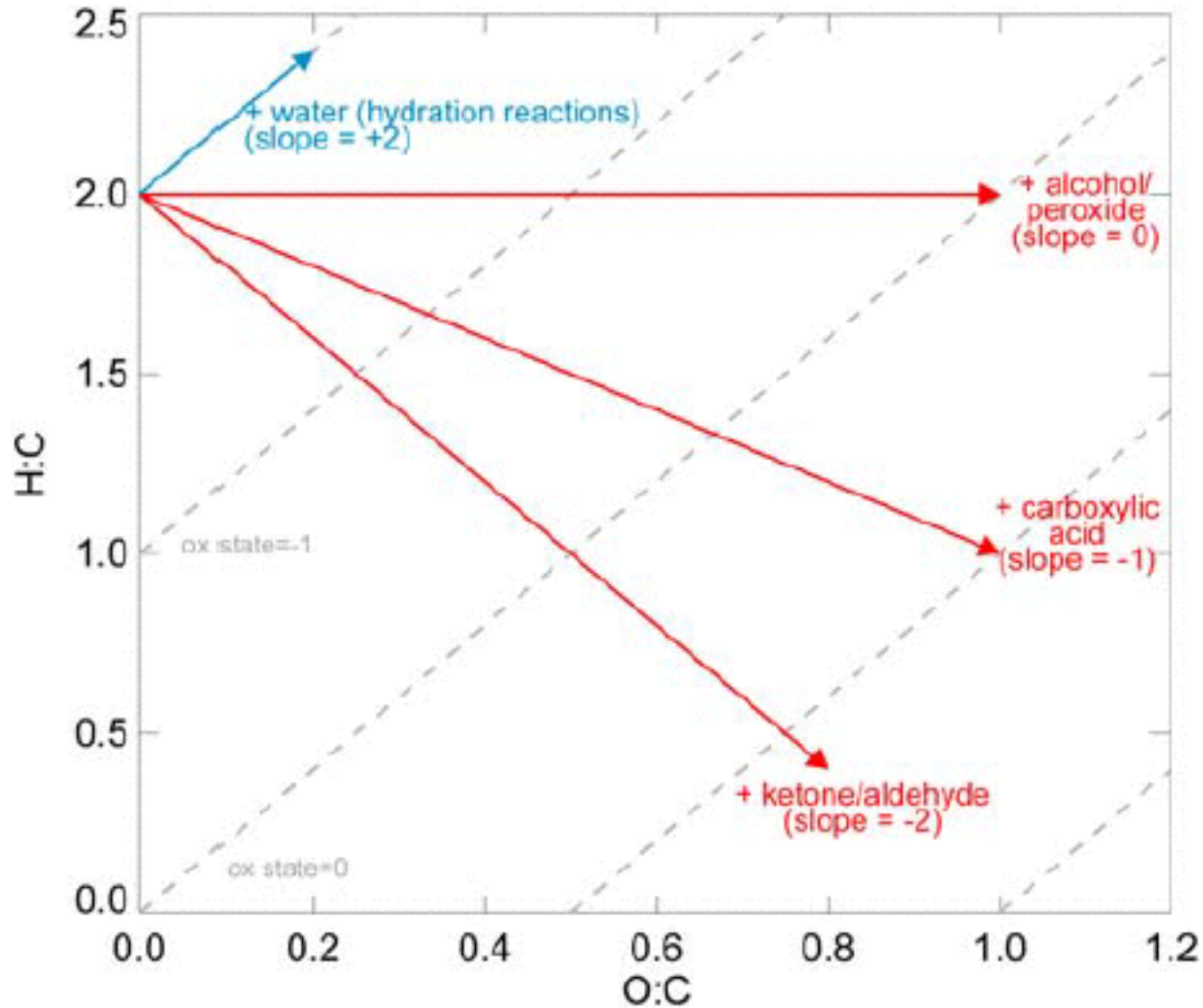
Suggests that SO<sub>2</sub> emission controls decrease organic aerosol as co-benefit

# Long-term trends of organic and sulfate aerosol in Southeast

## 1991-2013 trends in summertime organic aerosol and sulfate

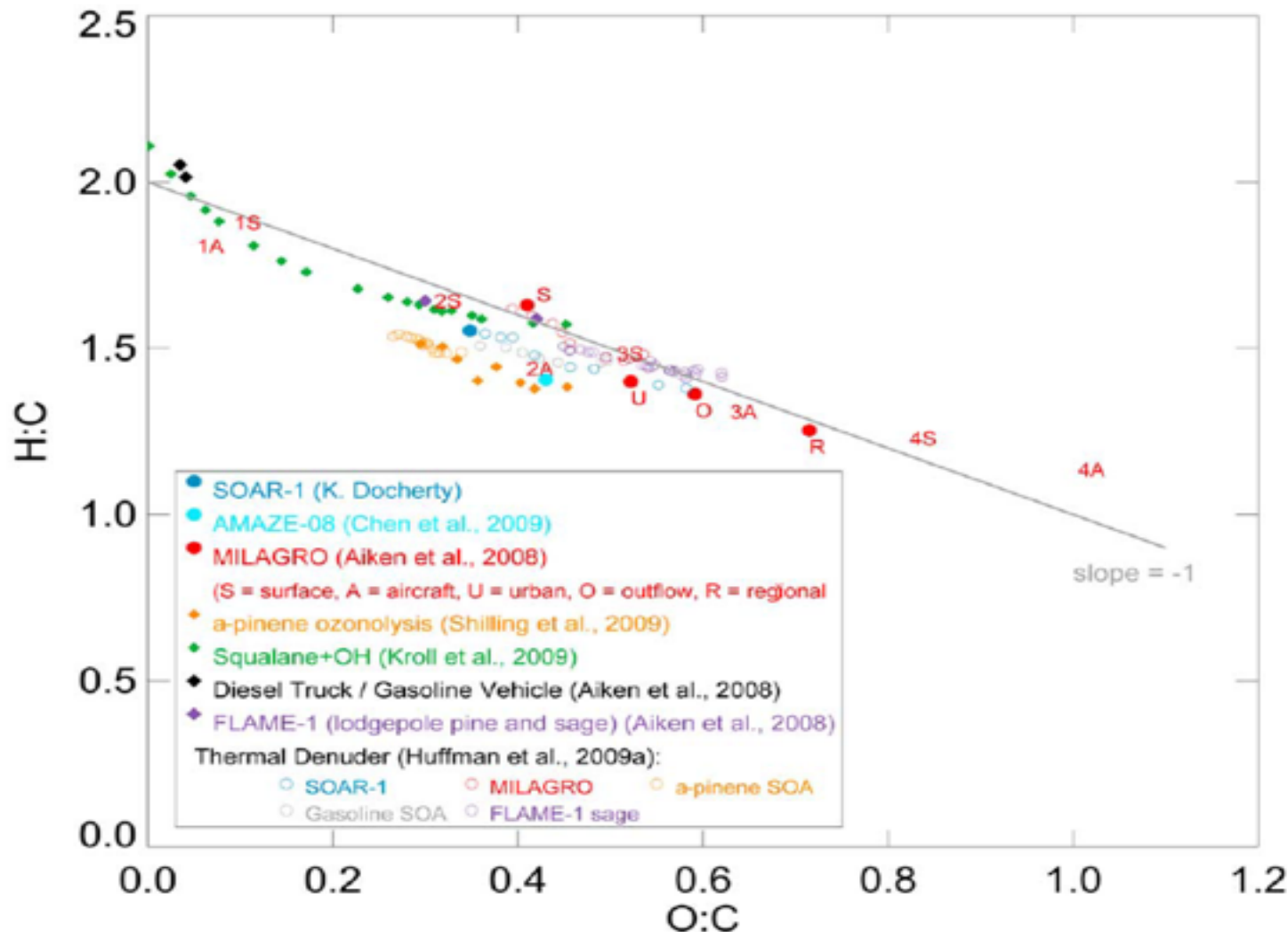


# Van Krevelen diagram for chemical aging of organic material



# Van Krevelen diagram: application to organic aerosol

-1 slope suggests aging by adding of  $-\text{COOH}$  functionalities





## Questions

1. In Regime 2 of sulfate-nitrate-ammonium (SNA) aerosol formation, decreasing  $\text{SO}_2$  emissions can actually cause an *increase* in total aerosol mass. Why? *[hint: sulfate has a molar mass of  $96 \text{ g mol}^{-1}$ , nitrate has a molar mass of  $62 \text{ g mol}^{-1}$ ]*
2. Whether secondary organic aerosol (SOA) forms in the organic phase or in the aqueous phase, there is a positive feedback effect in that the more aerosol you have, the more SOA you form. Explain.