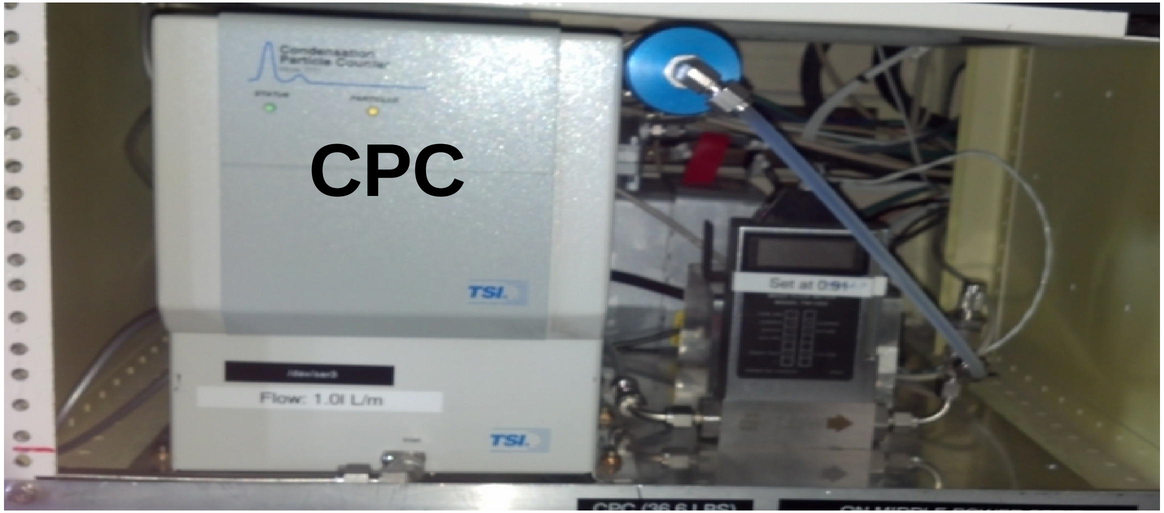
Atmospheric Aerosols



Definition of Aerosols

- Suspended Solid or Liquid Matter
- Small Settling Velocity

- Aerosols have residence times of days, to weeks.
- Atmospheric Aerosols are sometimes referred to as “particles”.

Image by Fred Remer, Saturday August 29, 2015 at 8000 ft over Devils Lake

Atmospheric Aerosol Size Range

10^{-9}m to 10^{-5} m

.001 µm to 10 µm

1 nm to 10,000 nm

Wavelength of Visible Light?

Size of a human hair?

Instrumentation Based Aerosol Definitions

Ultrafine Aerosols (UF)

- **Aerosols larger than 3 nm diameter.**

Condensation Nuclei (CN)

- **Aerosols larger than 10 nm diameter.**

Optical Aerosols ($D_{0.3}$)

- **Aerosols larger than 0.3 µm diameter.**

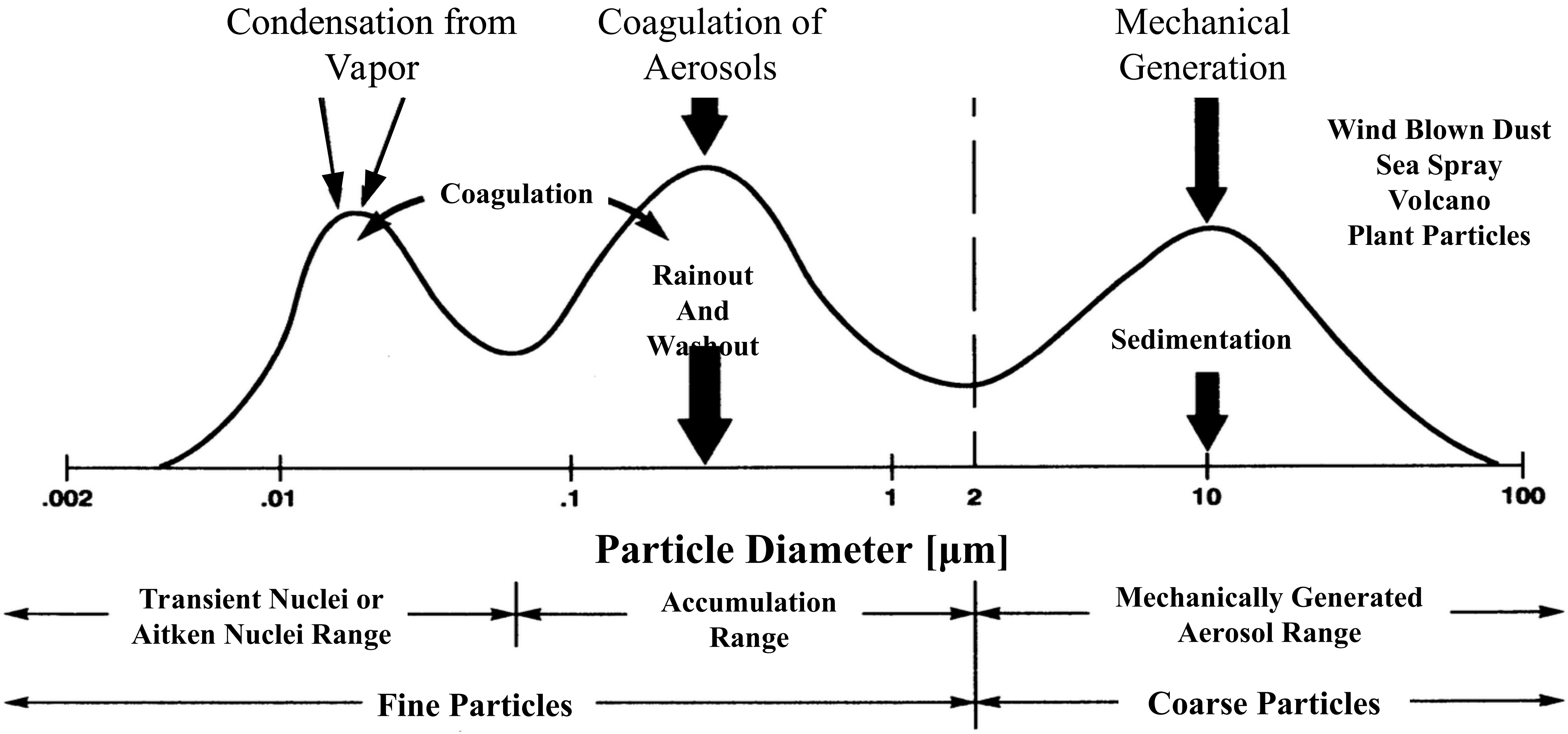
Cloud Condensation Nuclei (CCN)

- **Nuclei on which cloud droplets form.**

Ice Nuclei (IN)

- **Nuclei on which ice crystals form.**

Aerosol Modes



Adapted from Singh: Figure 5.4

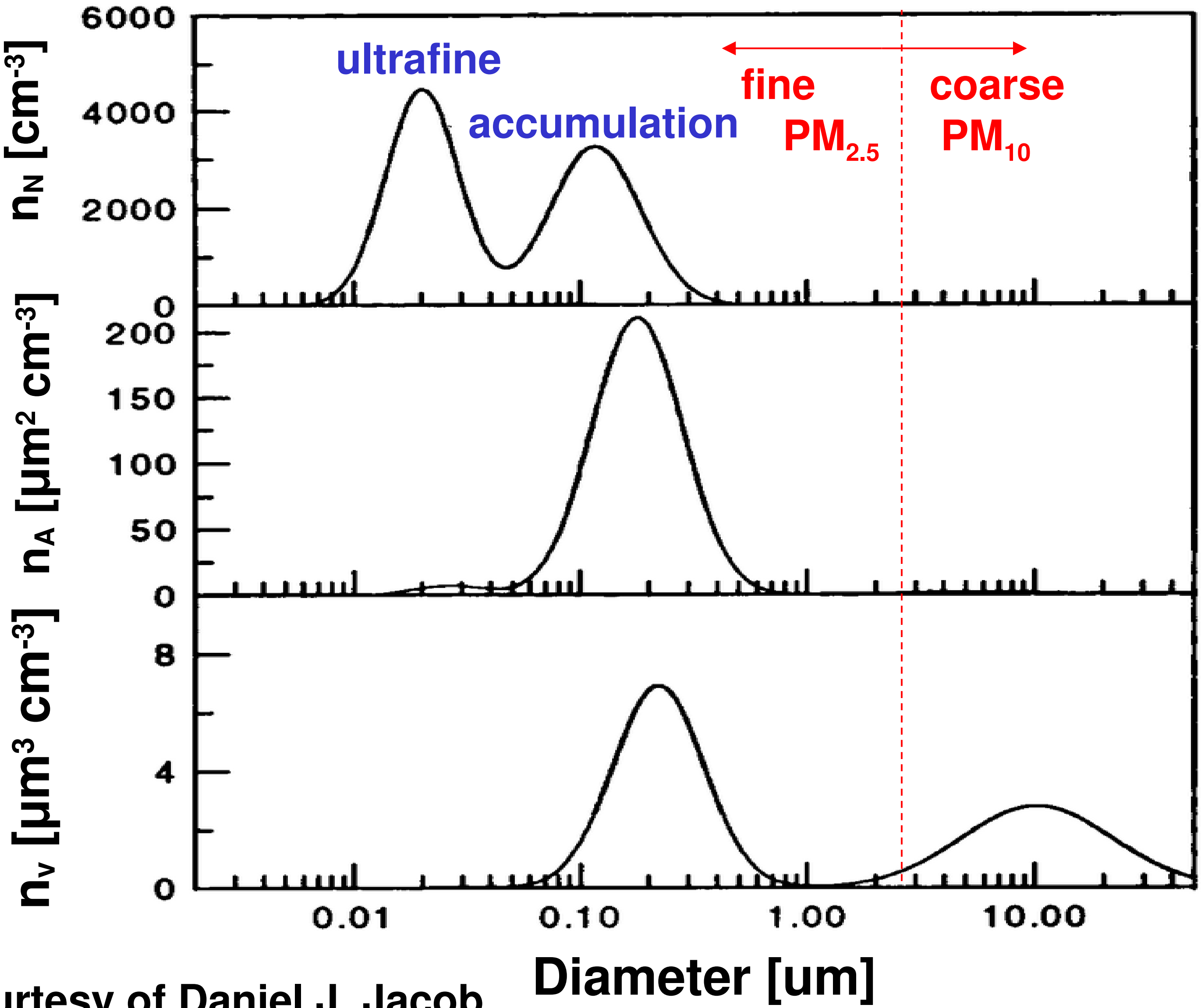
Aerosol Size Distribution

n_N – Particle Number (N) Concentration

n_s – Particle Area (A) Concentration

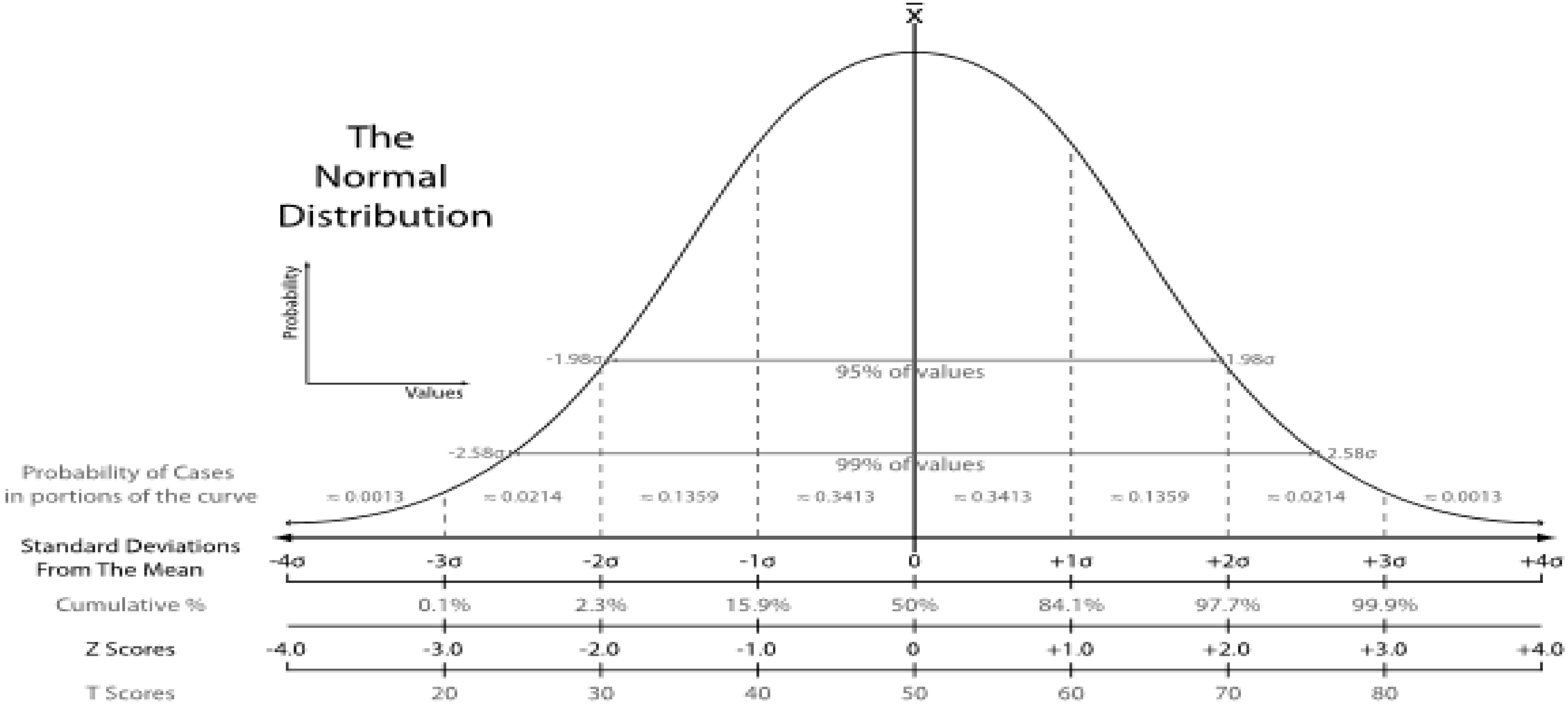
n_A – Particle Volume (V) Concentration

What volume is in terms of cm^{-3}? How about μm^3?



Courtesy of Daniel J. Jacob

Normal Distribution



Normal and Lognormal Distributions

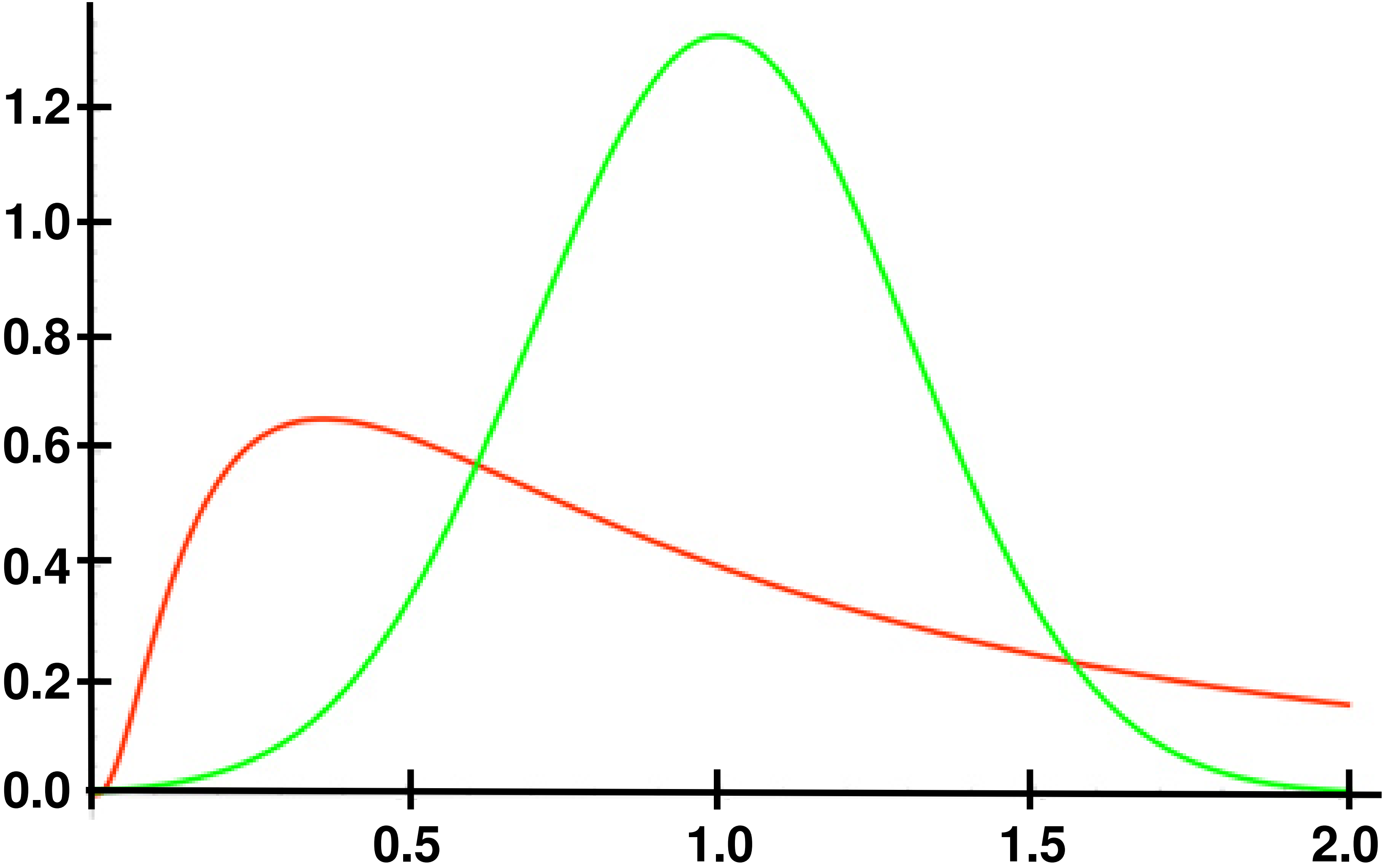
- Normal distribution has the characteristic bell shape, with maximum at the average ($\overline{u}$)

- Log-normal distribution is a distribution whose logarithm (natural log of u) is normally distributed. Appears as a normal distribution when x-axis is plotted on log scale.

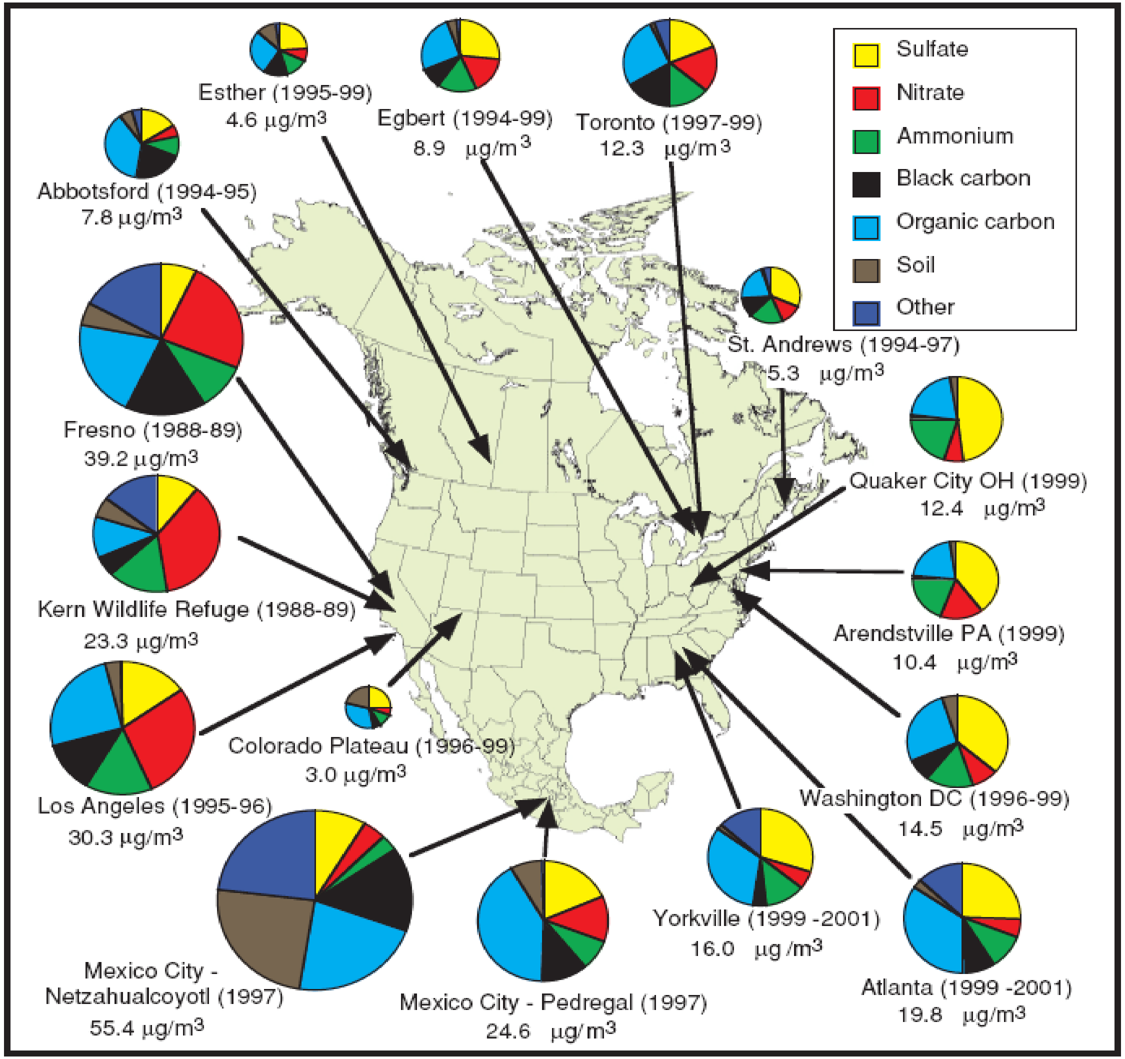
- **The log-normal distribution is a maximum entropy probability distribution.**

- Many physical systems tend to move towards maximal entropy configurations over time.

Lognormal and Normal Distribution Comparison



Annual mean $PM_{2.5}$ concentrations at North American Sites

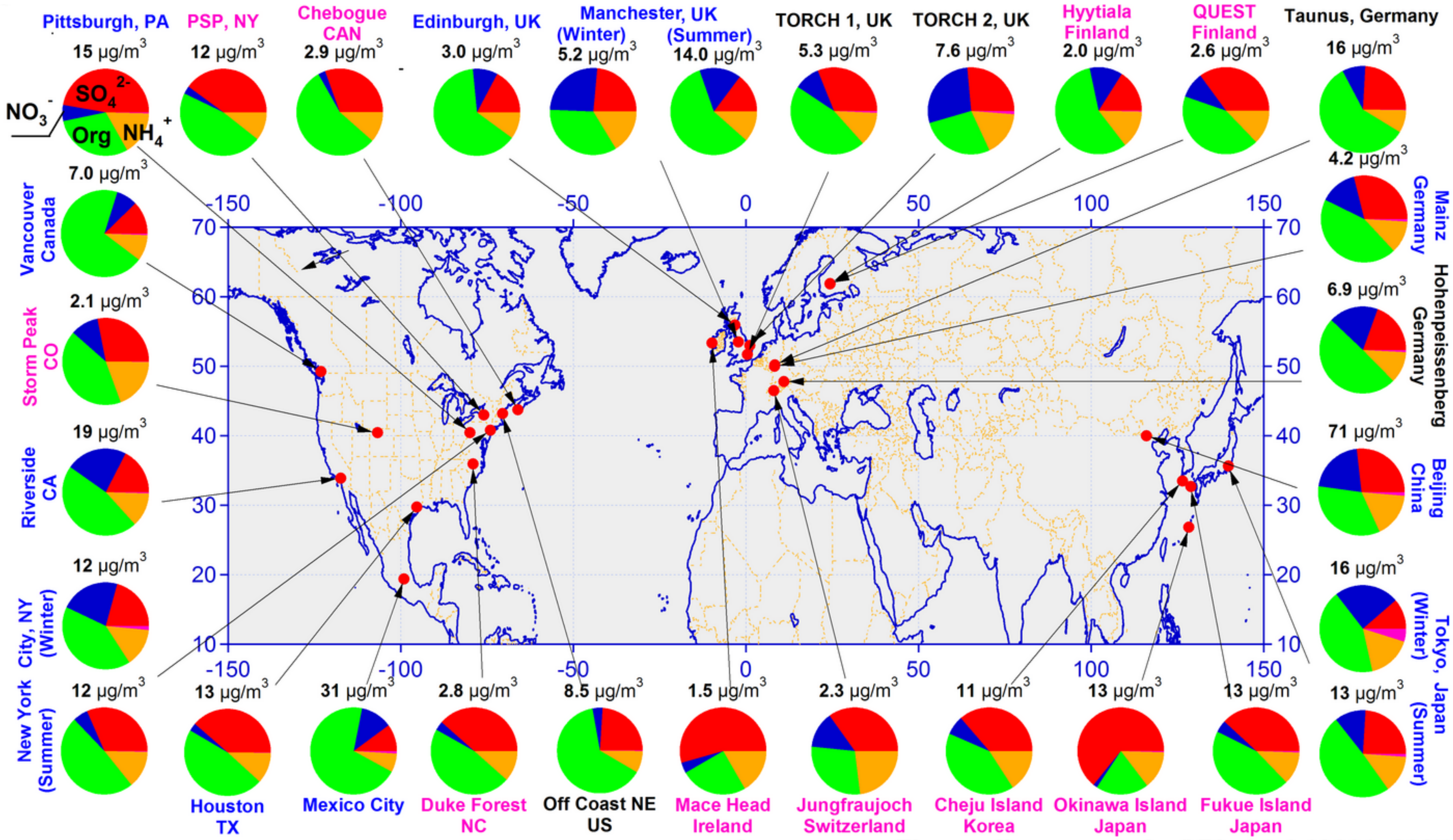


EPA revised the national air quality standards on December 14, 2012 to a annual mean $PM_{2.5}$ concentration of 12 $\mu g\ m^{-3}$. Old annual standard was 15 $\mu g\ m^{-3}$. The 24-hour fine particle standar is 35 $\mu g\ m^{-3}$. See http://www.epa.gov/pm/2012/decfsstandards.pdf.

NARSTO, 2004, Particulate Matter Science for Policy Makers, Edited by Peter McMurry, Marjorie Shepherd, James Vickery

Courtesy of Daniel J. Jacob

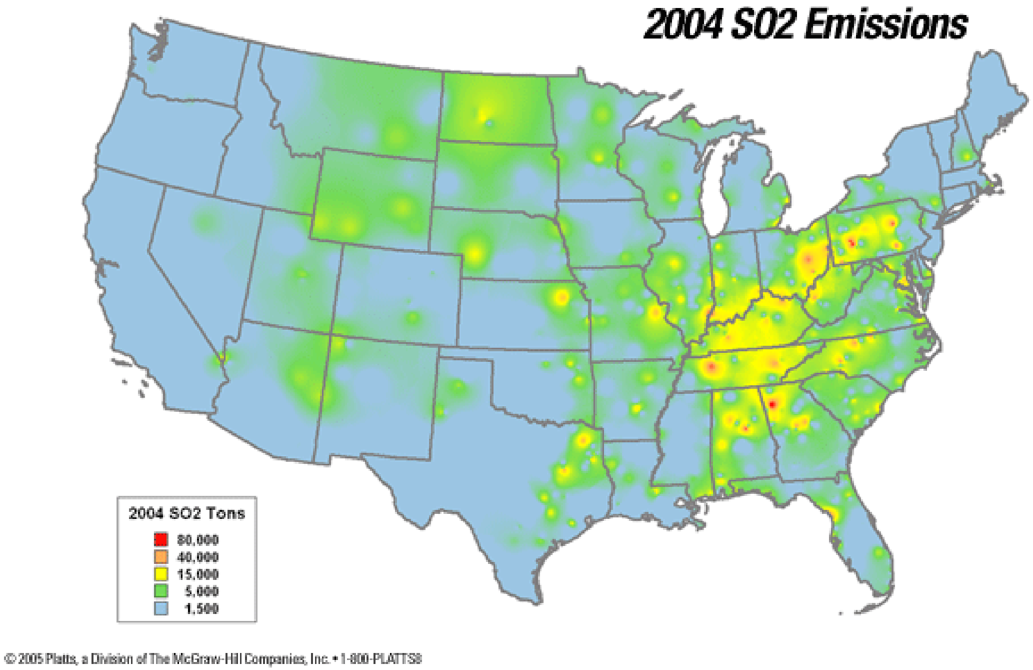
MEASUREMENTS OF FINE AEROSOL COMPOSITION



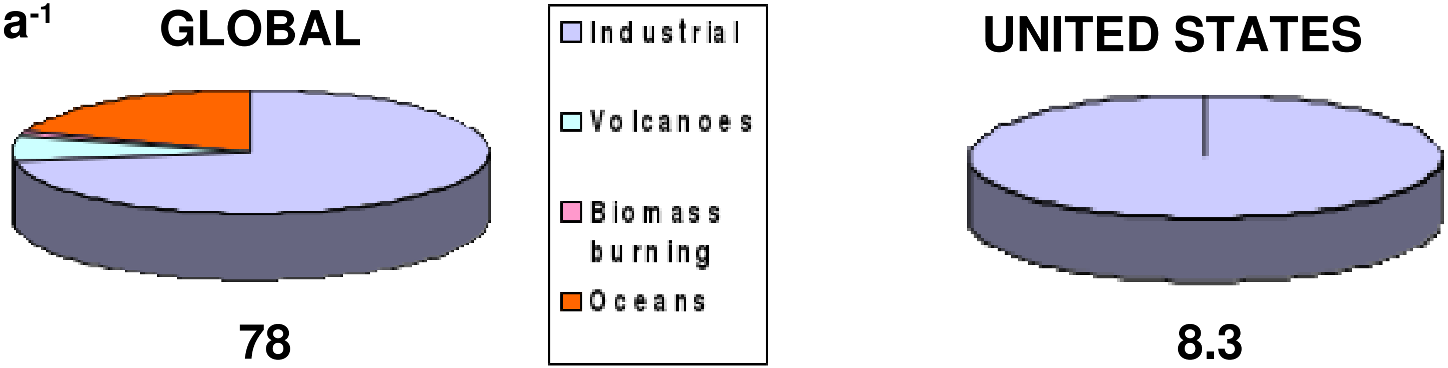
Zhang, Jimenez et al., *GRL*, 34, L13801, 2007

U.S. SO_2 EMISSIONS

Main source is coal combustion

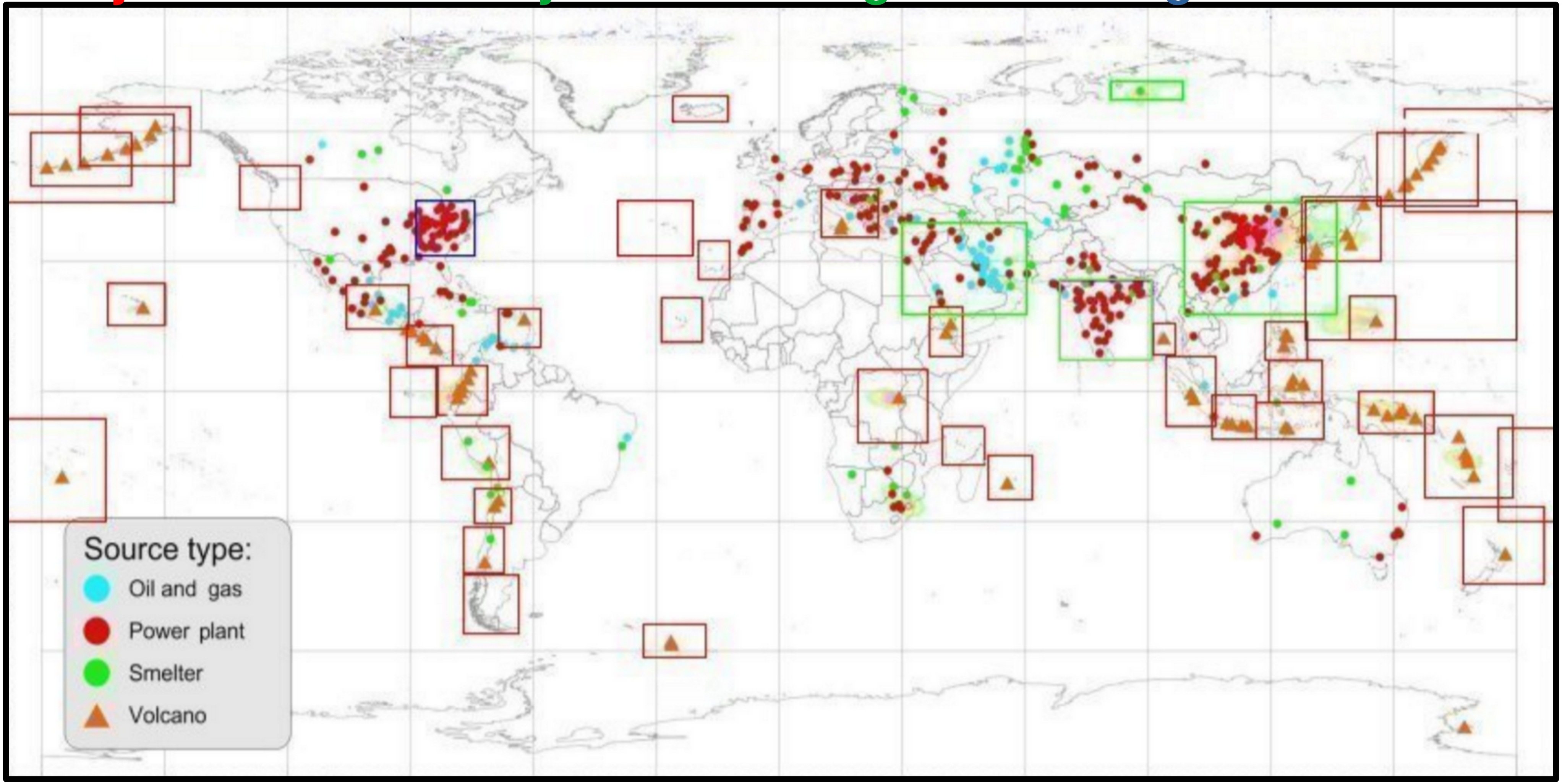


Sulfur Emissions, Tg a^{-1}



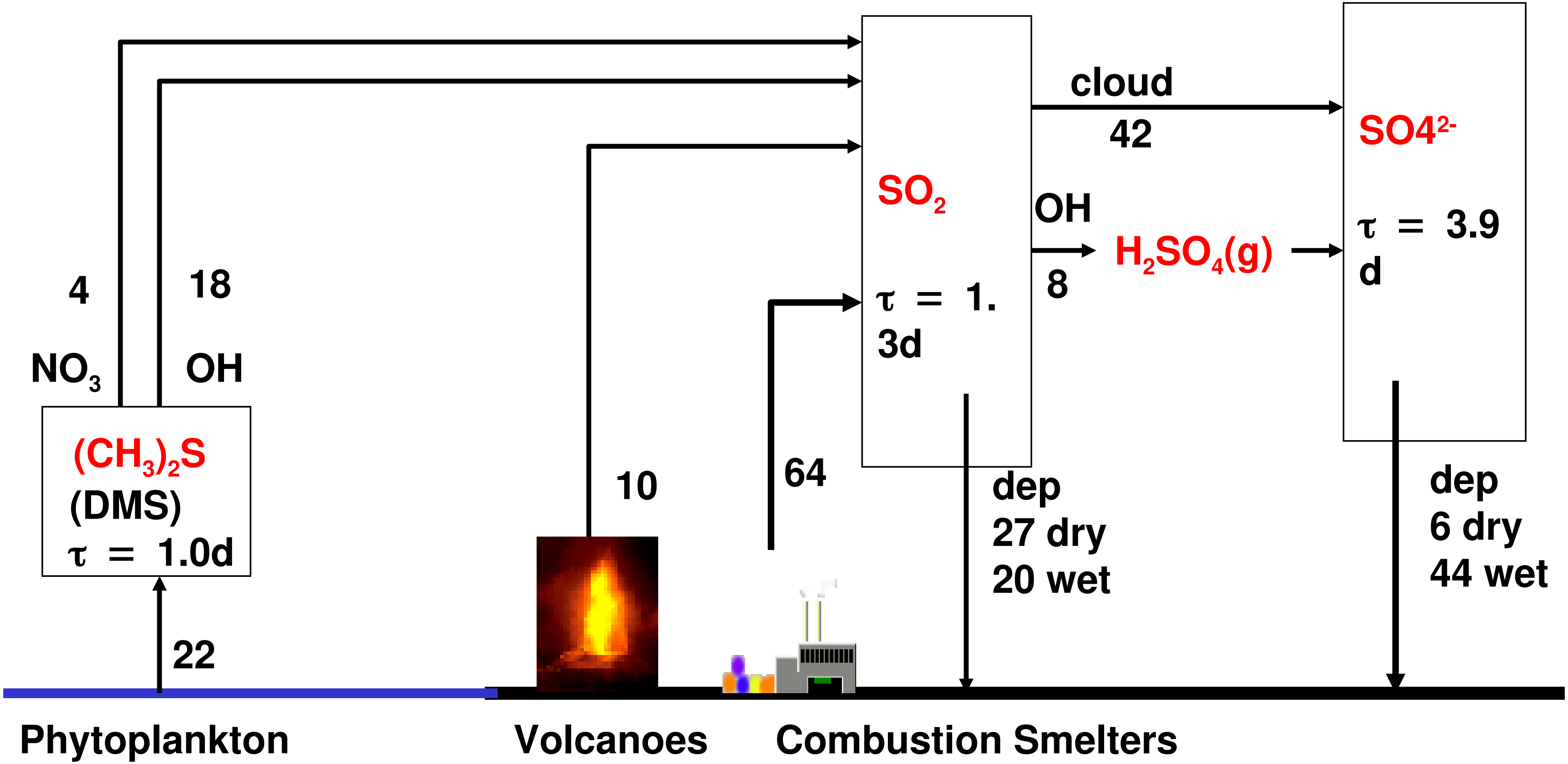
Courtesy of Daniel J. Jacob

Daily Volcanic **Daily Pollution Regions** **Long-term Pollution**



2024/10/17: Courtesy of https://so2.gsfc.nasa.gov/

SULFUR BUDGET [Chin et al., 1996] (flux terms in Tg S yr^{-1})



Courtesy of Daniel J. Jacob

FORMATION OF SULFATE-NITRATE-AMMONIUM AEROSOLS

Thermodynamic Rules:

$$H_2SO_4(g) \xrightarrow{H_20} SO_4^{2-} + 2H^+$$

Sulfate always forms an aqueous aerosol

$$NH_3(g) \xrightarrow{H_20} NH_4^+ + OH^-$$

Ammonia dissolves in the sulfate aerosol totally or until titration of acidity, whichever happens first

$$HNO_3(g) \xrightarrow{H_20} NO_3^- + H^+$$

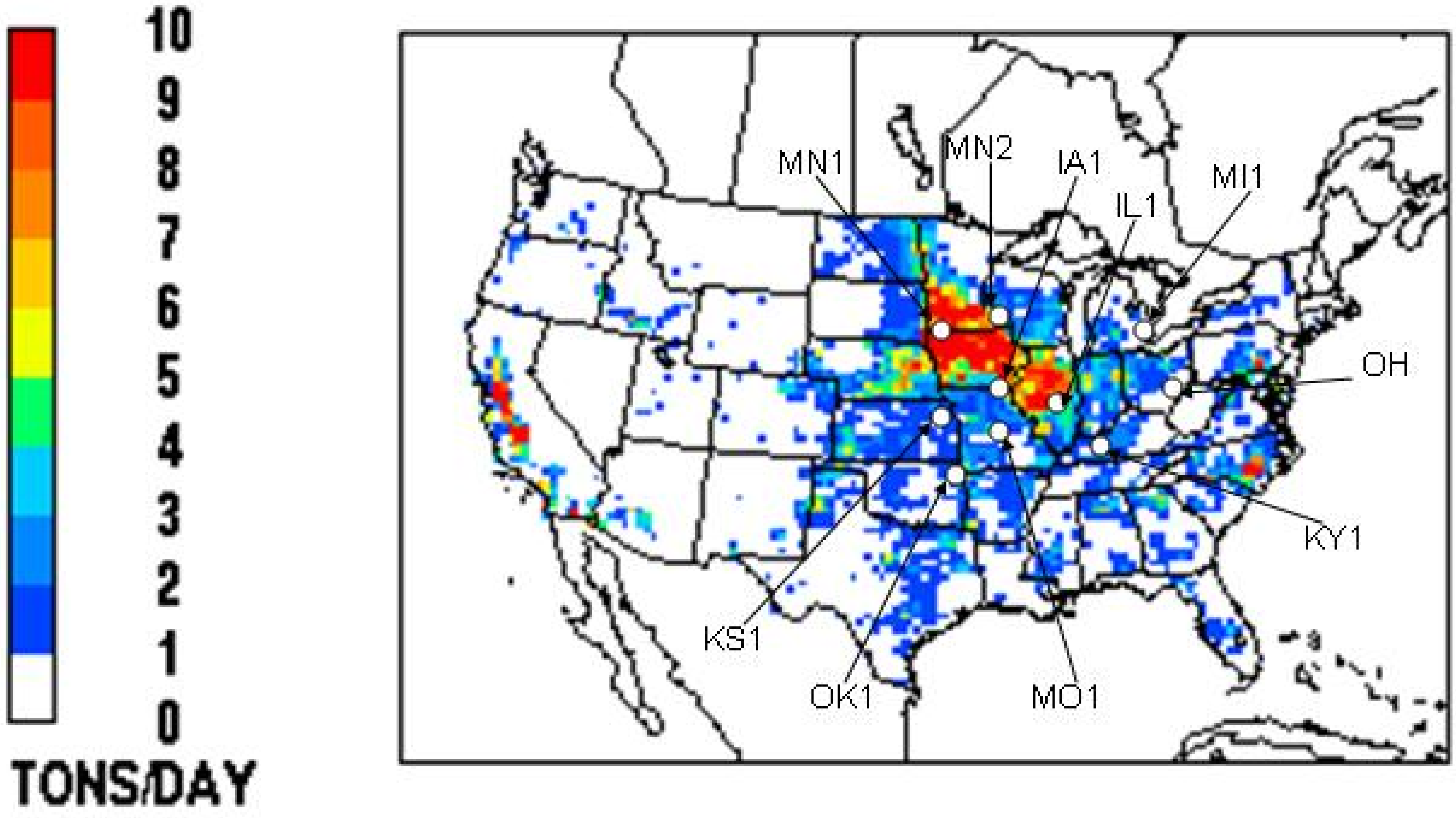
Nitrate is taken up by aerosol if (and only if) excess NH_3 is available after sulfate titration

$$NH_3(g) + HNO_3(g) \rightarrow NH_4NO_3(aerosol)$$

HNO_3 and excess NH_3 can also form a solid aerosol if RH is low

Condition	pH	Low RH	High RH
[S(VI)] > 2[N(-III)]	Acid	$H_2SO_4 \cdot nH_2O$, NH_4HSO_4, $(NH_4)_2SO_4$	(NH_4^+, H^+, SO_4^{2-}) solution
[S(VI)] ≤ 2[N(-III)]	Neutral	$(NH_4)_2SO_4$, NH_4NO_3	(NH_4^+, NO_3^-) solution

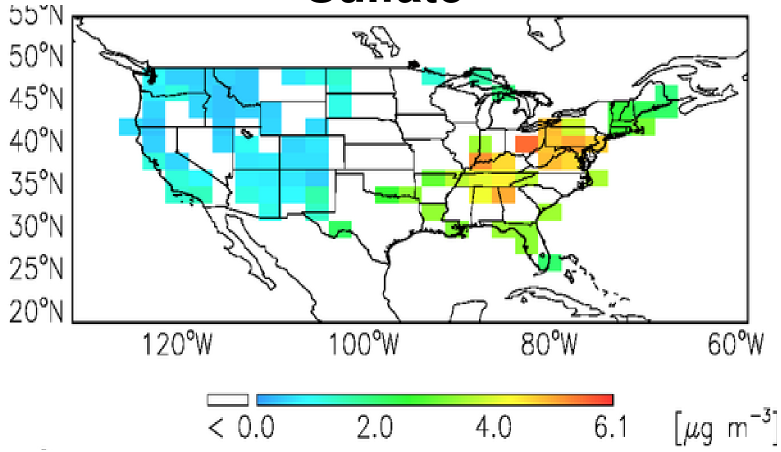
AMMONIA EMISSIONS



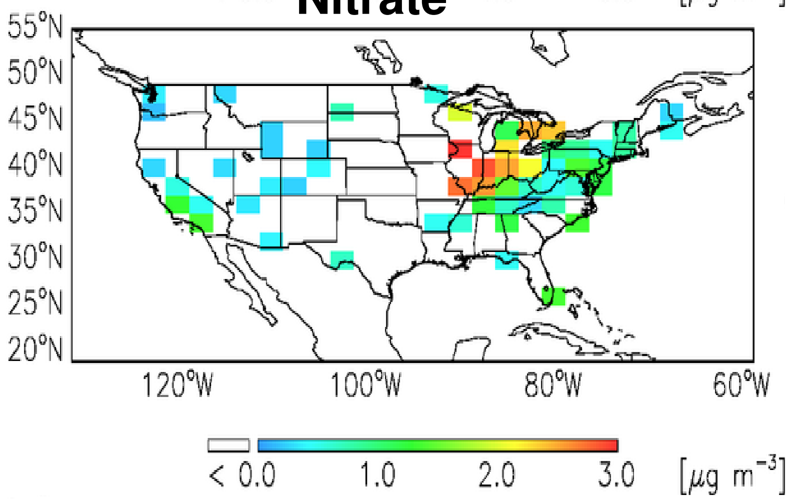
Ammonia, Tg N a^{-1}

SULFATE-NITRATE-AMMONIUM AEROSOLS IN U.S (2001)

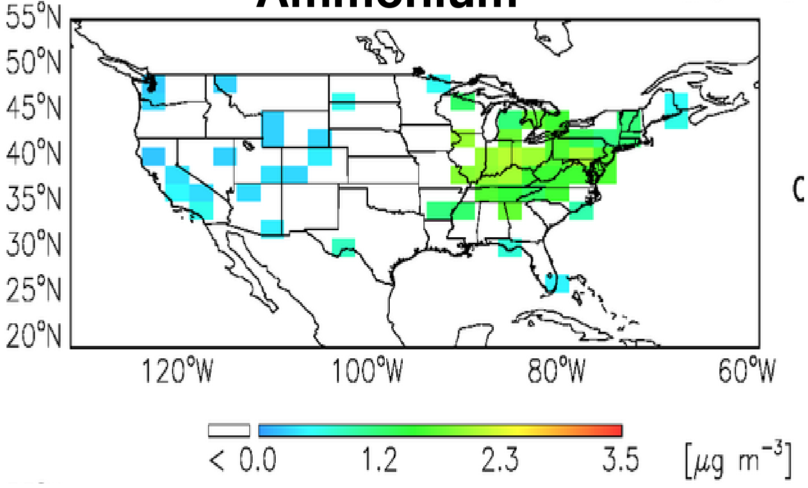
Sulfate

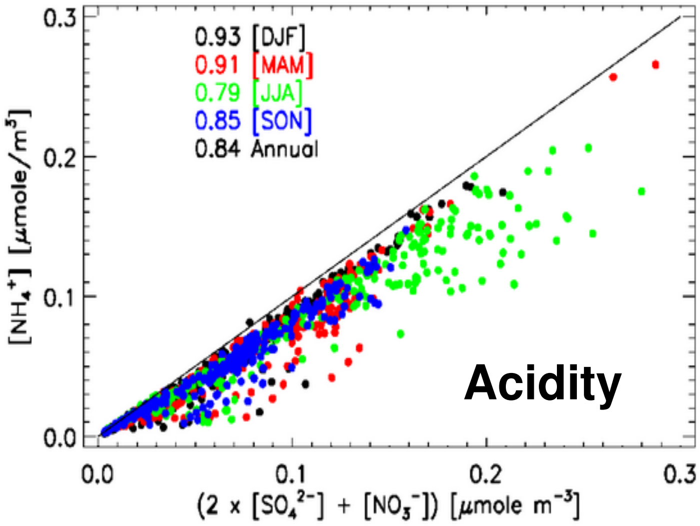


Nitrate



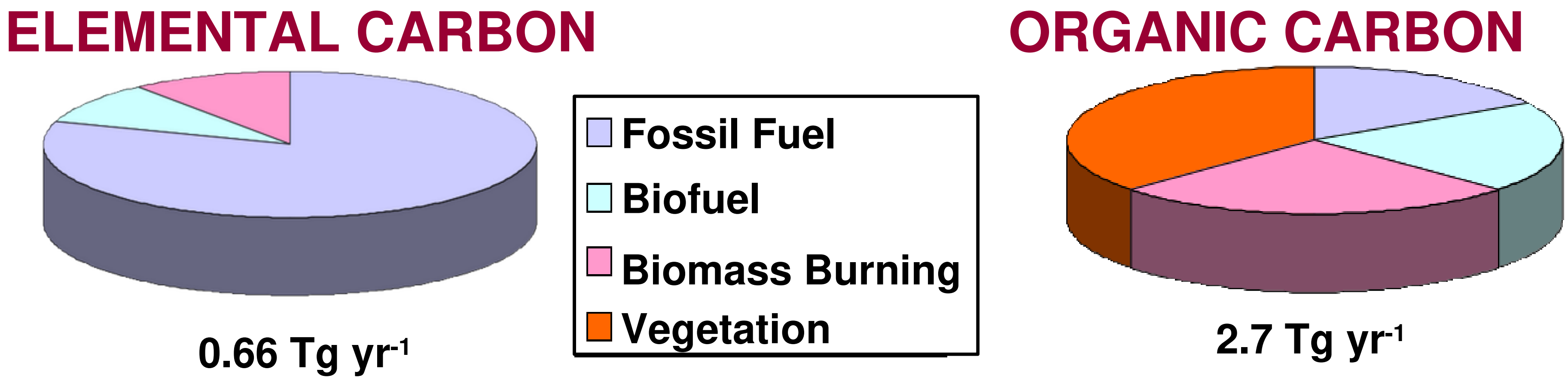
Ammonium





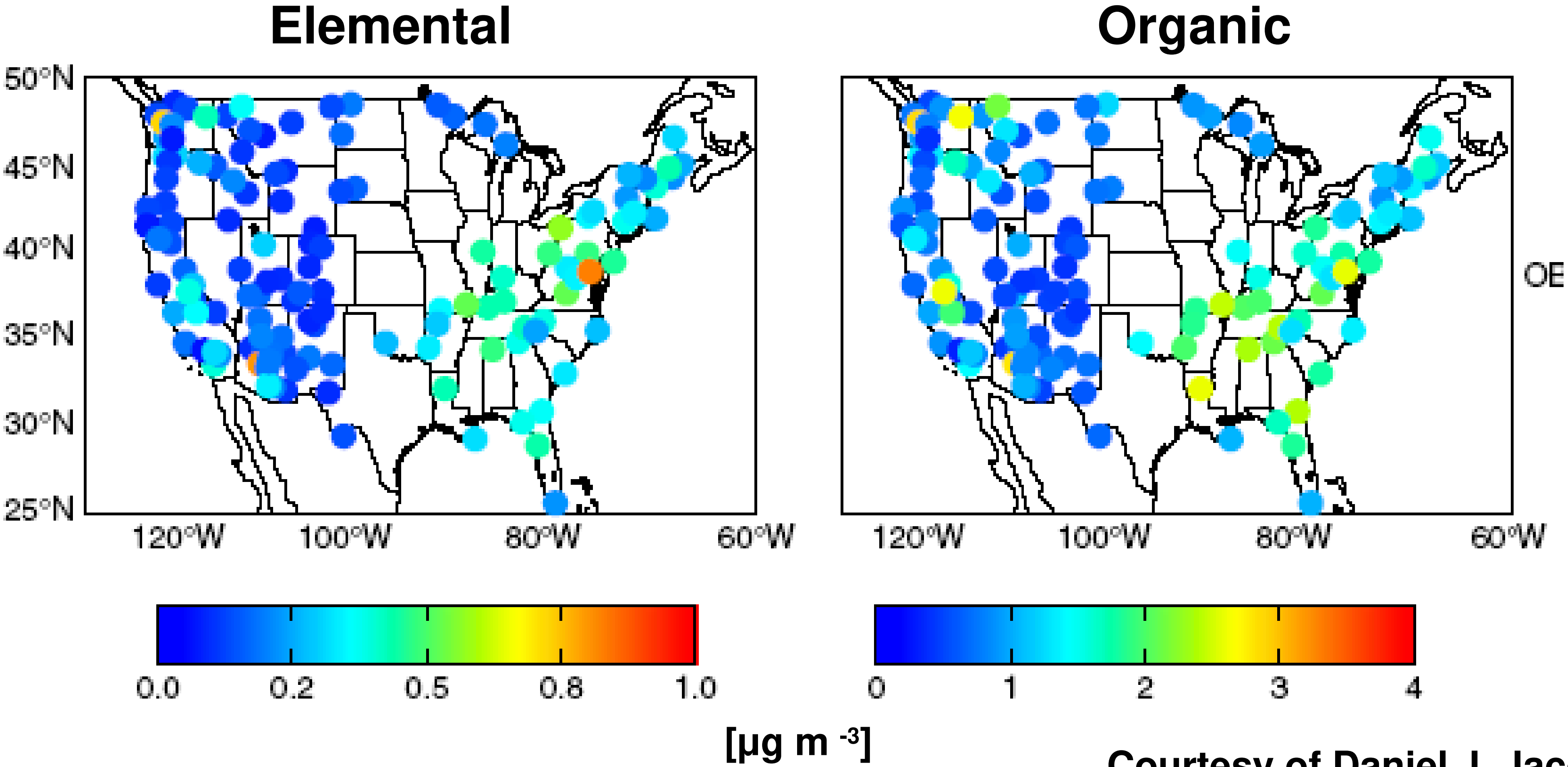
Courtesy of Daniel J. Jacob

CARBONACEOUS AEROSOL SOURCES IN THE U.S.



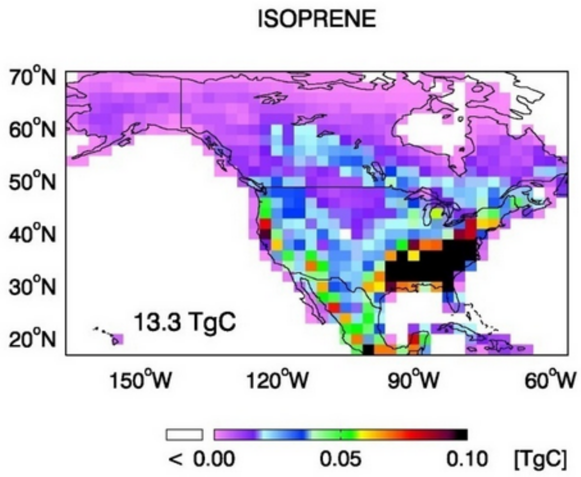
Courtesy of Daniel J. Jacob,
see http://image3.slideserve.com/6570266/carbonaceous-aerosol-sources-in-the-u-s-n.jpg

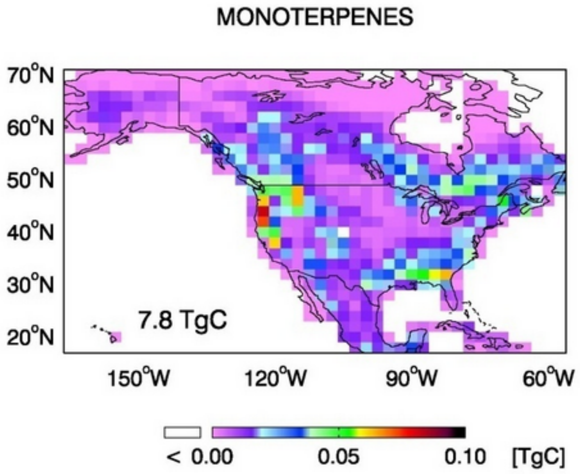
Annual Mean Concentrations (2001)

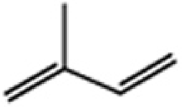


Courtesy of Daniel J. Jacob

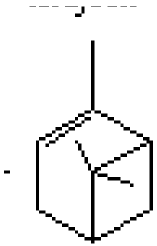
FORMATION OF ORGANIC AEROSOL FROM VEGETATIVE EMISSIONS







ISOPRENE



α-pinene

OH, O_3 →

Aldehydes
RC(O)H

Ketones
RC(O)R

Dicarbonyls
RC(O)-C(O)R

⟷ **absorption into aerosol**

↓ **oxidation**

Carboxylic acids
RC(O)OH

↓

polymerization

Courtesy of Daniel J. Jacob

Global SOA Budget

- **Bottom up estimates gives 50 to 90 Tg/yr (most estimates at low end).**

- **Top own estimates gives 140 to 910 Tg/yr.**

- **Difference suggests that chamber oxidation experiments substantially underestimate total SOA production.**

Source: Hallquist et al., 2009