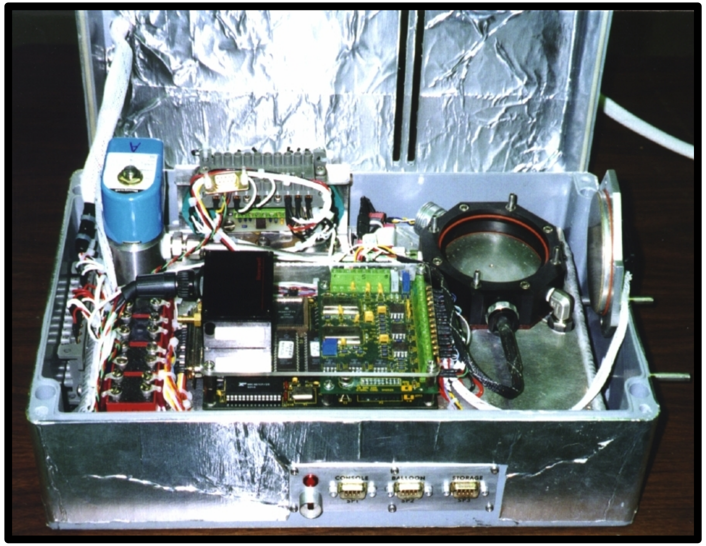
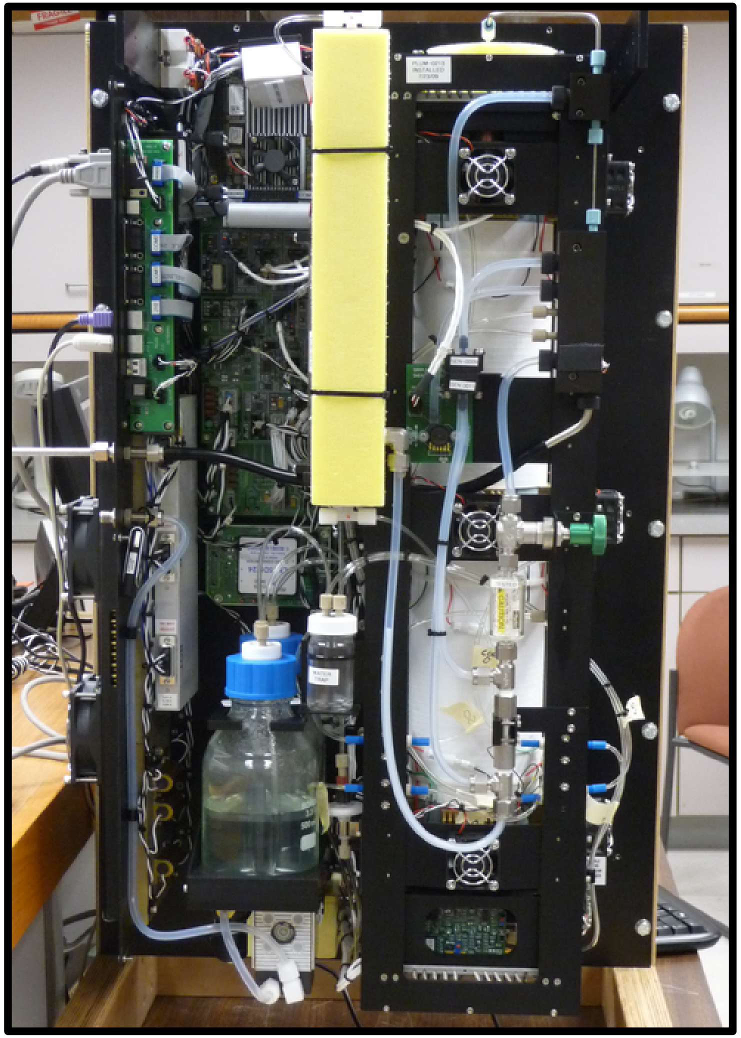
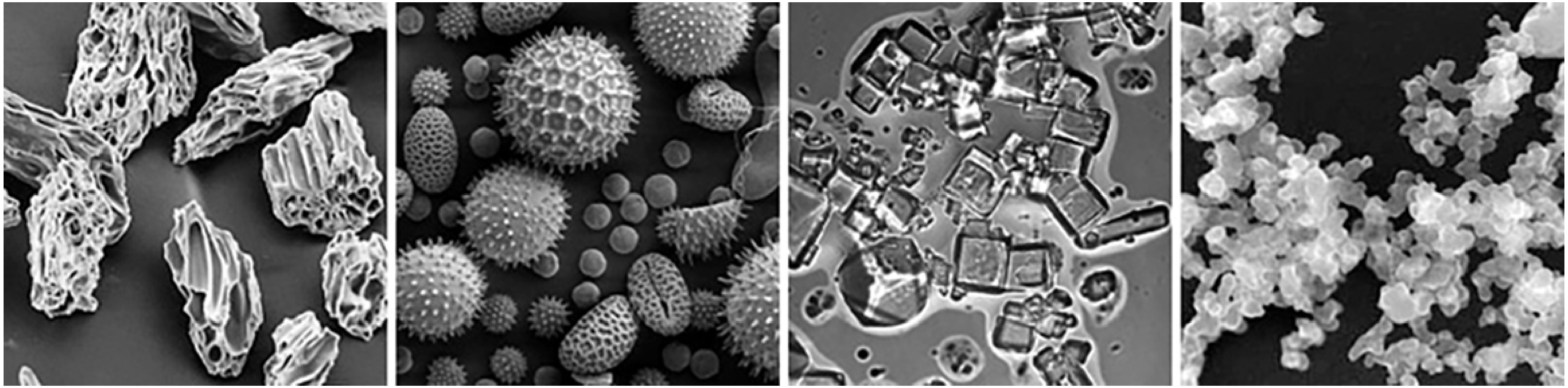
Atmospheric Aerosols and Particle Nucleation





What are Aerosols?

- Suspended particles in the air.
- May consist of liquids or solids, but not a gas.
- Suspended material in the Earth's atmosphere that have troposphere residence times (lifetimes) of days to a few weeks.
- Particles involved in the formation of water or ice are often referred to as “nuclei”.



These scanning electron microscope images (not at the same scale) show the wide variety of aerosol shapes. From left to right: volcanic ash, pollen, sea salt, and soot.
Images: NASA, compiled from USGS, UMBC (Chere Petty), and Arizona State University (Peter Buseck)

How do we know when present in the air?

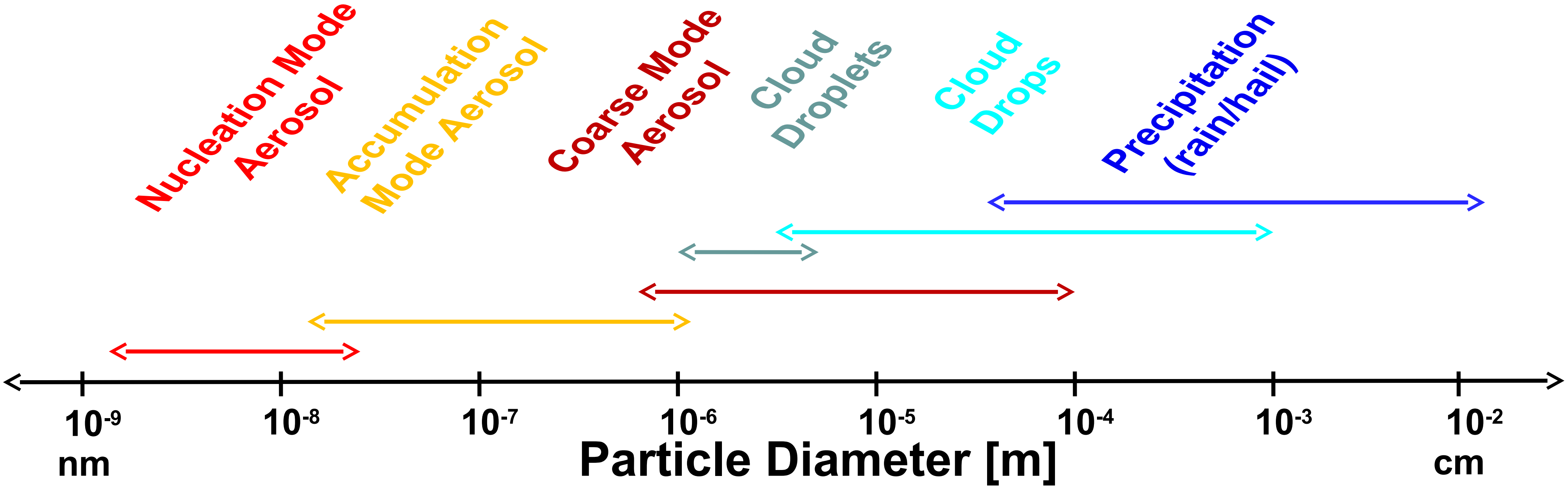
Aerosols and Water

- Hygroscopic Particles
  - Readily absorbing and holding water molecules (vapor).
    - Example: Sea Salt
- Hydrophobic Particles
  - Repel water molecules.
  - Nonpolar types of materials.
    - Example: Fresh Smoke, Soot

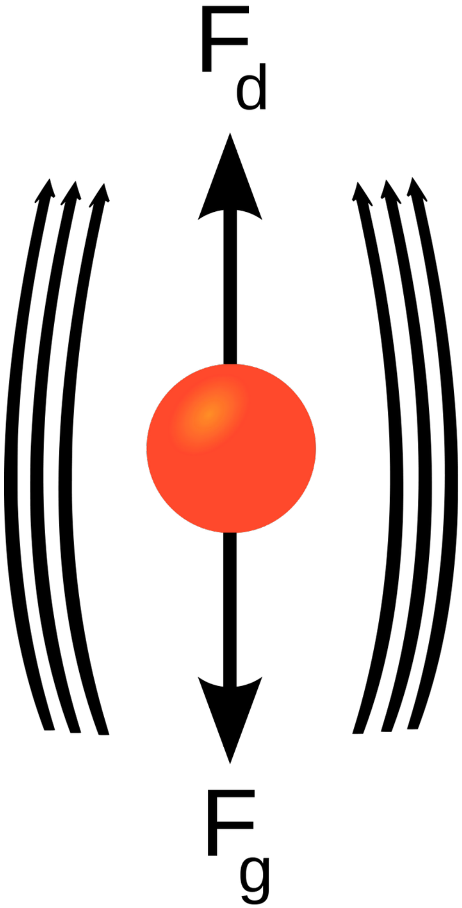
Atmospheric Particle Background

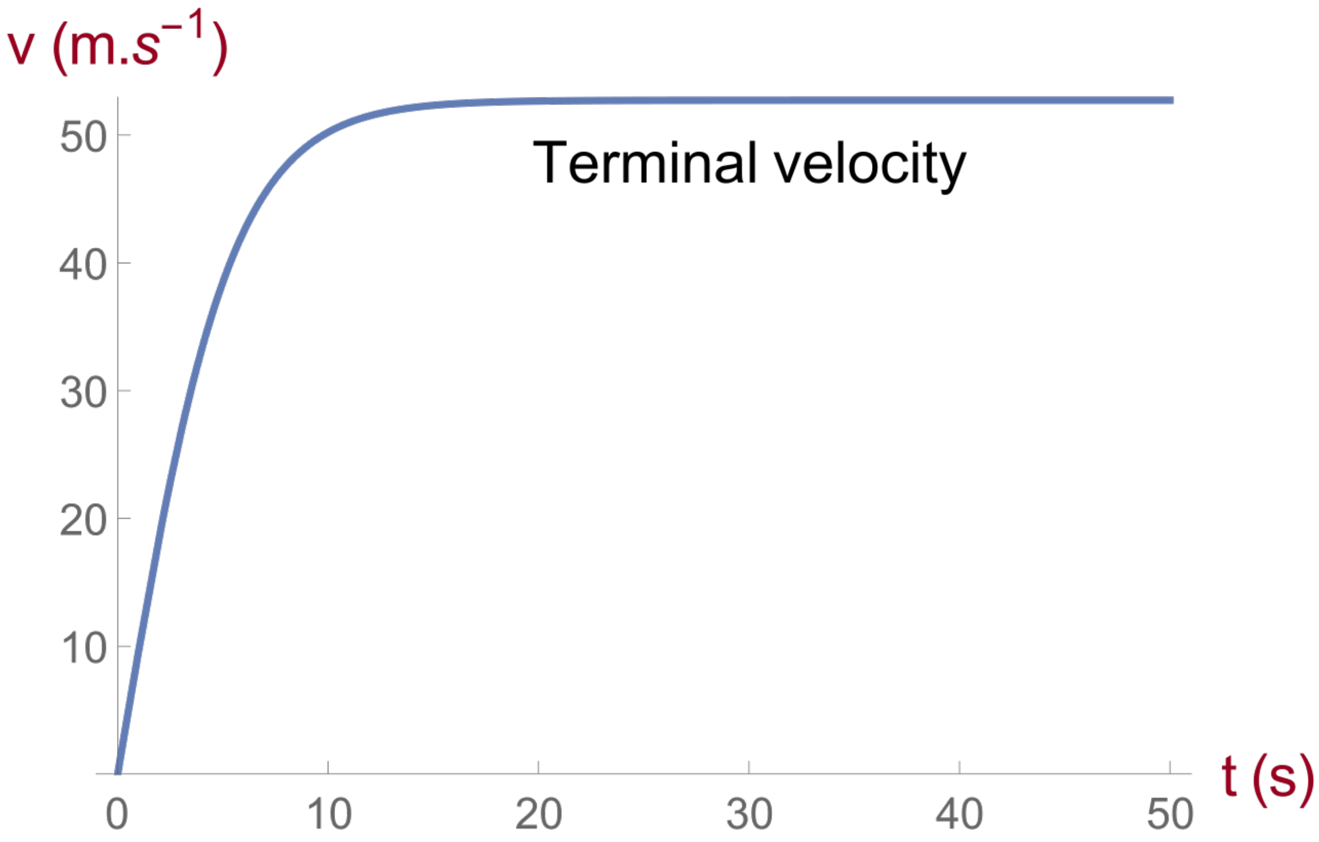
Atmosphere contains particles of all sizes.

- Suspended particles (aerosols) move with the average flow of gas molecules (atmospheric wind).
- Large particles (dust/drops/rain) have sufficient inertia to move independently of the wind.



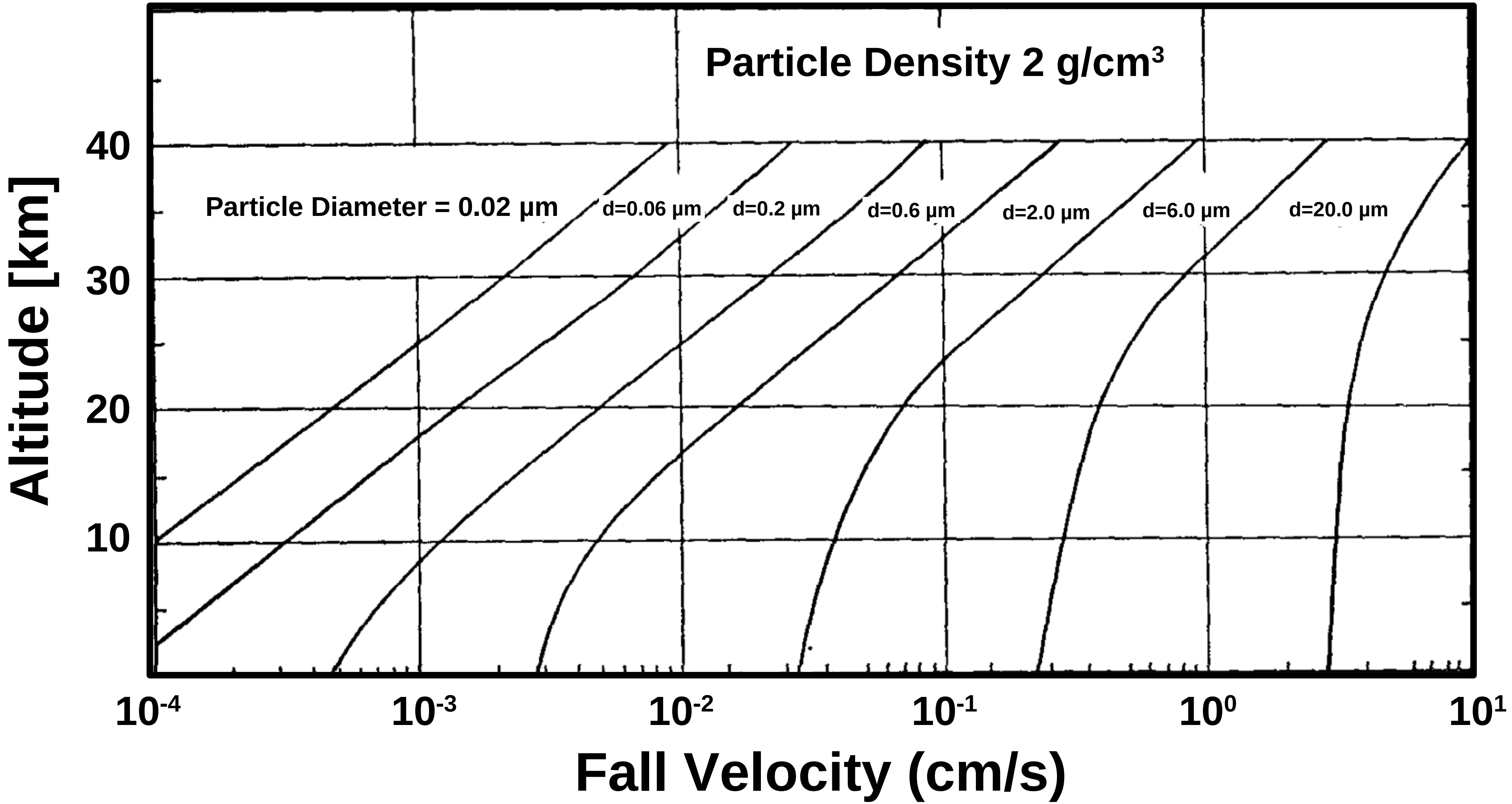
Terminal Velocity (Gravity = Drag Force)





Adapted from Wikipedia Terminal Velocity article.

Terminal Velocities of Aerosols



Adapted from Junge, Christian E., Charles W. Chagnon, and James E. Manson. "Stratospheric aerosols." Journal of Atmospheric Sciences 18, no. 1 (1961).

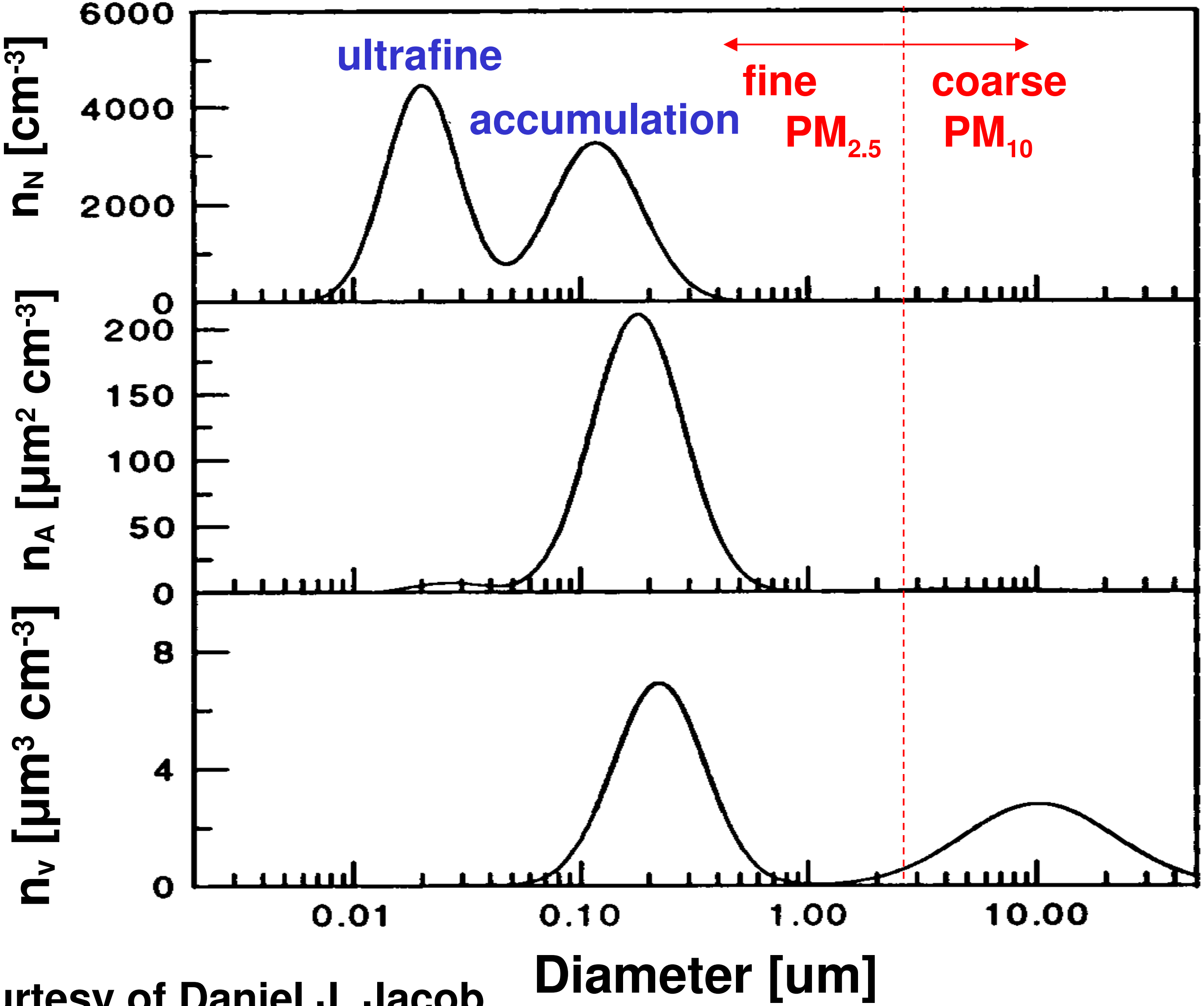
Aerosol Size Distribution

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

Lognormal Distribution

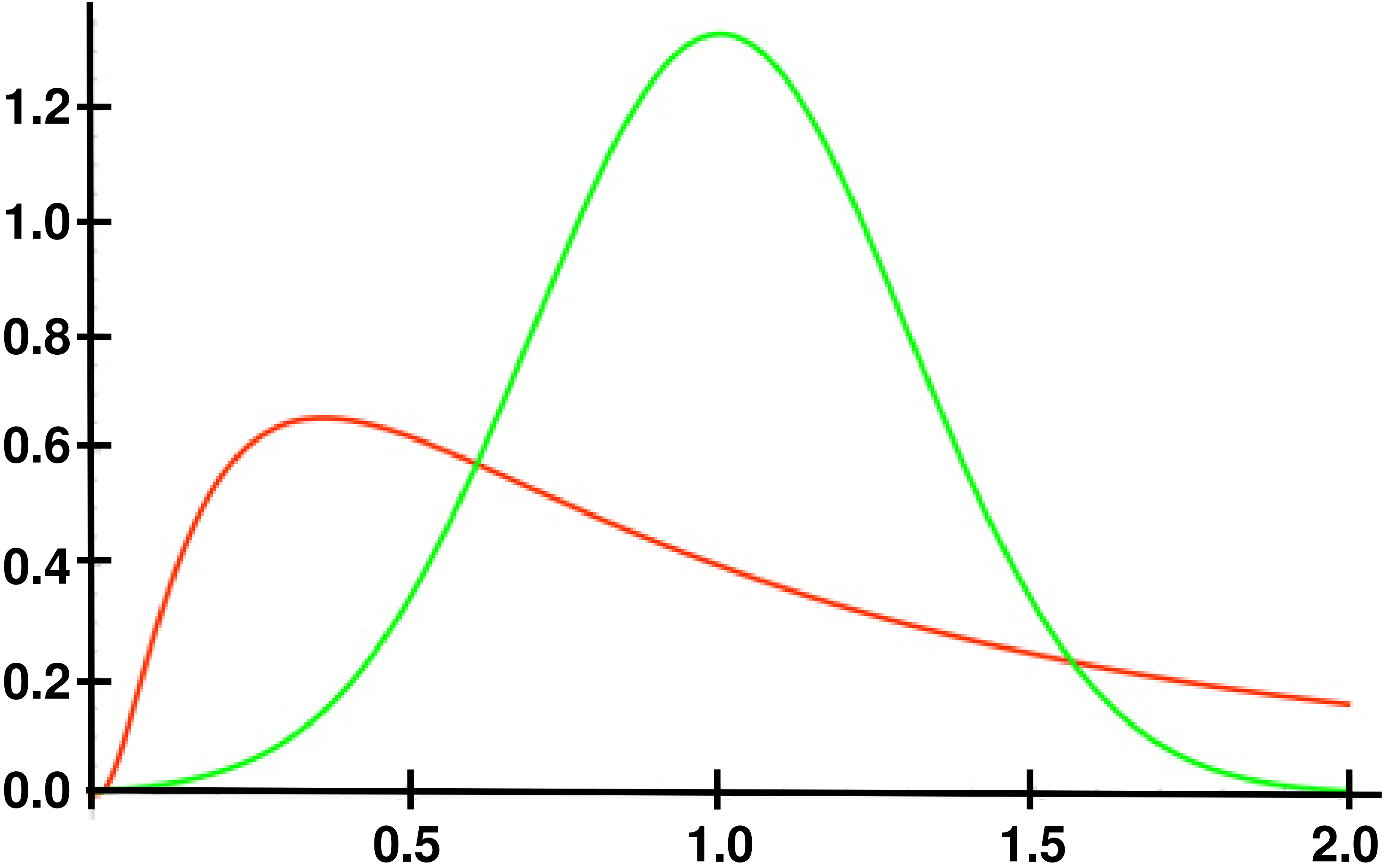
- Normal distribution has the characteristic bell shape, with maximum at the average ($\bar{u}$)

- 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.

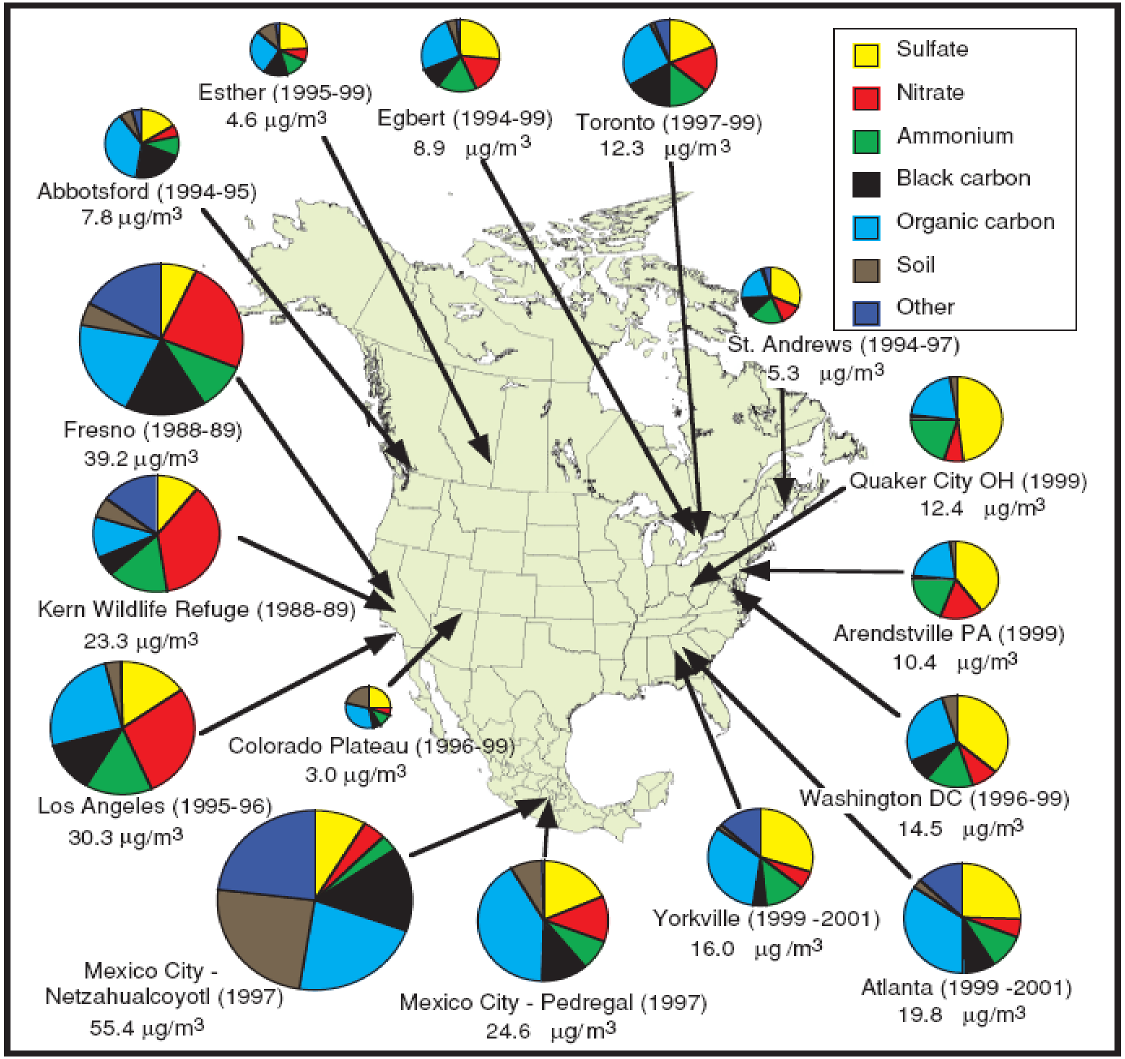
- **The log-normal distribution is a maximum entropy probability distribution.**

- 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

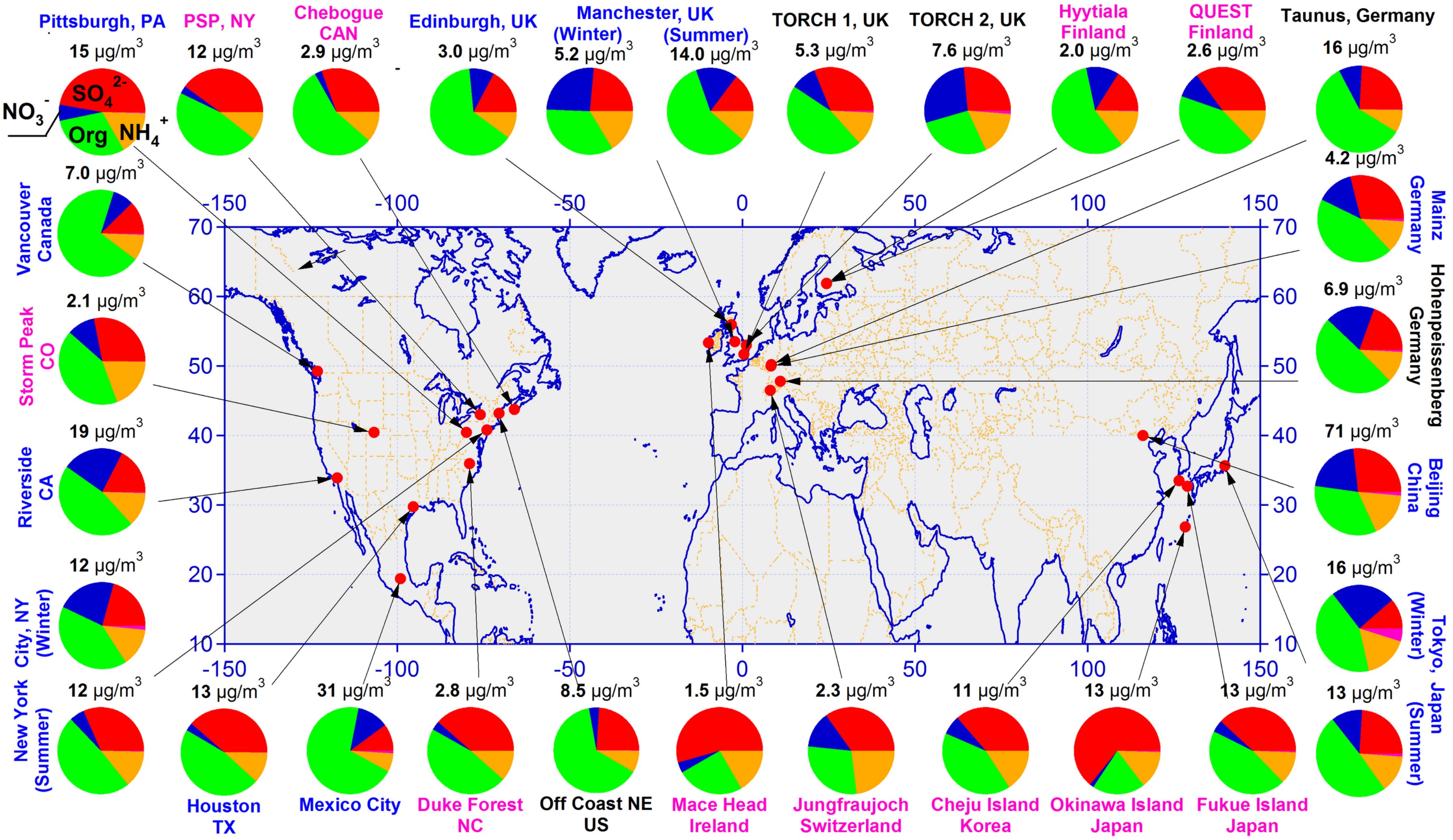


EPA revised the national air quality standards on December 14, 2012 to a annual mean $PM_{2.5}$ concentration of 12 μg m^{-3}. Old annual standard was 15 μg m^{-3}. The 24-hour fine particle standar is 35 μg m^{-3}. See http://www.epa.gov/pm/2012/decfsstandards.pdf.

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

Courtesy of Daniel J. Jacob

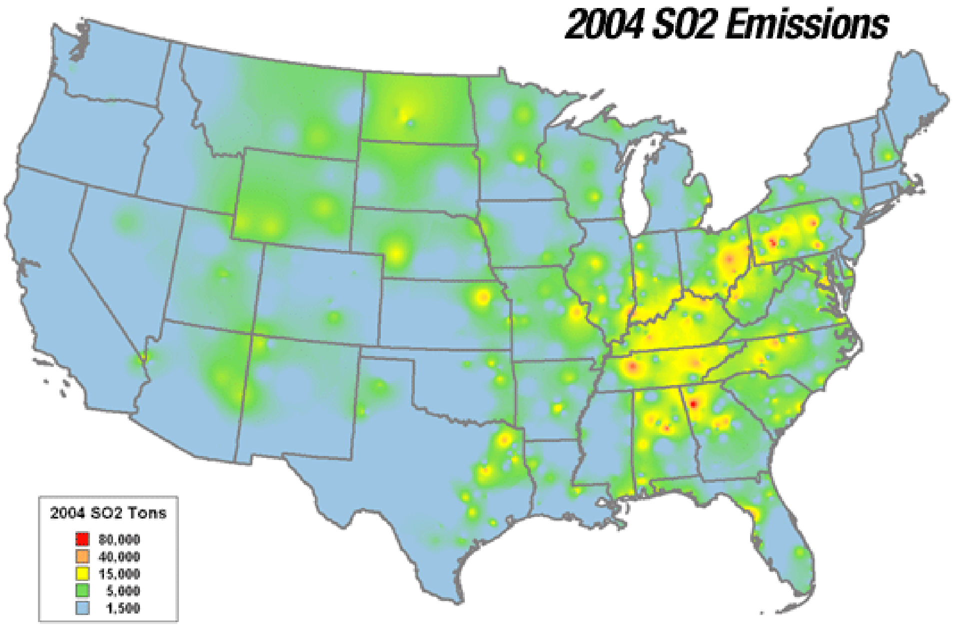
MEASUREMENTS OF FINE AEROSOL COMPOSITION



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

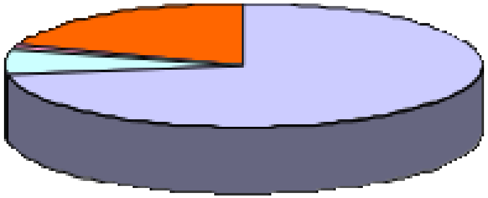
U.S. SO_2 EMISSIONS

Main source is coal combustion



Sulfur Emissions, Tg a^{-1}

GLOBAL



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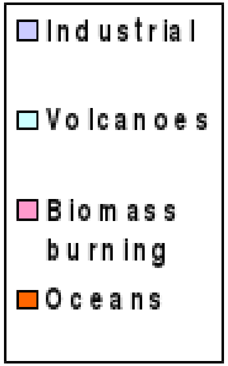
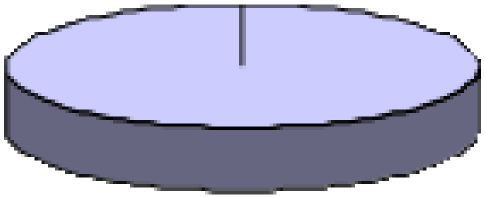


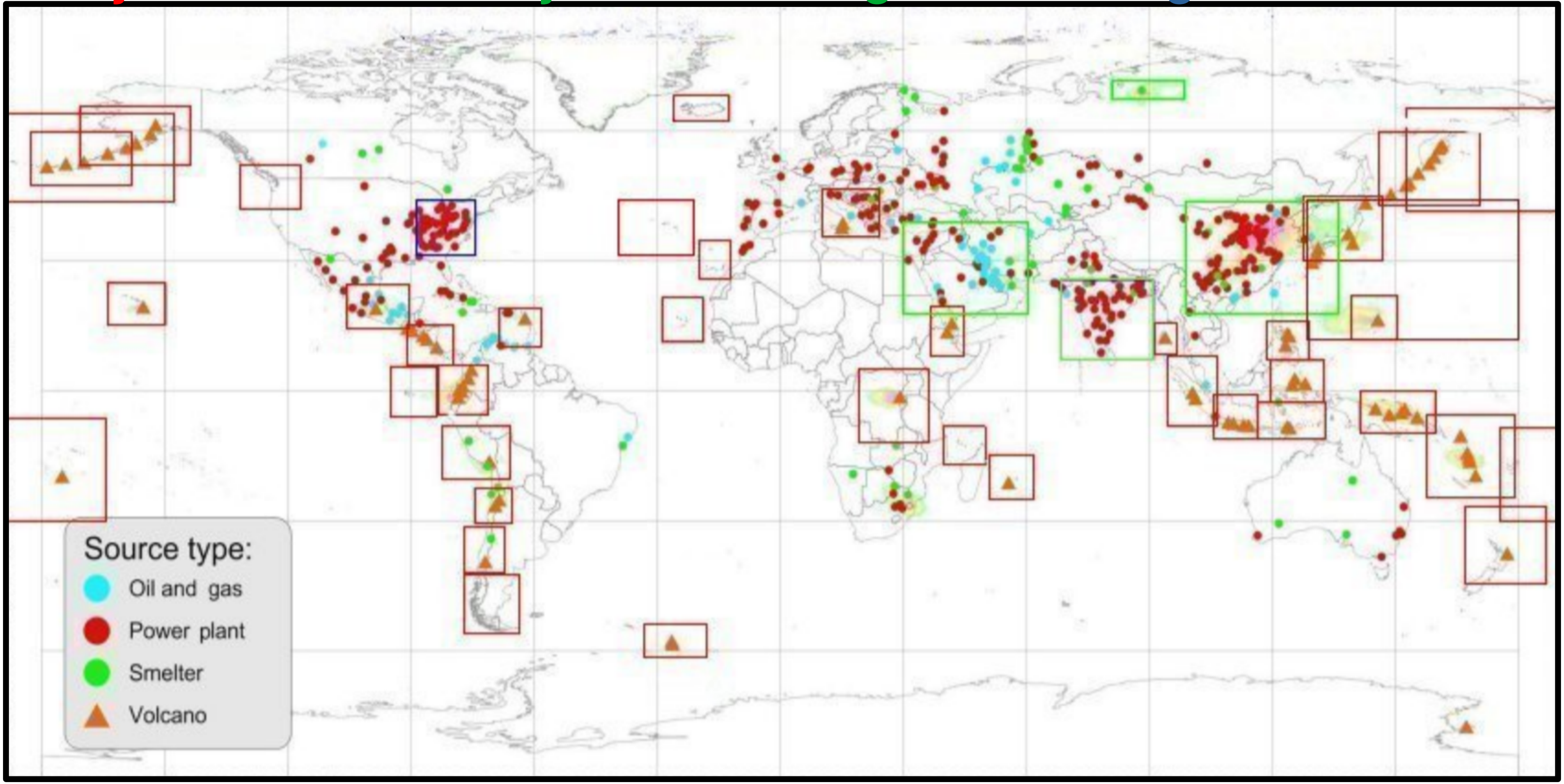
UNITED STATES



8.3

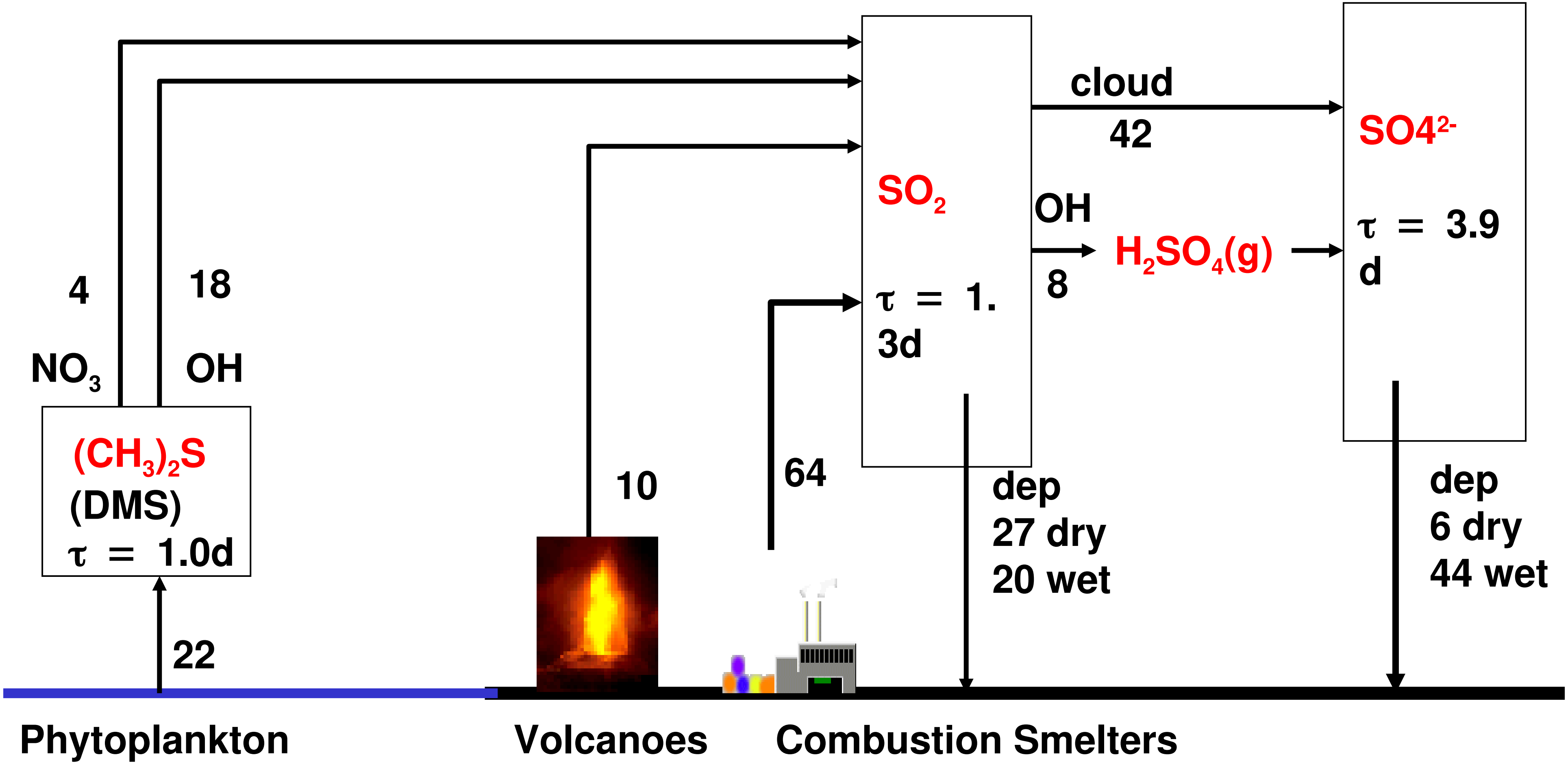
Courtesy of Daniel J. Jacob

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

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

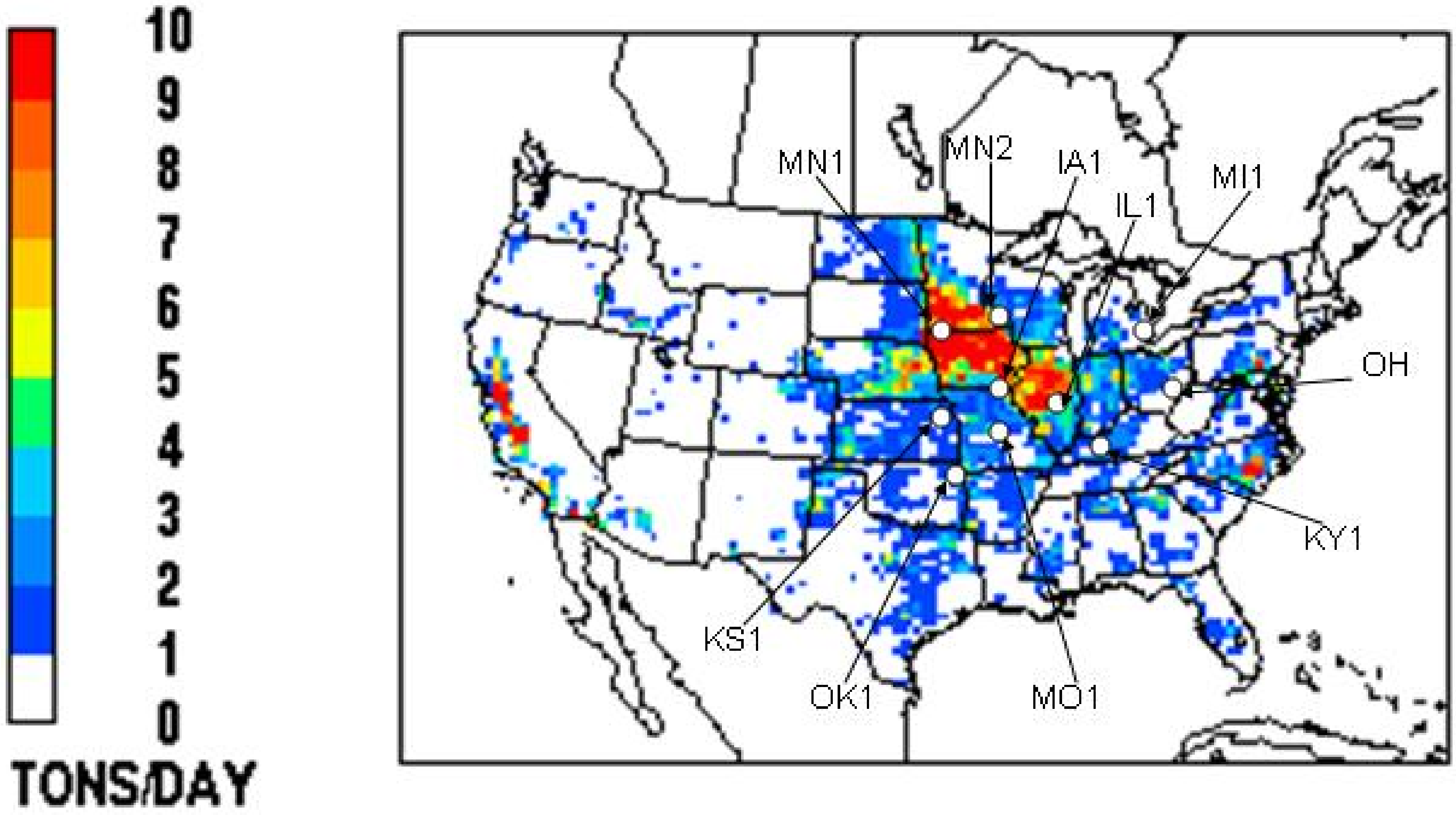
Nitrate is taken up by aerosol if (and only if) excess NH_3 is available after sulfate titration

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

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

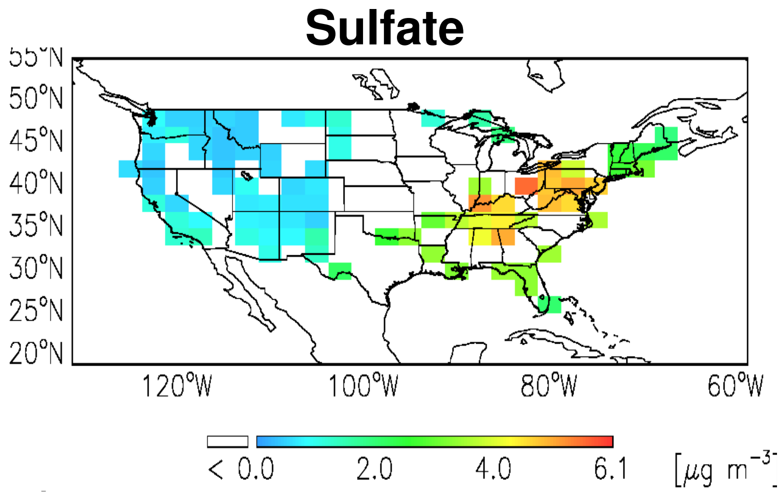
Condition	pH	Low RH	High RH
[S(VI)] > 2[N(-III)]	Acid	$H_2SO_4 \bullet nH_2O$, NH_4HSO_4, $(NH_4)_2SO_4$	(NH_4^+, H^+, SO_4^{2-}) solution
[S(VI)] ≤ 2[N(-III)]	Neutral	$(NH_4)_2SO_4$, NH_4NO_3	(NH_4^+, NO_3^-) solution

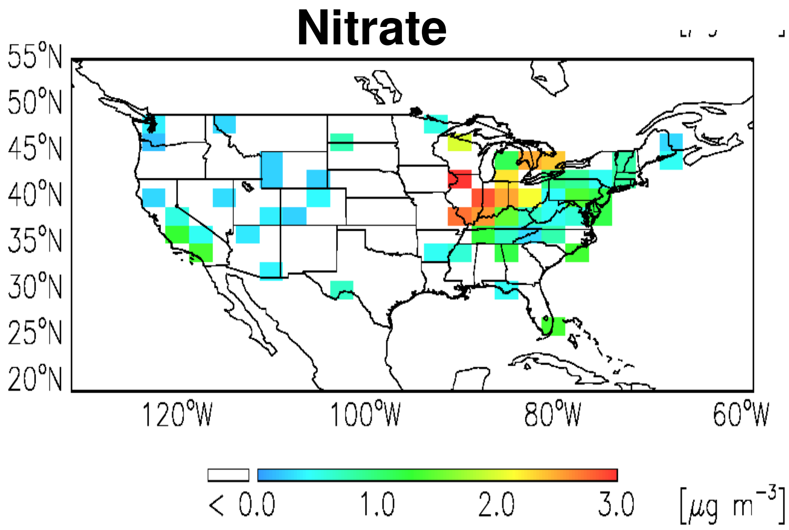
AMMONIA EMISSIONS

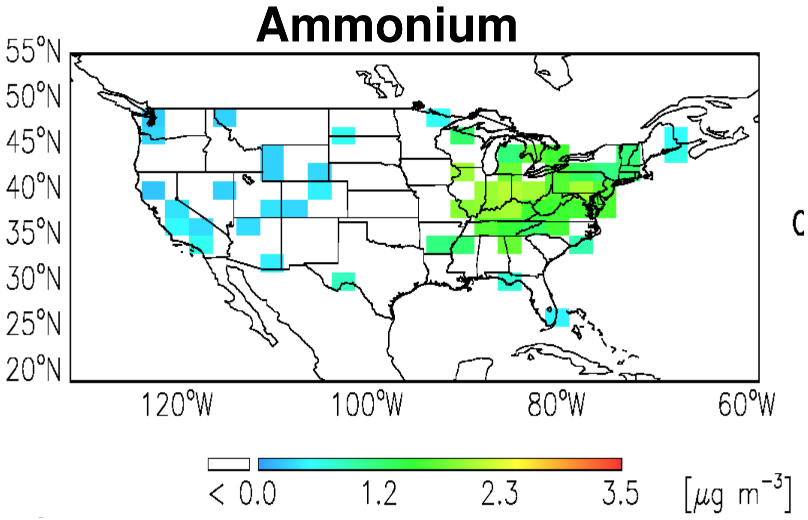


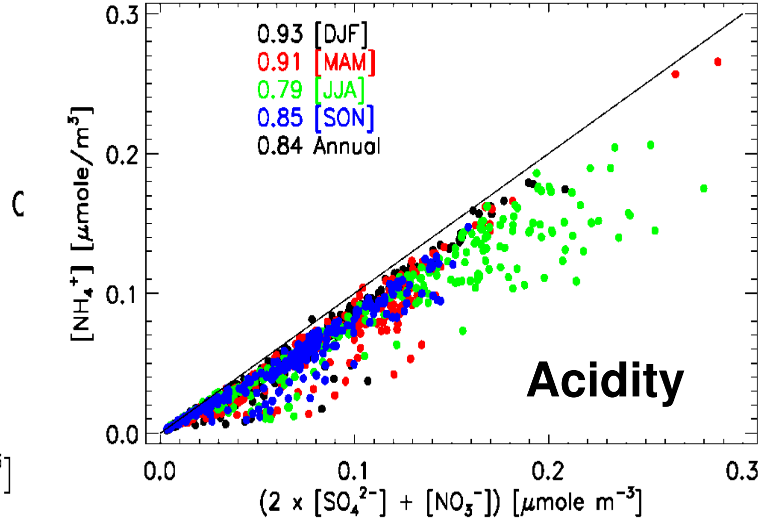
Ammonia,Tg N a^{-1}

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





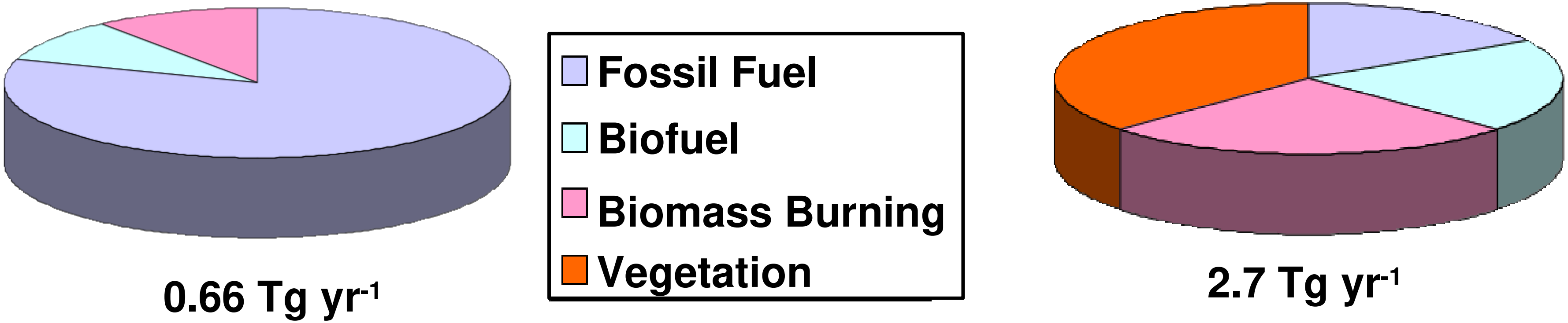




Courtesy of Daniel J. Jacob

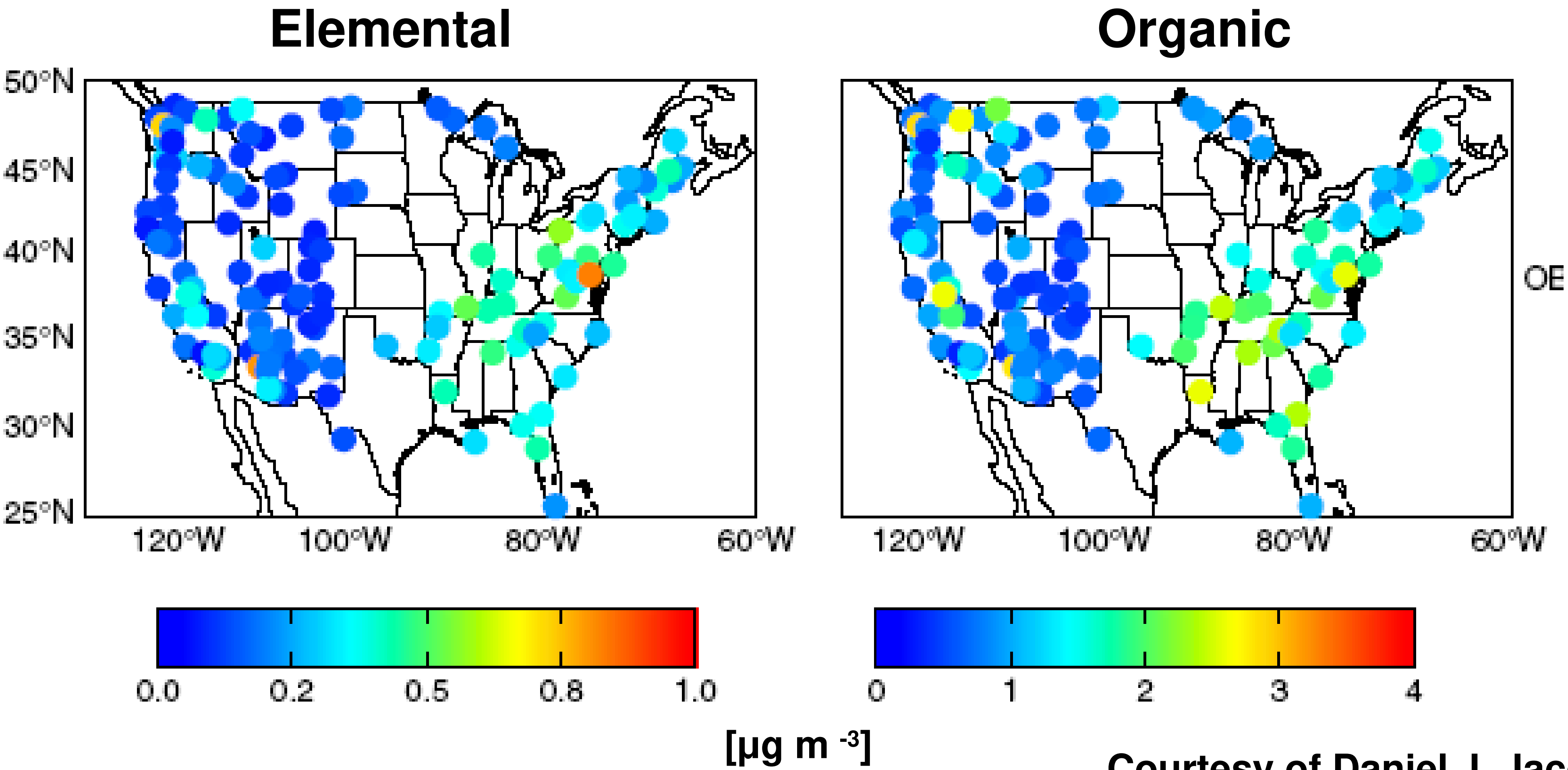
CARBONACEOUS AEROSOL SOURCES IN THE U.S.

ELEMENTAL CARBON | ORGANIC CARBON



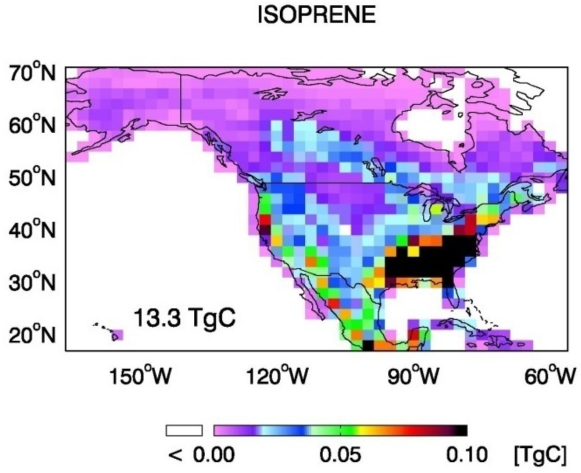
Courtesy of Daniel J. Jacob,
see http://image3.slideserve.com/6570266/carbonaceous-aerosol-sources-in-the-u-s-n.jpg

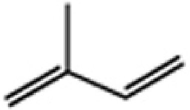
Annual Mean Concentrations (2001)



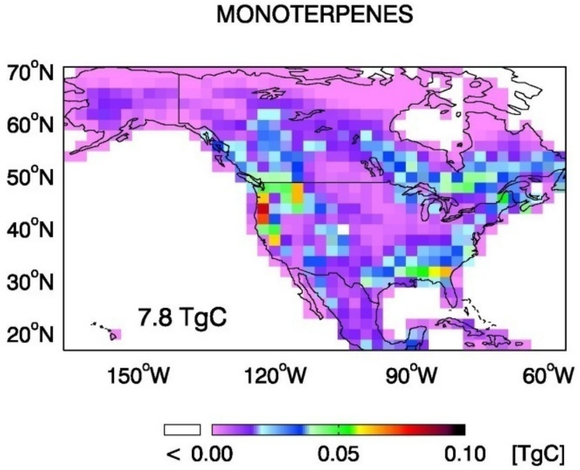
Courtesy of Daniel J. Jacob

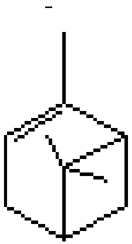
FORMATION OF ORGANIC AEROSOL FROM VEGETATIVE EMISSIONS





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

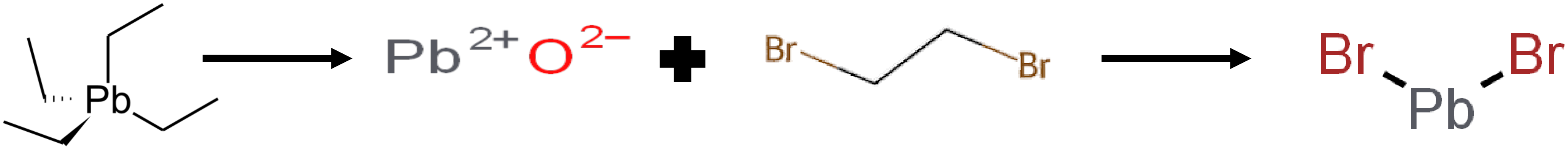
Courtesy of Daniel J. Jacob

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

Lead Aerosols from Aviation Fuel

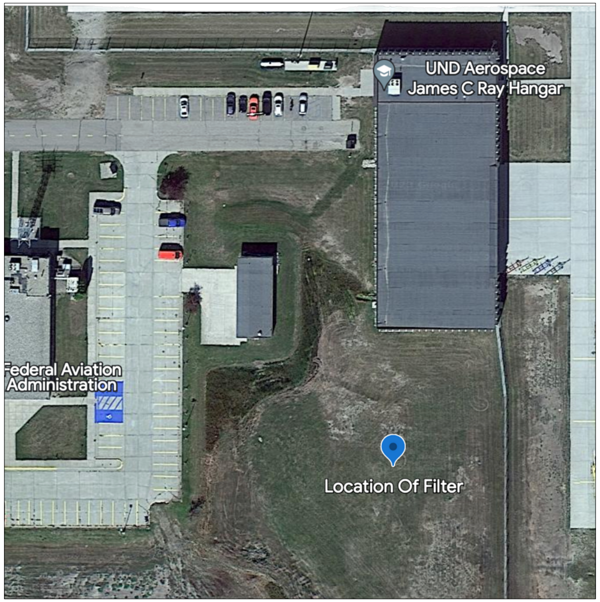


Tetra-ethyl-Lead (TEL) **Lead Oxide** **Ethylene Dibromide** **Lead (II) Bromide**

- As LL100 fuel burns, TEL naturally degrades to lead oxide which increases the octane rating.
- Deposits are formed due to lead oxides high melting point; these deposits are electrically conductive and is corrosive.
- To prevent deposits forming, ethylene dibromide is used to react with lead oxide to form lead bromide which is a gas at lower temperature to ensure that lead will be fully exhausted.

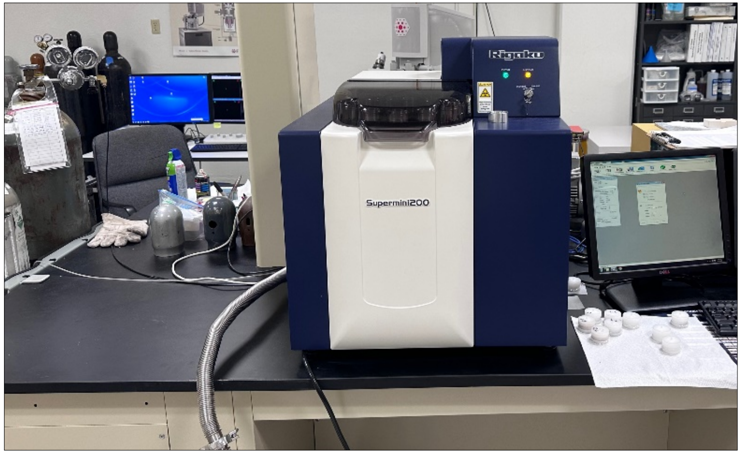
Lead Aerosols Transport

- Exhausted gas cools to the solid phase in the atmosphere where the lead exists/evolves into different leaded compounds and ions.
- Leaded compounds travel long distances in the air before going into the soil and possibly groundwater.
- Exposure to lead causes disruption of tightly regulated processes due to lead stronger a binding affinity compared to other metal ions (Ca2+, Mg, Zn, Fe, et…), which are known to be involved within biological systems.



Lead Aerosols Sampling

- UND Aerospace general aviation airport was chosen for the location of high-volume sampler. Daily and weekly samples were collected.
- 8” x 10” glass fiber filter daily and weekly samples were collected. Glass fiber samples were pre and post weighed. X-Ray Fluorescence (XRF) was used to analyze the elemental composition of each filter sample.



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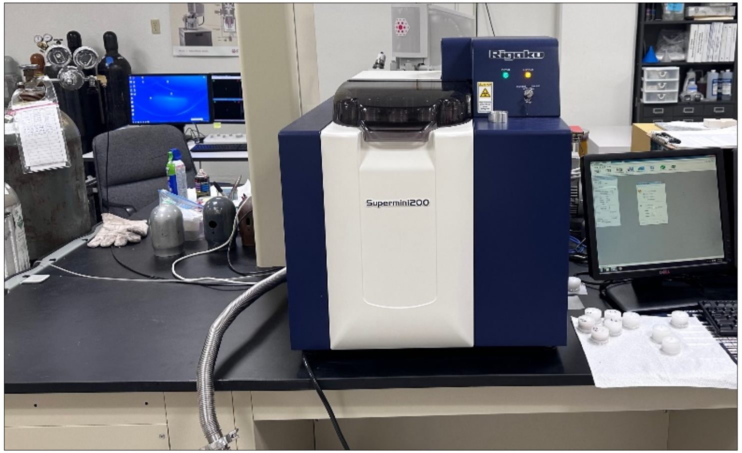
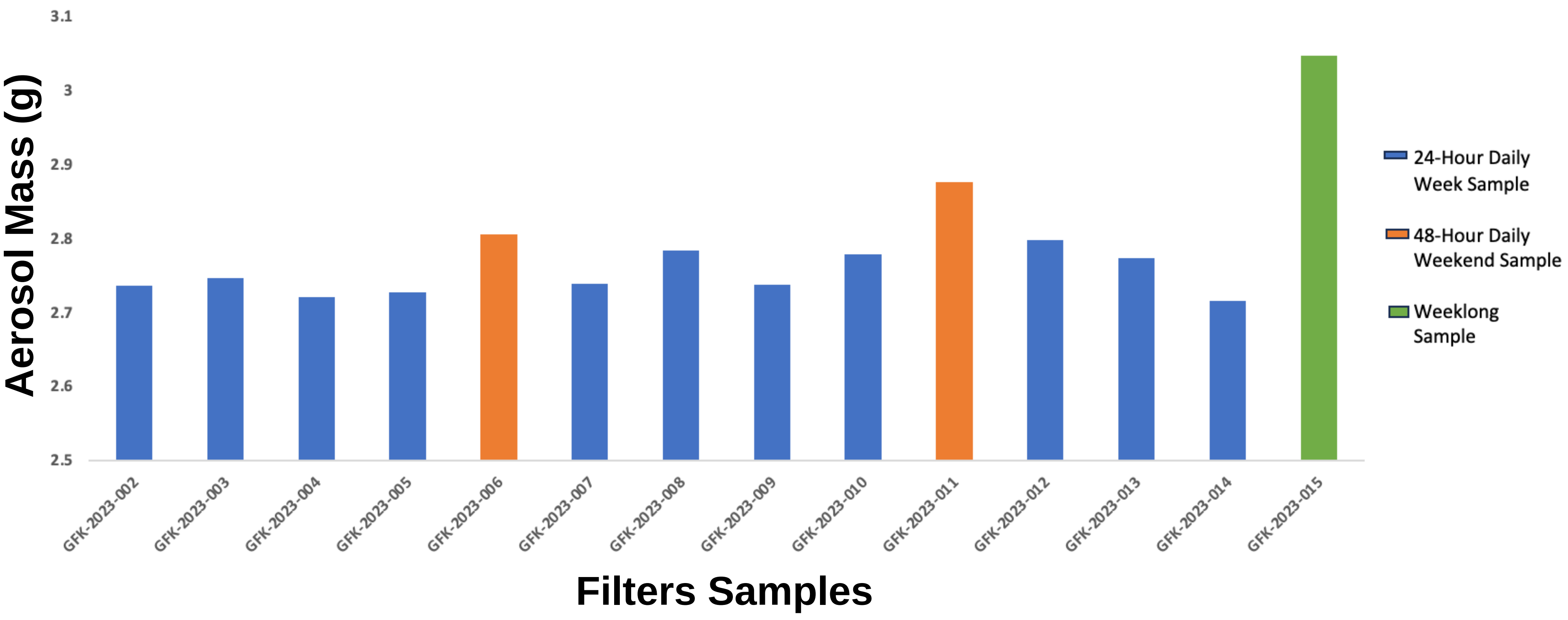
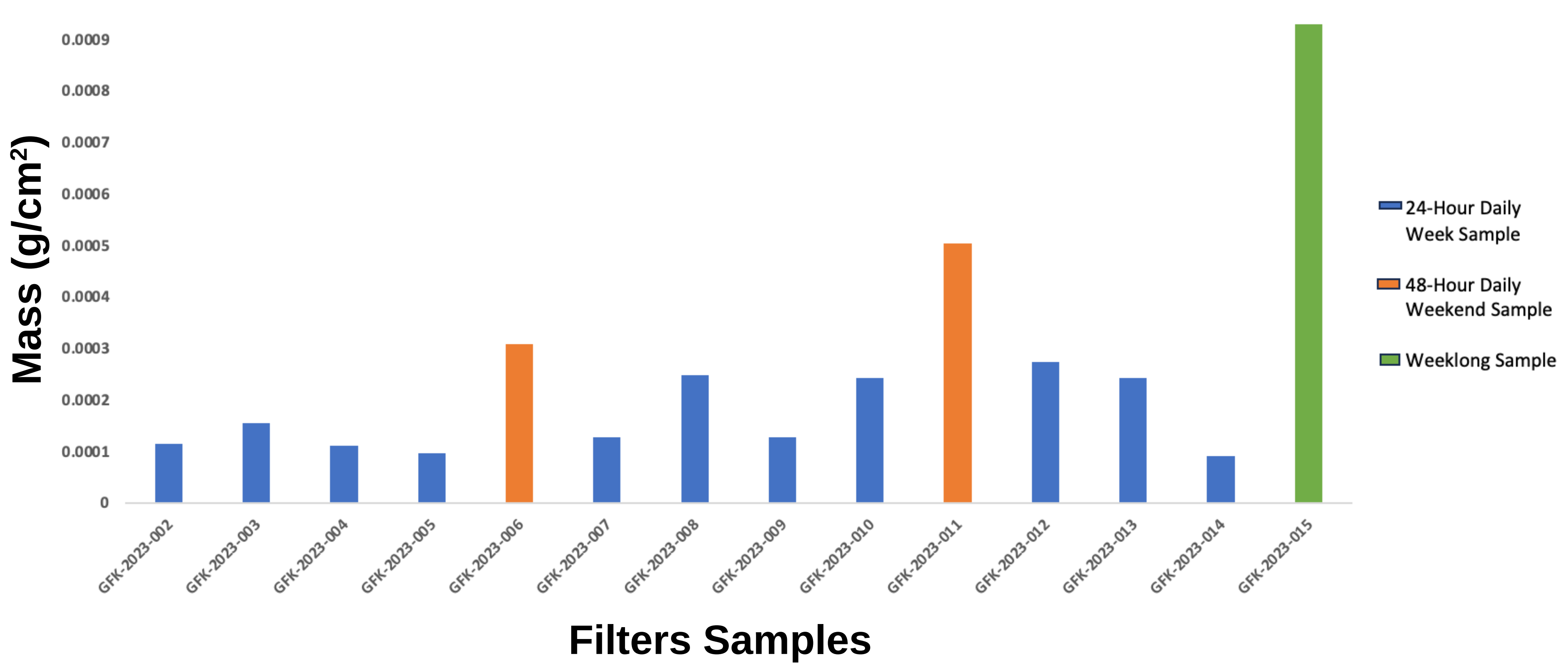


Collected Aerosol Mass on Particle Filter



Aerosol Mass on Particle Filter



Lead Aerosols GFK Conclusions

- Detected lead on daily samples, but detection issues.
- Based off results and discussion with XRF manufacture. Lead sulfide experiment was performed to determine if XRF was effective in detecting lead. Test was successful.
- Based off low concentrations of lead in daily airport samples and lead sulfide experiment. Decided to start running week-long samples beginning on the transition period (June 23rd).