Acid Rain

READING: Chapter 13 of text;

- Gas-Liquid Partitioning and pH of "natural" rain
- US Acid Rain Problem: Sulfur and NO_x oxidation
- Trends in Emissions and Deposition

Guiding Questions:

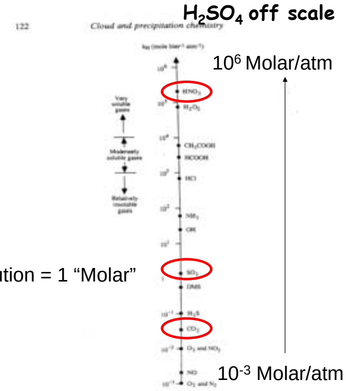
What is acid rain?

What chemistry explains the low pH rain in the NE US?

How do the natural sources of acidity compare to anthropogenic ones?

Henry's Law Constants

H_2SO_4 off scale



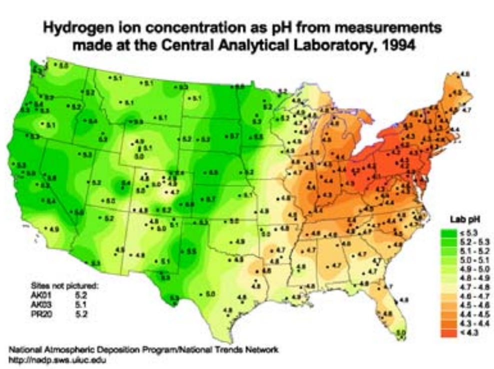
10^6 Molar/atm

1 mole/liter of solution = 1 "Molar"

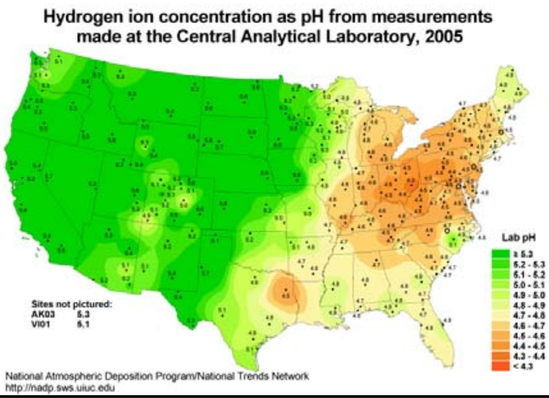
10^{-3} Molar/atm

From Hobbs *IAC*

pH of Precipitation Over U.S.



pH of Precipitation Over U.S.

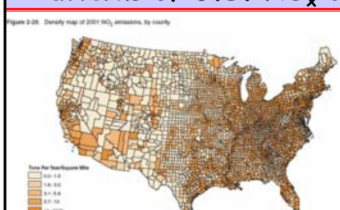


Chemical Composition of Precipitation

Table 13-1 Median Concentrations of Ions (μeq l^{-1}) in Precipitation at Two Typical Sites in the United States

Ion	*Rural New York State*	*Southwest Minnesota*
→ SO_4^{2-}	45	46
NO_3^-	25	24
Cl^-	4	4
HCO_3^-	0.1	10
Sum anions	74	84
→ H^+ (pH)	46 (4.34)	0.5 (6.31)
NH_4^+	8.3	38
Ca^{2+}	7	29
Mg^{2+}	1.9	6
K^+	0.4	2.0
Na^+	5	14
Sum cations	68	89

Patterns of U.S. NO_x and SO_2 Emissions



NO_x Emissions 2001

SO_2 Emissions 2001

SO_2 Oxidation in Cloud by H_2O_2

Henry's Law: $SO_{2(g)} \rightleftharpoons H_2OSO_{2\,(aq)}$

Aqueous acid dissociation: $H_2OSO_2 \rightleftharpoons H^+ + HSO_3^-$

Henry's Law: $H_2O_{2(g)} \rightleftharpoons H_2O_{2(aq)}$

Aqueous reaction: $HSO_3^- + H_2O_2 + H^+ \longrightarrow 2H^+ + SO_4^{2-} + H_2O$

What happens in remote regions where H_2O_2 is low?

SO_2 Oxidation in Cloud by Ozone

Henry's Law: $SO_{2(g)} \rightleftharpoons H_2OSO_{2\,(aq)}$

Aqueous acid dissociation: $H_2OSO_2 \rightleftharpoons H^+ + HSO_3^-$

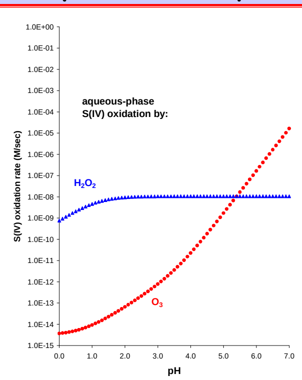
Aqueous acid dissociation: $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

Henry's Law: $O_{3(g)} \rightleftharpoons O_{3(aq)}$

Aqueous reaction: $O_3 + SO_3^{2-} \longrightarrow SO_4^{2-} + O_2$

Only important in remote regions or when cloud water pH > 6

pH dependence of aqueous-phase SO_2 oxidation



SO_2 = 0.2 ppb

H_2O_2 = 0.6 ppb

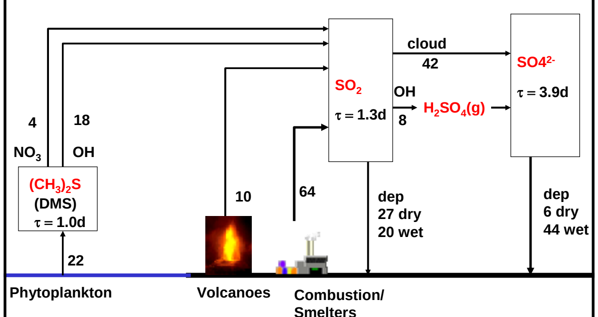
O_3 = 46 ppb

Question

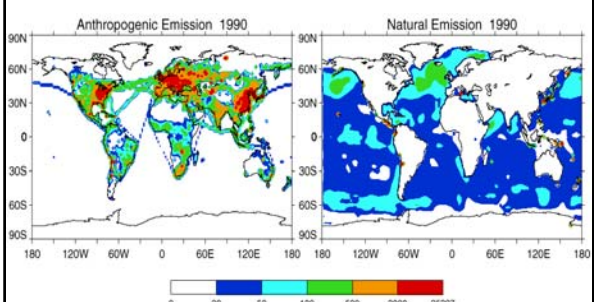
1. How is it that the O_3 oxidation mechanism actually increases the acidity of precipitation?

Global Sulfur Budget

Rates in Tg S yr^{-1}

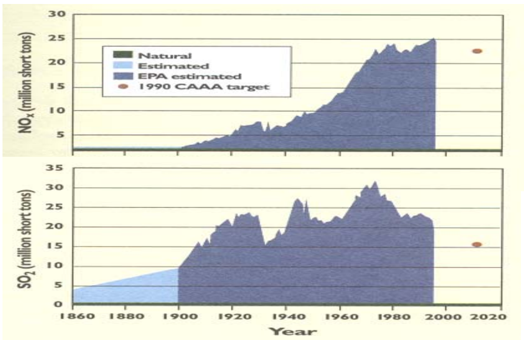


Global Sulfur Emission Patterns

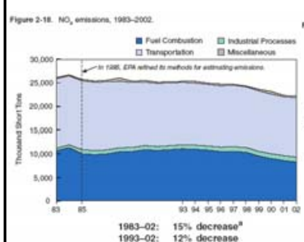


Chin et al. [2000]

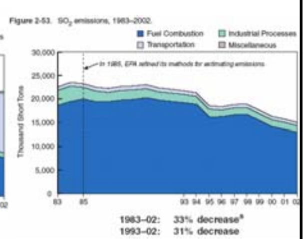
Trends in U.S. NO_x and SO_2 Emissions



Trends in U.S. NO_x and SO_2 Emissions

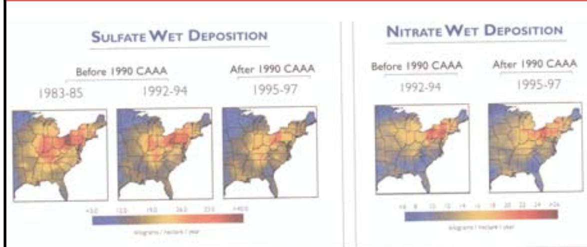


U.S. NO_x Emission Trends



U.S. SO_2 Emission Trends

Sulfate and Nitrate Wet Deposition Trends



Low Acid-Neutralizing Capacity (in black)

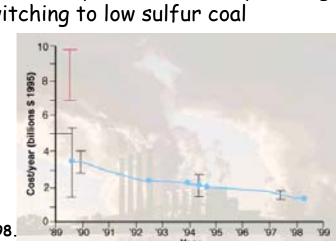
Cost-effectiveness of Acid Rain Program

- Costs = $3 billion/year.
- Benefits = $122 billion/year [PM→ human health; visibility; ecosystems]
- 40-to-1 benefit/cost ratio

Costs of 1990 Clean air act amendment

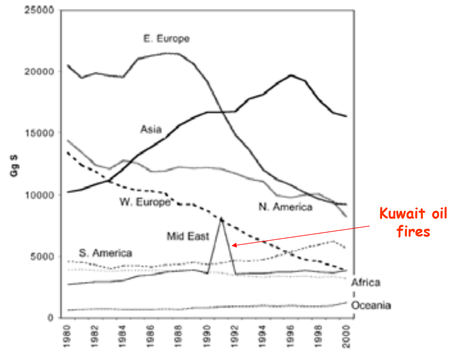
- Initially estimated to be ~$10 billion /year
- Actual costs ~$1-2 billion/year

→ cap and trade is more economical than strict regulations. Scrubbers turned out to be cheaper than expected and unexpected gains from switching to low sulfur coal



Kerr, Science, 1998.

Recent Trends in Sulfur Emissions (1980-2000)



Stern, Chemosphere 58 (2005)

Acid Rain Overview

Guiding Questions:

What is acid rain?

Precipitation (rain or fog) with a pH < ~ 5.5

What chemistry explains the low pH rain in the NE US?

Oxidation of Sulfur (SO_2) to H_2SO_4 primarily by in-cloud aqueous chemistry

Also, NO_2 + OH → HNO_3

How do the natural sources of acidity compare to anthropogenic ones?

Anthropogenic sources of sulfur and NO_x currently dominate the natural sources

Presentation Guidelines/Tips

1. **Aim for a 10 minute presentation (allowing 2 minutes for questions)**
   a. This isn't a whole lot of time—be judicious
2. **Typical presentation contains:**
   a. *Title slide*

   b. *Introduction:* define the problem and provide a "roadmap" or outline for your presentation

   c. *Motivation:* answer "why should we listen?"

   d. *Content:* What you did/learned and how does it relate to the course topics?

   e. *Summary and Conclusions:* What would be next?

Presentation Guidelines/Tips

3. Try to make slides clear and concise

a. This is 24 pnt font – smaller than this becomes hard to read

b. 1 or 2 main points per slide

c. Less text is better—more diagrams and figures

4. Speak loudly and clearly

a. notecards are OK but try not to read from a script.

Presentation Guidelines/Tips

5. Practice your presentation!

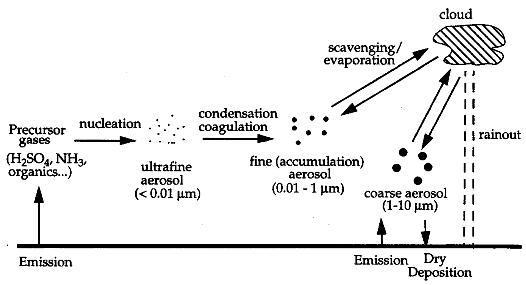
6. I will take a quick look if you want

Chapter 8: Atmospheric Aerosols

- What are the main sources and sinks of atmospheric aerosols?
- What is their chemical composition?
- Thermodynamics of aerosols
- Heterogeneous chemistry
- How big are they and why does size matter?
- Why do we care about atmospheric aerosols?
  - Health effects (pollution)
  - Visibility
  - Climate

Atmospheric Aerosols

Aerosol: dispersed condensed phases suspended in a gas
Size range: 0.001 mm (molecular cluster) to 100 mm (small raindrop)



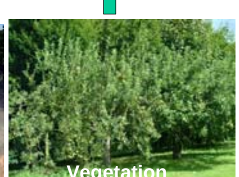
Environmental importance: health (respiration), visibility, climate, cloud formation, heterogeneous reactions, long-range transport of nutrients…

Urban Aerosol

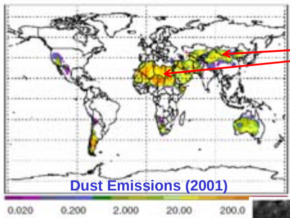
Rural and Remote Continental Aerosol

SOA

VOCs



Dust: Naturally Emitted Aerosol



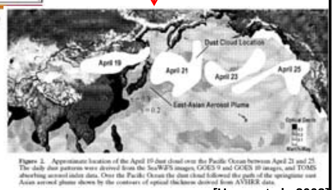
g m^{-2} y^{-1}

Fairlie et al. [2007]

Sources: arid / semi-arid regions

Emission in both fine and coarse mode, depends on surface properties and wind speed.

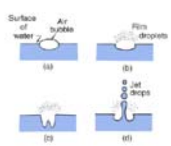
Resulting lifetime ~weeks



[Husar et al., 2002]

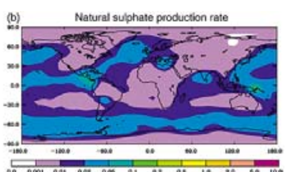
Marine Aerosols

Sea-salt aerosols

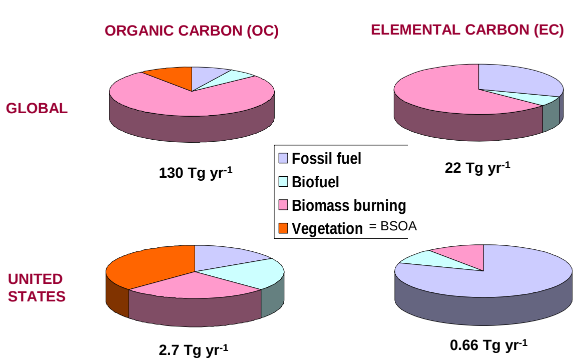


Emissions of dimethylsulfide (DMS) from marine phytoplankton:

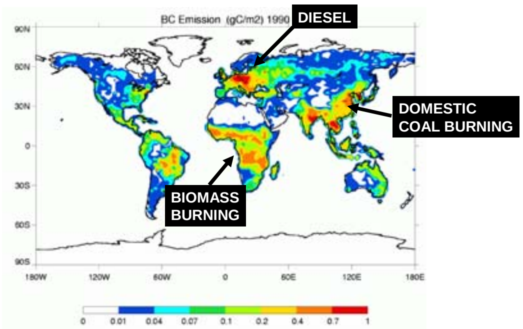
DMS →→ SO_2 →→ SO_4^{2-}



Carbonaceous Aerosol Sources



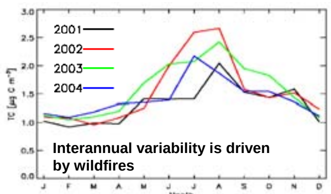
Black Carbon Emissions

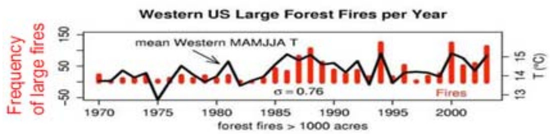


Wildfires

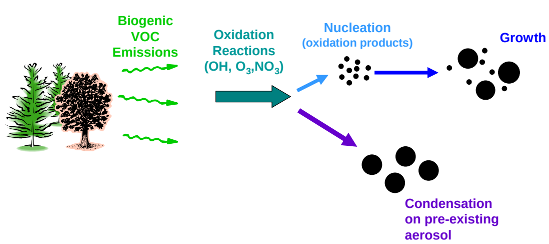
S. California fire plumes, Oct. 25 2004

Total carbonaceous (TC) aerosol averaged over U.S. IMPROVE sites



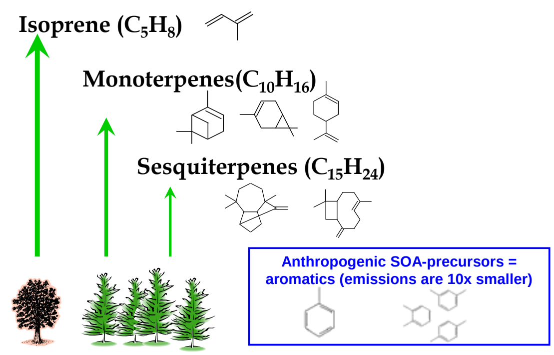


Secondary Organic Aerosol Production

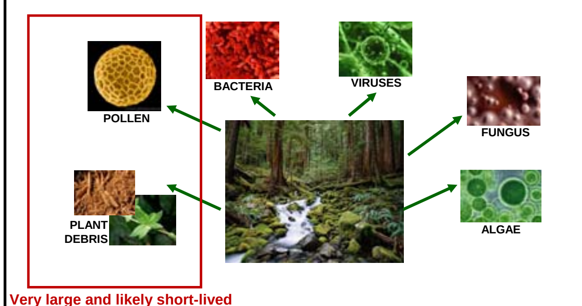


Over 500 reactions to describe the formation of SOA precursors, ozone, and other photochemical pollutants [Griffin et al., 2002; Griffin et al., 2005; Chen and Griffin, 2005]

Biogenic Hydrocarbons



Primary Biological Aerosol Particles (PBAP)

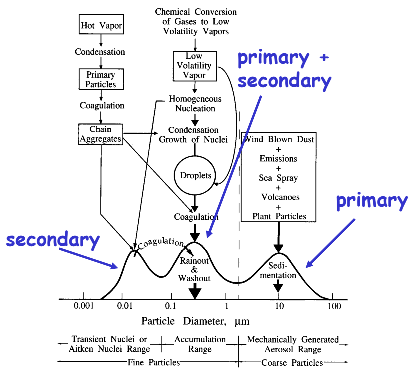


These particles have not traditionally been considered part of the OA budget, but this has been revised in recent years.
Not much is known about emissions, processing, climate effects.

Question

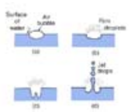
1. If the only form of PBAP (biological organic aerosol) emitted into the atmosphere were pollen, would we consider it important for the global aerosol budget? Why or why not?

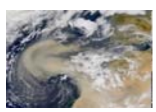
Common Modes of Atmospheric Aerosol



Coarse Mode Aerosol

$10\ \mu m < D_p < 10\ \mu m$





- Particles are generated by mechanical processes such as wind.
- Particles less than 1 μm are difficult to generate mechanically because they have large area-to volume ratios and hence their surface tension per unit aerosol volume is high.
- Particles larger than 10 μm are not easily lifted by the wind and have short atmospheric lifetimes because of their large sedimentation.

Gravitational Settling

Diam. (μm)	Time to Fall 1 km
0.02	228 y
0.1	36 y
1.0	328 d
10	3.6 d
100	1.1 h
1000	4 m
5000	1.8 m

from M.Z. Jacobson "Atmospheric Pollution"

Terminal settling velocity:

$$v_t \propto \frac{D_p^2}{\mu}$$

D_p = diameter of particle

μ = viscosity of air

Only particles smaller than 10 μm reach the global atmosphere

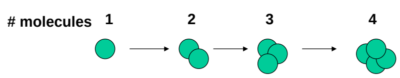
Nuclei Mode Aerosol

$D_p < 0.1\ \mu m$

- Generally form through processes of clustering (nucleation) of gas particles to form a new aerosol particle (a.k.a. gas-to-particle conversion).
- A common example is binary nucleation of sulfuric acid and water.
- Grow through condensation of low vapor pressure gases and coagulation with other fine mode particles.

Nuclei Mode Aerosol

Gas molecules: $10^{-4} – 10^{-3}\ \mu m$



Nucleation (clustering) of gas molecules to form a new aerosol particle = *secondary* aerosol particle

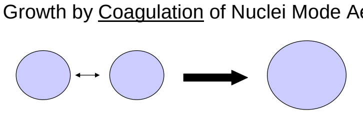
"gas-to-particle conversion"

Key example is binary nucleation by H_2SO_4(g) and H_2O(g)

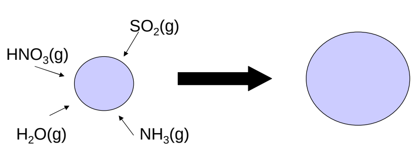
Where $SO_2 + OH (+ O_2 + H_2O) \rightarrow H_2SO_4(g) (+ HO_2)$

Growth of Nuclei Mode Aerosol

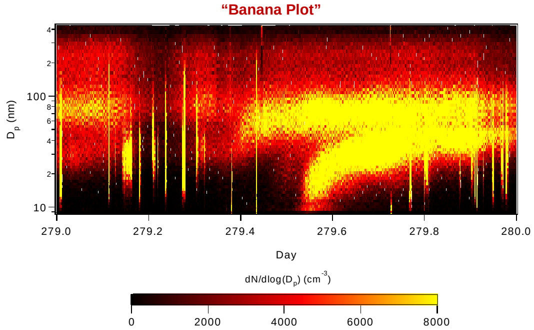
Growth by Coagulation of Nuclei Mode Aerosols



Growth by Condensation of Gases



Fine Particle Growth at Blodgett Forest



[Lunden et al., 2006]

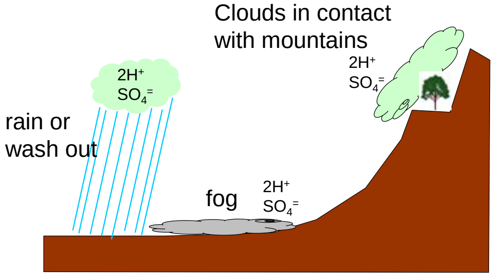
Accumulation Mode Aerosol

0.1 μm < D_p < 1 μm

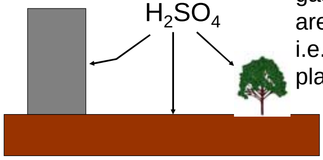
- Form from condensational and coagulational growth of nuclei mode aerosol, and direct emission from combustion sources.
- Growth beyond 1 mm is slow because the particles are by then too large to grow rapidly by condensation of gases, and because the slower random motion of larger particles reduces their coagulation rate.
- These particles are also too small to sediment at a particular rate, and are lost mainly from the atmosphere through wet deposition.
- Hence, they tend to accumulate in this size range.

Wet Deposition

Acids and other gases are taken up into water droplets, which are then deposited



Dry Deposition



Acids (and other gas molecules) are taken up by surfaces, i.e. ground, buildings, plants (also respiration)

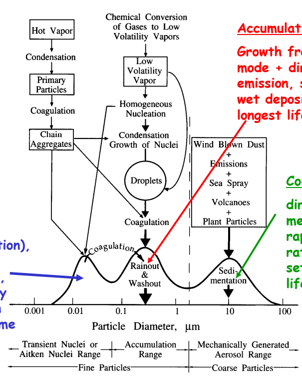
Factors that govern dry deposition rates:

→Level of atmospheric turbulence

→Chemical properties of depositing species

→Nature of surface itself

Common Modes of Atmospheric Aerosol



Accumulation mode:

Growth from nucleation mode + direct emission, small dry and wet deposition rates, longest lifetime (days)

Coarse mode:

direct emission from mechanical processes, rapid dry deposition rates (gravitational settling), short lifetime (hours)

Nucleation mode:

Gas-to-particle conversion (nucleation), rapid growth to accumulation mode, relatively rapid dry and wet deposition rates, short lifetime (hours)

Why Size Matters

(1) Toxicity

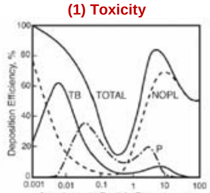
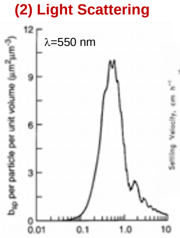


Figure 2.3. Particle deposition in the major regions of the human respiratory tract during normal respiration corrected for size dependent inhalability. (NOPL, naso-oro-pharyngo-laryngea) region; TB, tracheo-bronchial region; and P, pulmonary region). Developed from the National Council on Radiation Protection Model (NCRP, 1997) by Phalen (2002).

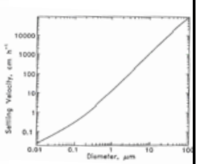
[NARSTO, 2003]

(2) Light Scattering



[Finlayson-Pitts & Pitts]

(3) Particle Lifetime



[Seinfeld & Pandis]

(4) Surface Reactions: smaller particles have greater relative surface area

Adverse Health Effects of PM

Epidemiological studies show that PM:
- affects cardiorespiratory system
- can cause cancer
- impairs lung development

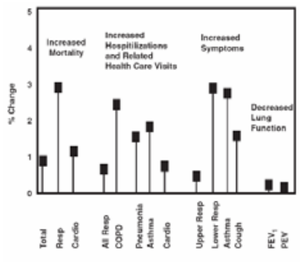
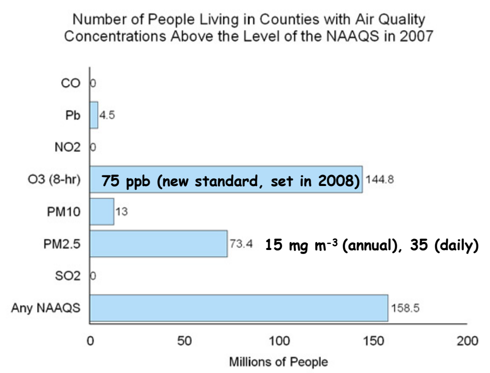


Figure 2.5. Stylized summary of acute exposure studies, percent change in health endpoint per 10 μg/m³ increase in PM... (Adapted from Pope

[NARSTO, 2003]

The EPA estimates that over 65,000 premature deaths per year can be attributed to PM. More deadly than car accidents!

Air Pollution in the U.S.

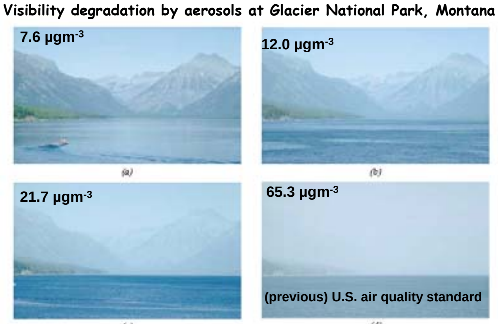


$PM_{2.5}$ ≡ Particulate Matter (aerosols) less than 2.5 mm diameter

EPA Regional Haze Rule

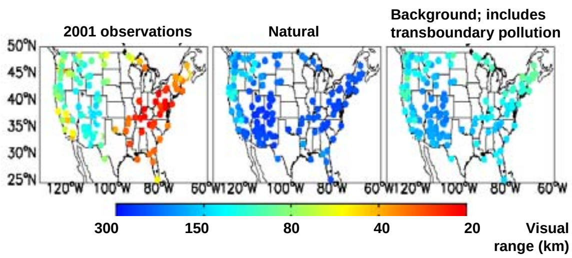
Wilderness Areas Must Achieve Natural Visibility Conditions by 2064

Visibility degradation by aerosols at Glacier National Park, Montana

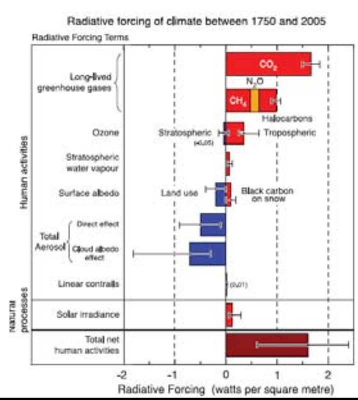


Natural aerosol concentrations are typically less than 2 mg m^{-3}

Visibility in U.S. Wilderness Areas



Aerosol Climate Forcing



IPCC [2007]

Scattering of Radiation by Aerosols

"Direct Effect"

By scattering solar radiation, aerosols increase the Earth's albedo

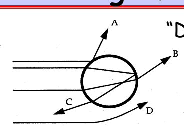


Fig. 8-3 Scattering of a radiation beam: processes of reflection (A), refraction (B), refraction and internal reflection (C), and diffraction (D).

Scattering efficiency is maximum when particle diameter = λ
⇨particles in 0.1-1 μm size range are efficient scatterers of solar radiation

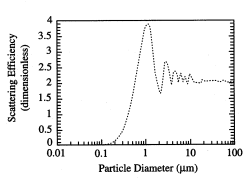
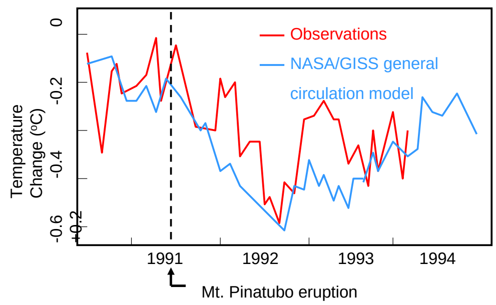


Fig. 8-4 Scattering efficiency of green light (λ = 0.5 μm) by a liquid water sphere as a function of the diameter of the sphere. Scattering efficiencies can be larger than unity because of diffraction. Adapted from Jacobson, M. Z. *Fundamentals of Atmospheric Modeling*. Cambridge, England: Cambridge University Press, 1999.

Evidence of Aerosol Effects on Climate

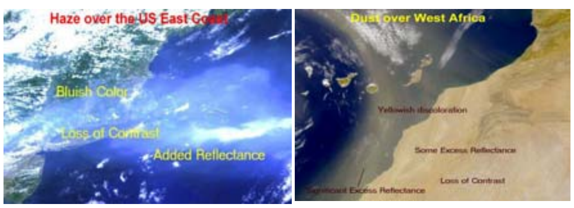
Temperature decrease following large volcanic eruptions



Scattering vs. Absorbing Aerosols

Scattering sulfate and organic aerosol over Massachusetts

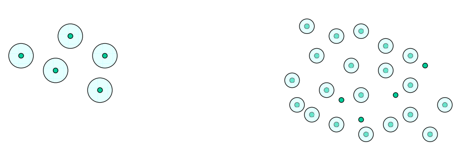
Partly absorbing dust aerosol downwind of Sahara



Absorbing aerosols (black carbon, dust) warm the climate by absorbing solar radiation

Aerosol "Indirect Effect"

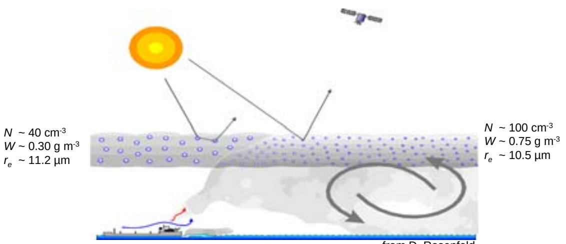
Clouds form by condensation on pre-existing aerosol particles ("cloud condensation nuclei") when RH>100%



clean cloud (few particles):
large cloud droplets
• low albedo
• efficient precipitation

polluted cloud (many particles):
small cloud droplets
• high albedo (1st indirect)
• suppressed precipitation (2nd indirect)

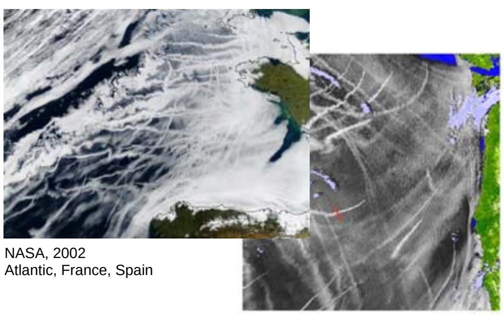
Evidence of Indirect Effect: Ship Tracks



from D. Rosenfeld

- Particles emitted by ships increase concentration of cloud condensation nuclei (CCN)
- Increased CCN increase concentration of cloud droplets and reduce their avg. size
- Increased concentration and smaller particles reduce production of drizzle
- Liquid water content increases because loss of drizzle particles is suppressed
- Clouds are *optically thicker* and brighter along ship track

Satellite Images of Ship Tracks



NASA, 2002
Atlantic, France, Spain

AVHRR, 27. Sept. 1987, 22:45 GMT
US-west coast

Other Evidence of Cloud Forcing

CONTRAILS AND "AIRCRAFT CIRRUS"

Aircraft condensation trails (contrails) over France, photographed from the Space Shuttle (©NASA).