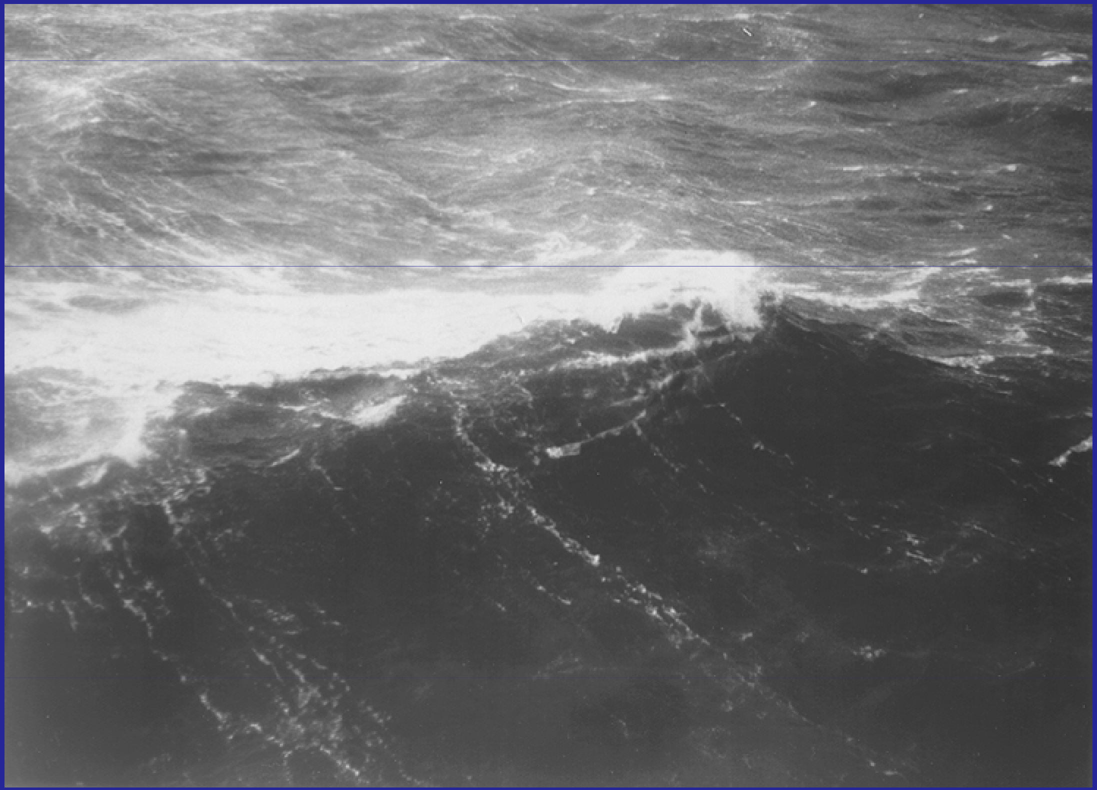
2009 SOLAS Summer School

Introduction to Marine Aerosols



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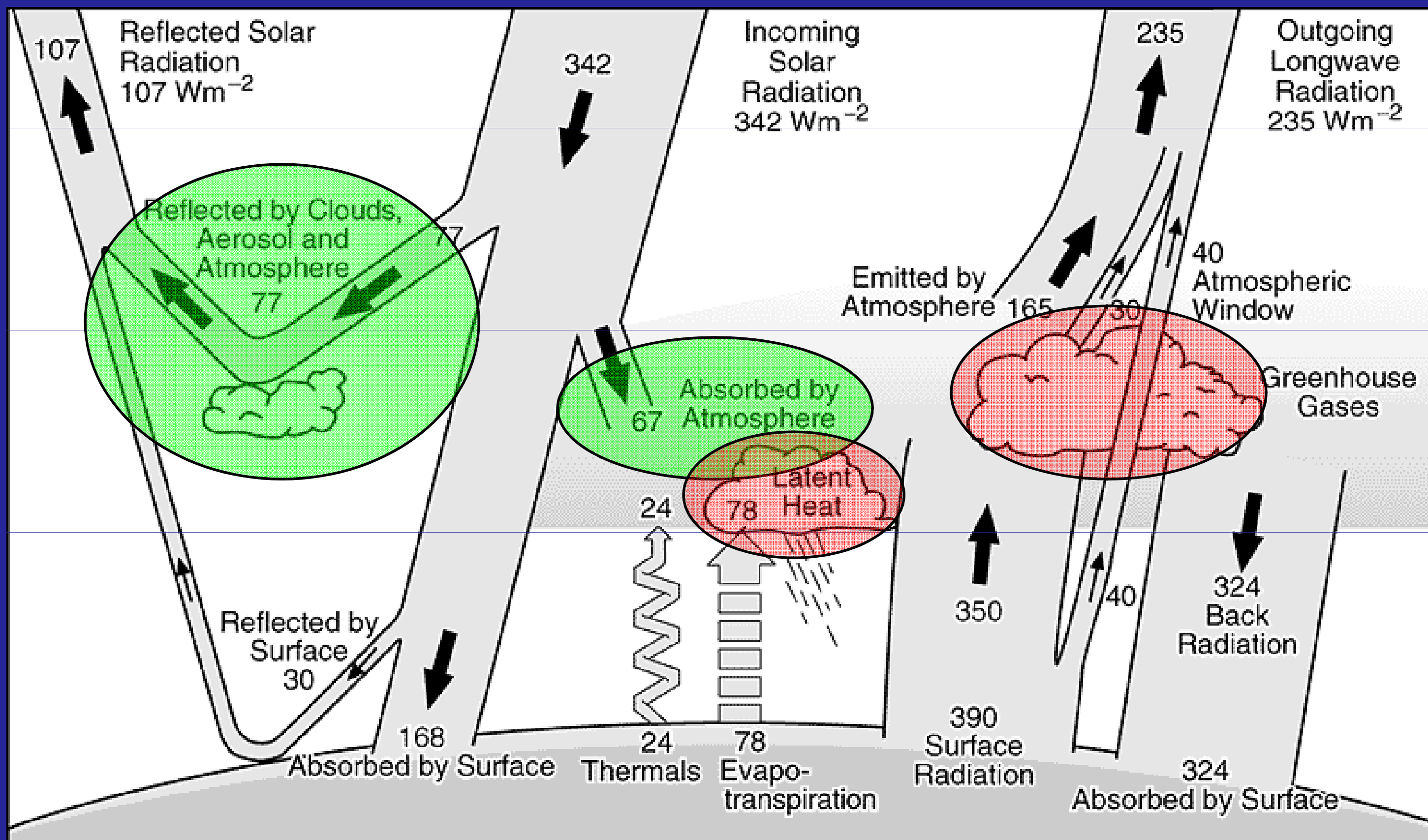
What is driving marine aerosol research?

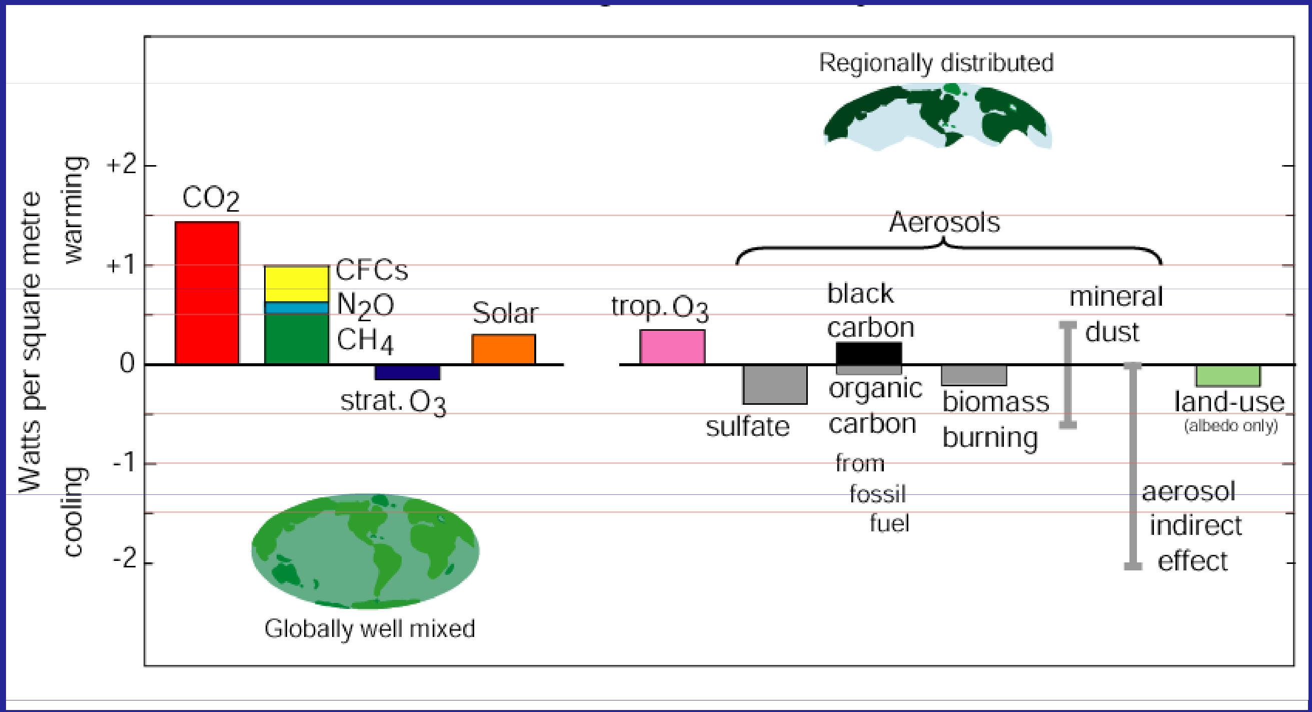
- *geochemical cycles*
  - *global elemental fluxes, transport properties*
- *acidification (sulfur, nitrogen)*
- *climate change*
  - *direct/indirect effects*
  - *aerosol optical properties, aerosol/cloud interactions*
  - *interactions between aerosols/oxidation capacity*
- *nutrients*
  - *N deposition*
  - *budgets in coastal, oligotrophic regions*
  - *desert dust and iron deposition, HNLC regions*
- *human health*
  - *air quality, airborne pathogen transport*

Earth's energy balance...



Aerosol effects on Earth's radiation budget

global radiative forcing
(2000 vs 1750)



IPCC

Direct effects (cloud-free):

- *scatter → cooling*
- *absorption → heating*

Indirect effects (clouds):

- *more (but smaller) droplets → scatter (Twomey)*
- *more droplets → longer cloud lifetime (Albrecht)*
- *absorption → heating → evaporates clouds*

Some questions...

- *What are marine aerosols made of ?*

- *Where do they come from?*

- *How long do they stay in the atmosphere? How are they removed?*

- *How do they evolve while in the atmosphere?*

- *How do they interact with the climate system?*
    - *forcing*
    - *feedback*

- *How will they change in the future as a result of industrialization and climate change?*

- *...what don't we know about marine aerosols that we need to know?*

Things we “know we know”... (or don’t)...

“...there are known knowns. These are things we know that we know. We also know there are known unknowns; that is to say we know there are some things we do not know. But there are also unknown unknowns. These are things we don't know we don't know.”

Donald Rumsfeld

“Unknown knowns” ...things we know that might not be true

Eric Saltzman

- *“nucleation is rare”*
- *“sulfate is <u>the</u> source of CCN over the oceans”*
- *“sea spray doesn’t make submicron aerosols“*
- *“organics in marine aerosols are derived from land”*
- *“there’s not enough iodine out there to matter...”*

Terminology...

•*aerosol* - a dispersion of solid and liquid particles suspended in gas (air).

note: “aerosol” is defined as the dispersion of both particles and gas, but in common practice it is used to refer to the particles only!

•*primary aerosol* - emitted directly into the atmosphere.
- •soot, fly ash
- •Saharan dust, pollen
- •sea spray

•*secondary aerosol* - created by nucleation of new particles, aggregation of existing particles, or growth of preexisting particles from gas phase molecules (gas to particle conversion).

either type may be natural or anthropogenic or both

•*internal vs. external mixtures* – in an internally mixed aerosol all particles have the same composition

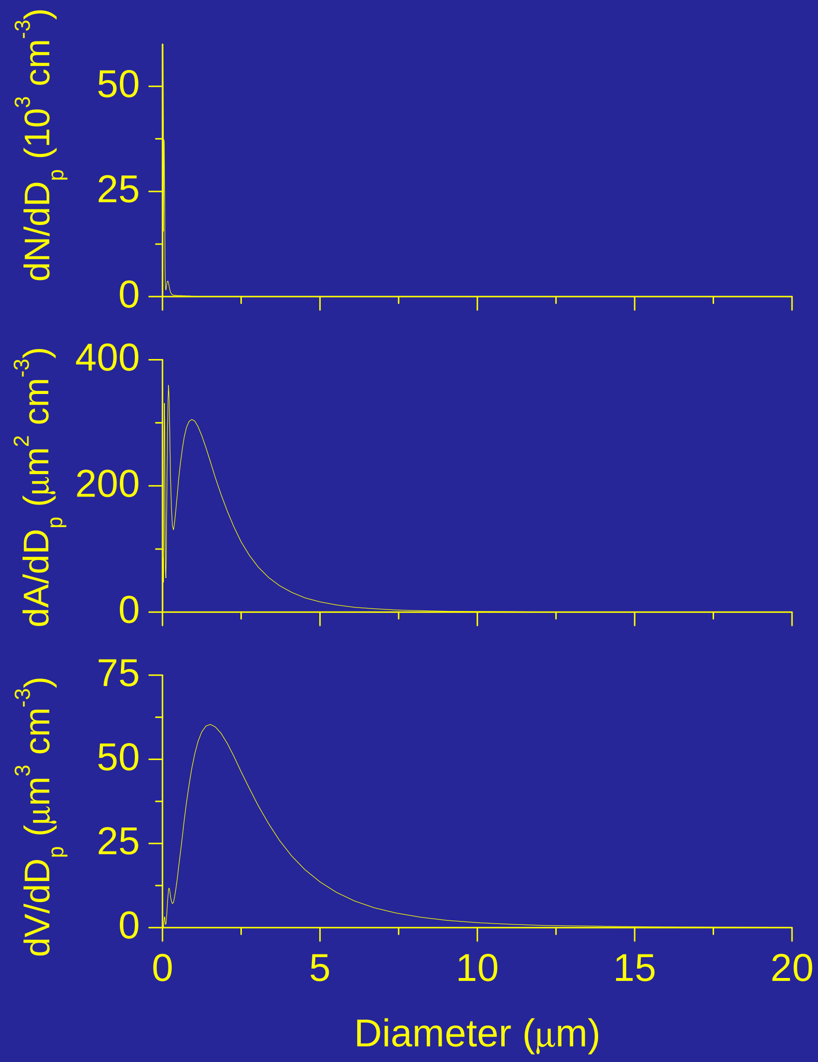
How much aerosol is there? typically ~10’s of ug/m^3 (air ~1kg/m^3)

The aerosol size distribution...

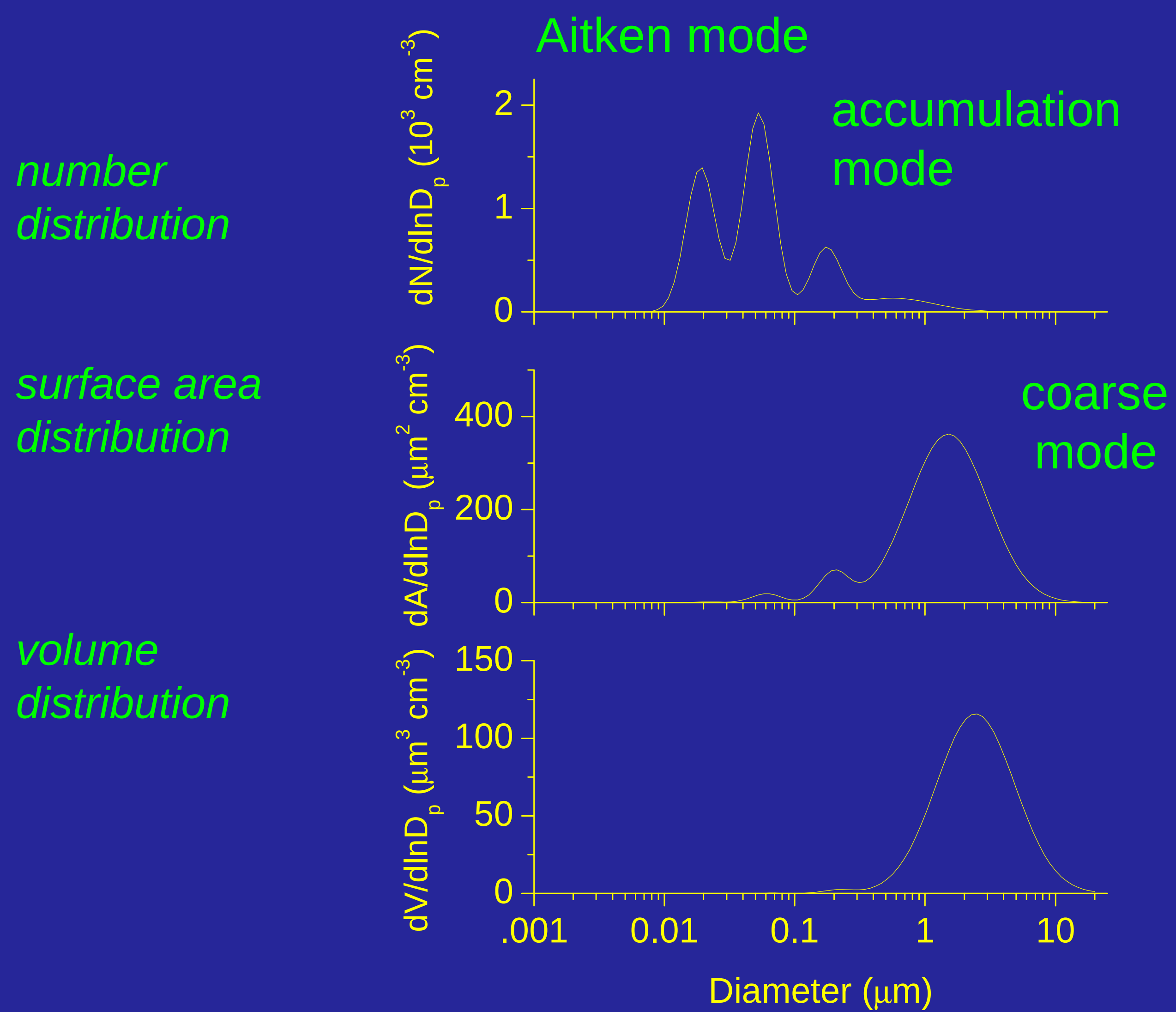
number distribution

surface area distribution

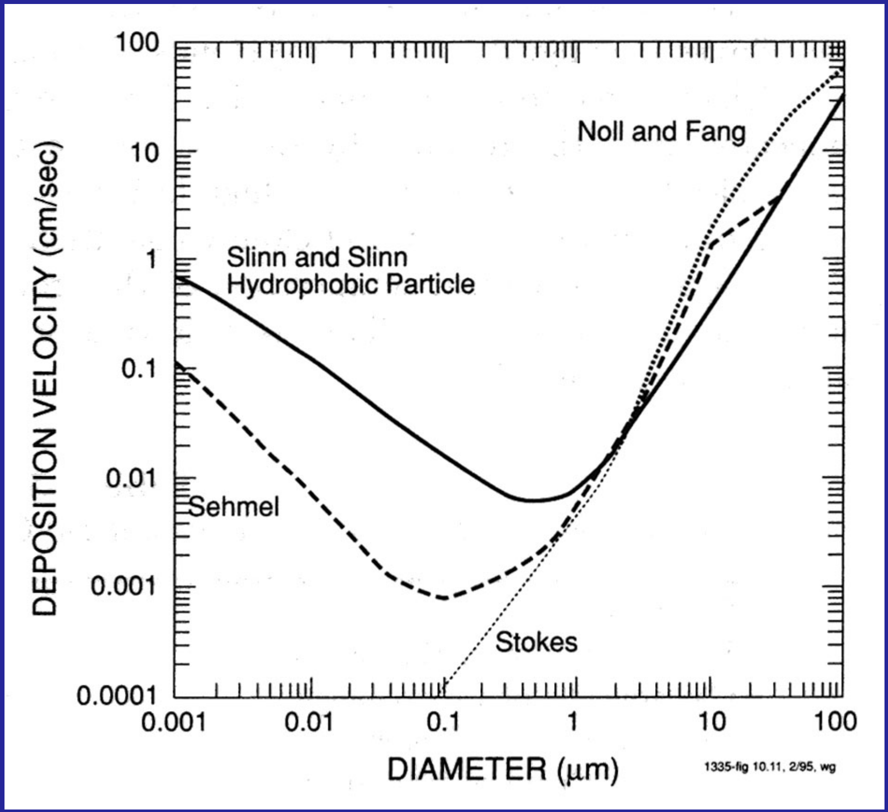
volume distribution

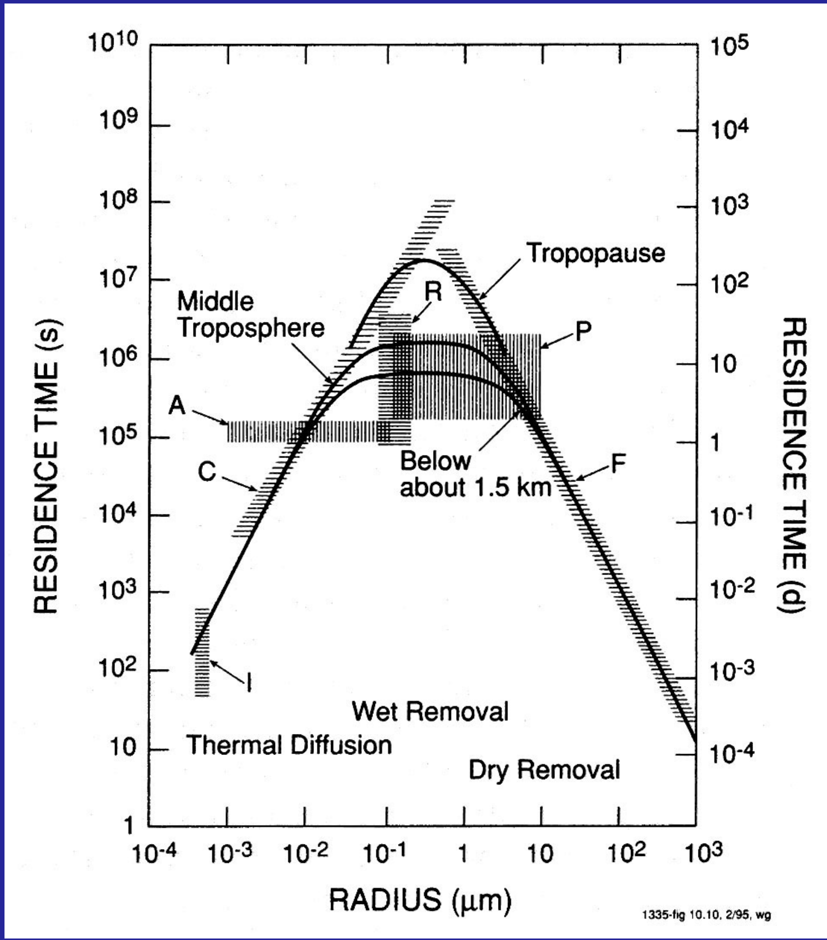


The log-normal aerosol size distribution...



aerosol removal and lifetimes...



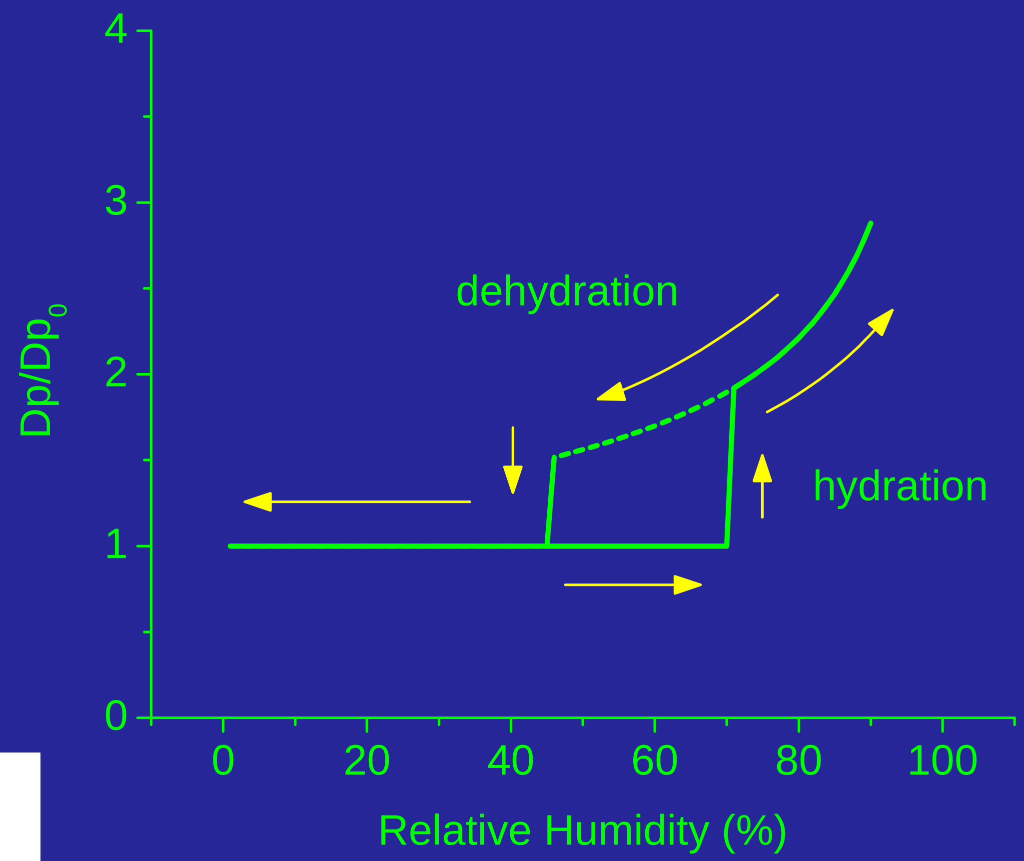


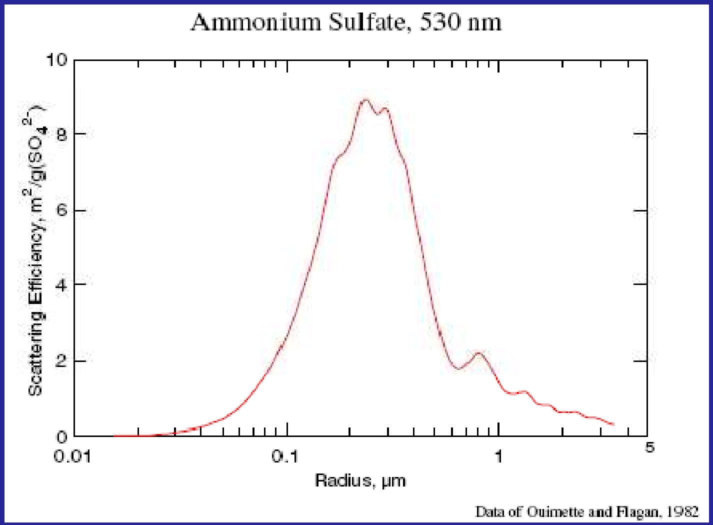
impaction, settling →

← **diffusion, coagulation**

Humidity and aerosol size...

- hygroscopic aerosols grow/shrink with RH (with hysteresis)





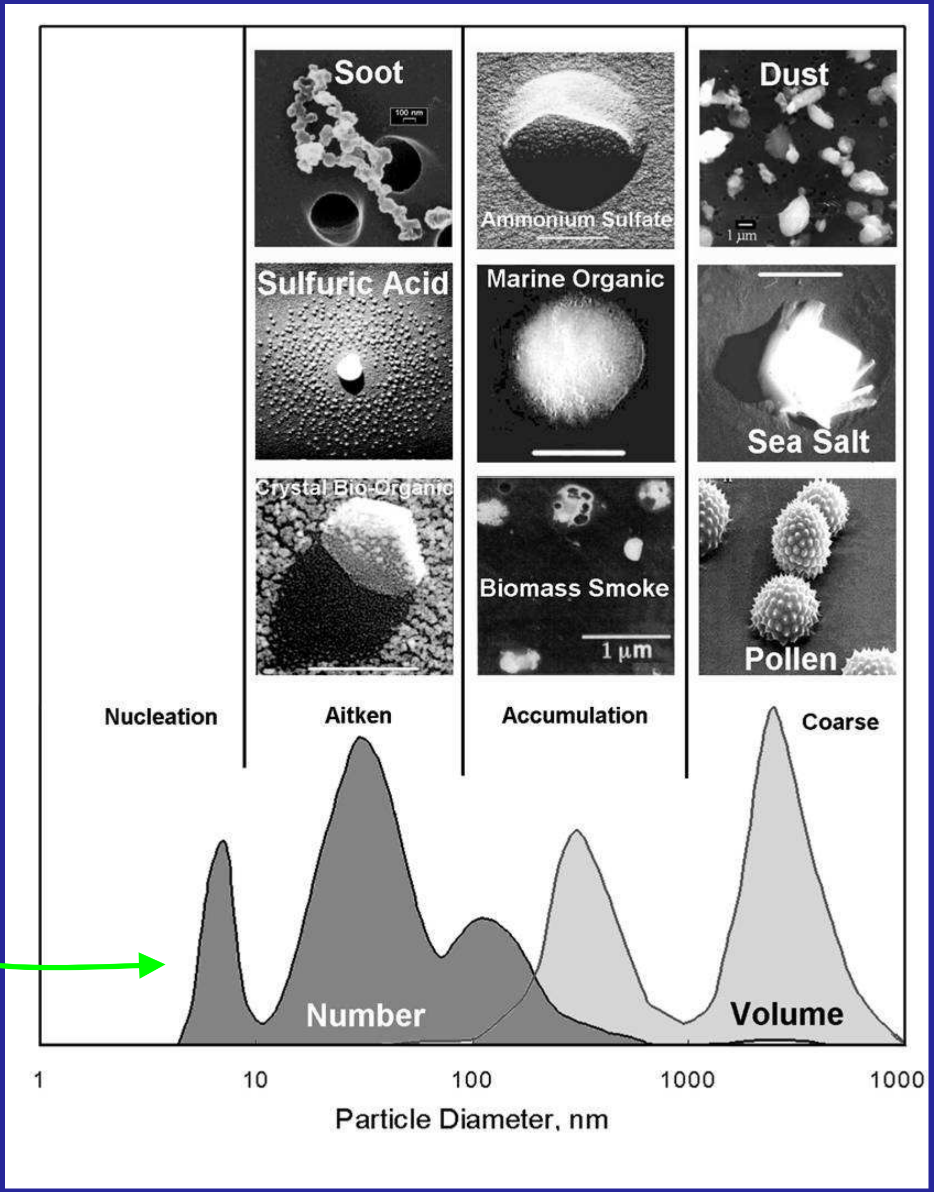
- aerosol size strongly affects light scattering cross-section

The aerosol modes...

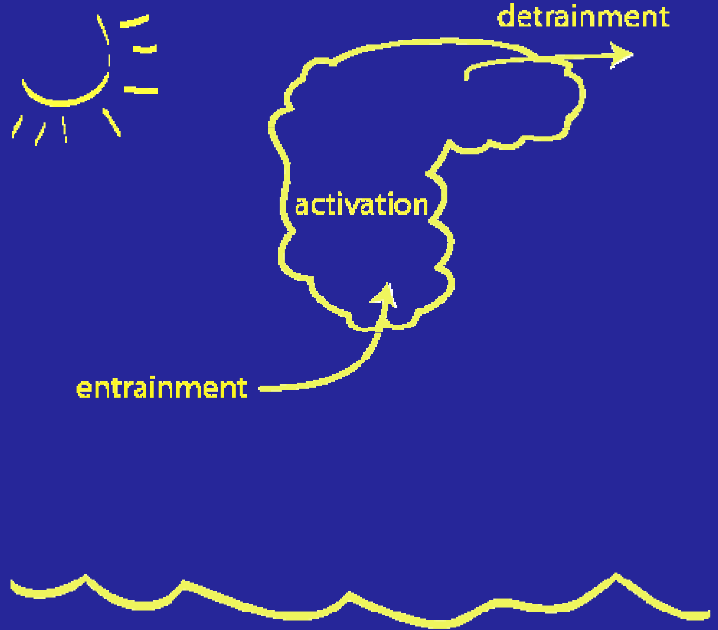
- *Aitken mode – 0.01-0.1 um*
- *accumulation mode – 0.1-1 um*
- *coarse mode - >1 um*

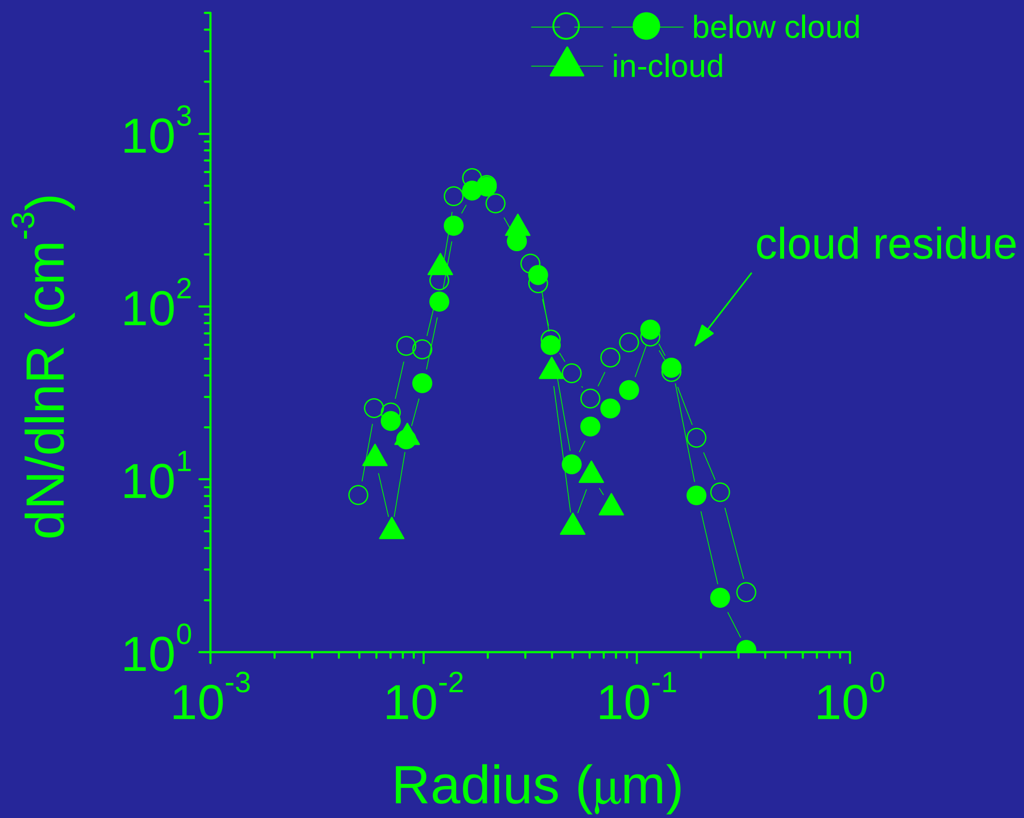
and sometimes, the elusive

- *nucleation mode <0.01 um*



Cloud processing ...

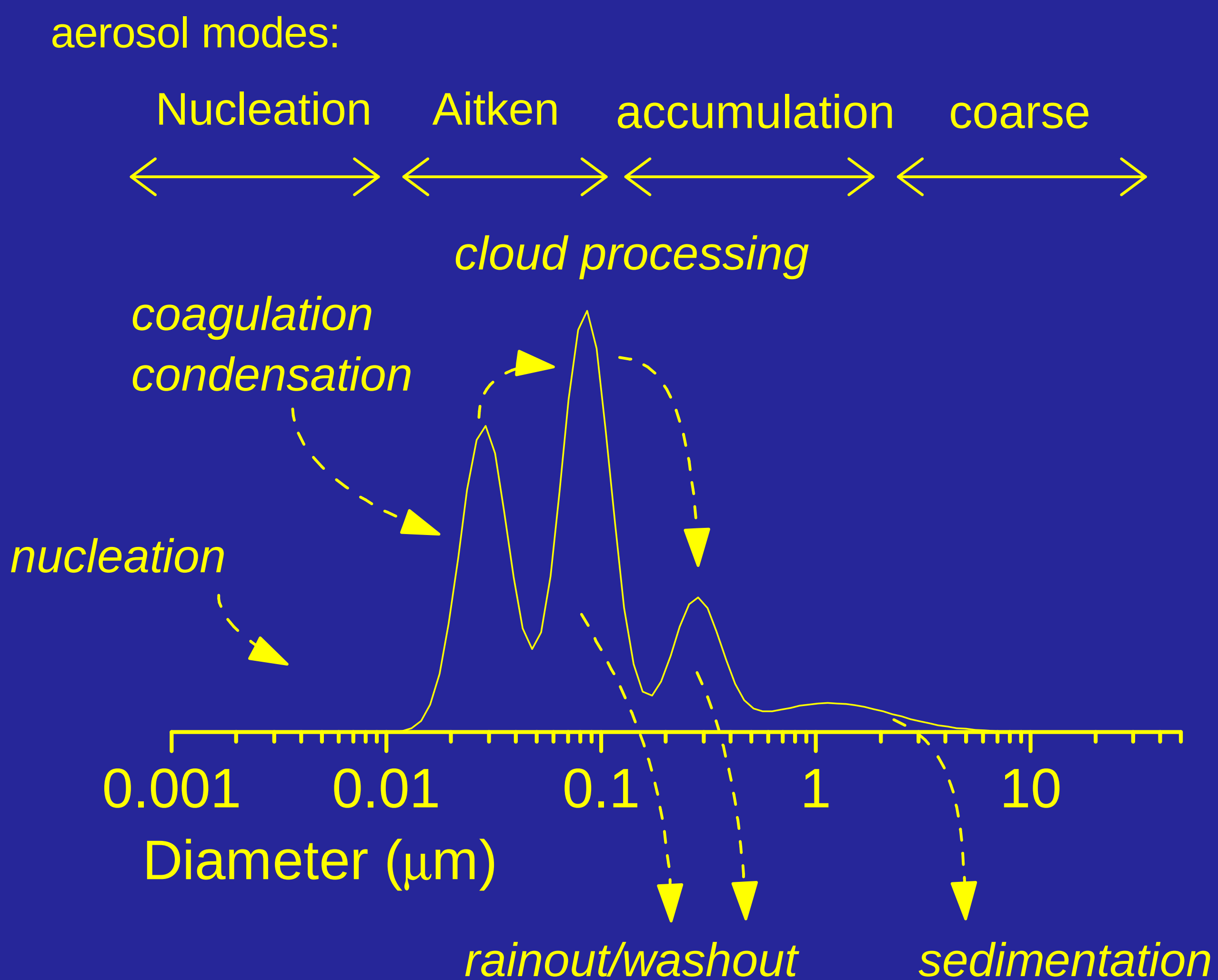




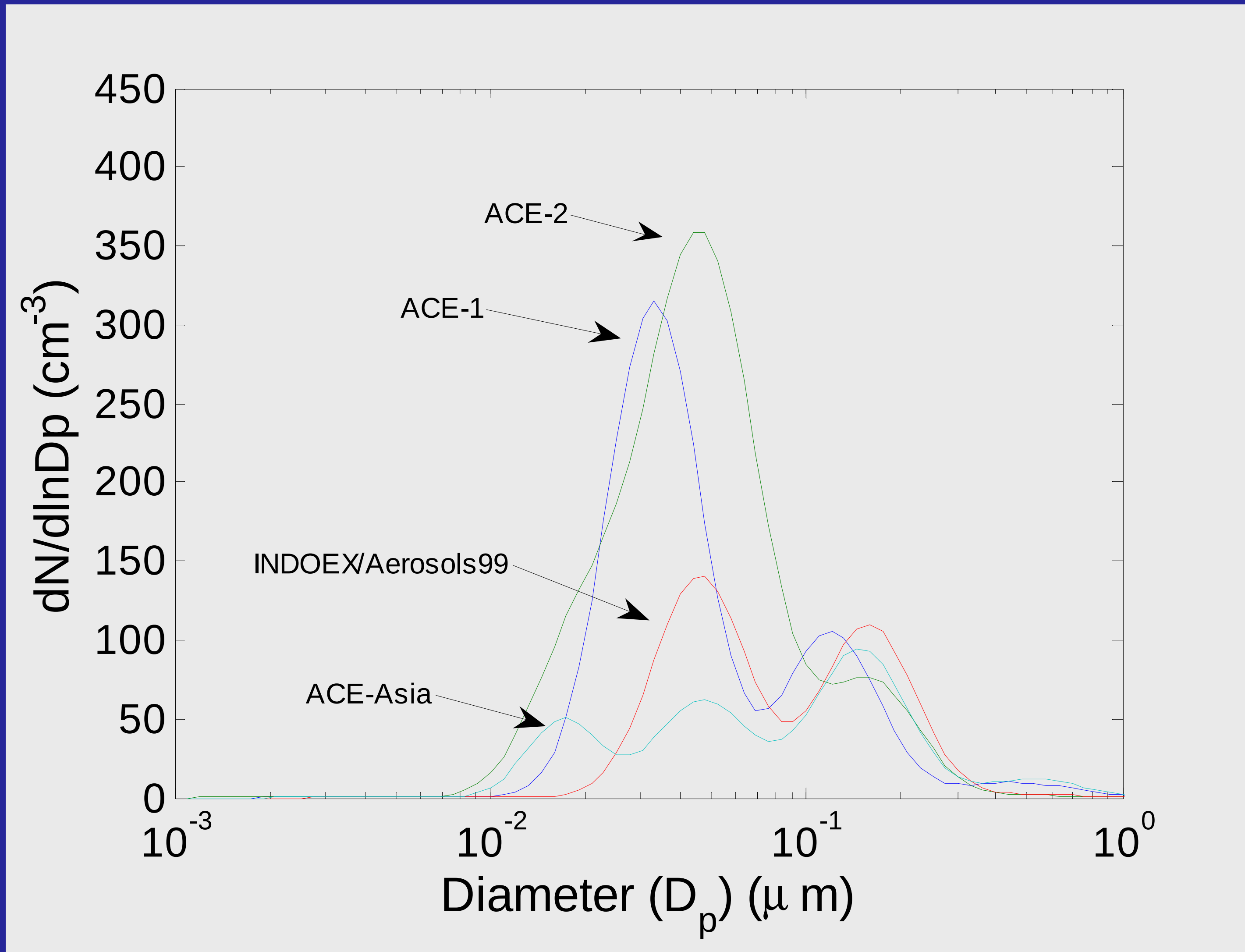
- *cloud residue mode due to evaporation of cloud droplets*
- *"splits" Aitken mode in marine air.*

a process-oriented view of the size distribution

... competition between production/transformation/removal

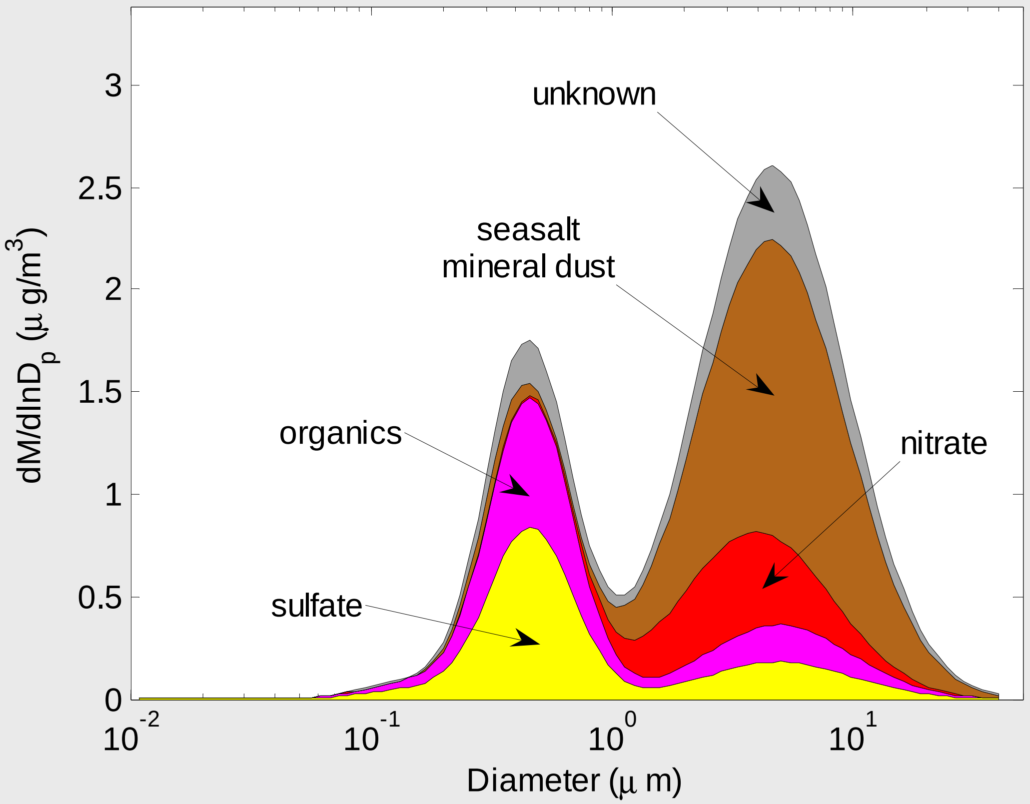


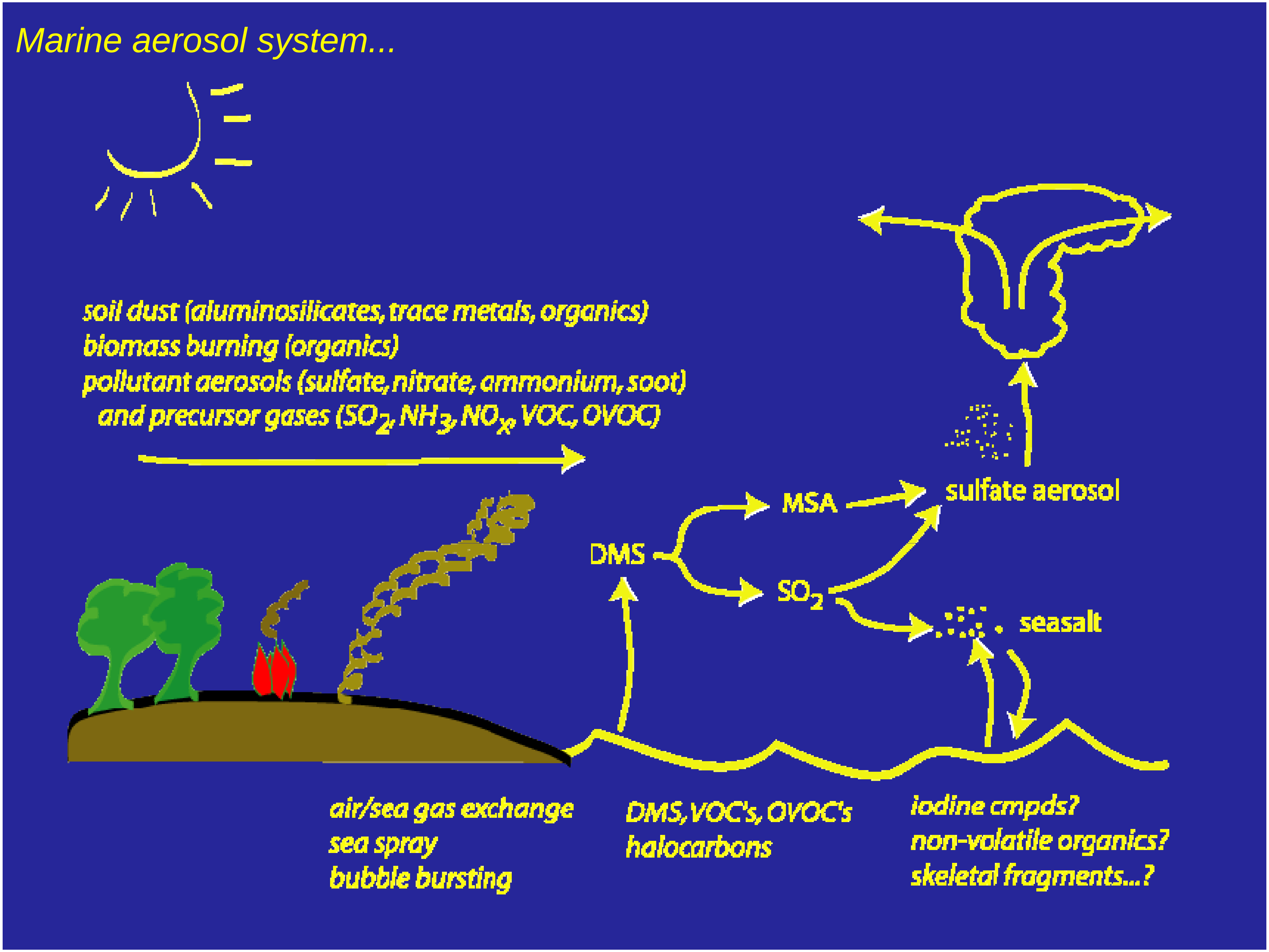
Observed marine aerosol number distributions (>10,000!)



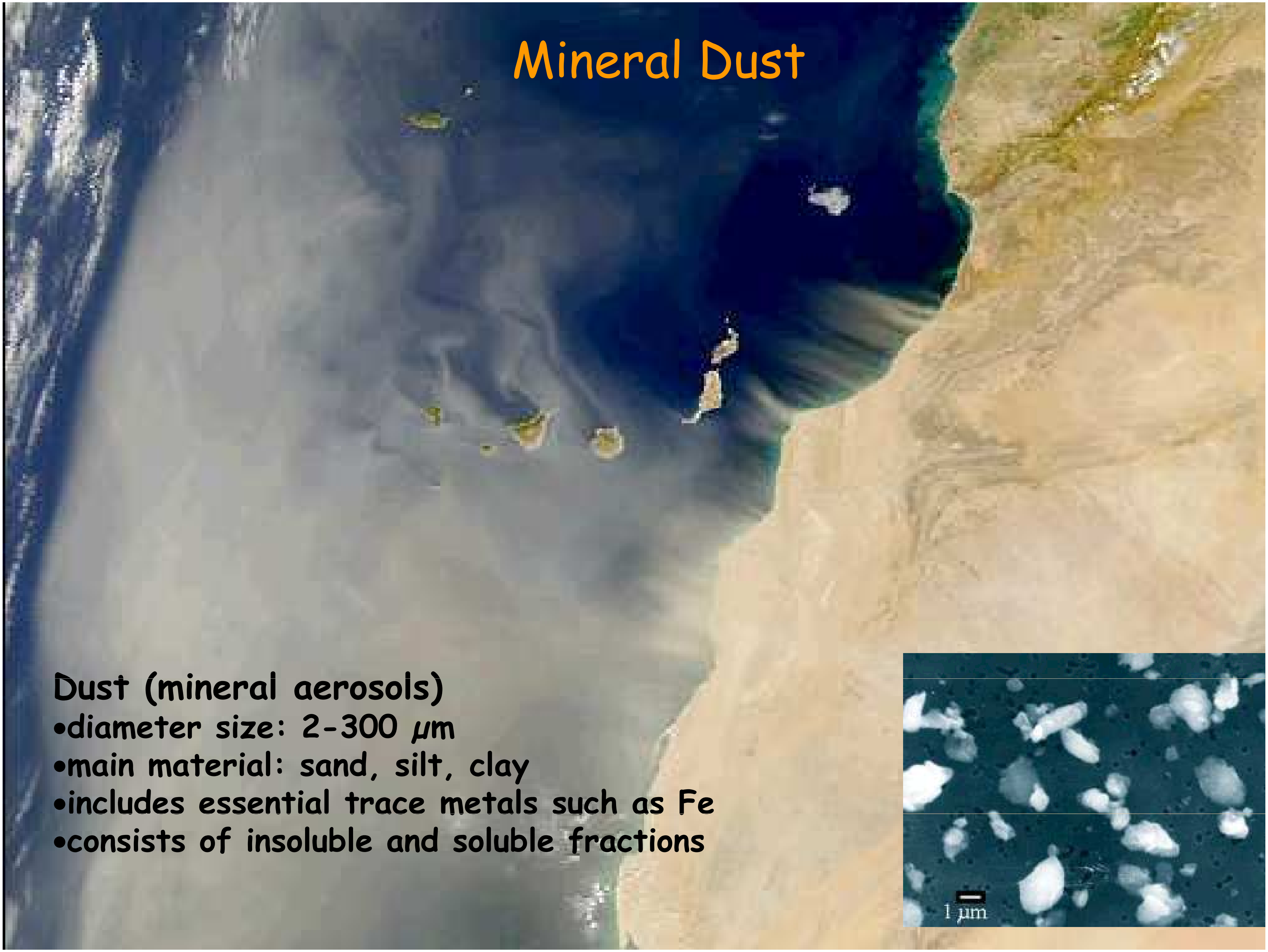
The chemical perspective ... a chemical size distribution

- *chemical size distributions resemble mass, not number*
- *sulfate and organics dominate the accumulation mode, but there's a surprising amount of seasalt*
- *there are <u>a lot</u> of unidentified organics*
- *the coarse mode has the expected mechanically generated aerosols, but also nitrate and sometimes sulfate*




Marine aerosol system...
soil dust (aluminosilicates, trace metals, organics)
biomass burning (organics)
pollutant aerosols (sulfate, nitrate, ammonium, soot)
and precursor gases (SO2, NH3, NOx, VOC, OVOC)
DMS
MSA
SO2
sulfate aerosol
seasalt
air/sea gas exchange
sea spray
bubble bursting
DMS, VOC's, OVOC's
halocarbons
iodine cmpds?
non-volatile organics?
skeletal fragments...?

Mineral Dust



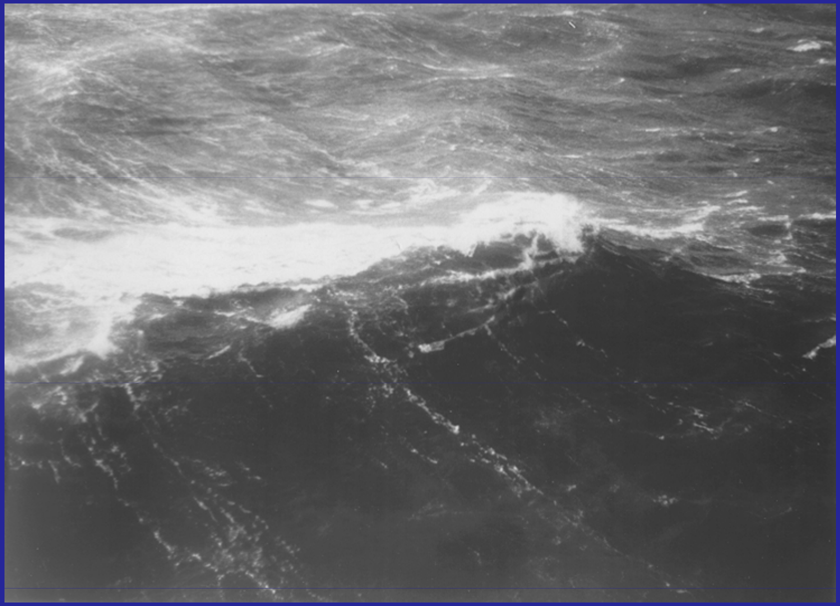
Dust (mineral aerosols)

- diameter size: 2-300 μm
- main material: sand, silt, clay
- includes essential trace metals such as Fe
- consists of insoluble and soluble fractions

Seasalt aerosols...

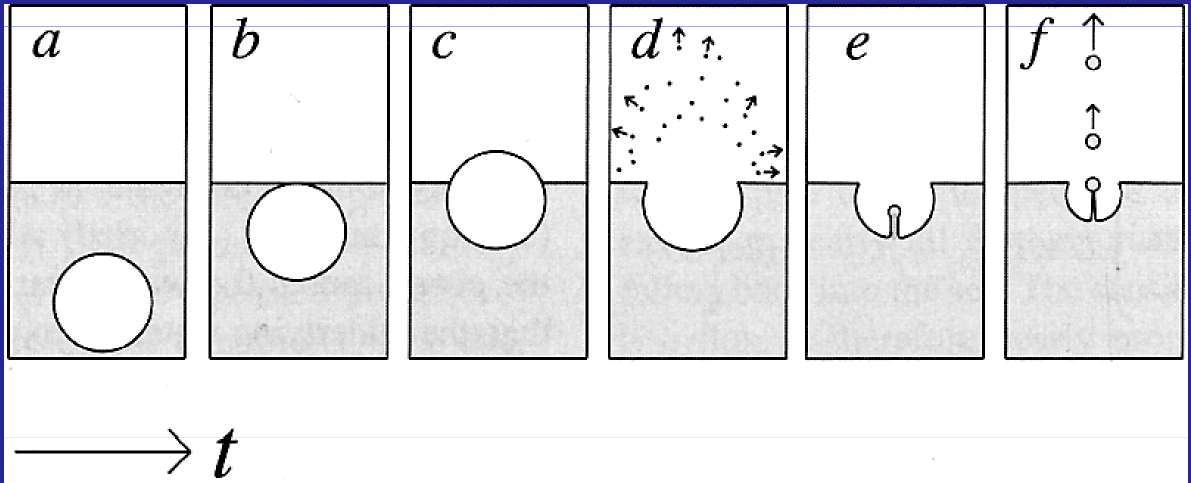
wind → bubbles → spray

whitecap coverage W α U^{3+}*!*

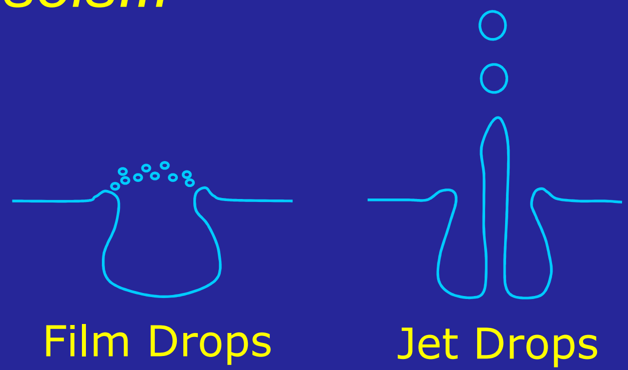


seasalt production via bubble bursting...

- film drops (many, small, organics)
- jet drops (fewer, larger)



Seasalt aerosols...

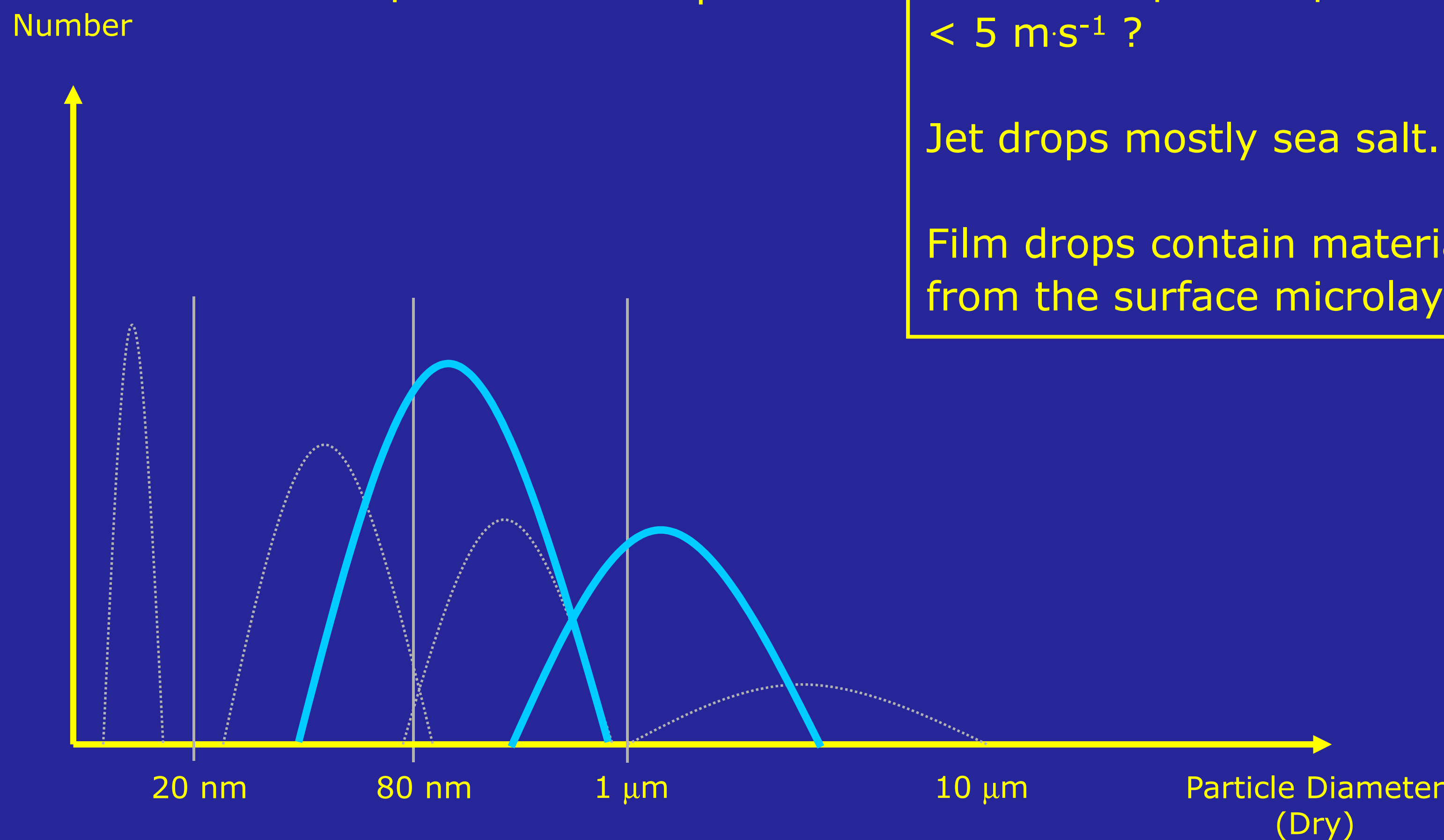


Strong wind speed (U) dependence (exponential), U > 5 m·s^{-1}.

Non-wind speed dependence, U < 5 m·s^{-1} ?

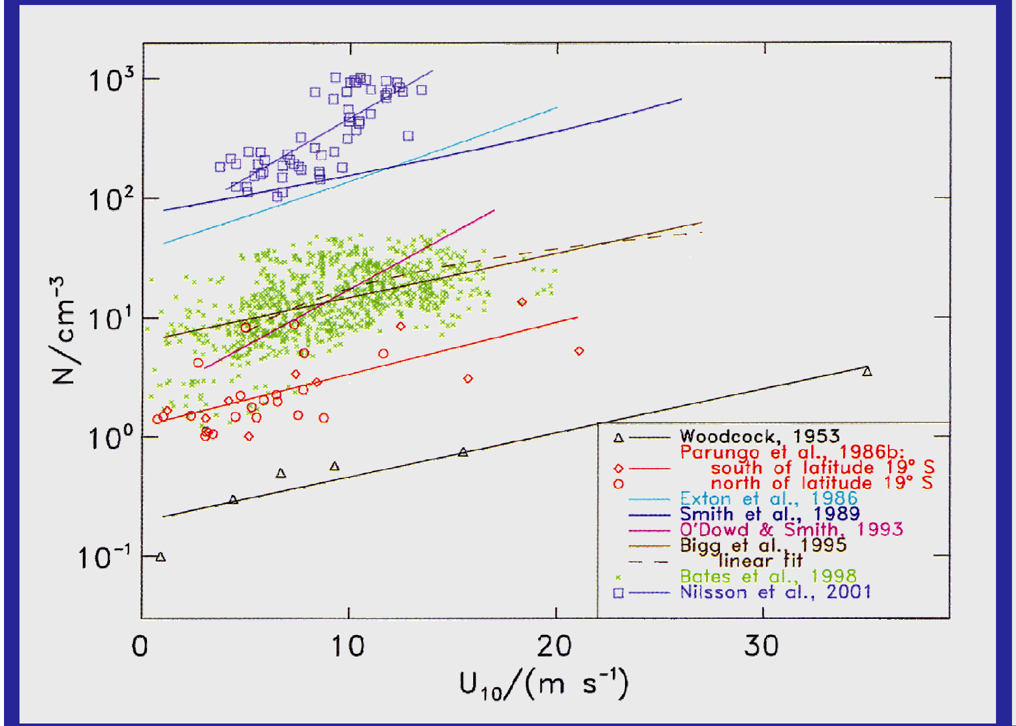
Jet drops mostly sea salt.

Film drops contain material from the surface microlayer.

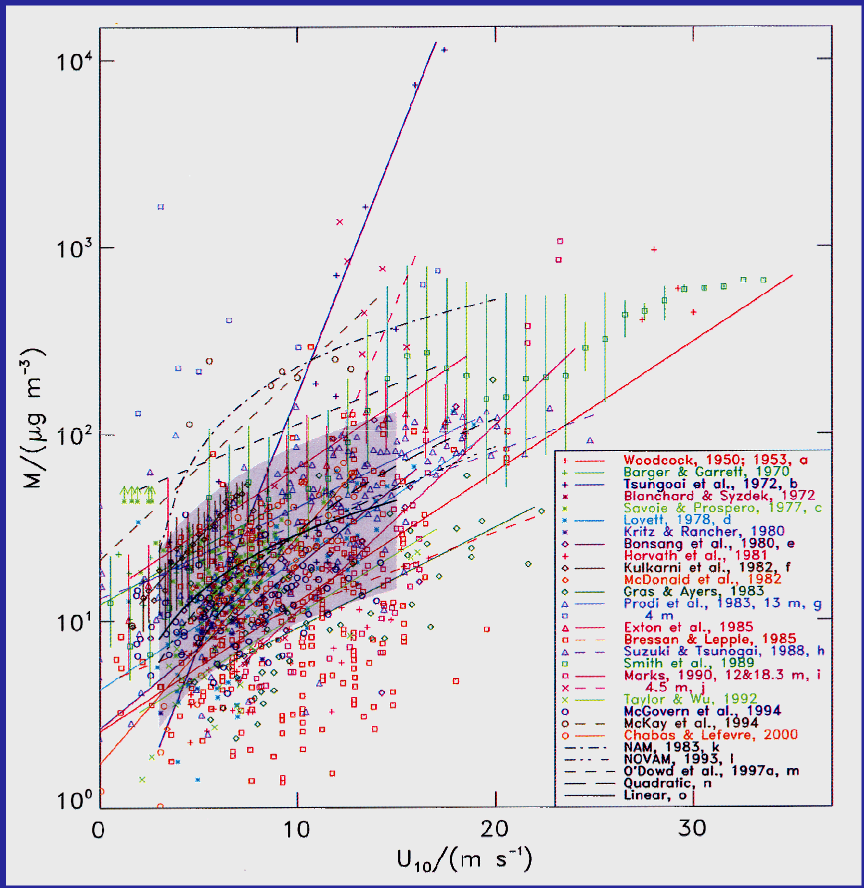


(from C. Leck)

Seasalt – number and mass as a function of surface wind speed



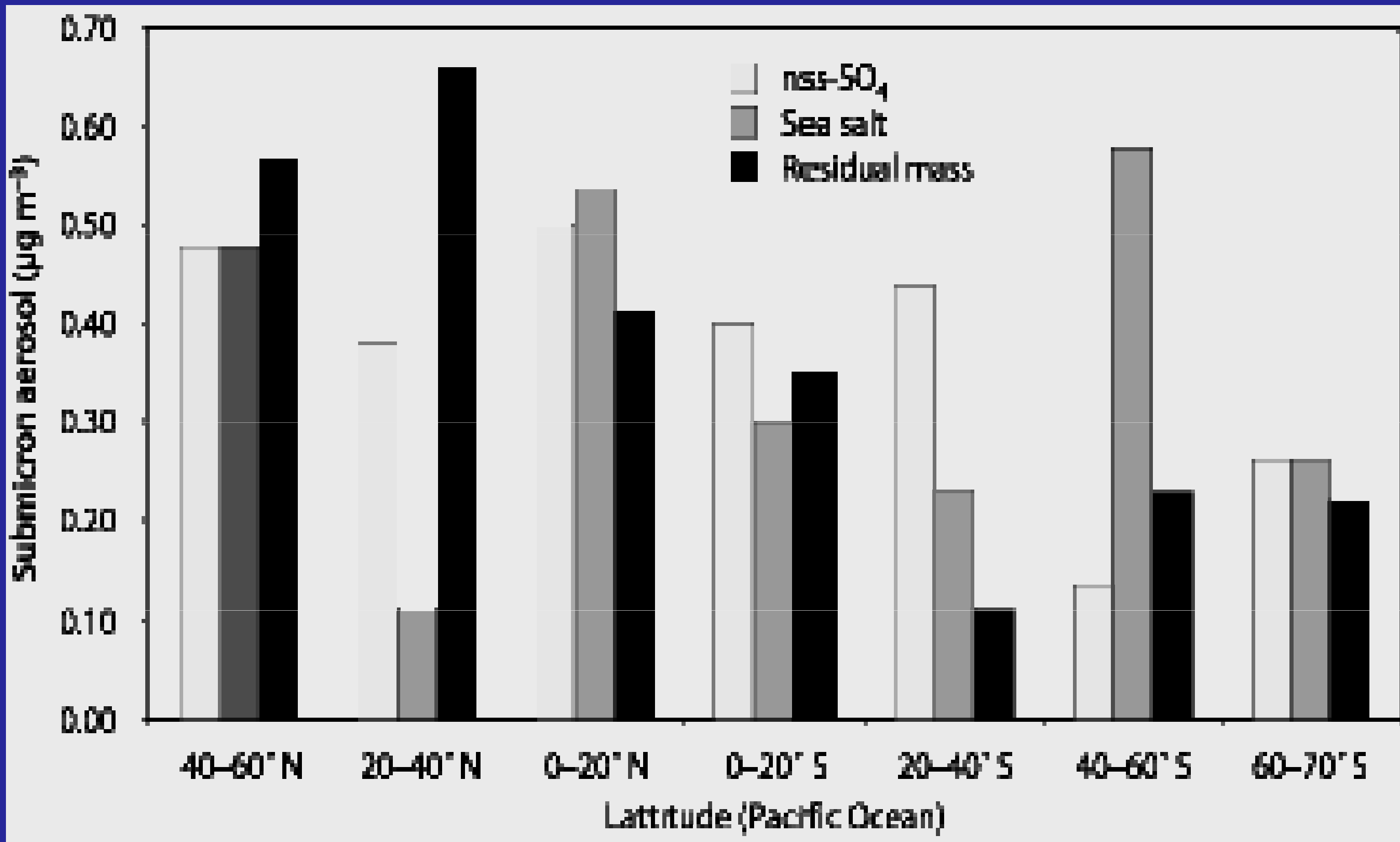
seasalt particle number



seasalt mass

(compiled by Lewis and Schwartz, 2004)

Marine aerosol mass fractions...

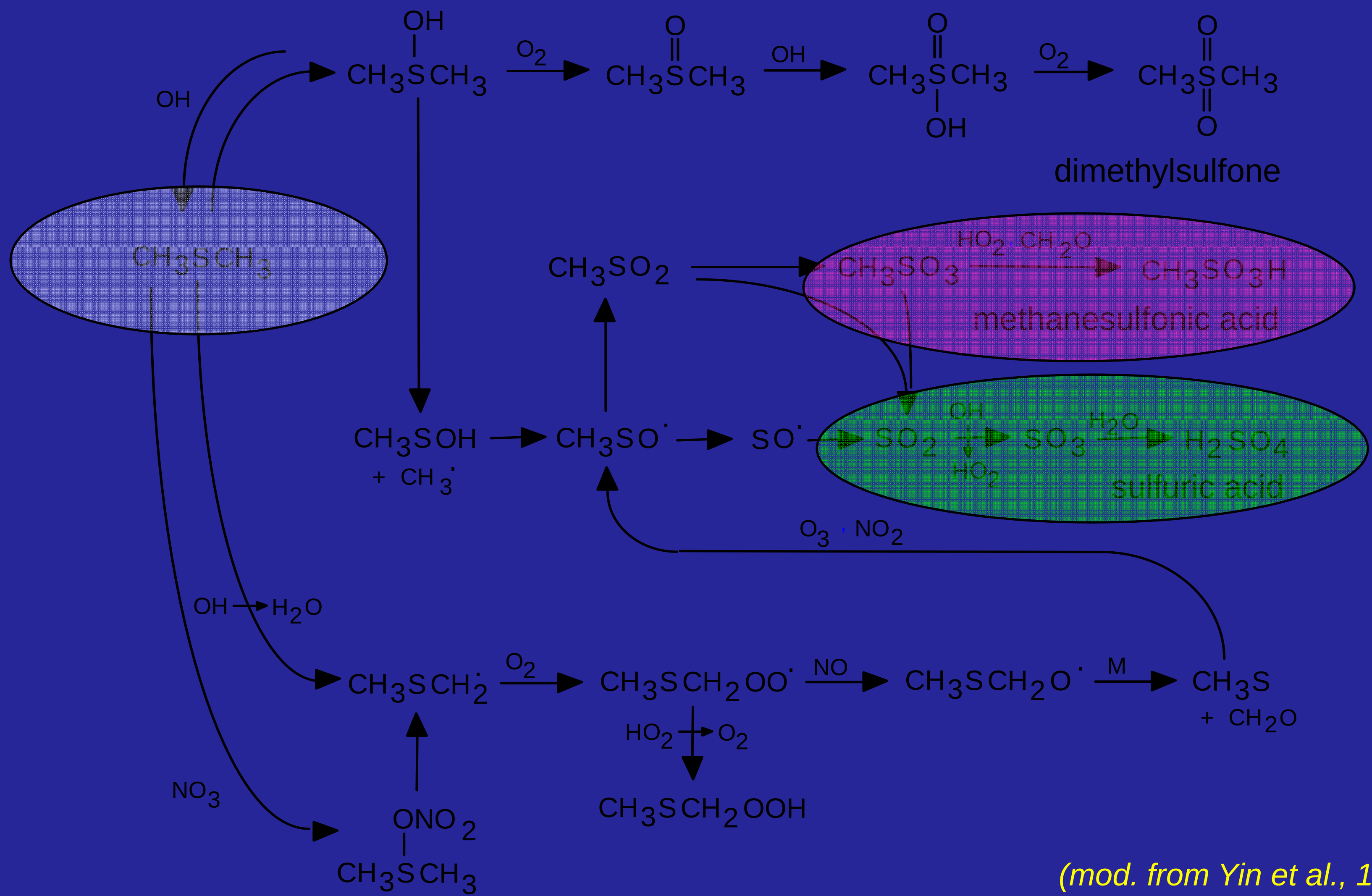


Fraction of submicron aerosol derived from nss sulfate, sea salt and "residual"

Quinn et al., 2000

The sulfur story (in brief) ...

- emissions: fossil fuel SO_2, volcanic SO_2, oceanic DMS
- DMS oxidation ... gas phase ... complex!



(mod. from Yin et al., 1990)

Happily, gas phase SO_2 oxidation is simple...

$$SO_2 + OH \xrightarrow{M} HOSO_2$$

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3$$

$$SO_3 + H_2O + H_2O \longrightarrow H_2SO_4 + H_2O$$

sadly, most SO_2 oxidation occurs in the aqueous phase...

some basics...

$$SO_2(g) \longleftrightarrow SO_2(aq)$$

$$SO_2 + H_2O \xrightarrow{pK_1 \sim 4} HSO_3^- + H^+$$

$$HSO_3^- + H_2O \xrightarrow{pK_2 \sim 8} SO_3^= + H^+$$

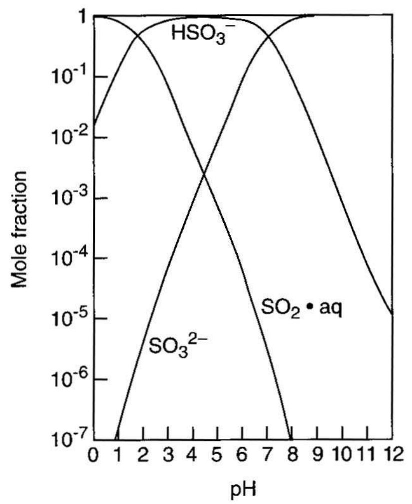


FIGURE 8.7 Mole fraction of sulfur species in solution at different acidities (adapted from Martin and Damschen, 1981).

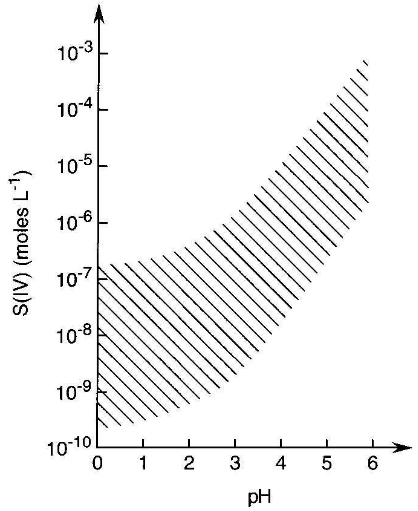
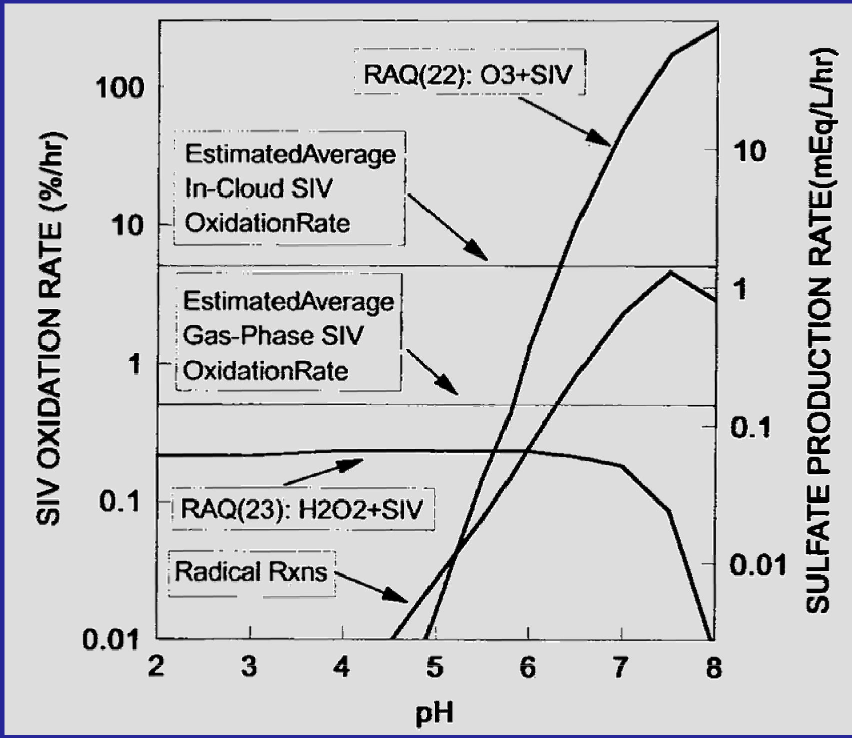


FIGURE 8.8 Range of expected aqueous S(IV) concentrations as a function of acidity for gas-phase SO_2 concentrations of 0.2–200 ppb (adapted from Martin, 1984).

heterogeneous oxidation of SO_2

- *in-cloud oxidation*
  - *weakly buffered, pH ~4*
  - *oxidation by H_2O_2*
  - *aerosol growth, split Aitken mode*



- *seasalt aerosols*
  - *strongly buffered by carbonate system*
  - *rapid oxidation by O_3*
  - *then slower oxidation by H_2O_2 (also OH, halogen radicals...)*
  - *rapid loss by deposition*

(Chameides and Stelson, 1992)

Organic aerosols - burning

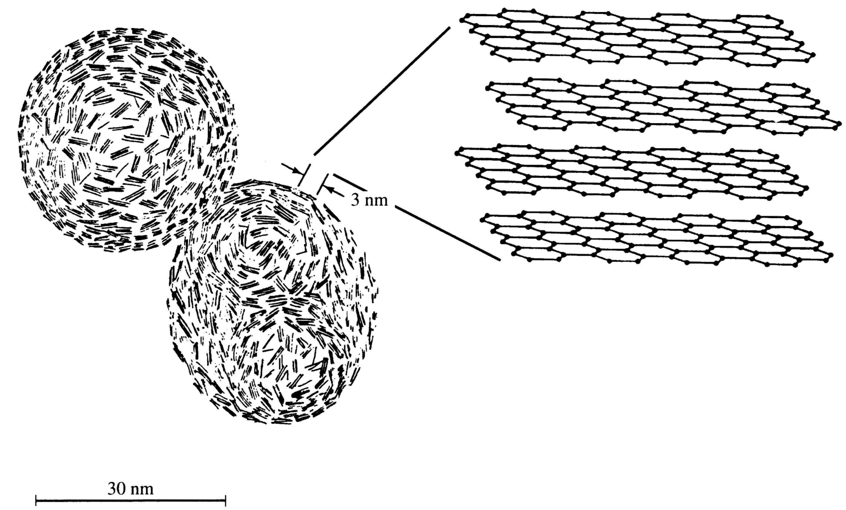


FIGURE 13.1 Schematic of soot microstructure.

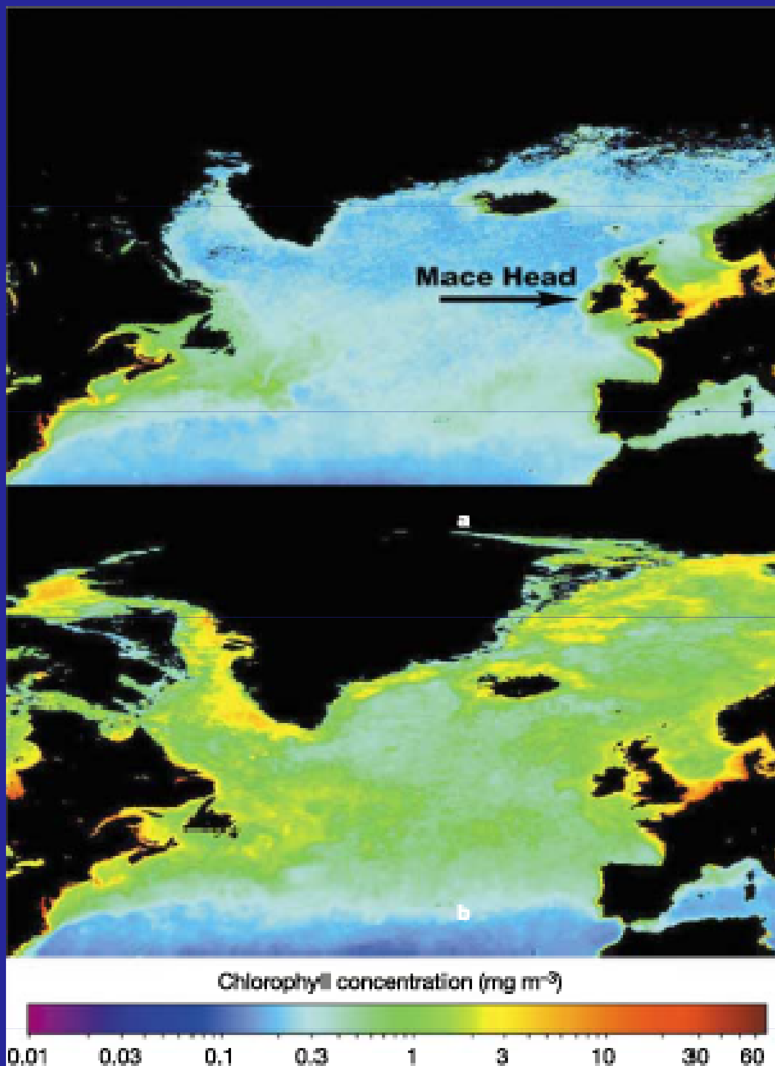
soot – "elemental carbon"

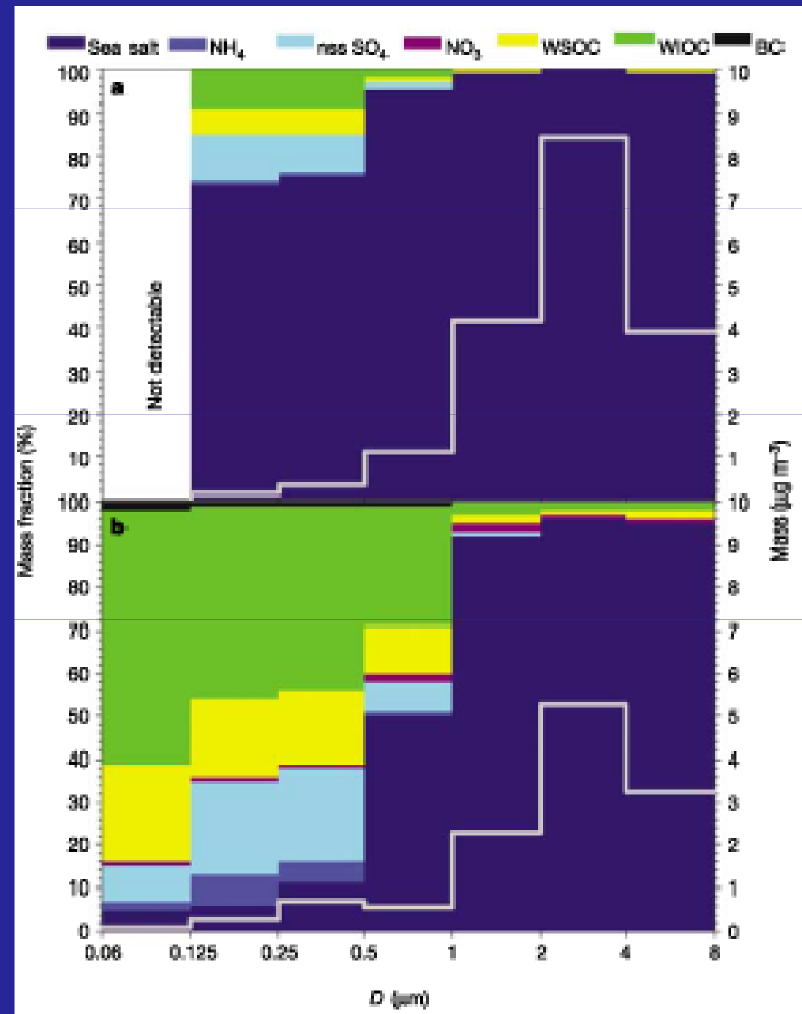
- *formed in flames*
- *little spectral dependence*
- *carbon-only*

"brown carbon":

- *sugars*
- *alcohols*
- *aromatics (and methoxy)*
- *di/tri acids*
- *ketoacids*
- *hydroxyacids*

Marine-derived organic aerosols...

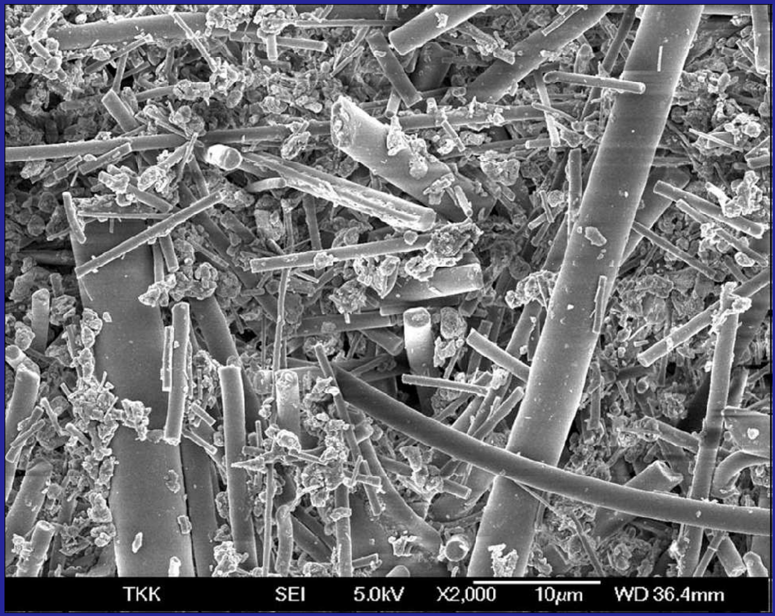




(O'Dowd et al., 2004)

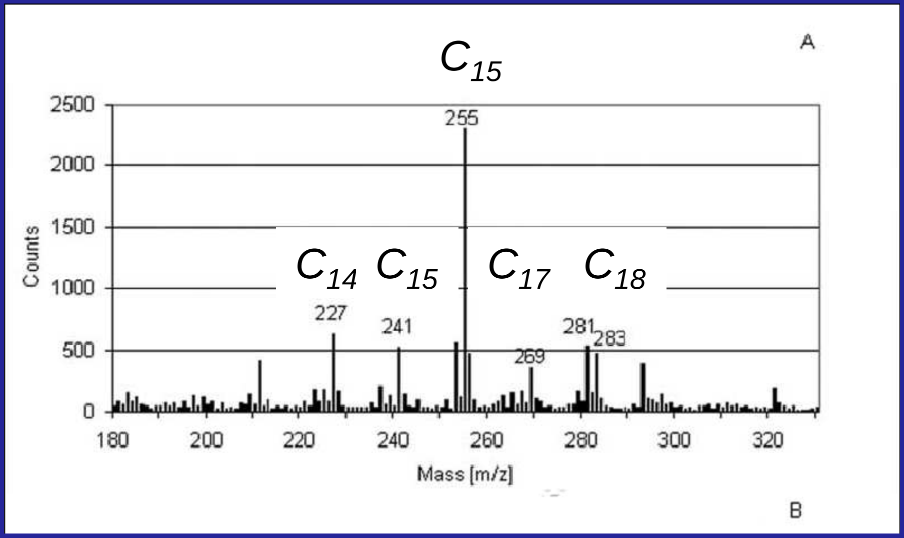
More organics in marine aerosols ...

SEM micrograph of an Arctic marine aerosol sample. Single particles (diameter 1 µm) and groups of particles are lying between the fibers of the filter. About half of the particles are coated by an organic layer.



Negative TOF-SIMS spectra of marine aerosol.

mass 255 → $C_{15}H_{31}COOH$ (palmitic acid)



Tervahattu et al., 2002

Iodine and nucleation...

- *coastal I_2 emissions*
  $\rightarrow I_2O_5$
- *macroalgae*
- *open ocean CH_2I_2, I_2 ... ?*
- *broader importance?*

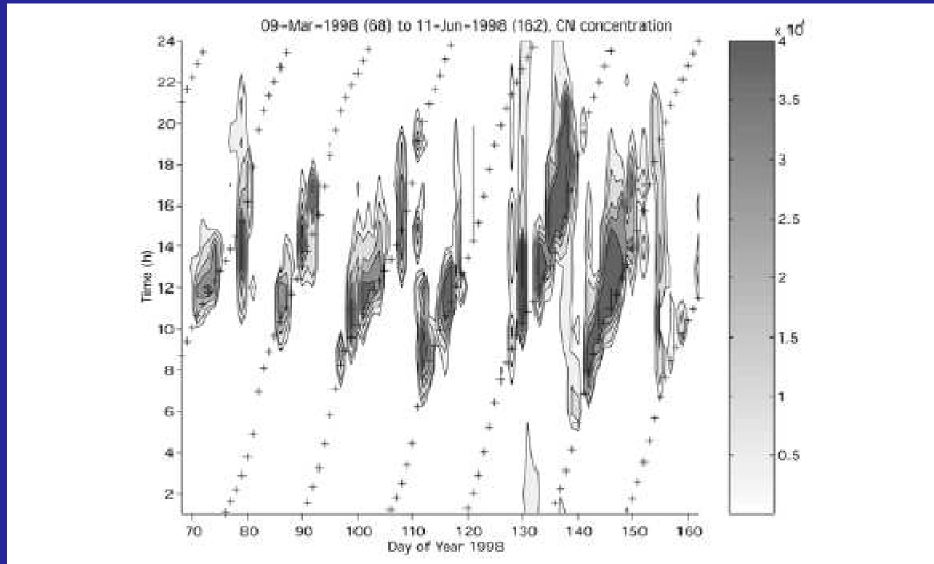
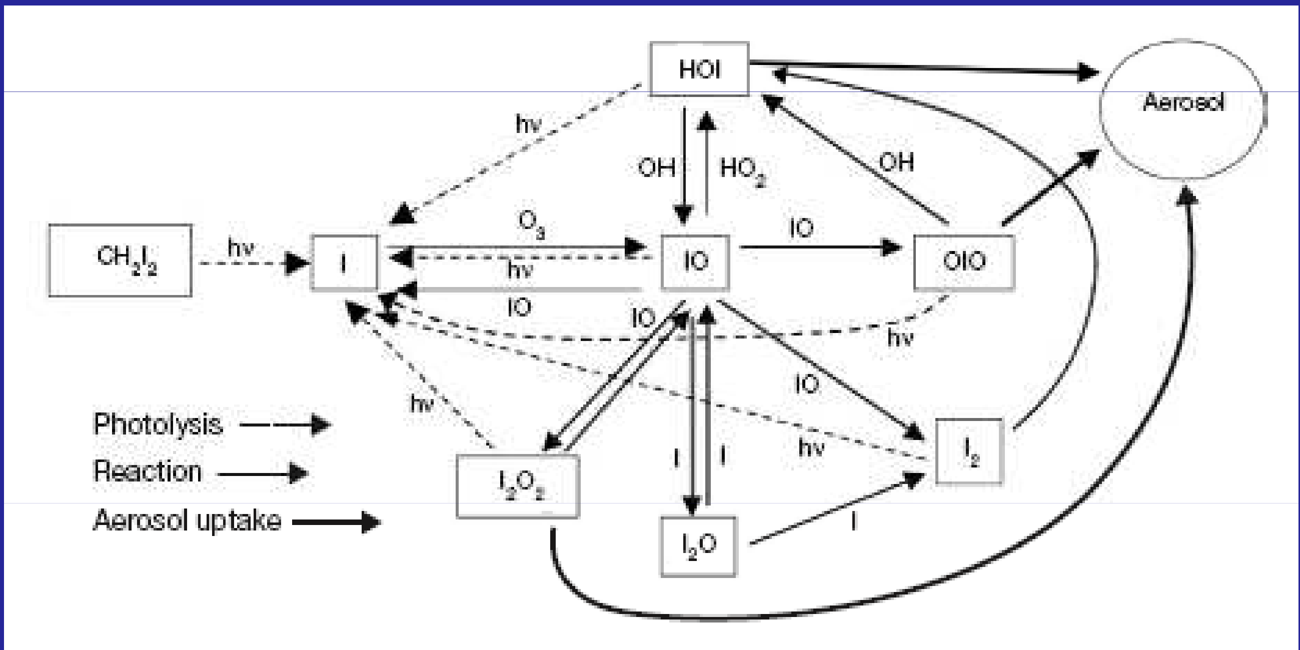
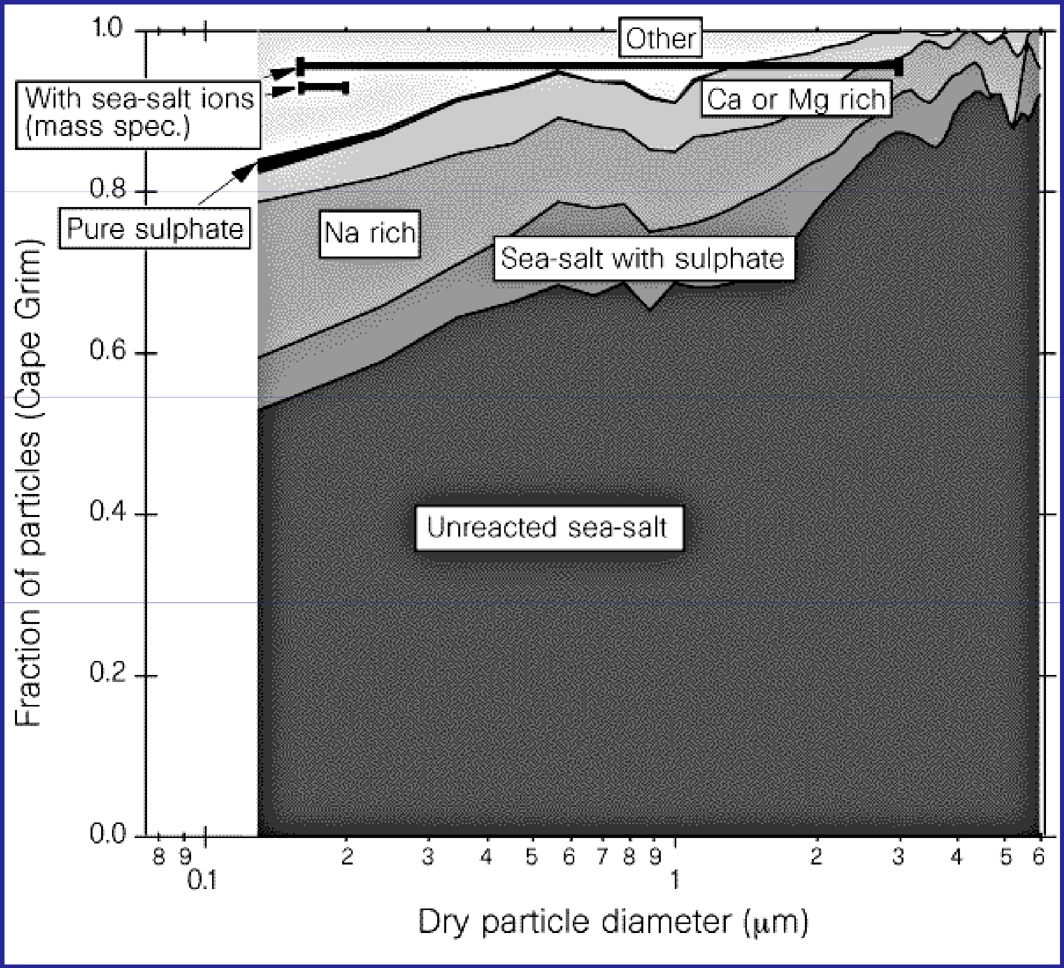


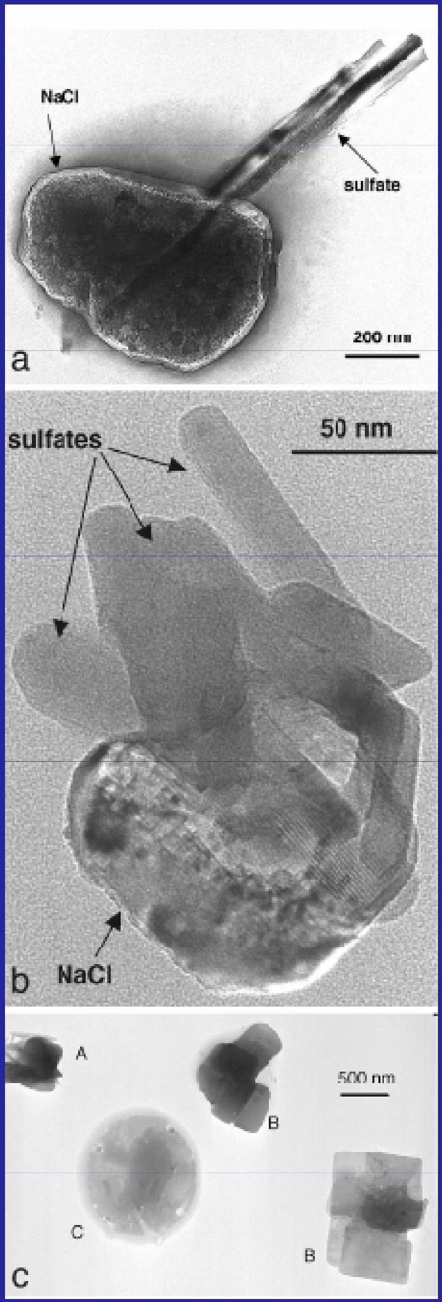
Figure 2. Total particle concentration over a 3-month period at Mace Head. Low tide is marked with a cross. Units of color scale are cm^{-3}. Particle concentrations are 1-hour averages.



O'Dowd et al., 2002a,b

The single-particle view...



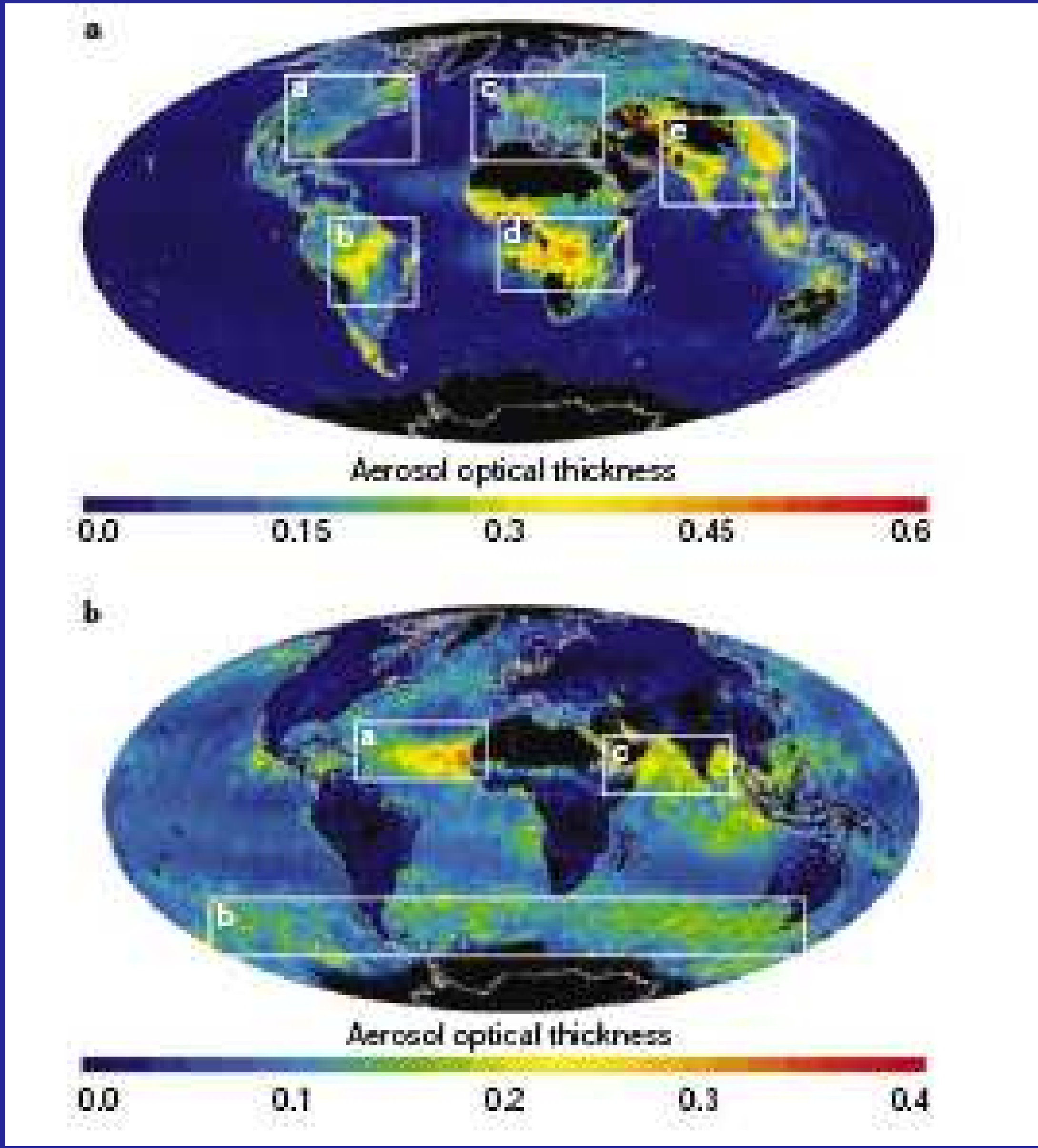


Murphy et al., 1998; Buseck and Posfai, 1999

Global view of aerosol optical depth... MODIS Sept. 2000

fine particles
- *urban pollution*
- *biomass burning*

coarse particles
- *mineral dust*



(Kaufman et al., 2002)

Aerosol properties from space...

- *Aersol Optical Thickness*

Aerosol size info

- *angstrom coefficient*

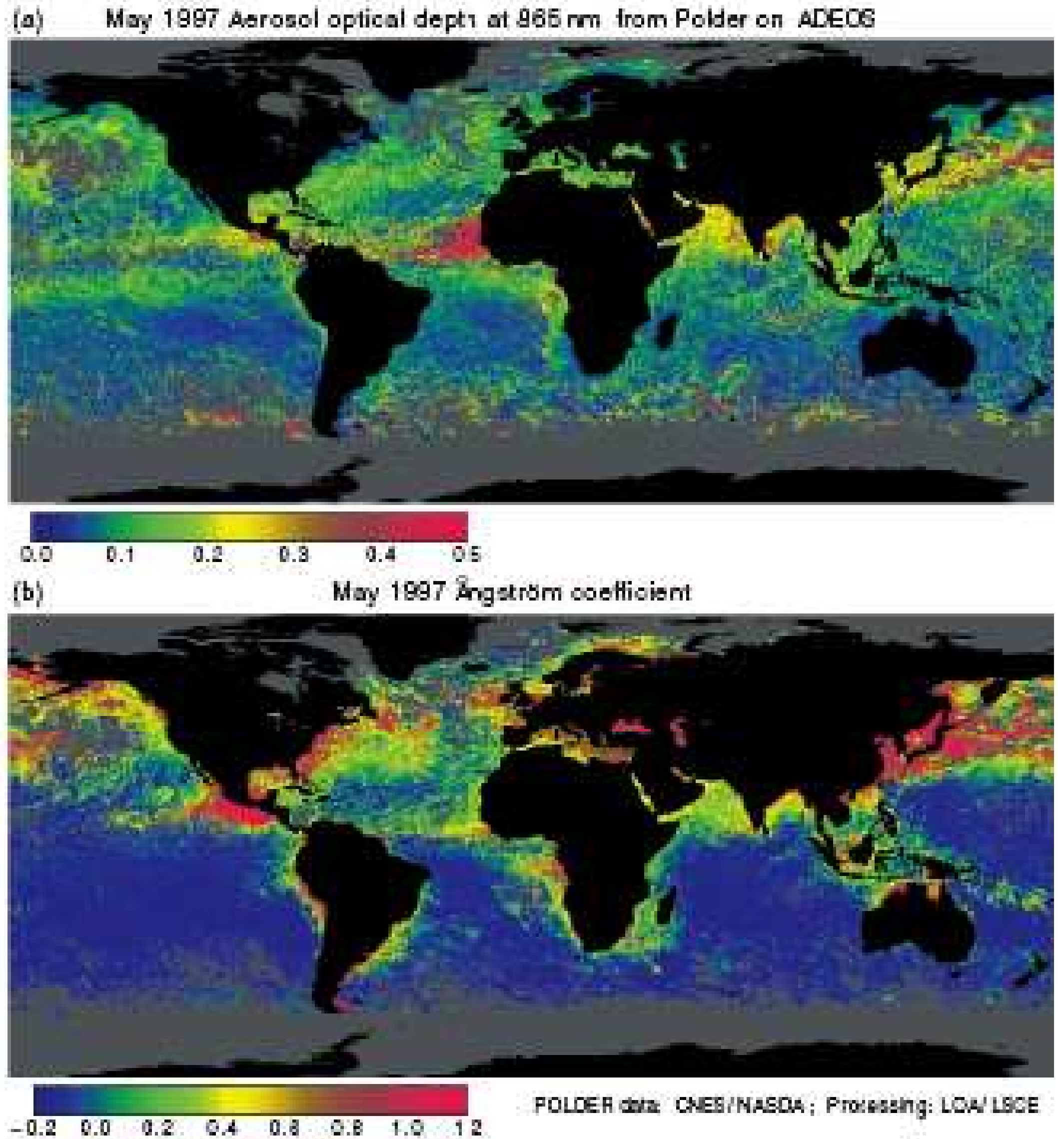
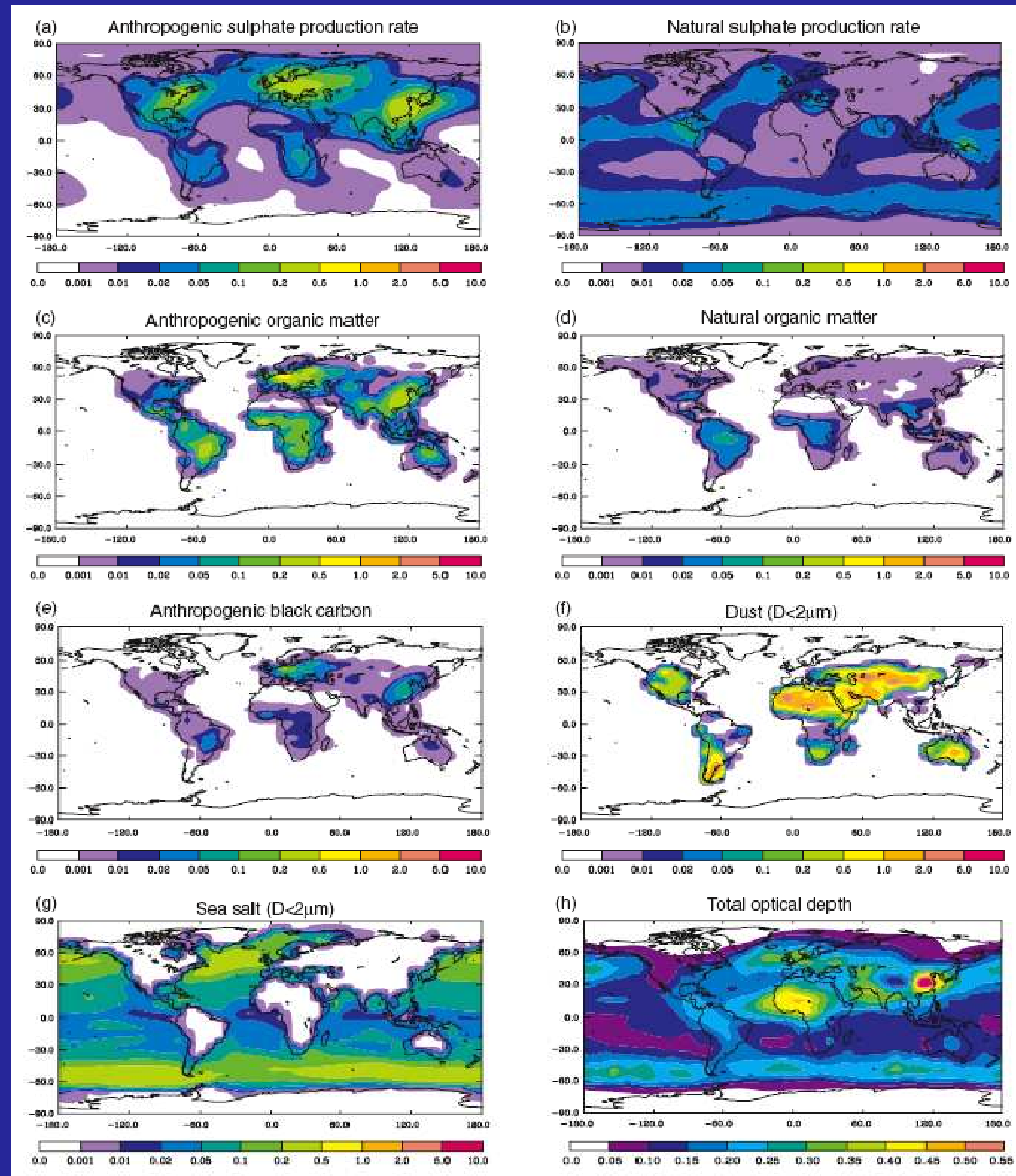


Figure 5.3: (a) Aerosol optical depth and (b) Ångstrom exponent from POLDER satellite data for May 1997 (Deuzé et al., 1999). The largest optical depths over the Atlantic Ocean are from north African dust. The Ångstrom exponent expresses the wavelength dependence of scattered light between 670 and 865 nm. The African dust plume has a small Ångstrom exponent due to the importance of coarse mode aerosols whereas the larger Ångstrom exponents around the continents show the importance of accumulation mode aerosols in those locations.

POLDER-1 (IPCC, Deuze et al., 1999)

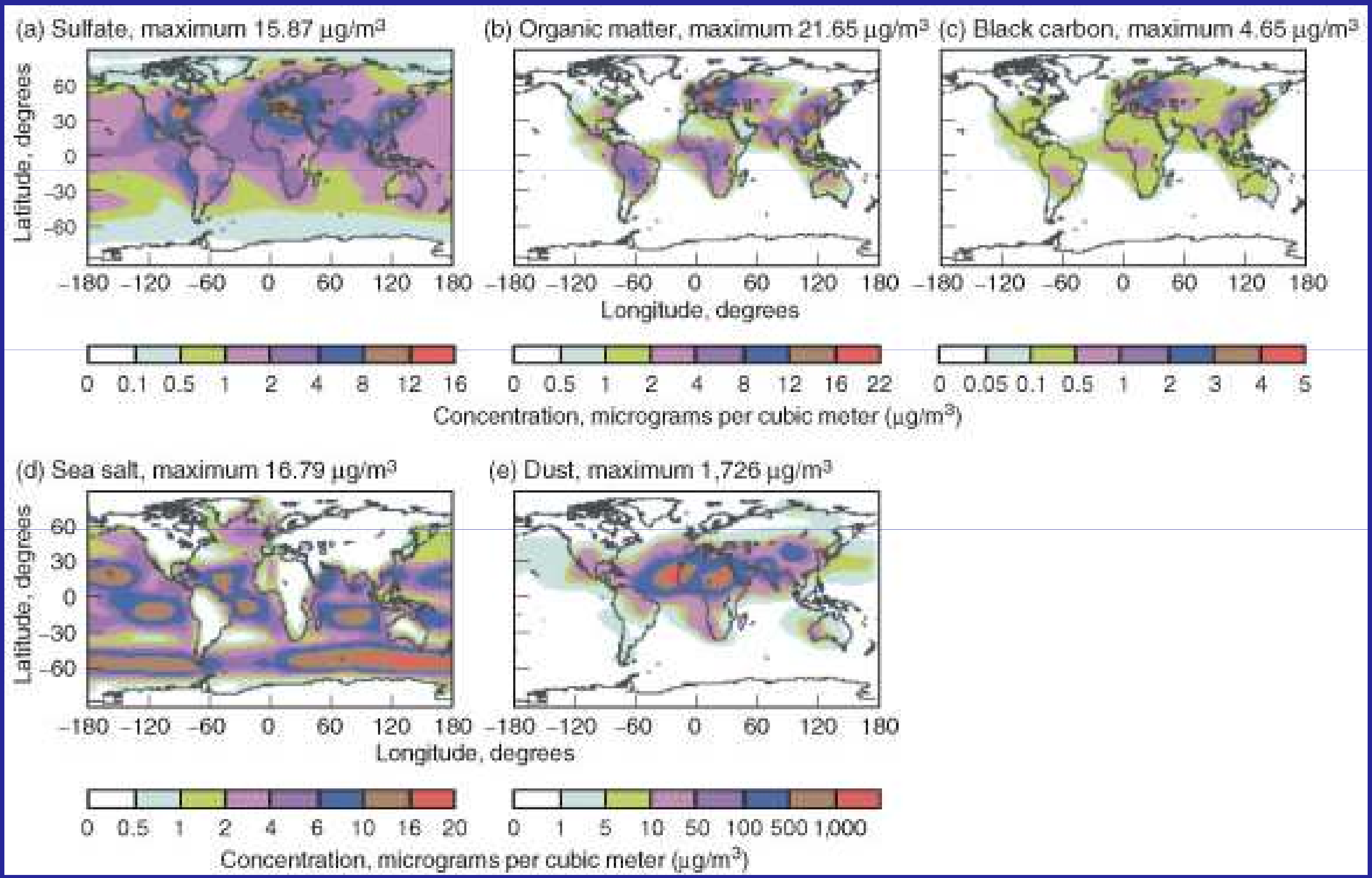
Understanding forcing/feedback requires realistic aerosols in climate models...



annual average sources (kg km^{-2} hr^{-1})

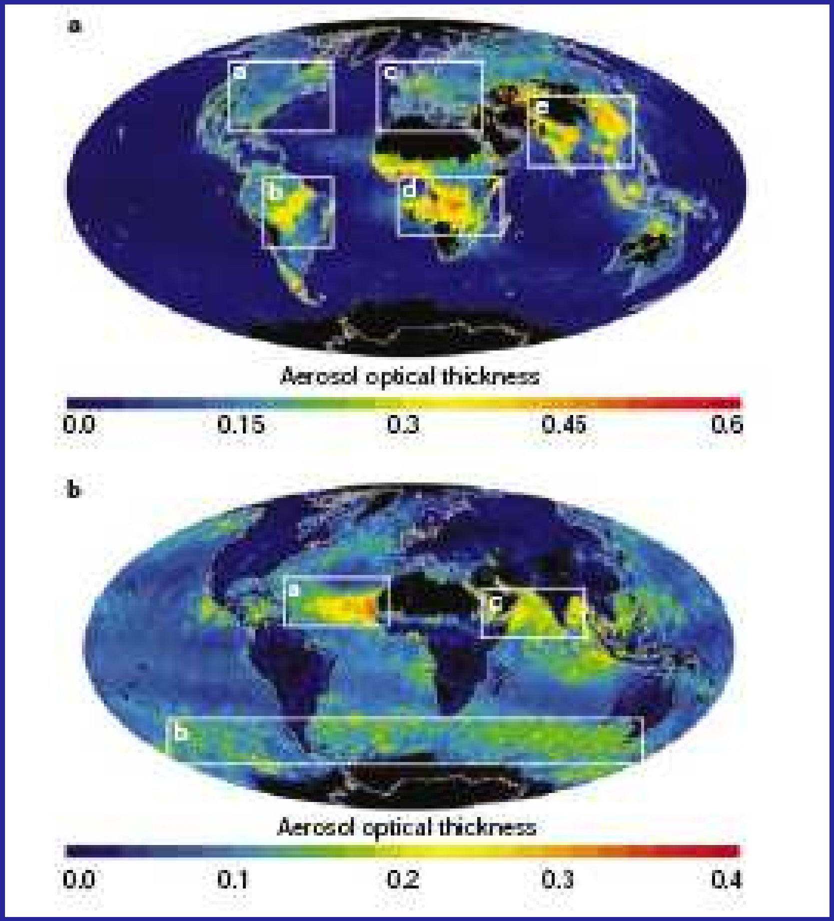
IPCC, 2001

Modeled atmospheric aerosols...



Measurements and models...

Sept. 2000, AOT 0.55 µm

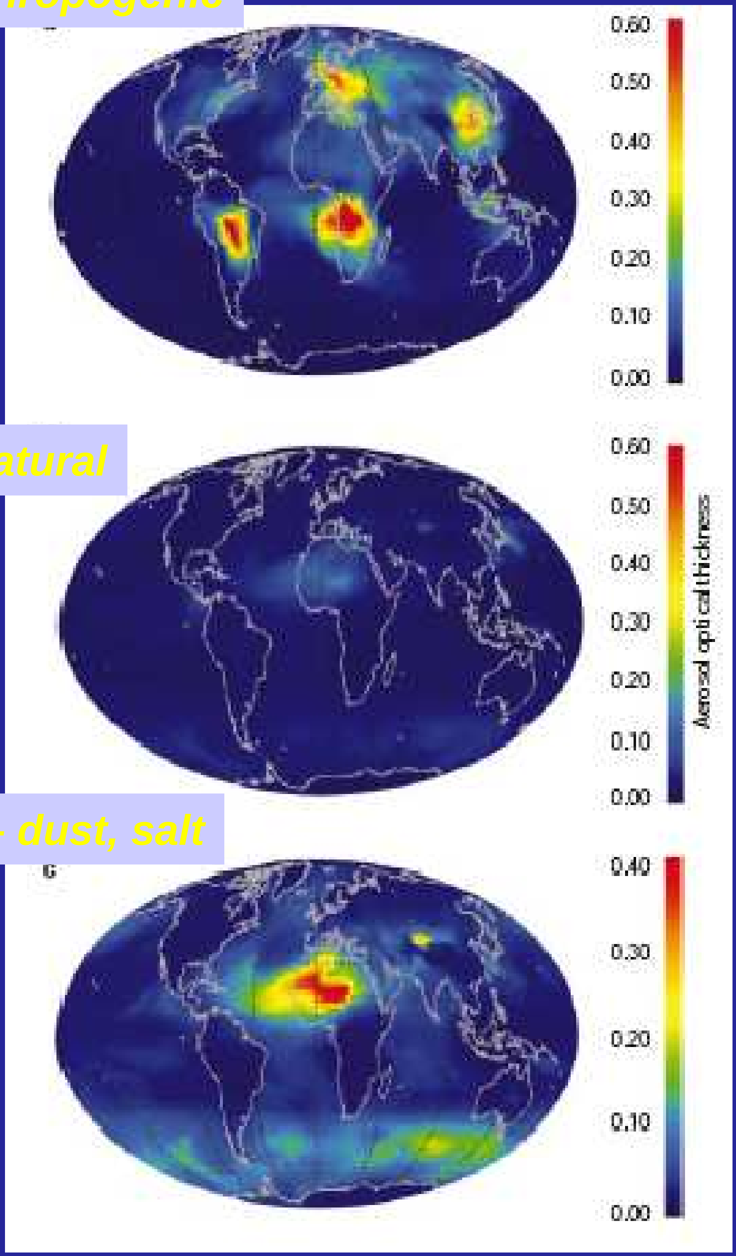


MODIS (Kaufman et al., 2002)

fine - anthropogenic

fine-natural

coarse – dust, salt



GOCART model (Chin et al., 2002)

What’s left to do...?

- *in situ* aerosol/cloud radiation experiments
- understand the satellite signals
- model “real” aerosols (shapes, internal/external mixtures)
- marine microlayer
- “life cycle” of marine aerosol organics
- gas phase $\rightarrow$ aerosol chemistry (sulfur, iodine, organics)
- aerosol $\rightarrow$ gas phase cycling (halogens)
- coupled aerosol/chemistry/climate experiments and models

- *marine aerosols are woefully undersampled!*

… the end!!

The end.

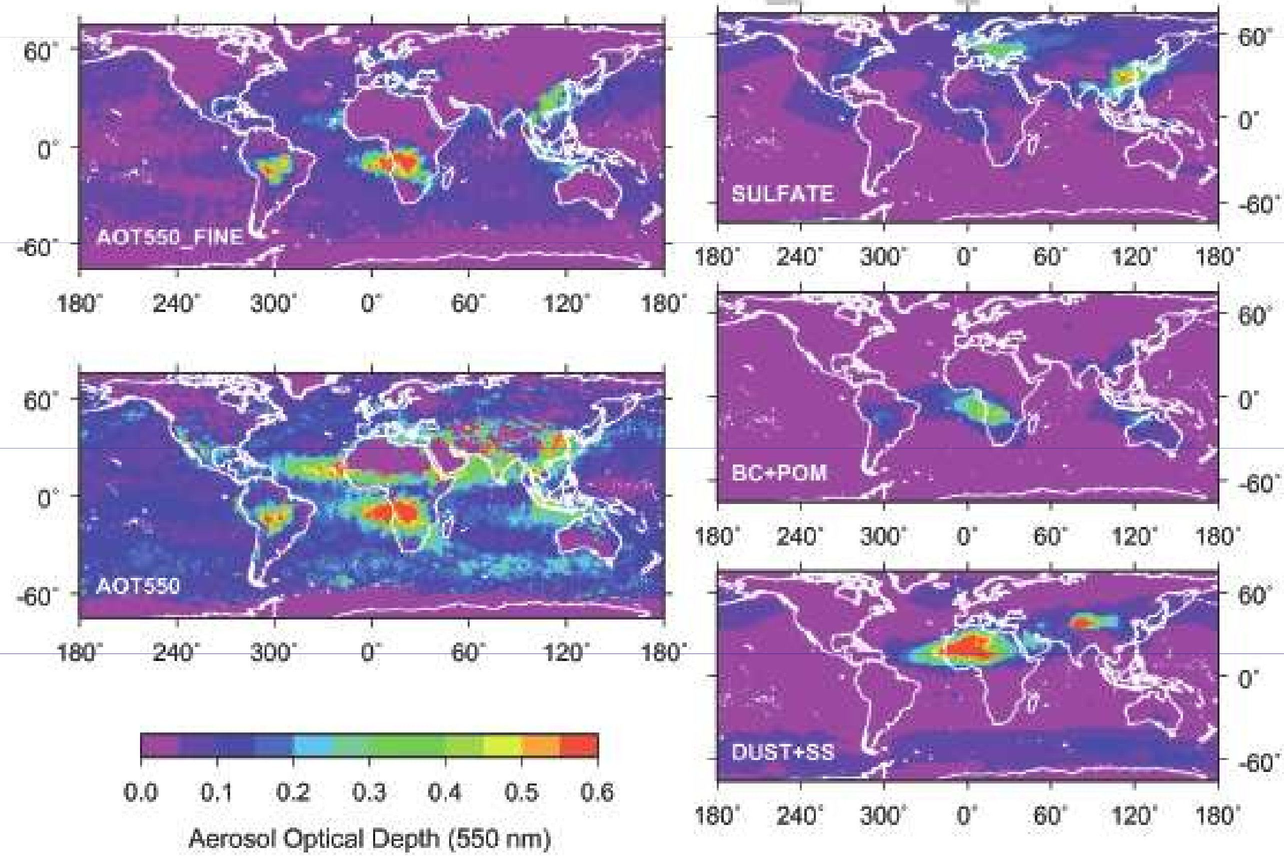


Plate 2. Satellite observations and model simulations of global aerosol optical thickness (at 0.55 μm) for September, 2000. Left, NASA Moderate Resolution Imaging Spectroradiometer (on EOS) satellite observations of (upper left) fine aerosols and (lower left) total aerosols. Right, results from the GOCART model simulating sources, transport, and deposition of (upper right) anthropogenic sulfate, (middle right) black carbon and particulate organic matter, and (lower right) dust and sea salt. Data obtained from the NASA Giovanni online data system (http://disc.sci.gsfc.nasa.gov/giovanni). See *Kaufman et al.* [2002] and *Chin et al.* [2002] for further information.