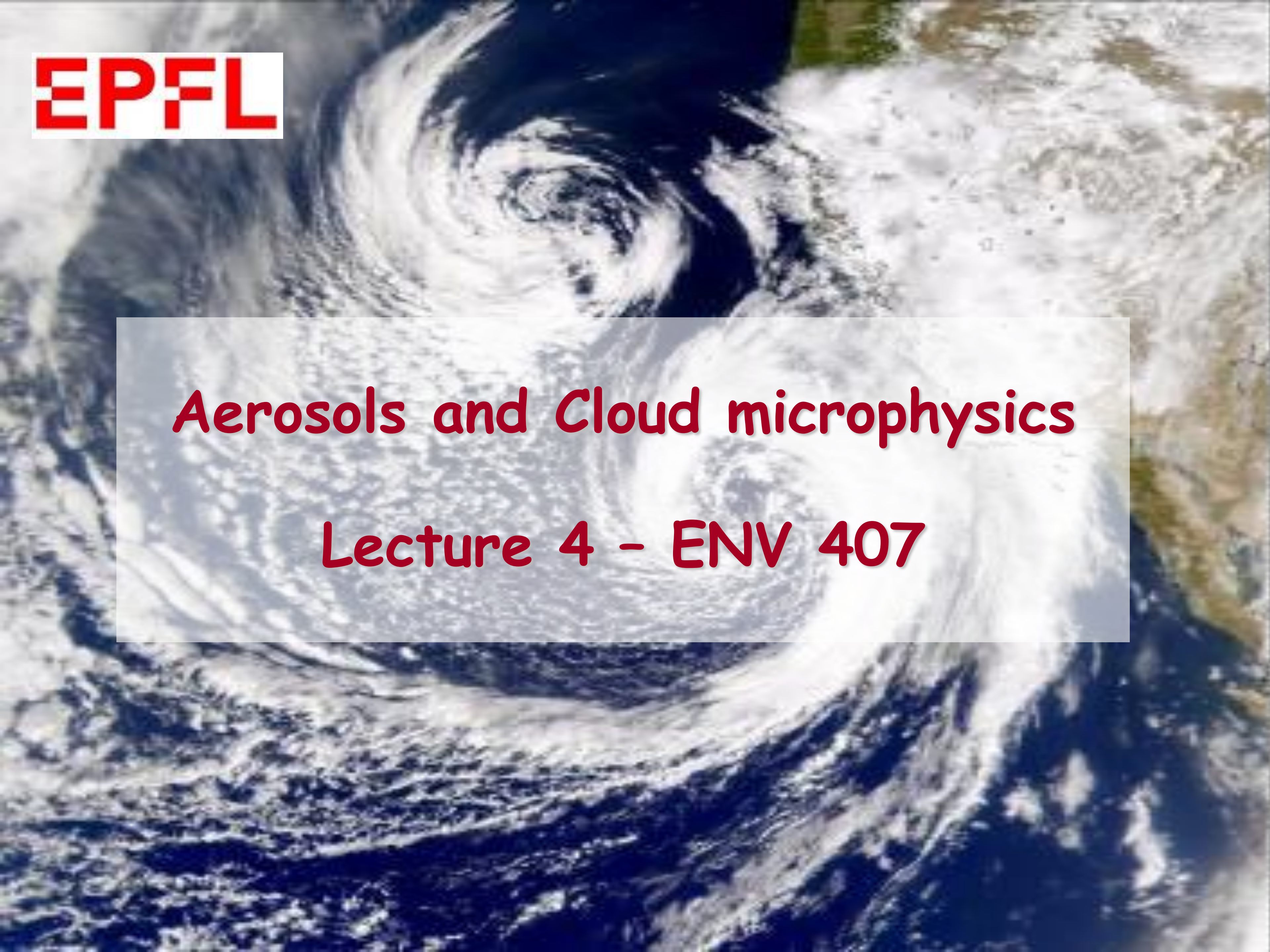
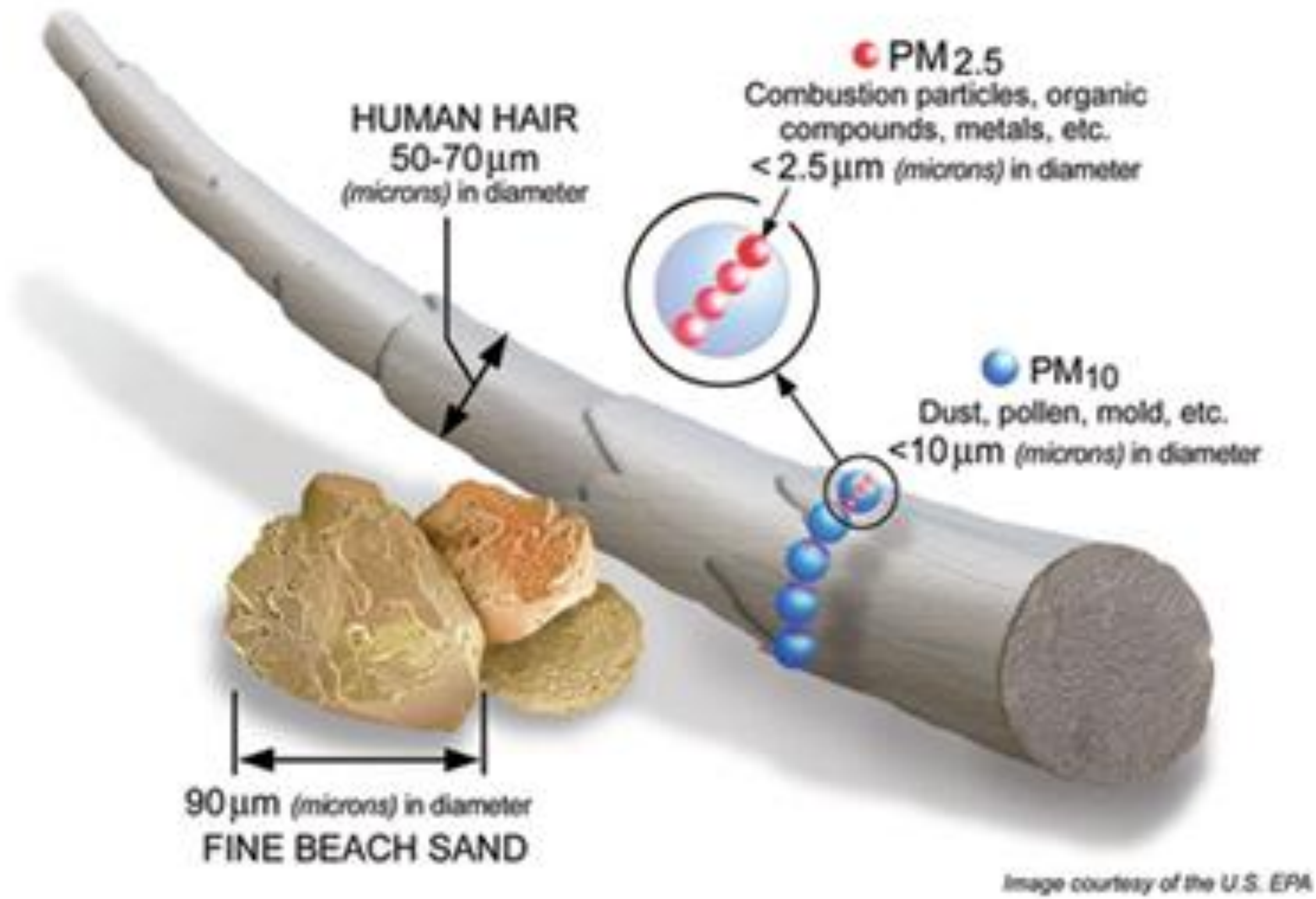


EPFL

# Aerosols and Cloud microphysics

## Lecture 4 – ENV 407

# Aerosol sizes and "names"



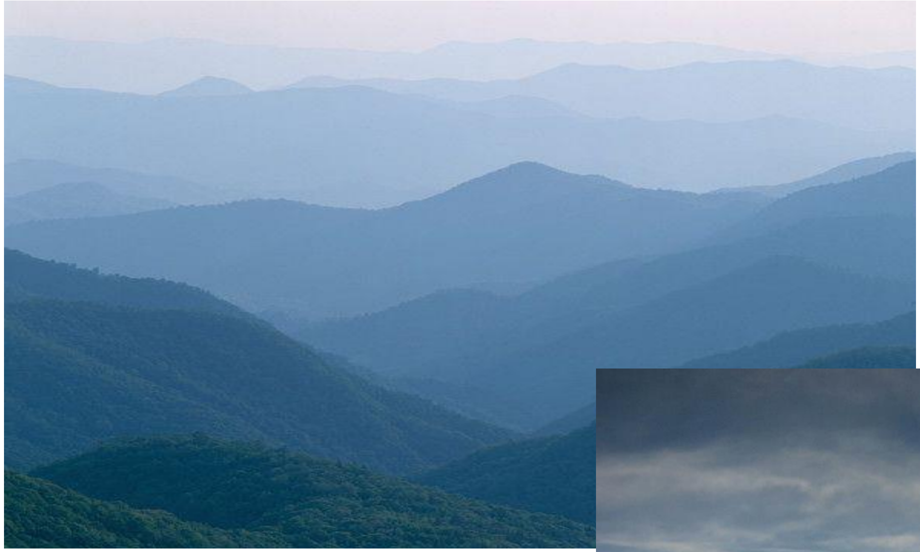
# Aerosols: Significance

Health Effects

Visibility

Atmospheric Optics

Cloud Formation



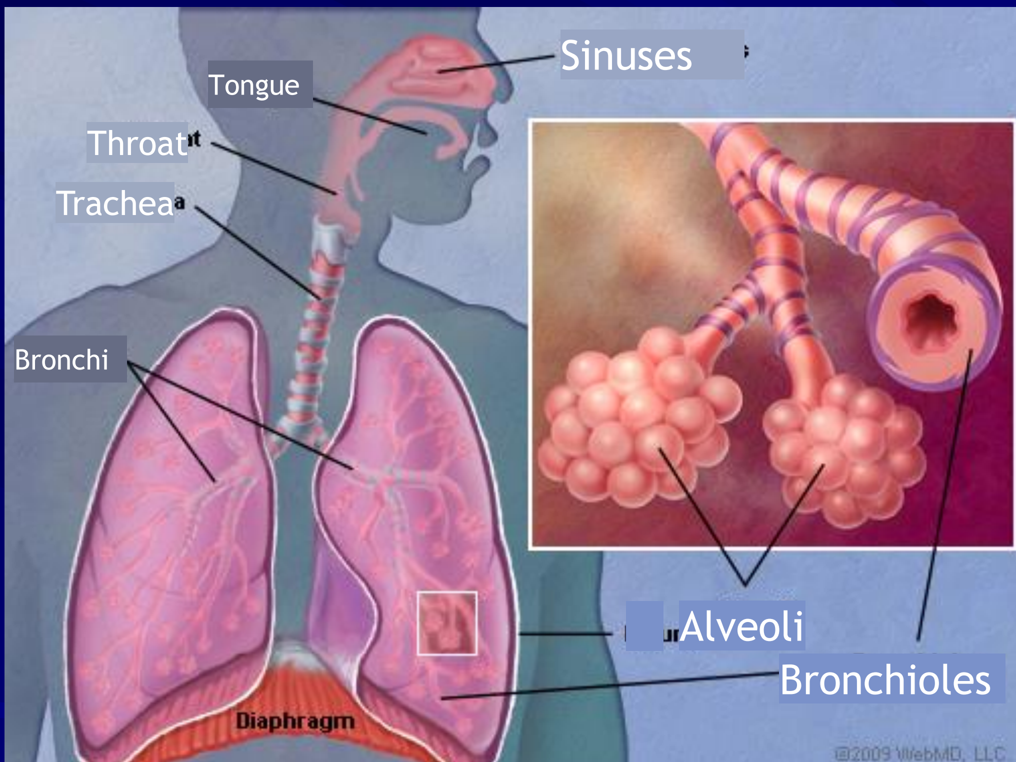
# Aerosols directly scatter/absorb light

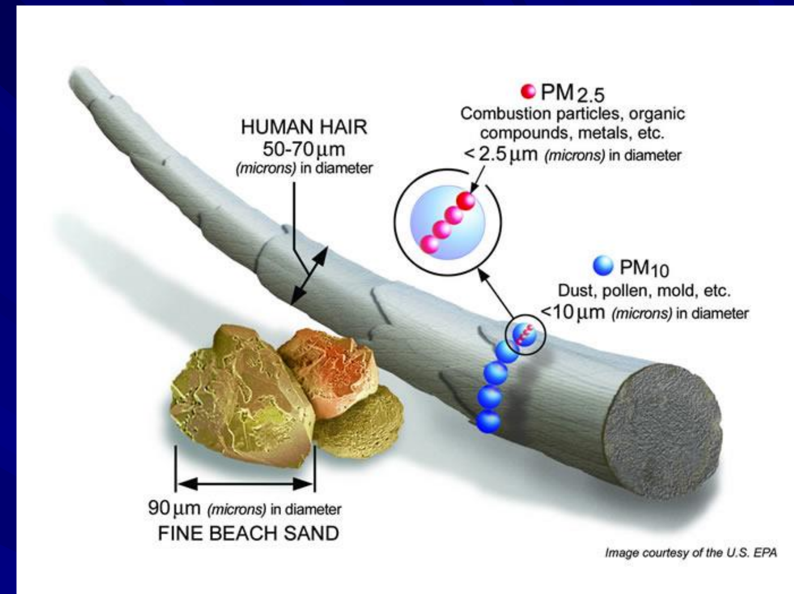
"direct radiative forcing" of aerosol.


Dust and smoke over East Mediterranean


Soot from Kuwaiti oil fires

# Effects of $PM_{2.5}$ on Human Health




- Irritation of the airways
- Reduced lung function
- Aggravated asthma
- Chronic bronchitis
- Irregular heartbeat
- Nonfatal heart attacks
- Some cancers



http://www.epa.gov/ord/ca/quick-finder/particulate-matter-image.htm

http://www.webmd.com/lung/picture-of-the-lungs

# Aerosols: other effects

- Snow/Ice albedo modification
  - ✓ Black carbon («soot») on snow and ice causes them to darken.
  - ✓ May have high regional importance for melting glaciers and ice pack.
- Nutrient deposition to ocean
  - ✓ Some oceanic ecosystems limited by various micronutrients (e.g. Iron, P).
  - ✓ Deposition of nutrient containing aerosol (dust, geoengineering) can stimulate ocean biota, and affect the carbon cycle.

# Origins of Aerosol


## Primary emissions

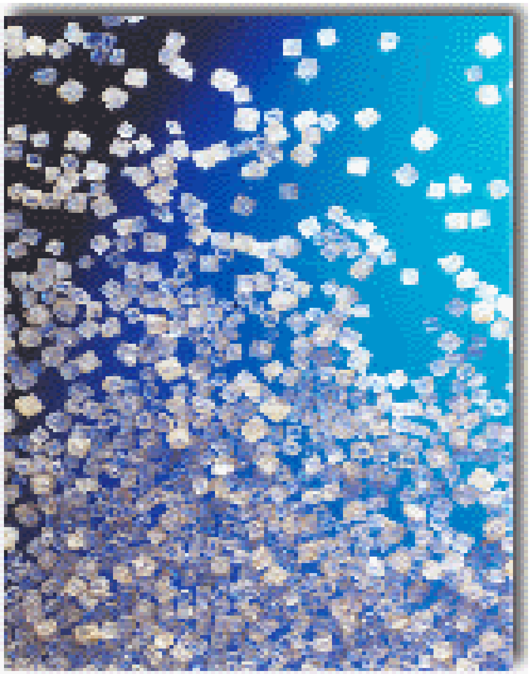
automobiles, industry, domestic, vegetation, forest fires..

## Secondary compounds

Oxidation of precursors (by $O_3$, $H_2O_2$, OH, $NO_3$, etc.)

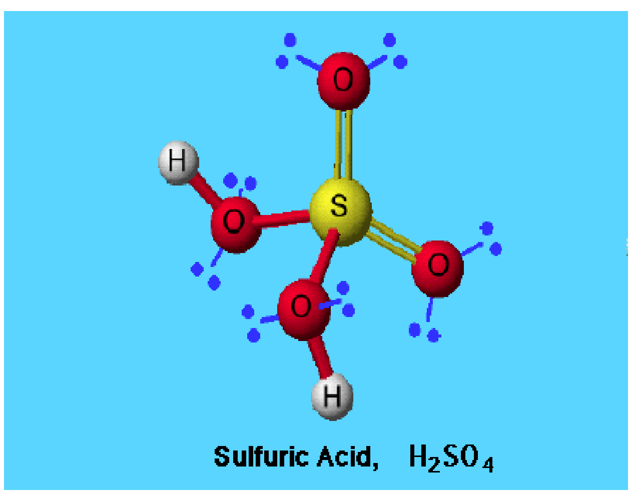
Reaction of volatile bases ($NH_3$) with acids to form $NH_4NO_3$, $(NH_4)_2SO_4$, etc…

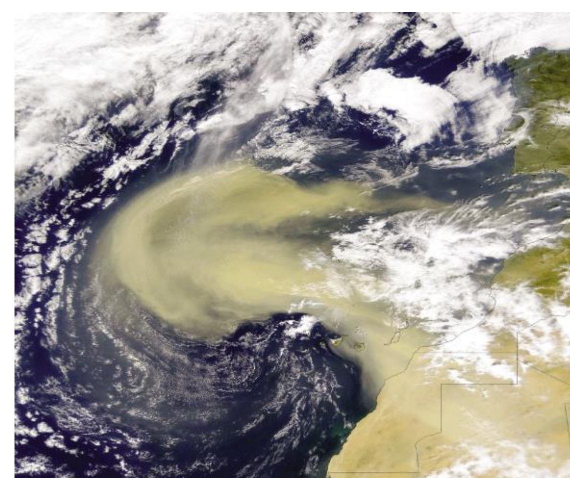
# Aerosol constituents



## Some inorganic components:

- Ammonium sulfate & bisulfate
- Sulfuric acid
- Seasalt (NaCl)
- Crustal material ($CaCO_3$, Mg & K salts)
- Nitrate salts ($NH_4NO_3$, $NaNO_3$)
- Chloride salts (KCl, $NH_4Cl$)



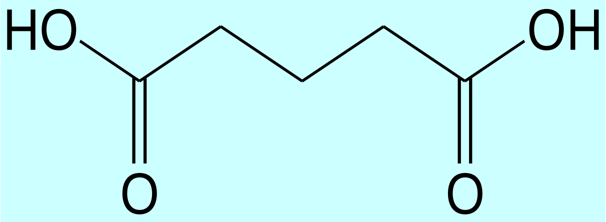



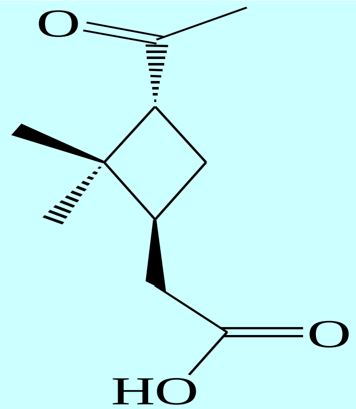
# Aerosol constituents

Some (of many) organic compounds:

## Glutaric Acid

Both primary (biomass combustion) and secondary (cyclohexene oxidation) species

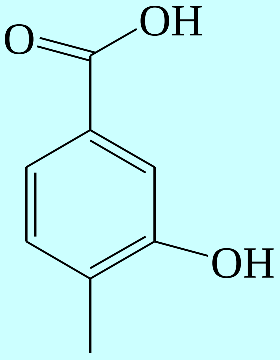


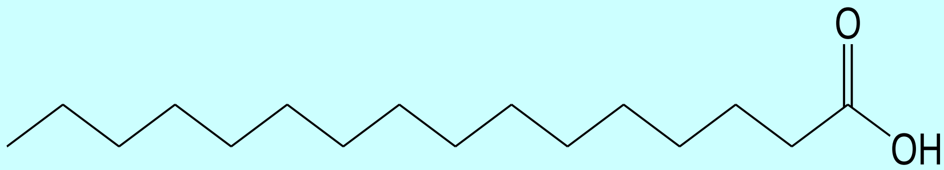

## Pinonic Acid

From oxidation of terpenes

## HydroxyMethyl Benzoic Acid




Both primary (gasoline combustion) and secondary (aromatic oxidation) aerosol species



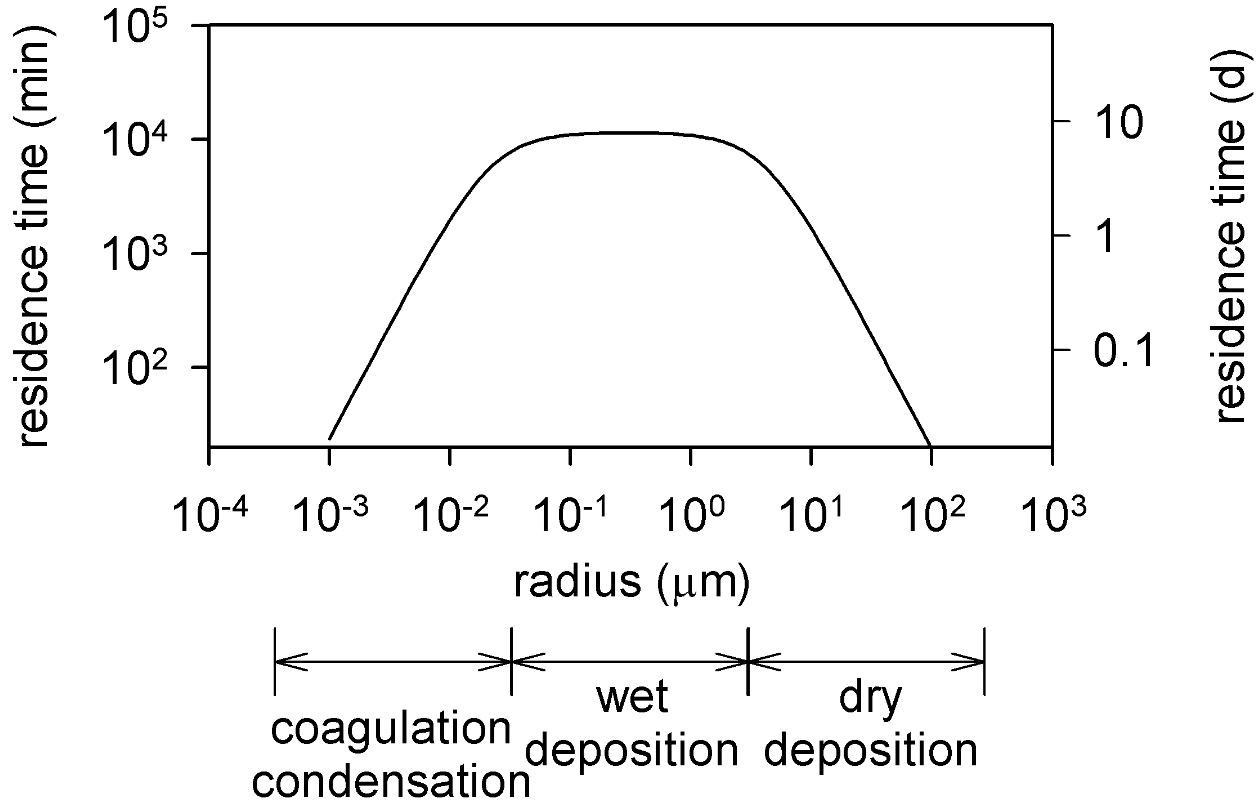

## Palmitic Acid

Common plant wax, primary aerosol constituent

## And many thousands more…

# Size Is a Key Aerosol Property

- Properties and lifetime of Aerosol Particles Depend on Their Size



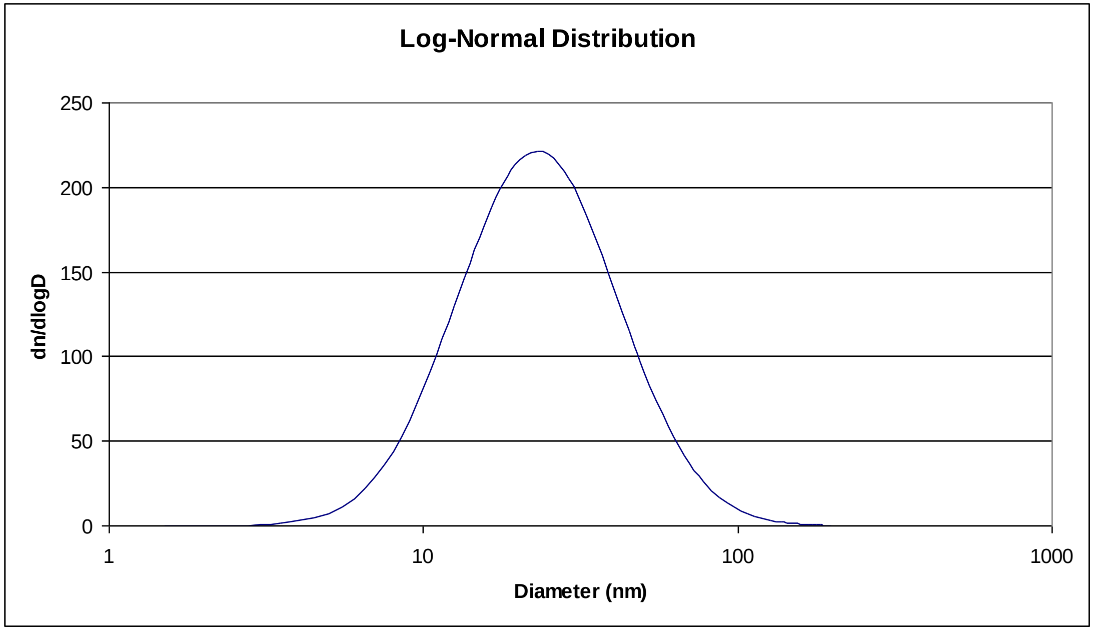
# Size Is important

- Many Properties of Aerosol Particles Depend on Their Size
- Most Aerosols have Log-Normal Size Distributions
- Common Types of Size Distributions
  - Number (number of particles of given size)
  - Mass (or Volume)
  - Surface Area

# Lognormal distributions

- Appears as a normal distribution when x-axis is plotted on log scale

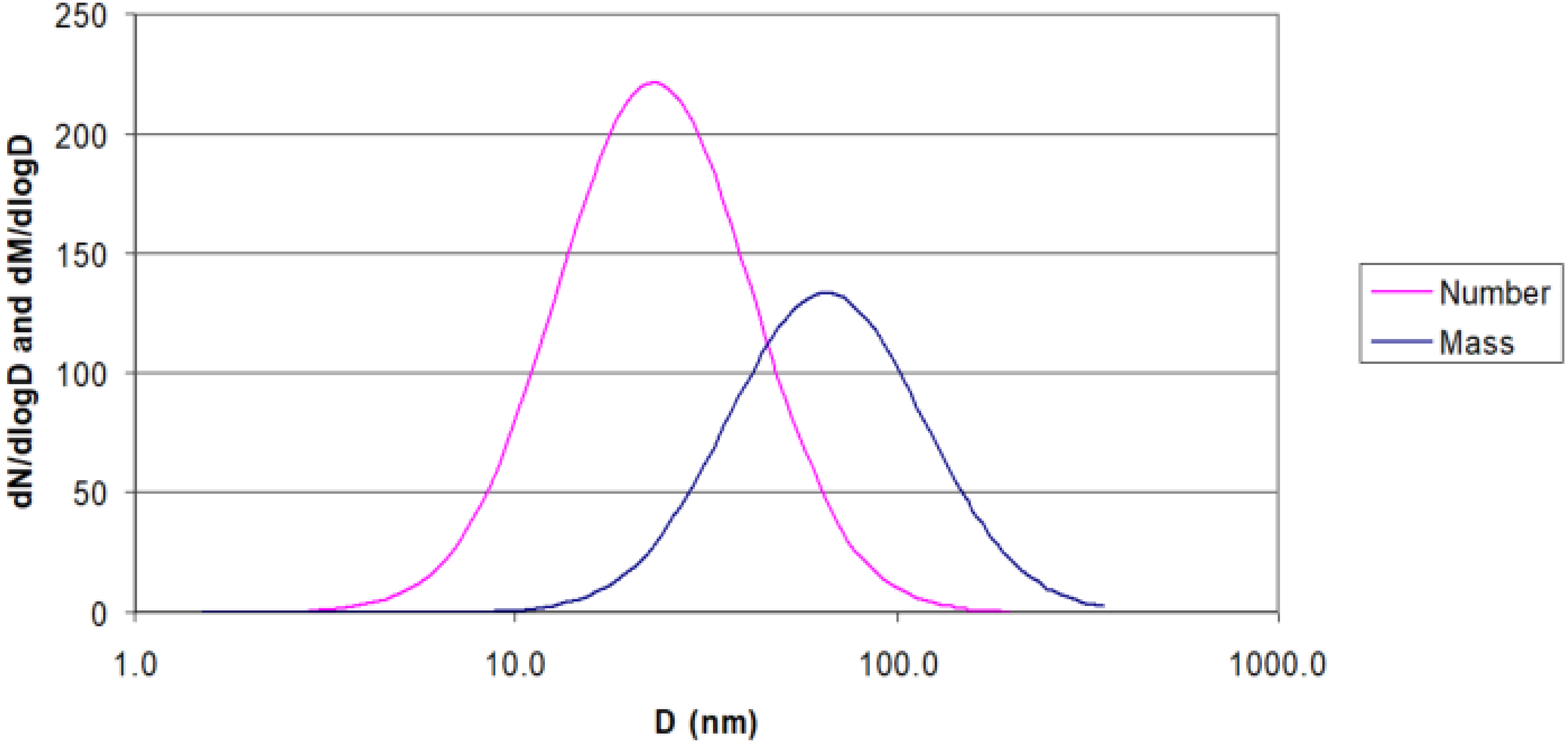
$$n(D) = \frac{N}{(2\pi)^{1/2}\ln\sigma_D}\exp\left[-\frac{(\ln D - \ln D_g)^2}{2\ln^2\sigma_D}\right]$$




Geometric Mean Diameter = 23 nm; Geometric Standard Deviation (σ) = 1.8

# Number vs. Mass Distributions

Mass distribution is "shifted" with respect to the number distribution because of the large difference in volume between small and large particles.



# Calculation Example

- How many 10 nm particles would have the same volume as one 100 nm particle?

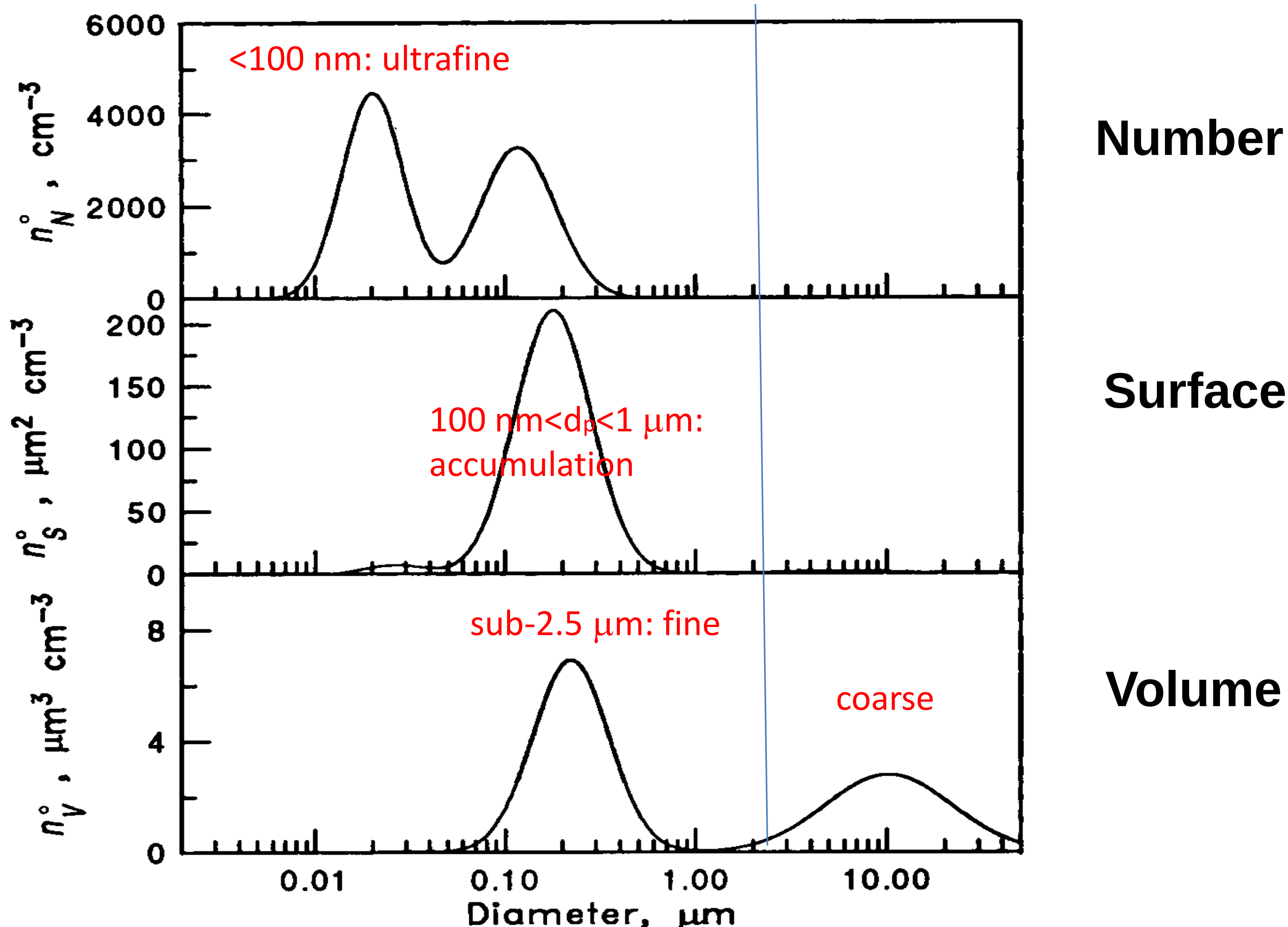
- How many 10 nm particles would have the same surface area as one 100 nm particle?

# Calculation Example

- How many 10 nm particles would have the same volume as one 100 nm particle?
  - $N*[\pi(10\ nm)^3/6] = 1*[\pi(100\ nm)^3/6]$
  - $N = (100/10)^3 = 1000$

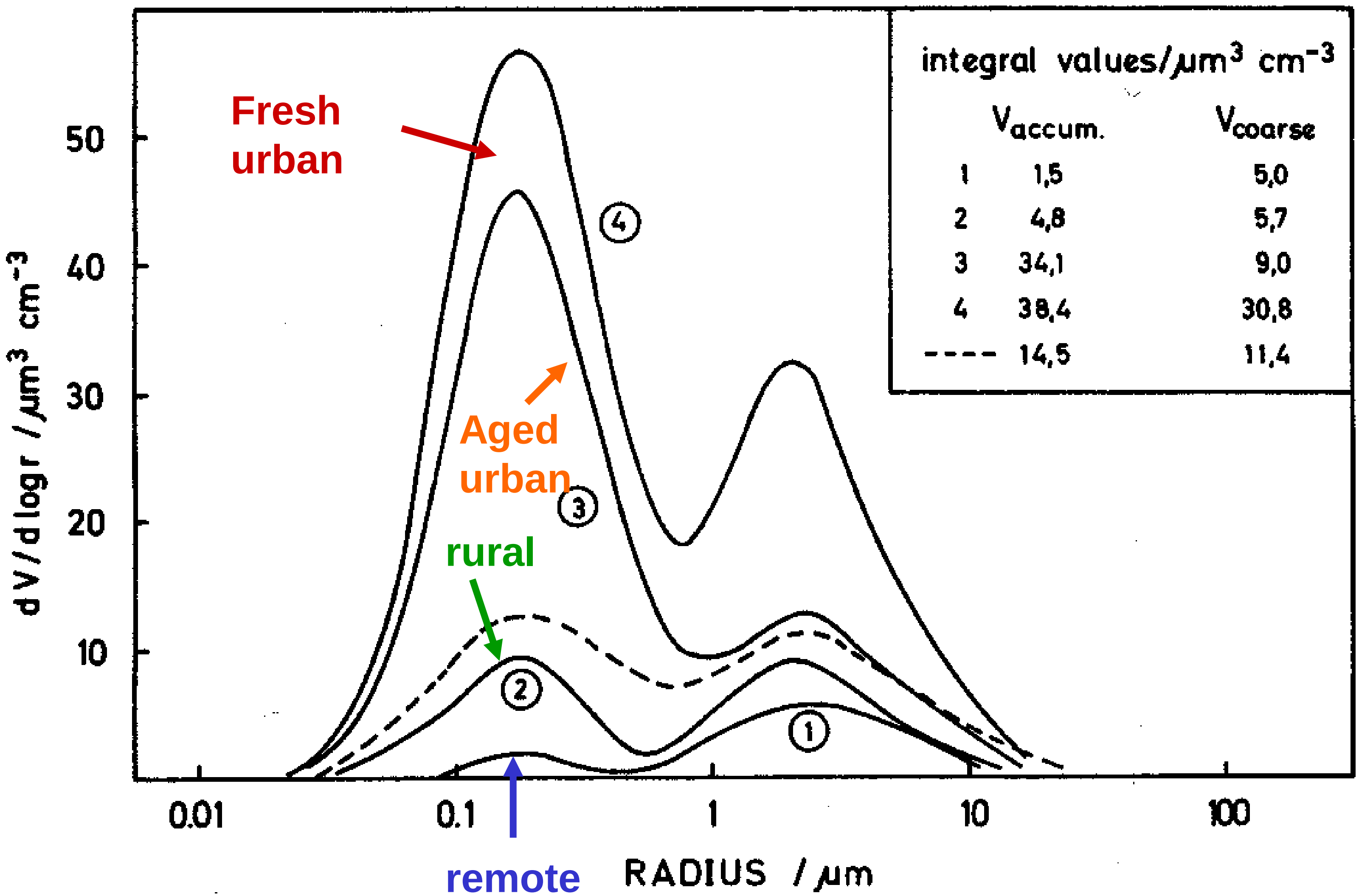
- How many 10 nm particles would have the same surface area as one 100 nm particle?
  - $N*[\pi(10\ nm)^2] = 1*[\pi(100\ nm)^2]$
  - $N = 100$

# Size Distribution: Remote continental air



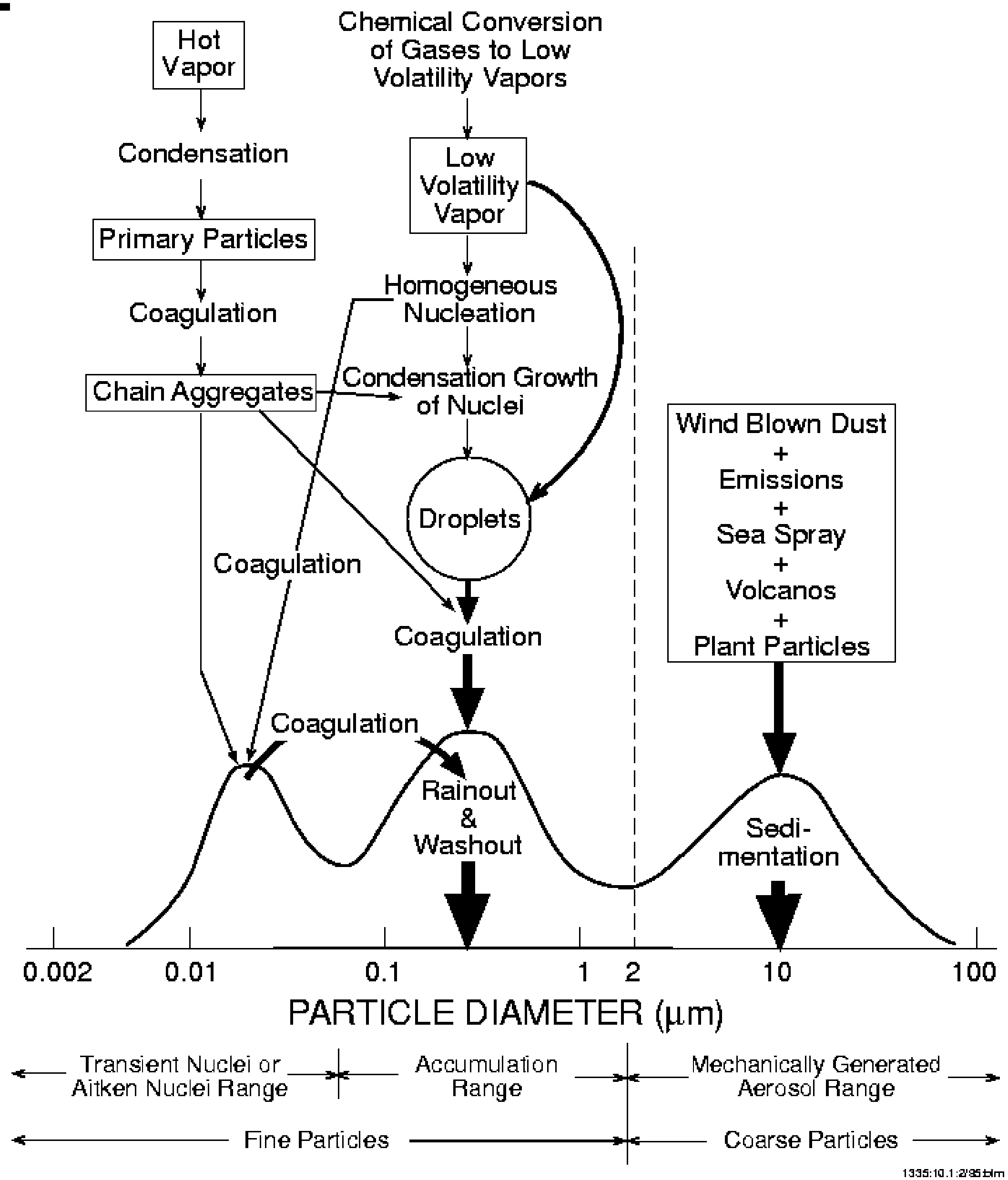

Seinfeld and Pandis

# Size distributions vary a lot



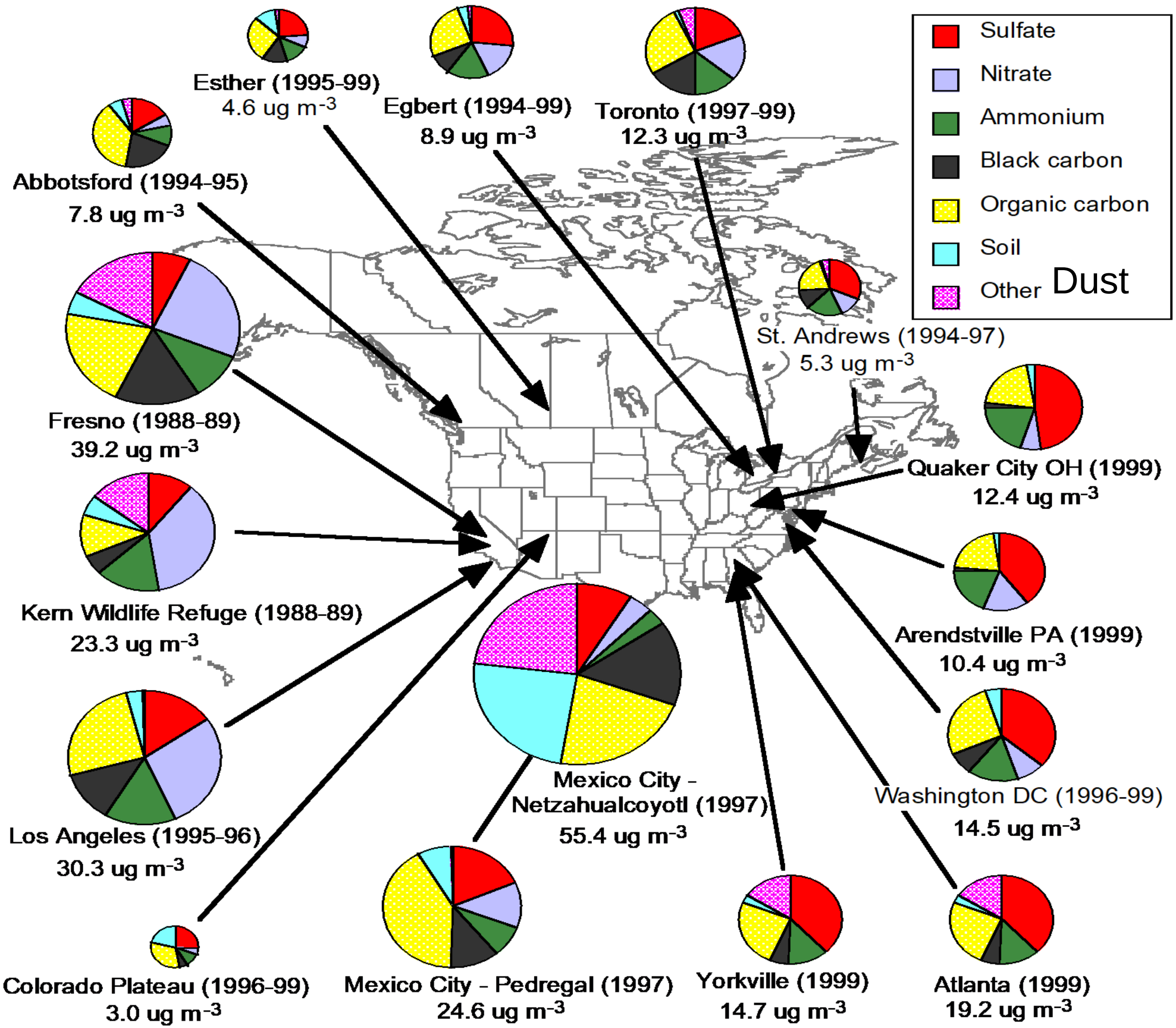

Warneck [1999]

# Size distribution is shaped by the processes present




Seinfeld and Pandis

# Aerosol composition is complex and highly variable




Now let's switch
to clouds

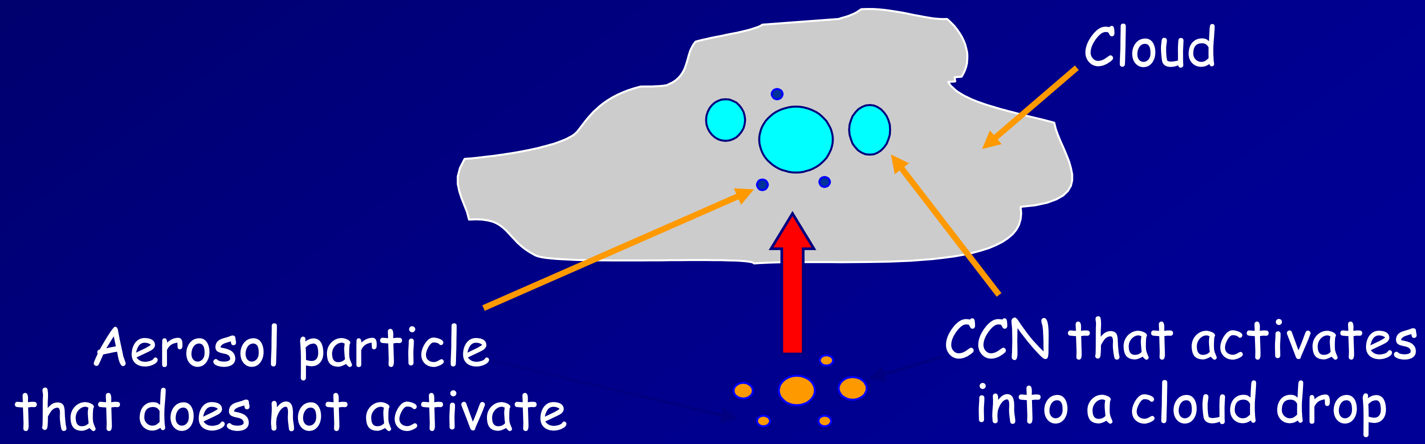
# How do (liquid water) clouds form?

Clouds form in regions of the atmosphere where there is too much water vapor (it is “supersaturated”).

This happens when air is cooled (primarily through expansion in updraft regions and radiative cooling).

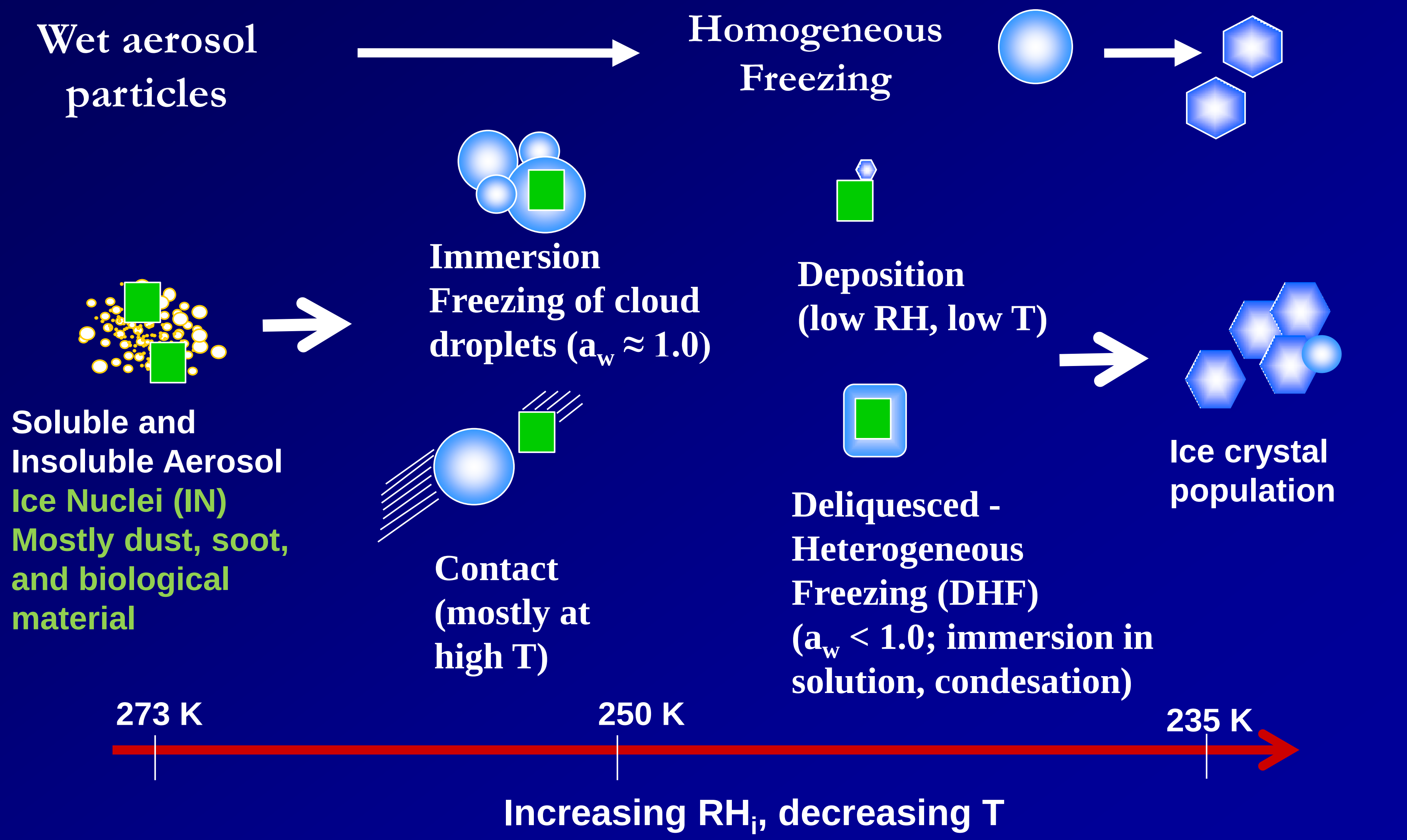
Cloud droplets nucleate on pre-existing particles found in the atmosphere (aerosols) with ~ 0.1μm diameter.

Aerosols that can become droplets are called cloud condensation nuclei (CCN).



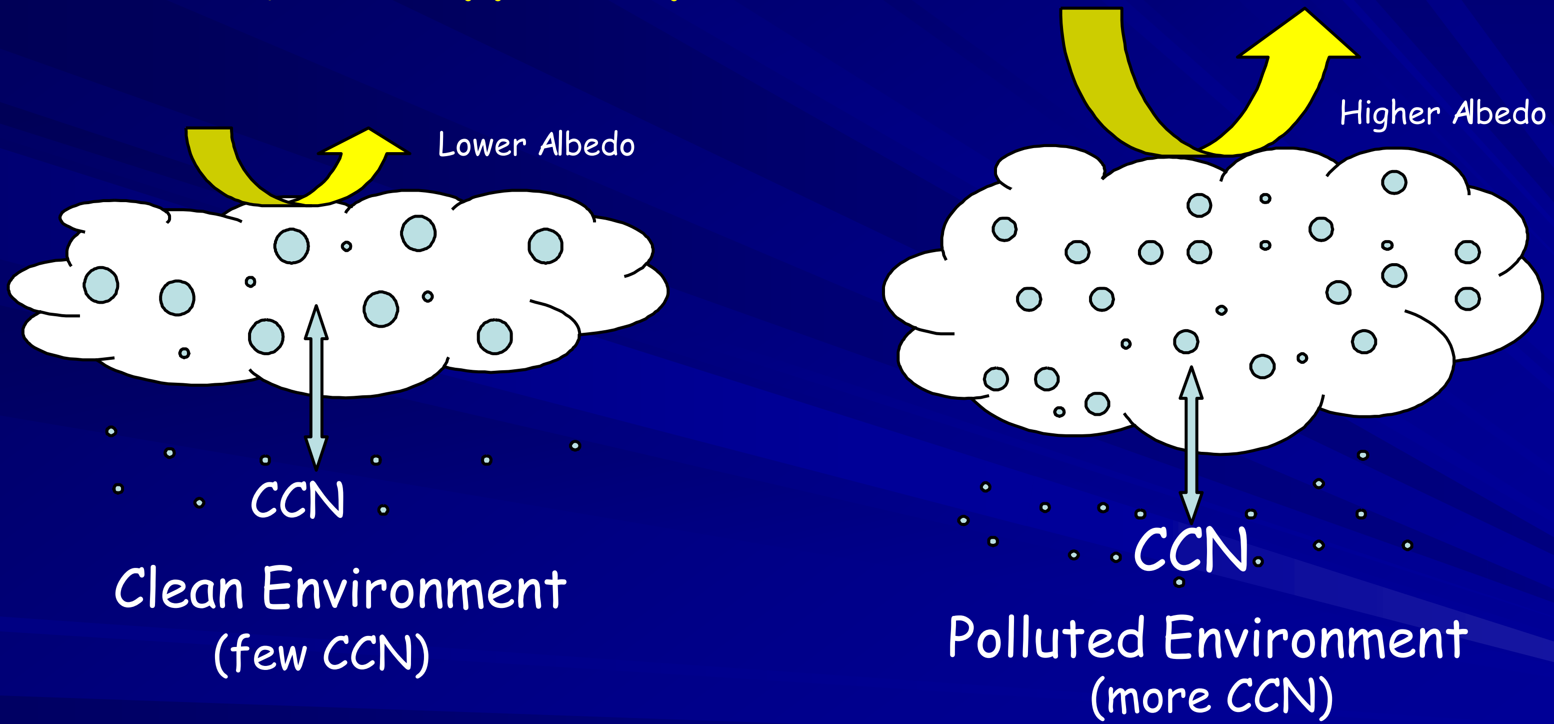
# Ice formation mechanisms

*Multiple* mechanisms for ice formation can be active.



# Increases in aerosol affects warm clouds

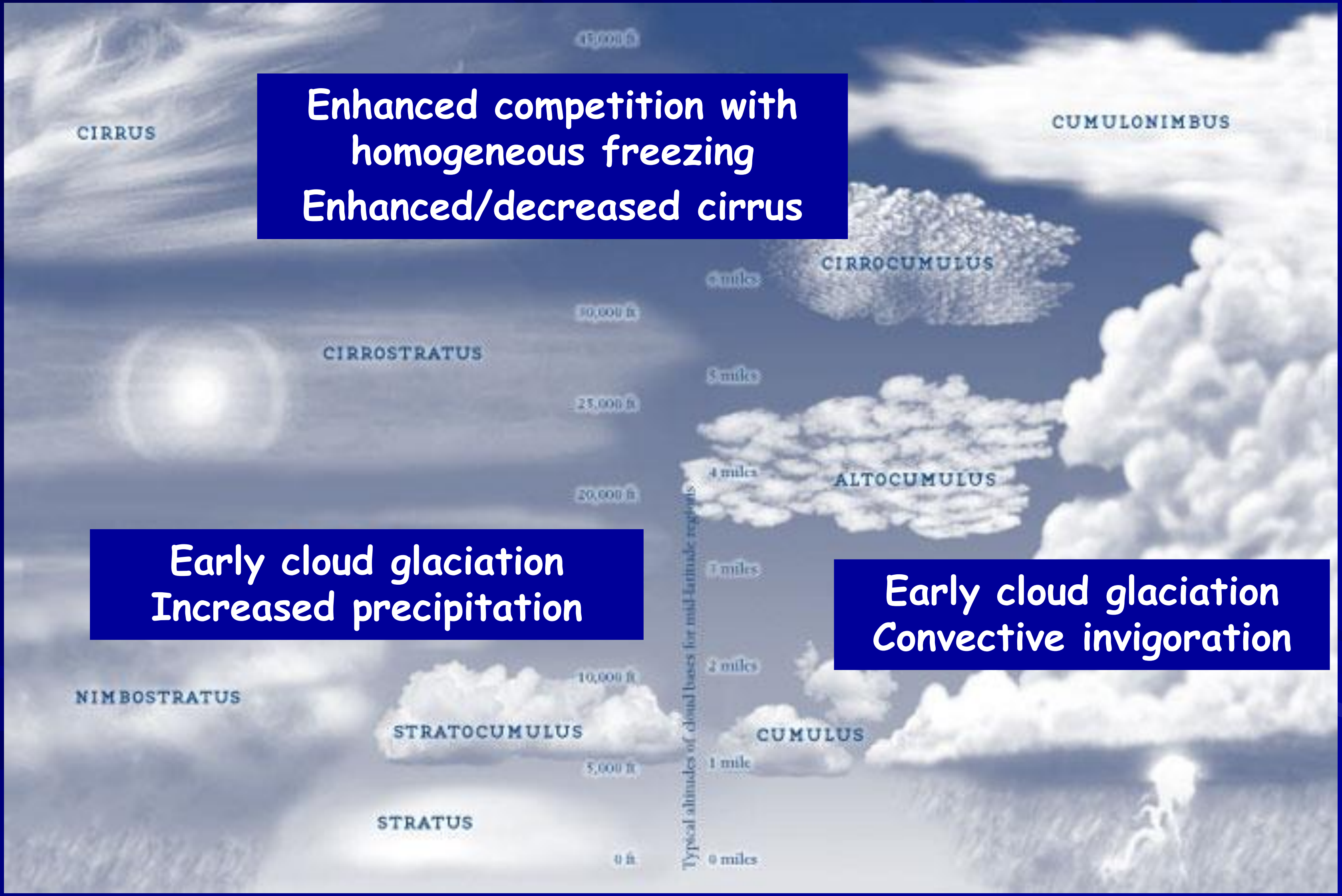
You make clouds that are "whiter", precipitate less (persist longer) and potentially cover larger areas of the globe. This is thought to yield a net cooling on climate and is termed as the "**indirect climatic effect of aerosols**".




Increasing particles tends to cool climate (potentially alot).

Quantitative assessments done with climate models.

# Aerosol effects on ice clouds and climate




Enhanced competition with homogeneous freezing

Enhanced/decreased cirrus

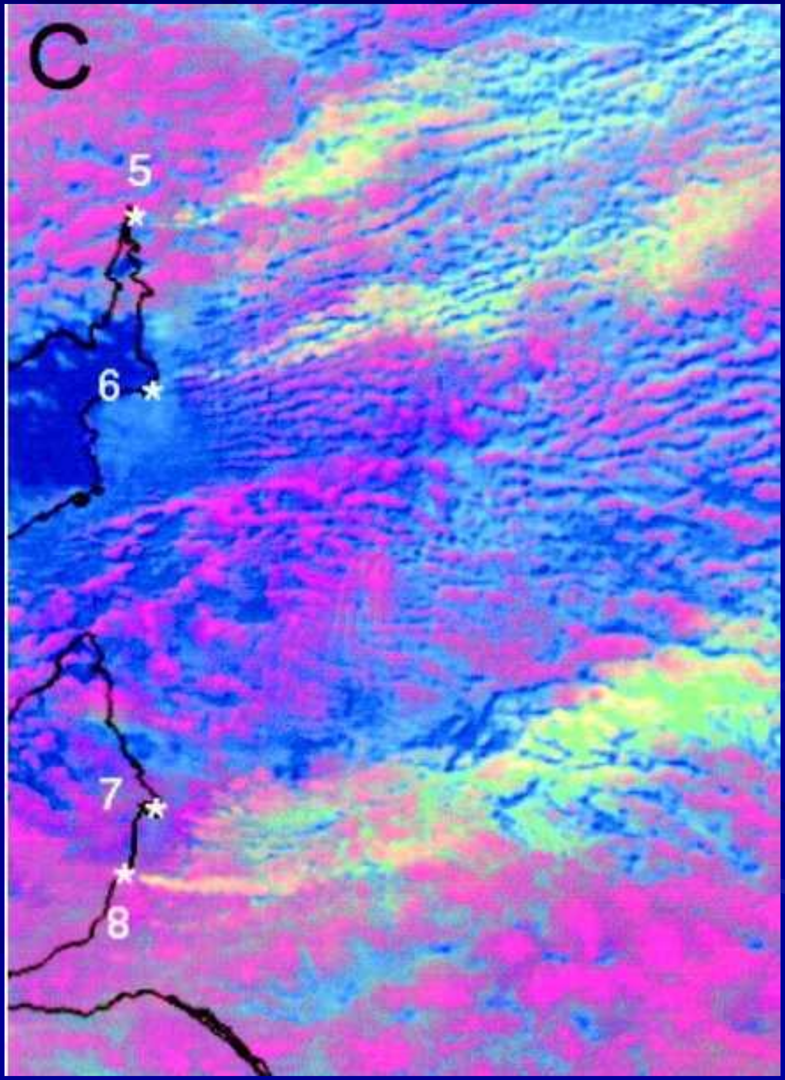
Early cloud glaciation
Increased precipitation

Early cloud glaciation
Convective invigoration

Courtesy: D.Barahona

# Observational evidence of indirect effect

Satellite observations of clouds off W. Australia.




Red: Clouds with low reflectivity.

**White**: Clouds that reflect alot.

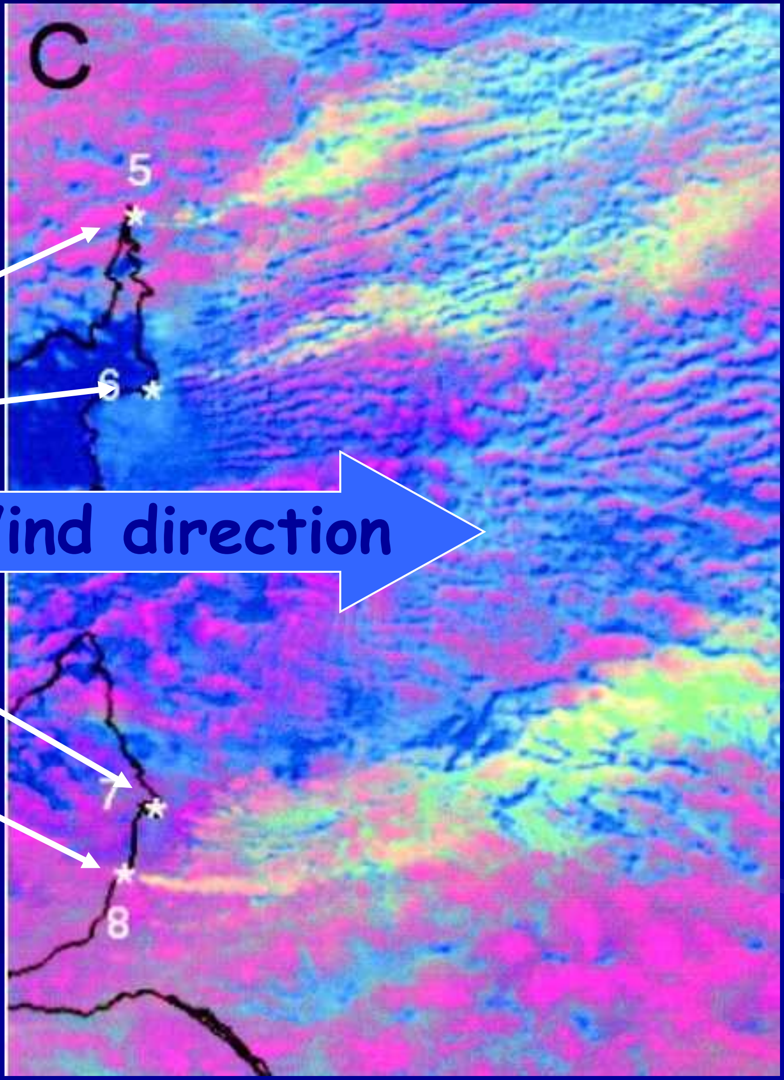
Blue: Clear sky.

*Rosenfeld et al., Science*

# Observational evidence of indirect effect

## Air pollution can affect cloud properties

Satellite observations of clouds off W. Australia.




Red: Clouds with low reflectivity.

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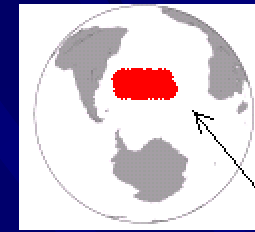
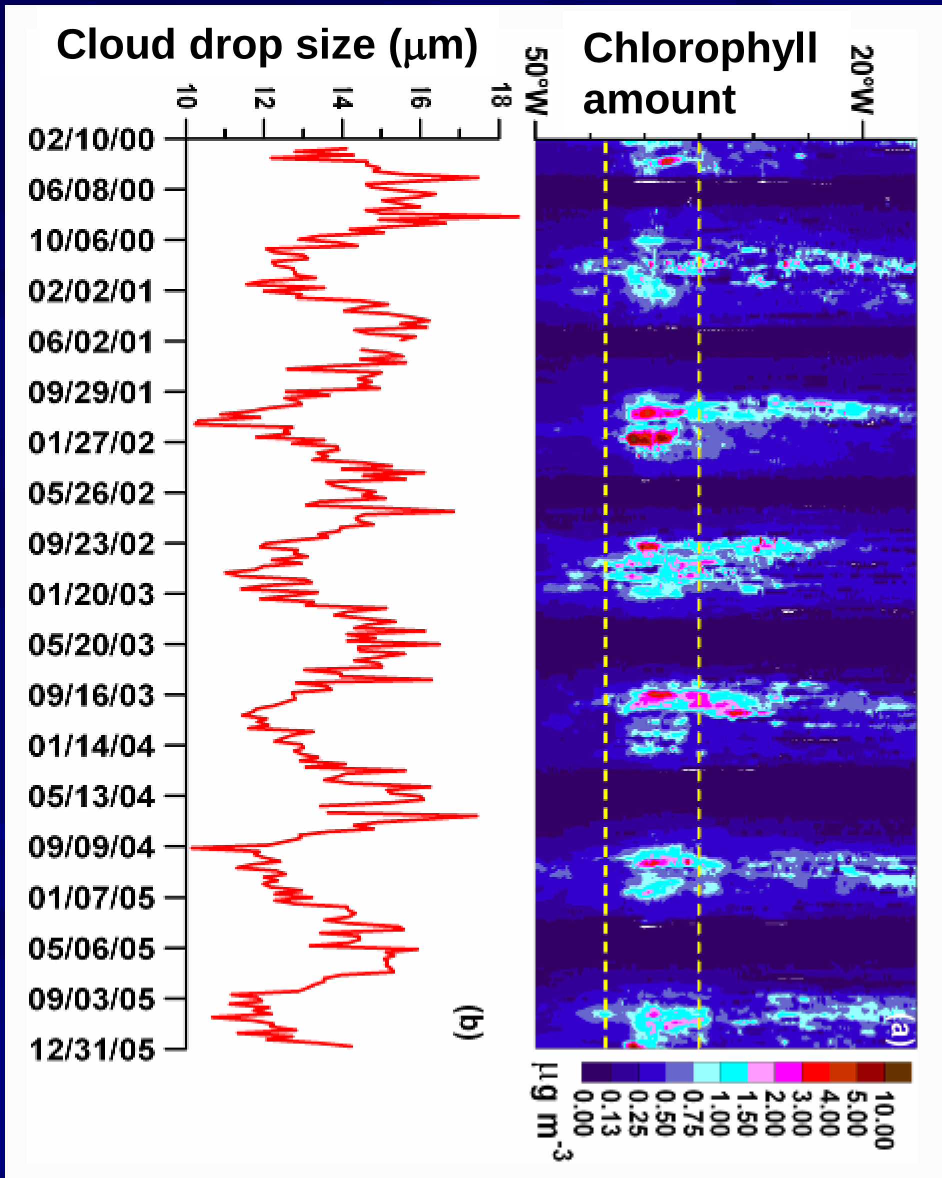
*Rosenfeld et al., Science*

# Phytoplankton affect clouds too…

Location: East of Patagonia (South America)






*Meskhidze and Nenes, Science, 2006*

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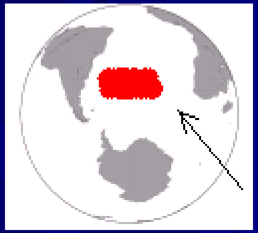

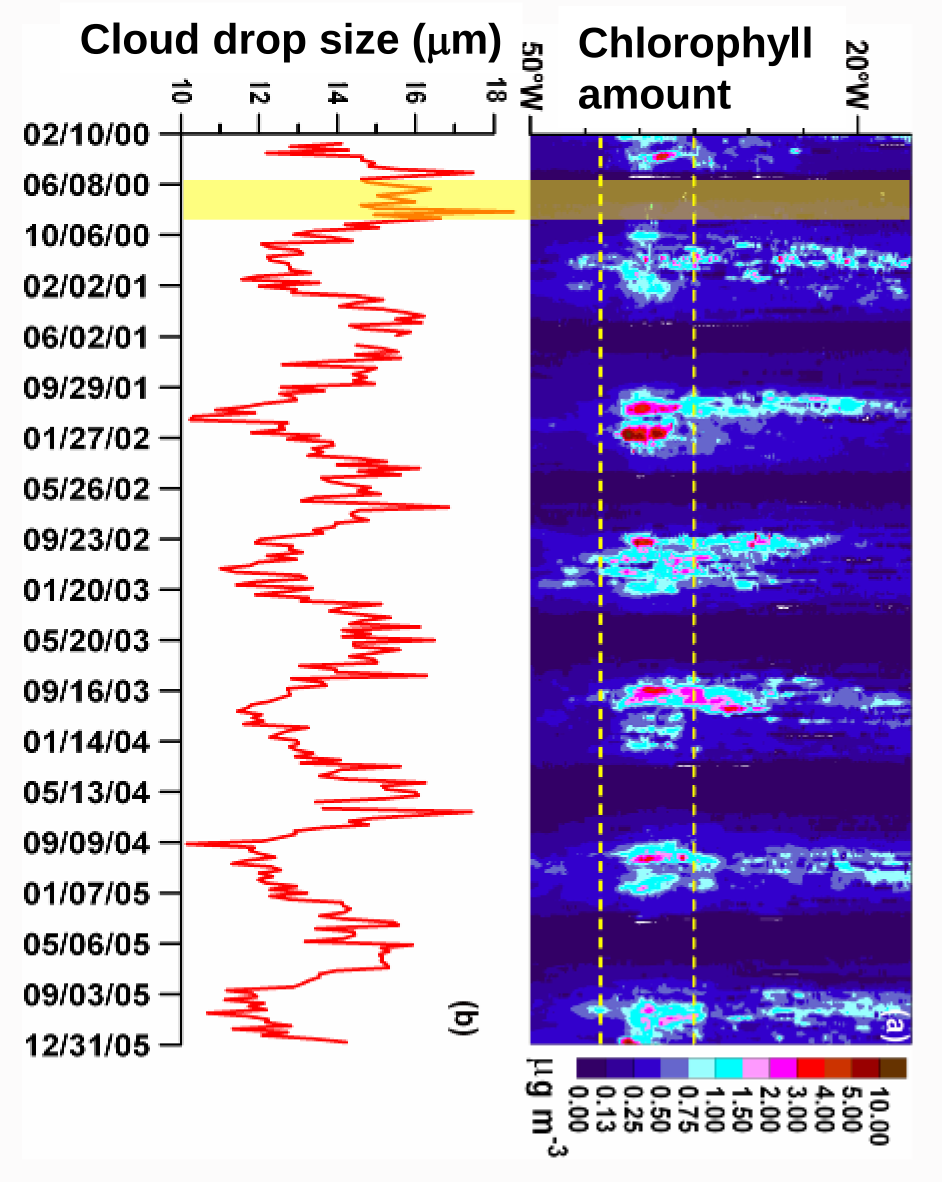


Low chlorophyll period, clouds have large drops (not very reflective)

*Meskhidze and Nenes, Science, 2006*

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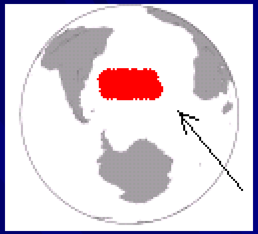

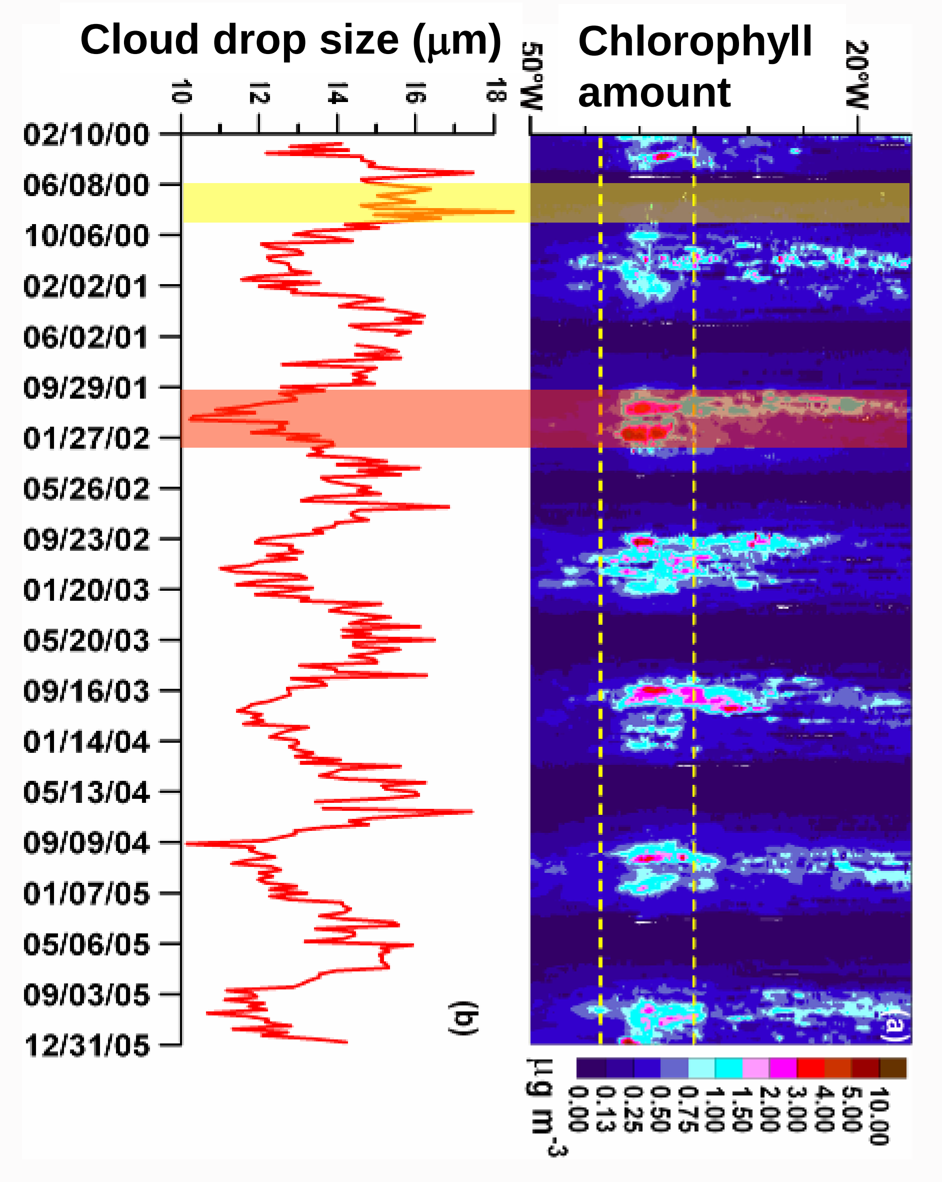


Low chlorophyll period, clouds have large drops (not very reflective)

High Chlorophyll period, Clouds have small drops (very reflective)

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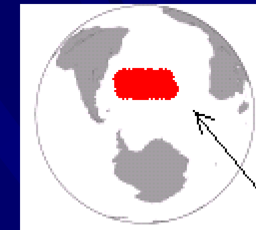
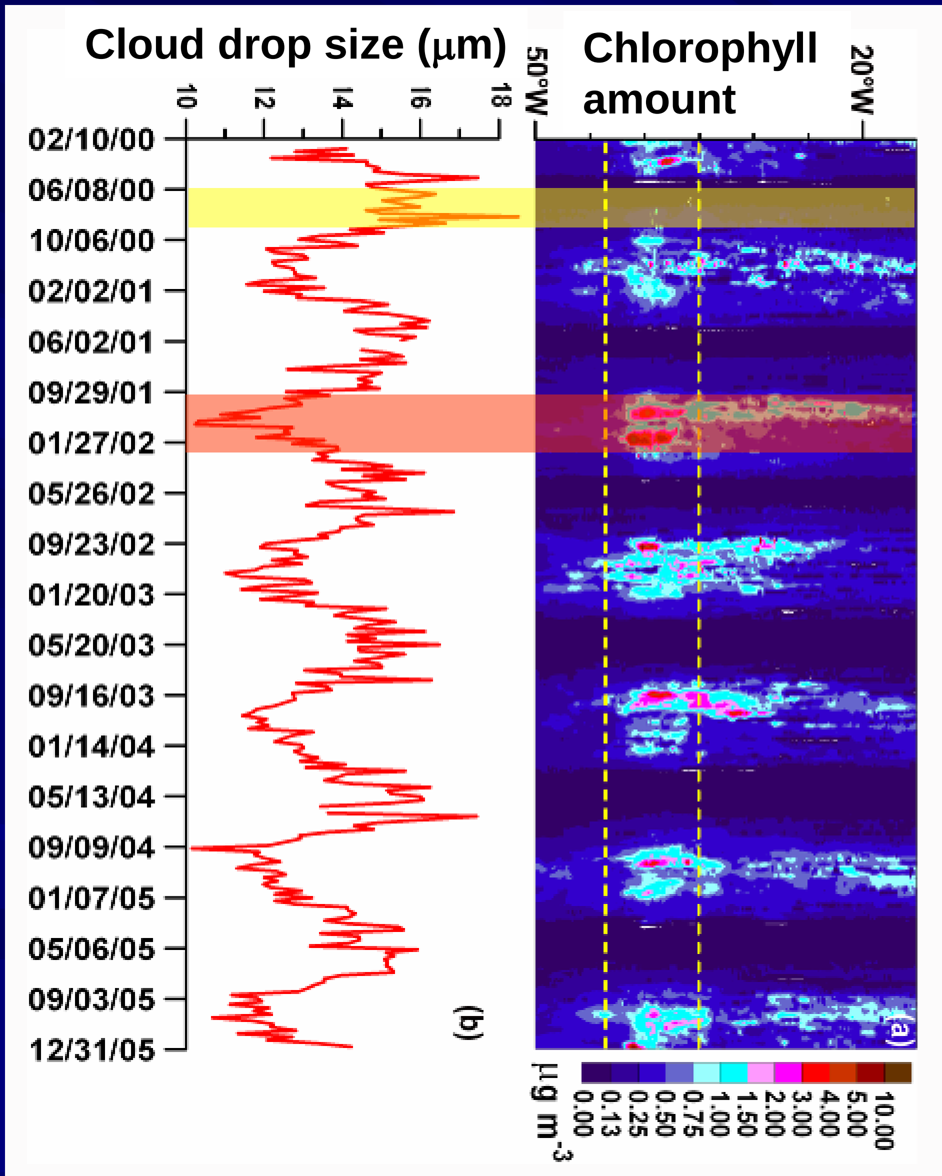





Low chlorophyll period, clouds have large drops (not very reflective)

High Chlorophyll period, Clouds have small drops (very reflective)

Phytoplankton emissions increase particle loads, and strongly impact clouds.

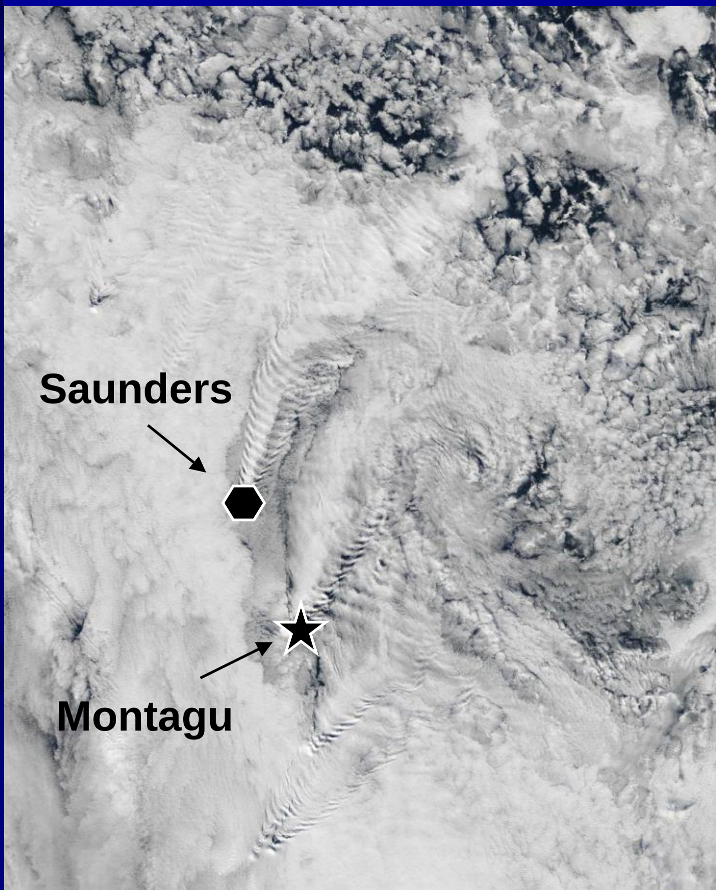
Biology-cloud interactions affect radiation in the region.

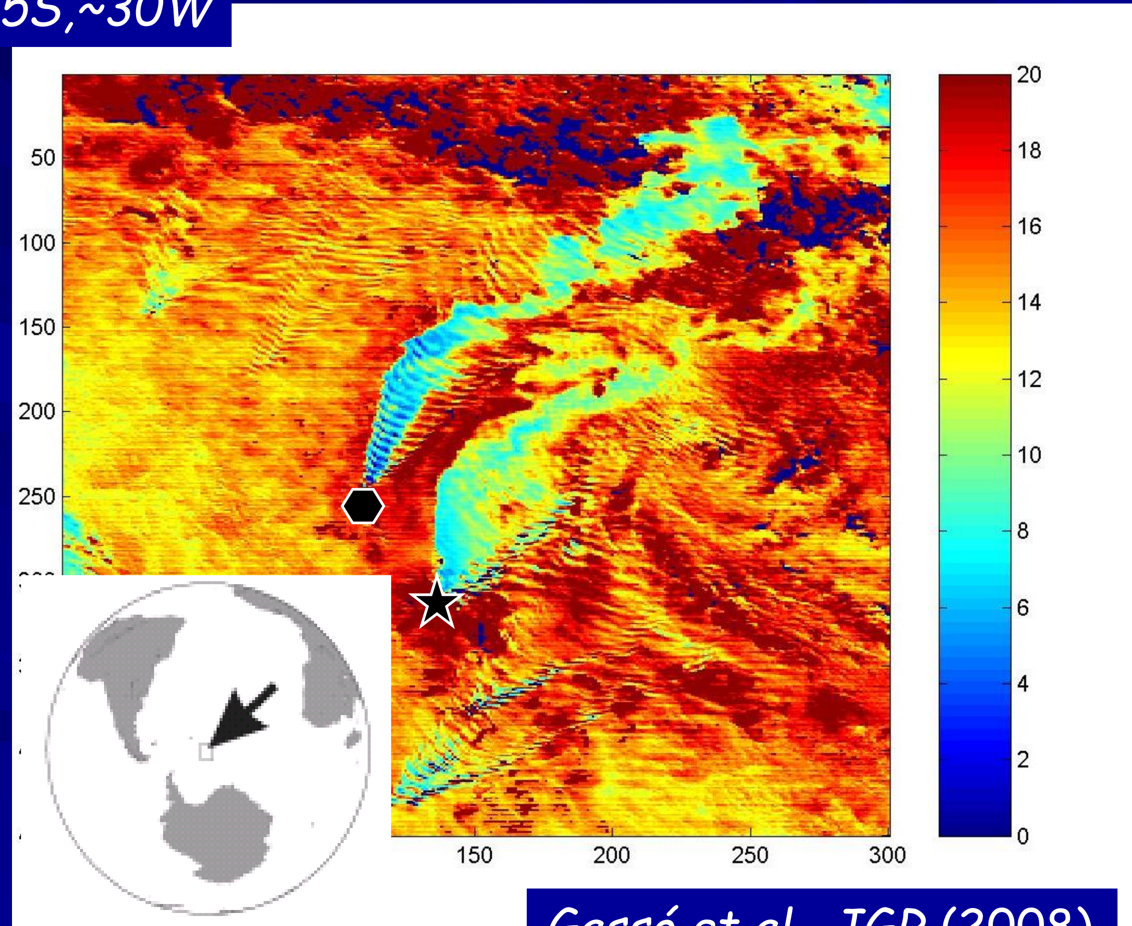
*Meskhidze and Nenes, Science, 2006*

# So do volcanoes (even when "sleeping") …

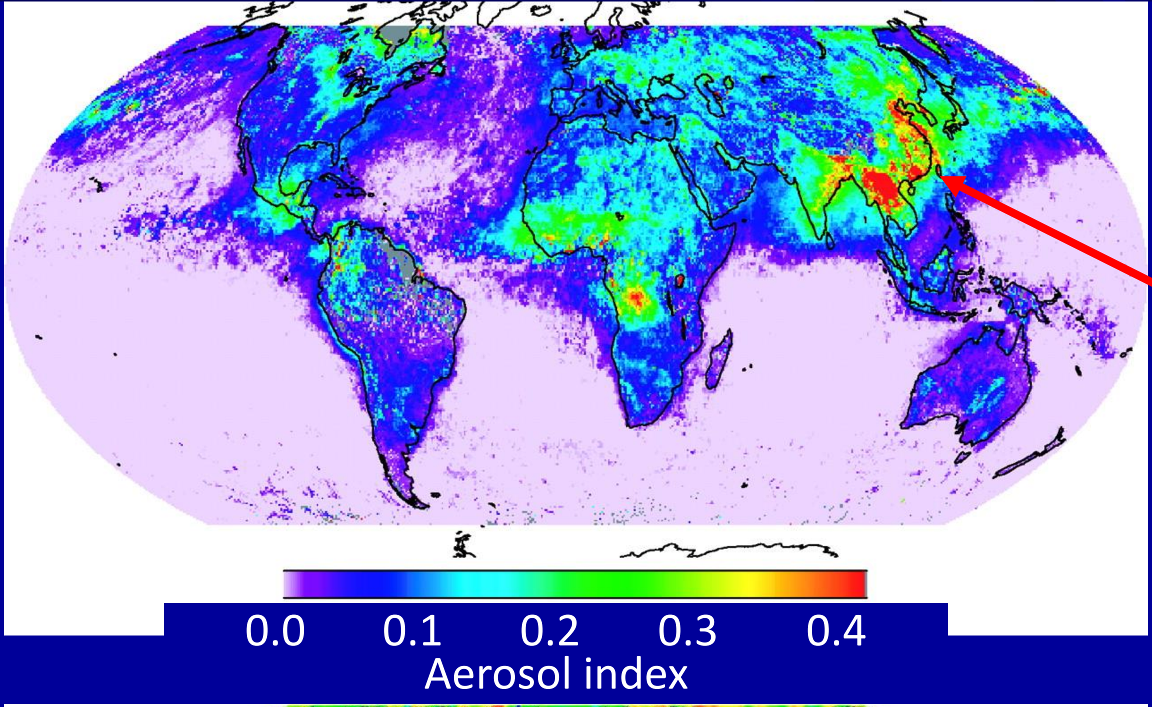
Volcanoes continuously emit $SO_2$ which becomes sulfate aerosol.
The aerosol can substantially increase CCN in volcanic plumes.
Clouds in the plume are much more reflective than outside.

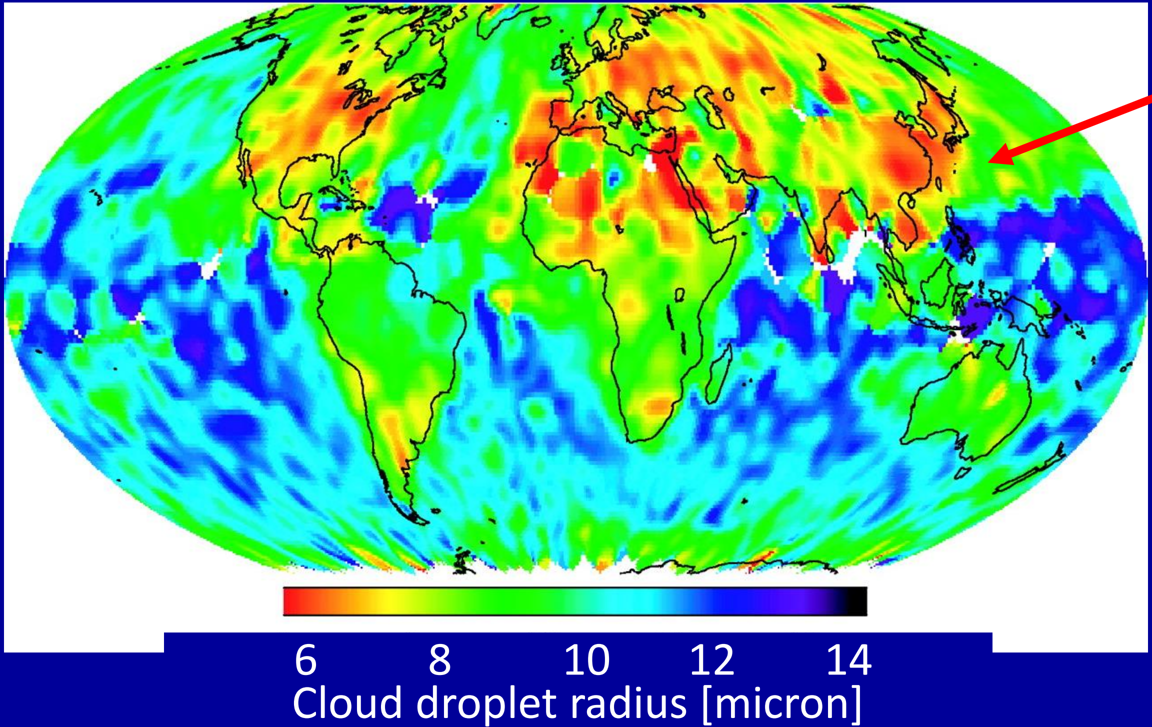
*Location: Sandwich Islands , ~55S,~30W*




*Gassó et al., JGR* (2008)




**A remote sensing global picture…**

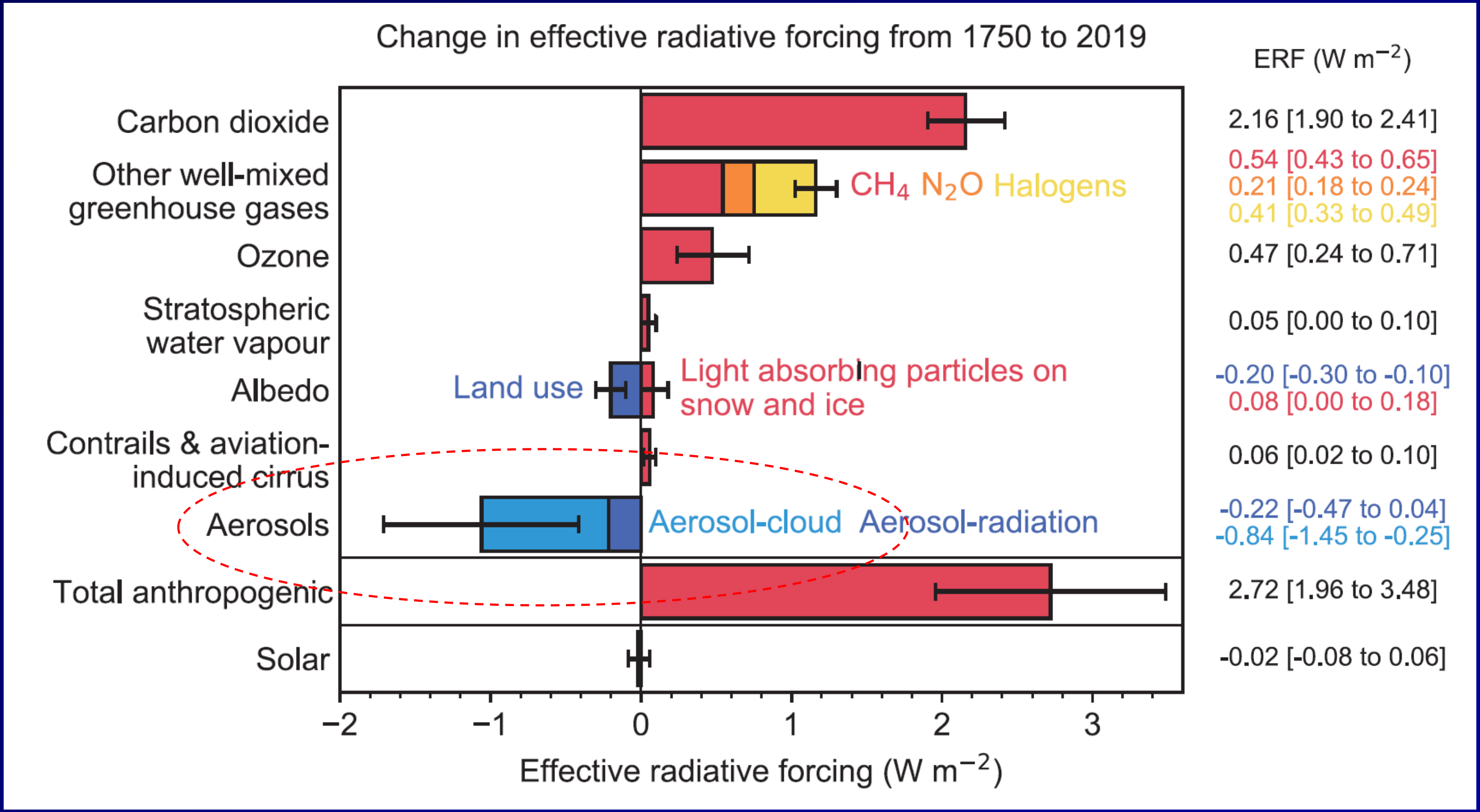
A lot of aerosol…

…gives smallest cloud droplets

**We see the same on all satellite platforms…**

Breón et al. (2002)

# Aerosol-cloud interactions are important for climate - but highly uncertain




Forster et al. (2021), IPCC AR6

# LIQUID cloud microphysics


- **Ice (cold) clouds**: Made of ice crystals at $T < 235$ K.
- **Mixed Phase clouds**: Mixture of liquid droplets and ice for $T$ between 235 and 273K
- **Liquid (warm) clouds**: Made of liquid droplets at $T > 273$ K

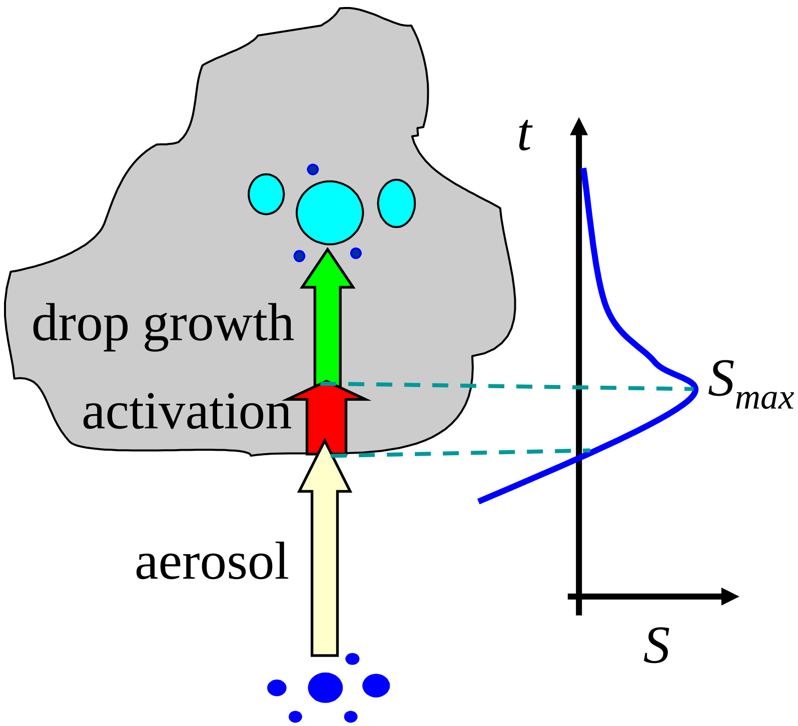
Cloud particles are not created directly from the vapor phase but from **suspended aerosol particles**

http://www.ucar.edu/news

# Droplet formation: The essence

**Goal: Link cloud droplet concentration with precursor aerosol**

**Approach**: Use the "simple story of cloud formation".

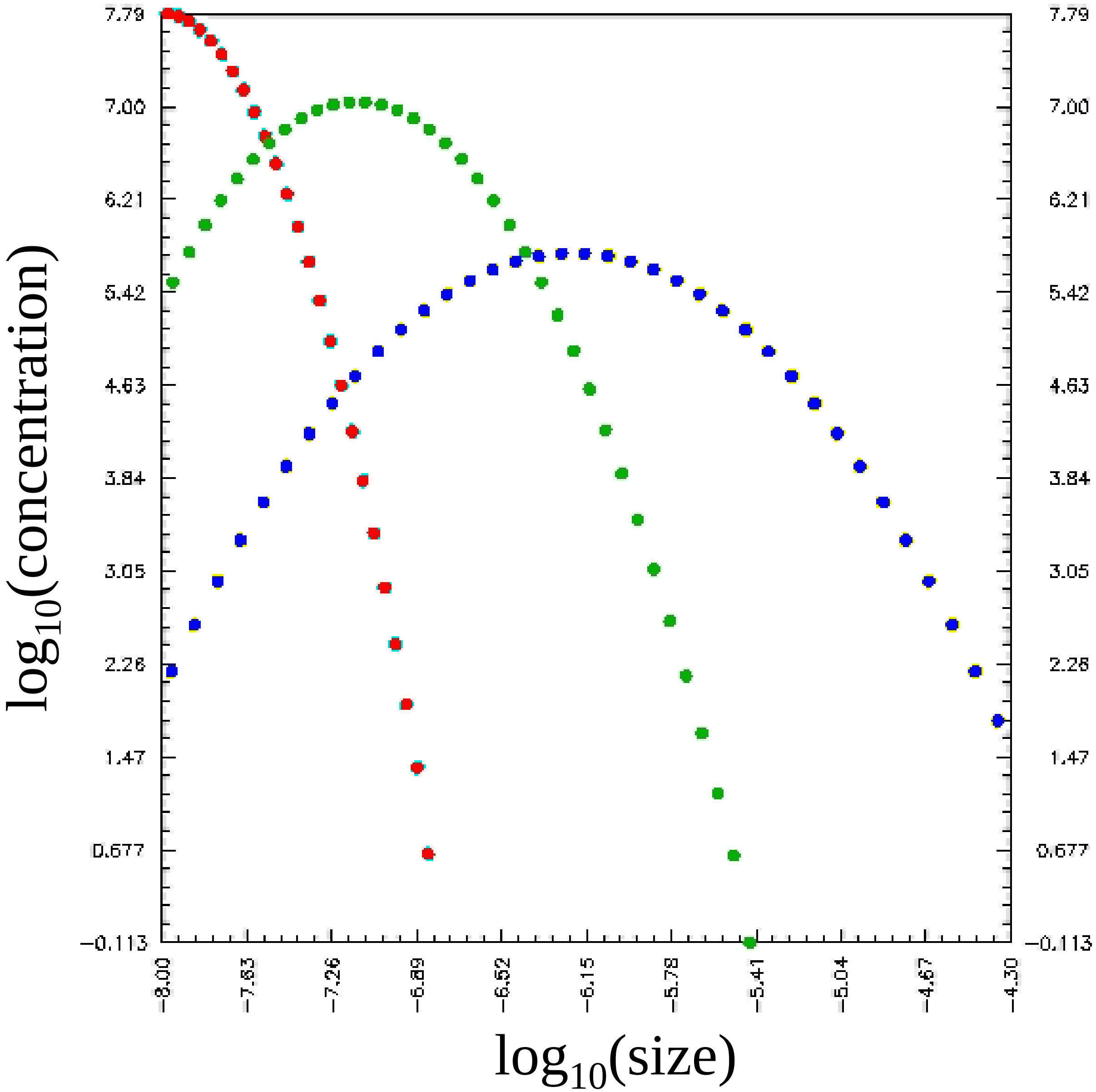


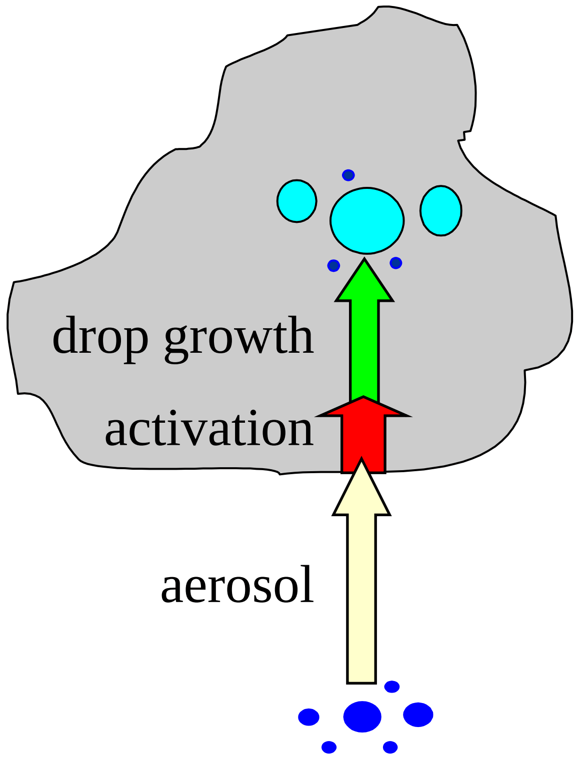

**Conceptual steps are:**

- Air parcel cools, exceeds dew point
- Water vapor is **supersaturated**
- Droplets start forming on existing CCN.
- Condensation of water on droplets becomes intense.
- Humidity reaches a **maximum**
- No more additional drops form

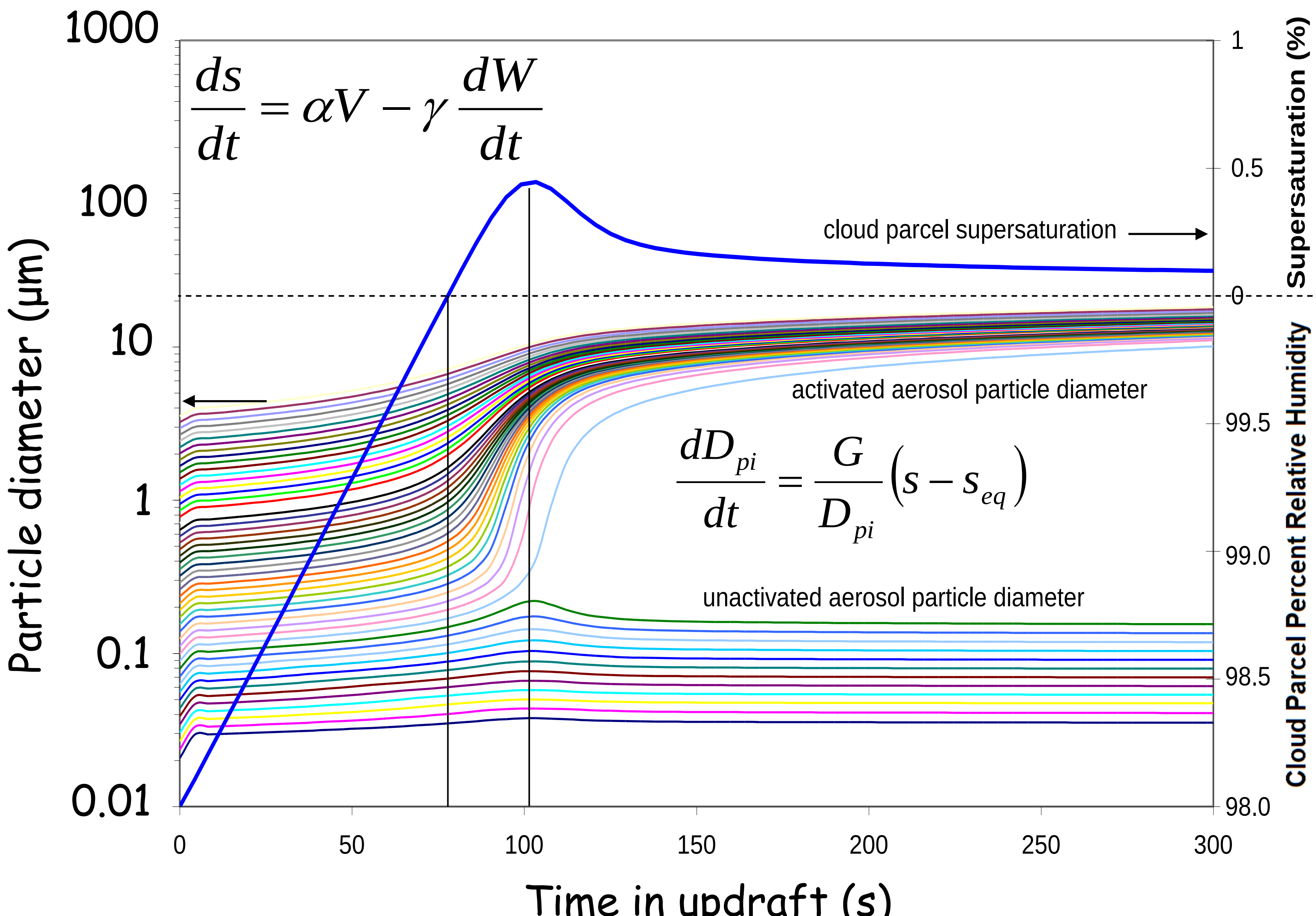
**A "classical" nucleation/growth problem**

# Simulation of cloud droplet formation



# Simulation of cloud droplet formation



# Drop formation: coupled nonlinear system

Supersaturation (and $s_{max}$) depends strongly on the expansion rate (updraft velocity $V$) and the condensation rate of water:

$$\frac{ds}{dt} = \alpha V - \gamma\left(\frac{dW}{dt}\right)$$

Water condensation rate on droplets

Water condensation rate on droplets determined from the contribution of each aerosol "size class" $i$

Mass transfer coefficient of water from the gas phase

$$\frac{dD_{p,i}}{dt} = \frac{G_i}{D_{p,i}}\left(s - s_{eq,i}\right)$$

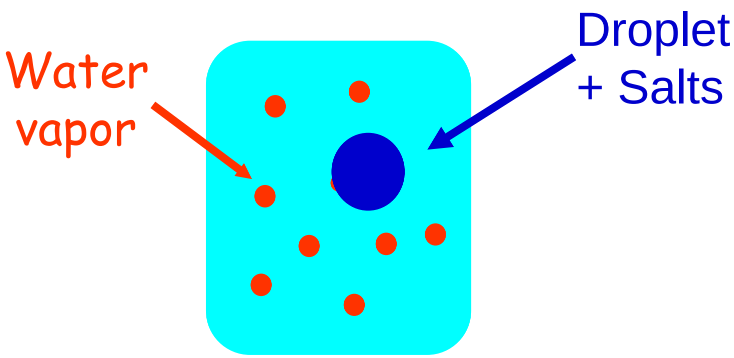
Equilibrium saturation (relative humidity) of droplet

**We need to know:**

1. $S_{eq,i}$ for aerosol and droplets (thermodynamics)
2. $G_i$ depends on the water vapor diffusivity (P,T) and the *water vapor mass transfer coefficient* (kinetics).

# Thermodynamics 101: essentials

- Equilibrium vapor pressure of water over pure water




$$P_{H_2O_{(g)}} = P_{sat}(T)$$

- Effects of dissolved solutes

Dissolved salts decrease the energy of your system (why?).

This reduces the equilibrium $P_{H_2O_{(g)}} < P_{sat}(T)$

Mol fraction of water in solution $\frac{n_w}{n_w + n_{salts}}$

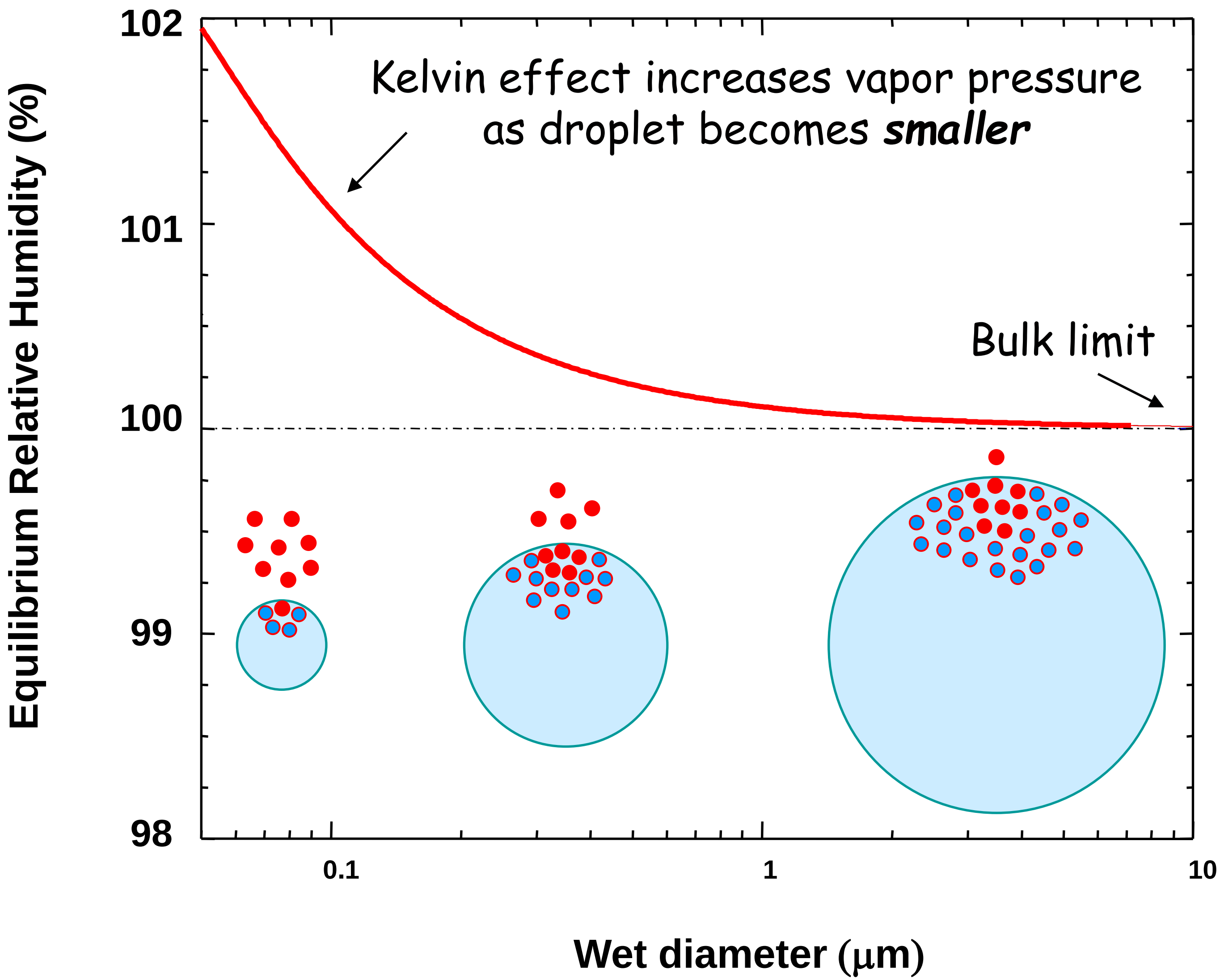
$$P_{H_2O_{(g)}} = P_{sat}(T)x_{H_2O_{(l)}}$$ **Raoult's Law (for ideal solutions)**

# Droplet thermo: special considerations

- Aerosol thermo mentioned before considered aerosol as a "bulk" system, where there is an infinite amount of each phase for interaction.
- "Bulk" thermodynamics thus assume that interfaces are "flat".
- Sometimes this is not a good approximation.
- "Curvature" effects may need to be included in the thermodynamic expressions.
- Main parameters expression curvature effects:
  - Interfacial tension ("surface tension")
  - Radius of curvature (most often, aerosol/drop radius)

# Including curvature: Thermodynamics of droplets

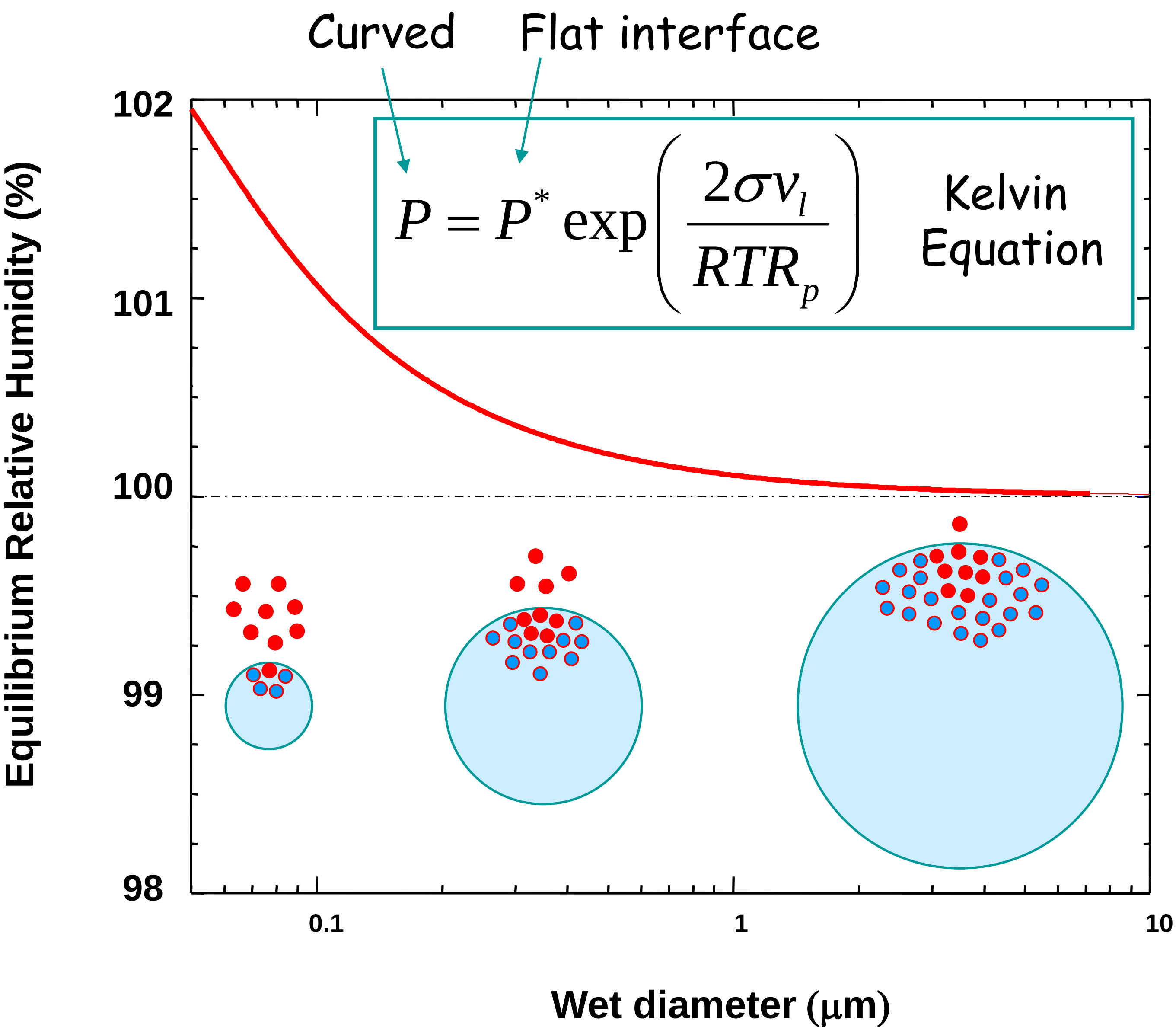
## Impact of curvature: "the physical explanation"




As the droplet size decreases, its equilibrium vapor pressure increases ("Kelvin effect")

Less molecules around in small drops to "keep" $H_2O$ in the droplet phase

# Including curvature: Thermodynamics of droplets




As the droplet size decreases, its equilibrium vapor pressure increases ("Kelvin effect")

Hugely important equation.

Needed for any nucleation process

# Thermodynamics of droplets: Köhler equation

Apply Kelvin equation to a pure water droplet (i.e., $\sigma_w$ and $v_l = \frac{M_w}{\rho_w}$ )

$$P = P^* \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p}\right)$$

Dissolved substances in the drop depress water vapor pressure. If $\sigma_w, v_l \sim$ **const**. then only $P^*$ changes (given by Raoult's law: $P^* = P^{sat}\gamma_w x_w$ )

$$\boxed{\frac{P}{P^{sat}} = x_w\gamma_w \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p}\right) \quad \text{Köhler Equation}}$$

Equilibrium relative humidity of a particle when it has absorbed water and acquired a wet diameter, $D_p$

# Thermodynamics of droplets: Köhler equation

One can then invoke simplifying assumptions:

$$x_w = \frac{n_w}{n_w + in_s} = 1 - \frac{in_s}{n_w + in_s} \sim 1 - \frac{in_s}{n_w} = 1 - \frac{in_s}{\frac{\pi}{6} D_p^3 \frac{\rho_w}{M_w}} = 1 - \frac{\frac{6}{\pi}\frac{M_w}{\rho_w} in_s}{D_p^3}$$

$$= 1 - \frac{B}{D_p^3} \quad \text{where} \quad B = \frac{6}{\pi}\frac{M_w}{\rho_w} in_s$$

Moles of solute in droplet

van't Hoff factor of solute in droplet

$$\gamma_w \sim 1 \quad \text{and} \quad \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p}\right) \sim 1 + \frac{A}{D_p} \quad \text{where} \quad A = \frac{4M_w\sigma}{RT\rho_w}$$

Substitution into full Köhler equation, and considering leading terms:

$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$

Simplified Köhler equation

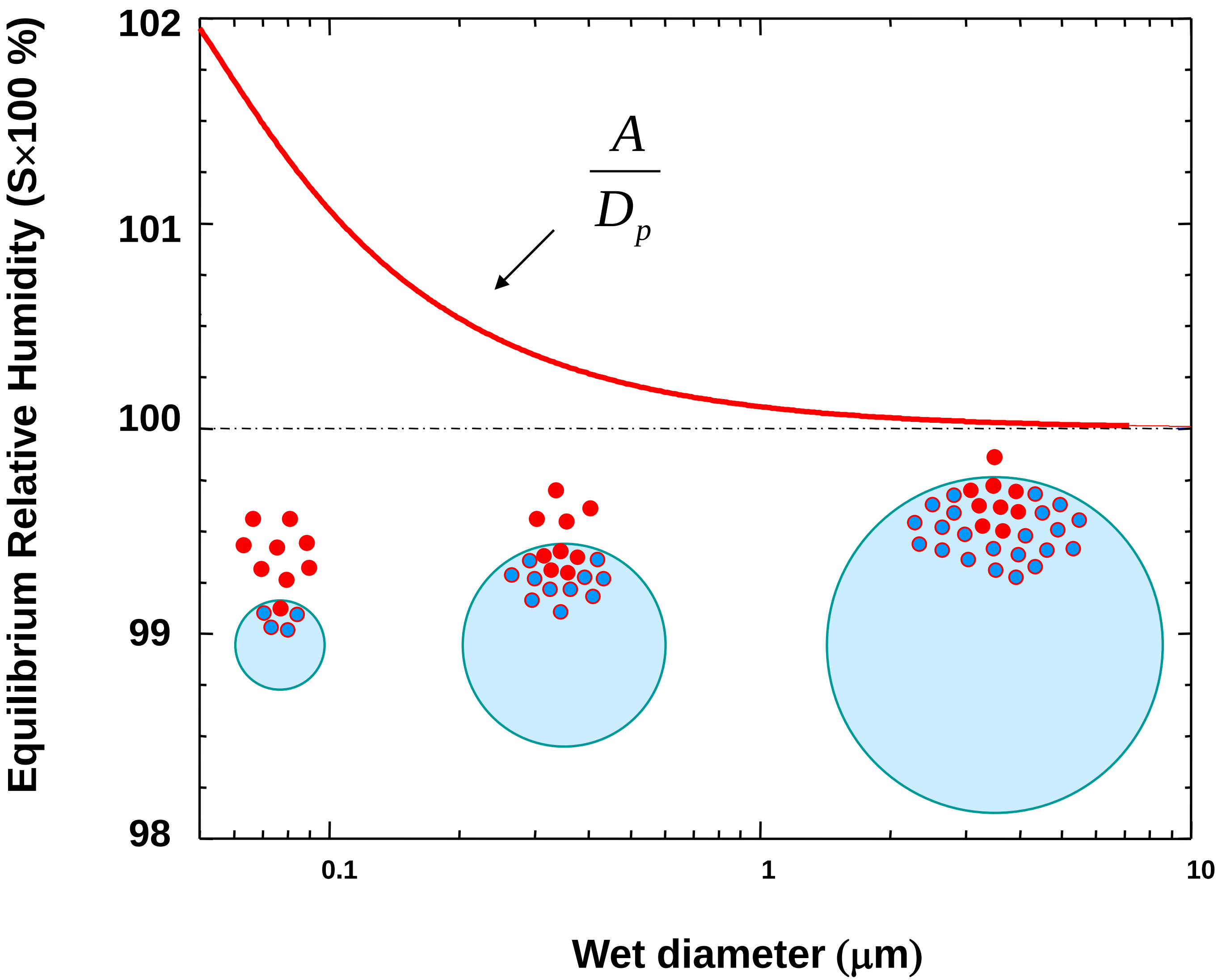
Saturation ratio

"Kelvin" term

"Raoult" term

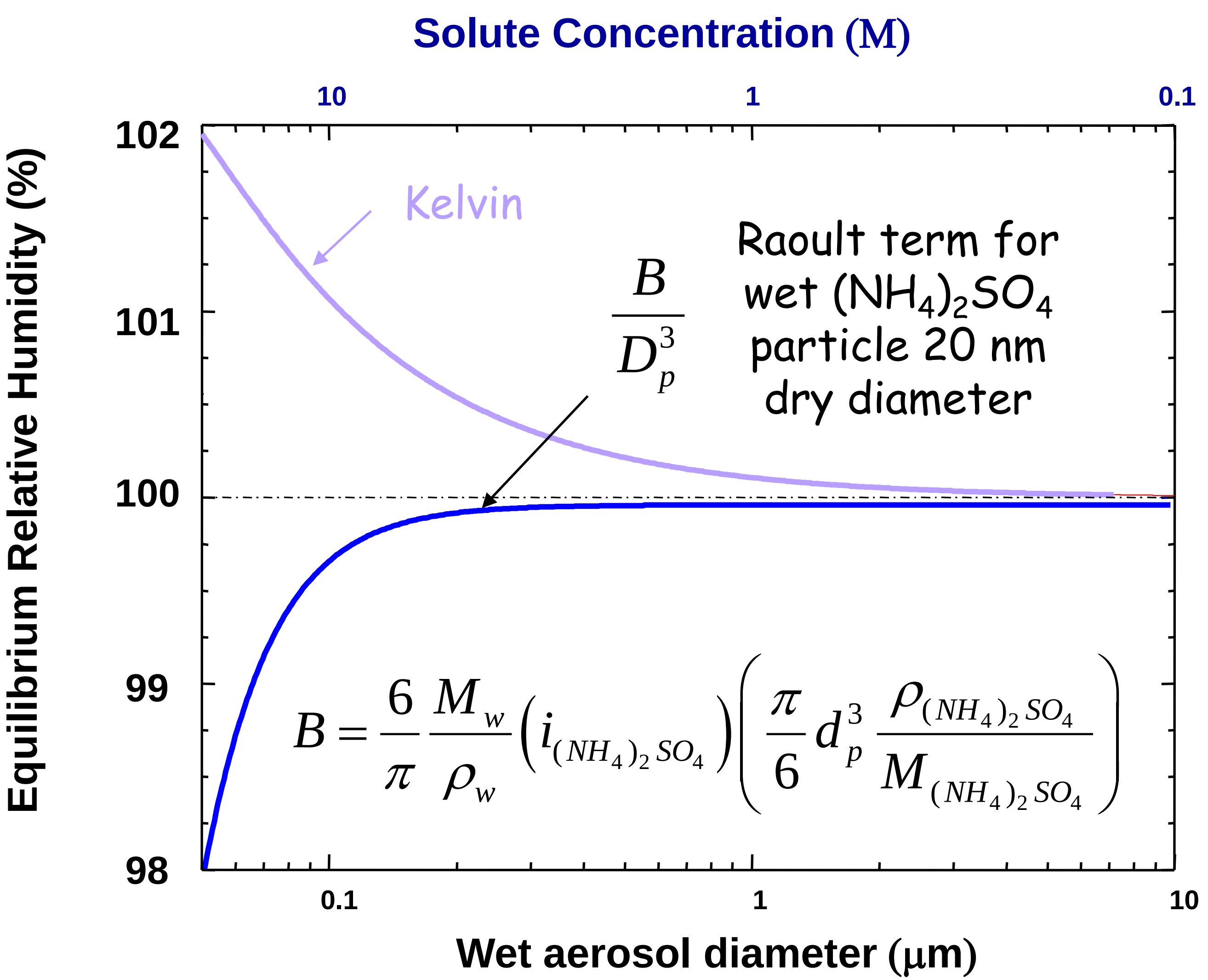
# Thermodynamics of droplets: Köhler equation

## First plot the Kelvin term



# Thermodynamics of droplets: Köhler equation

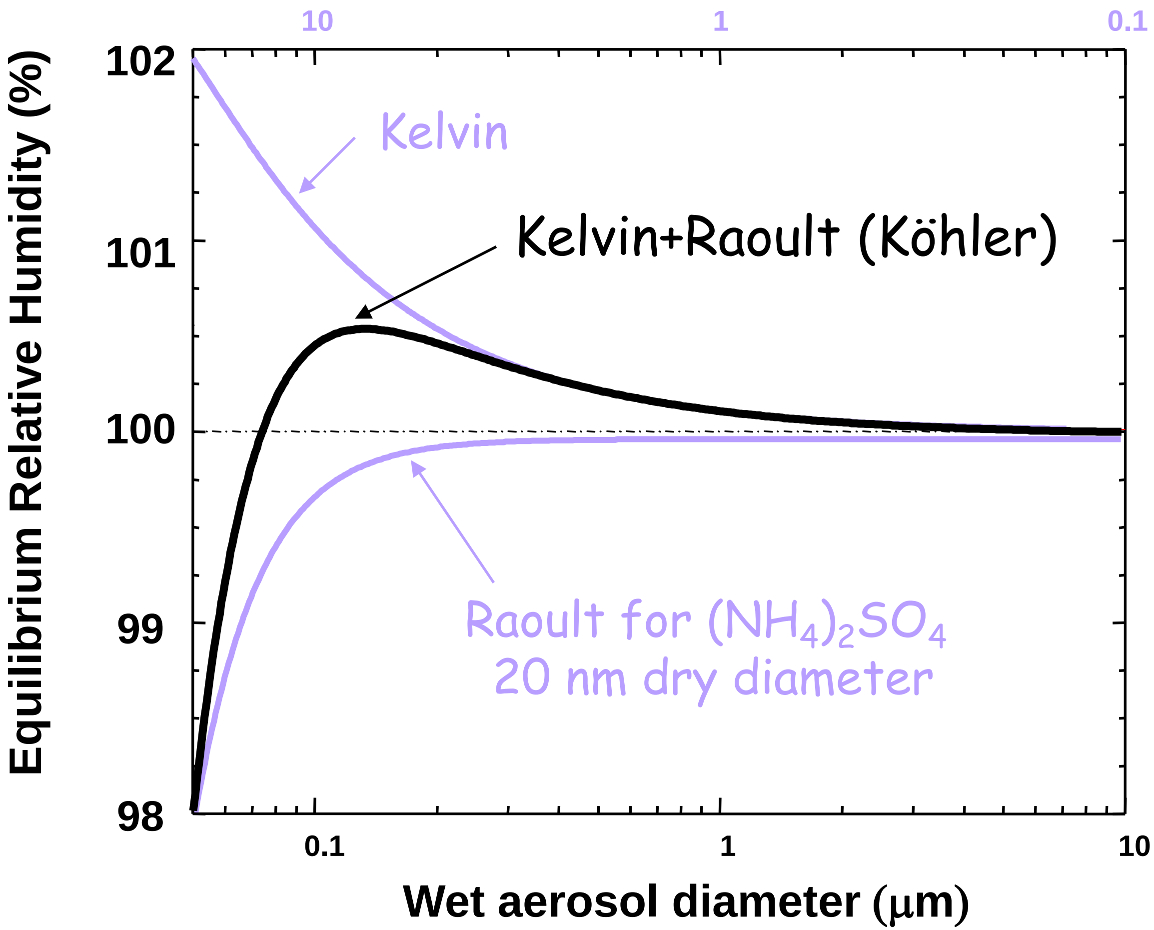
## …then plot the Raoult term



# Thermodynamics of droplets: Köhler equation

Both effects together: equilibrium vapor pressure of a wet aerosol.

$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$

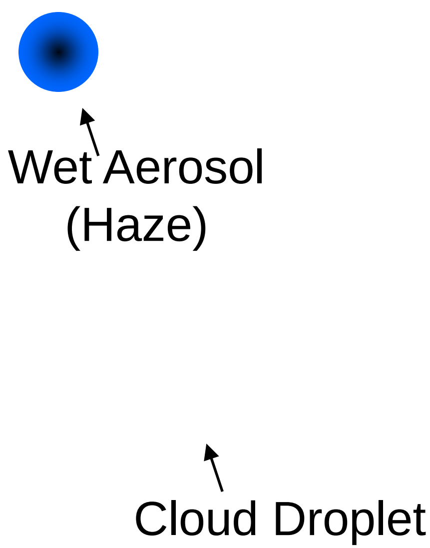


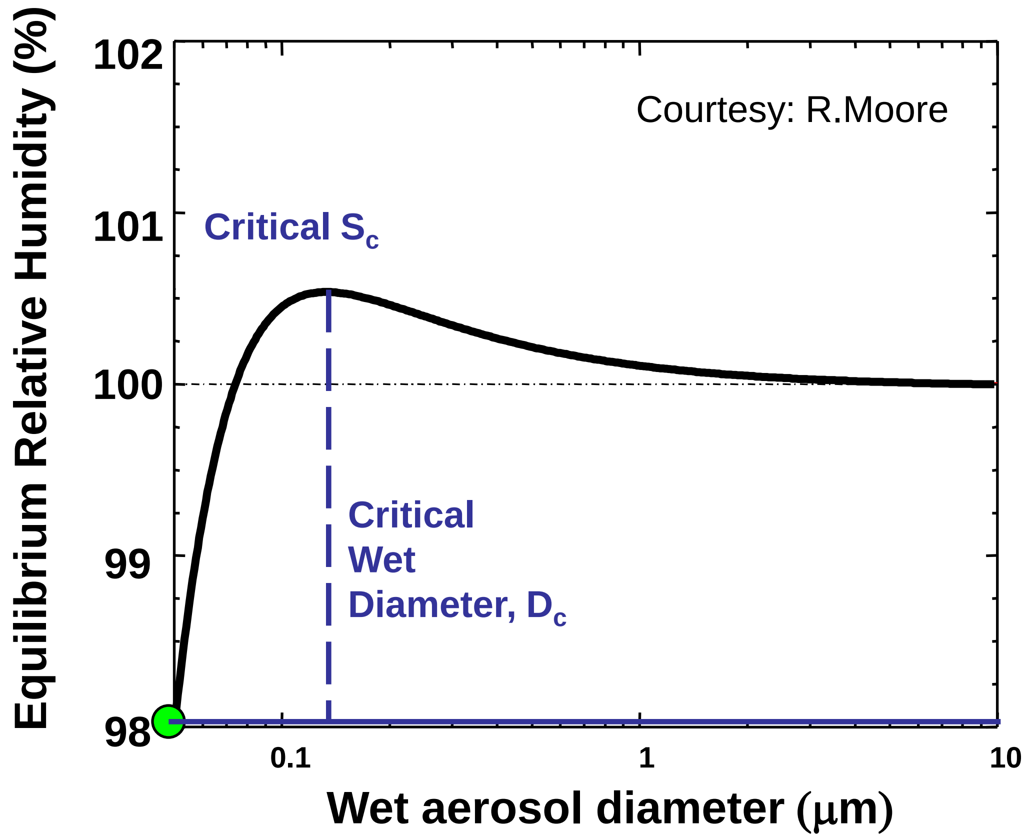

The combined Kelvin and Raoult effects is the simplified **Köhler equation**.

You can be in equilibrium **even if you are above saturation**.

# Regions of stability/instability of ambient droplets

Dynamical behavior of an aerosol particle in a variable RH environment.



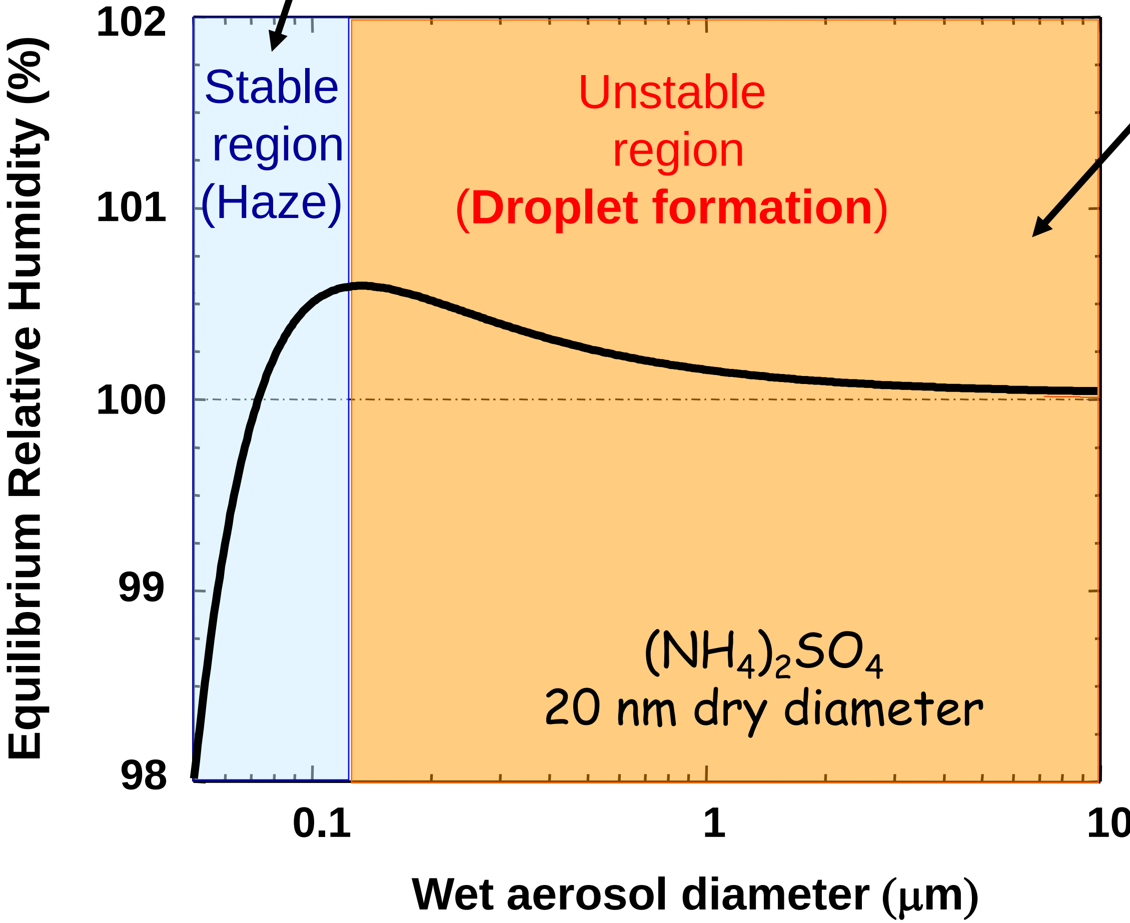




**If ambient S exceeds the maximum, particles grow uncontrollably. They are said then to act as Cloud Condensation Nuclei (CCN)**

# When does an aerosol particle act as a CCN ?

Ambient RH **less** than $S_c$ -> *stable* equilibrium.

Ambient RH **above** $S_c$ -> unstable equilibrium. Particles act as CCN and make droplets



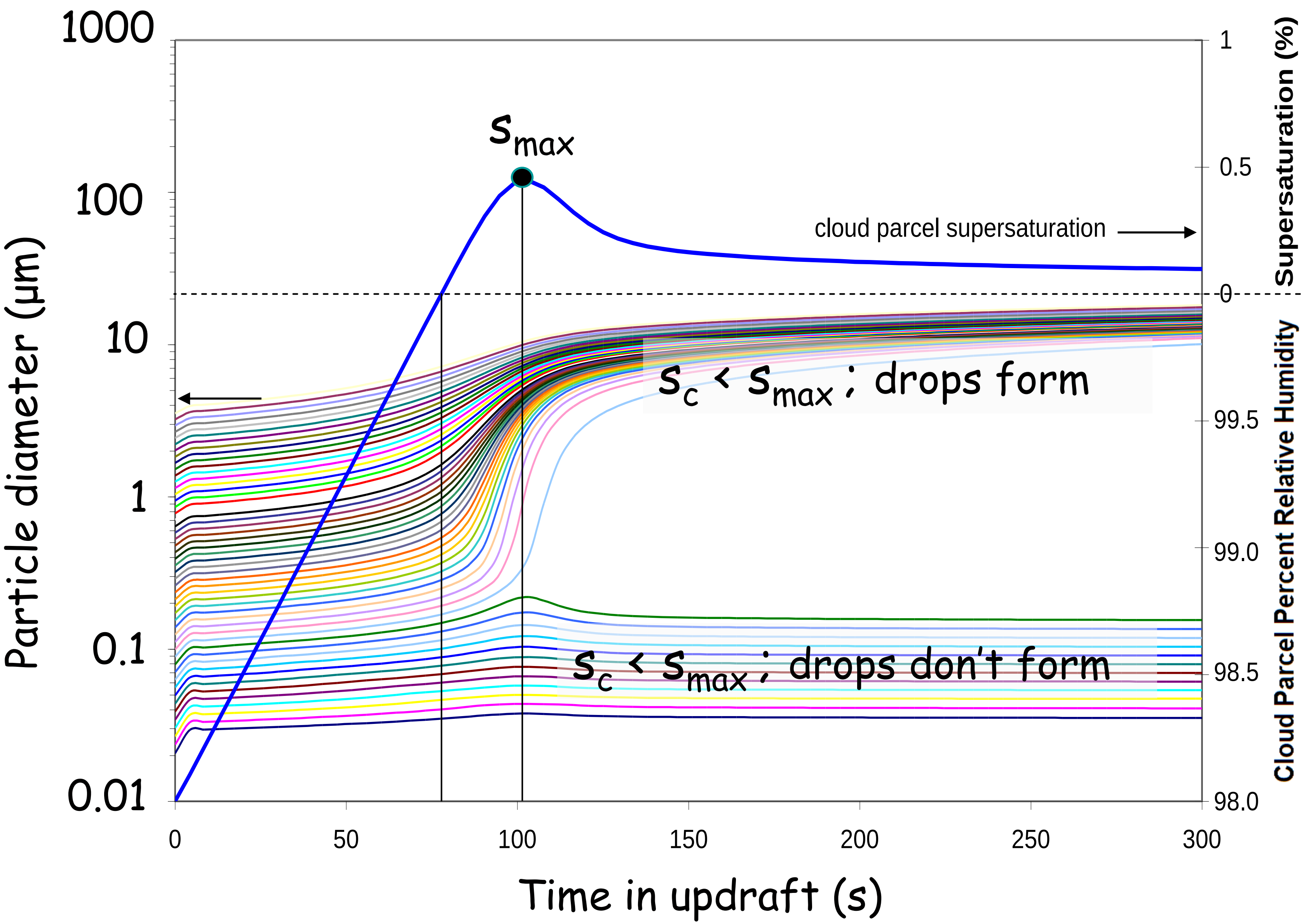

**Köhler theory:**

$$s_c = \left( \frac{4A^3}{27B} \right)^{1/2}$$

$$s_c \sim d_{dry}^{-3/2}, \varepsilon_{\mathbf{soluble}}^{-1/2}$$

Size is more important than composition

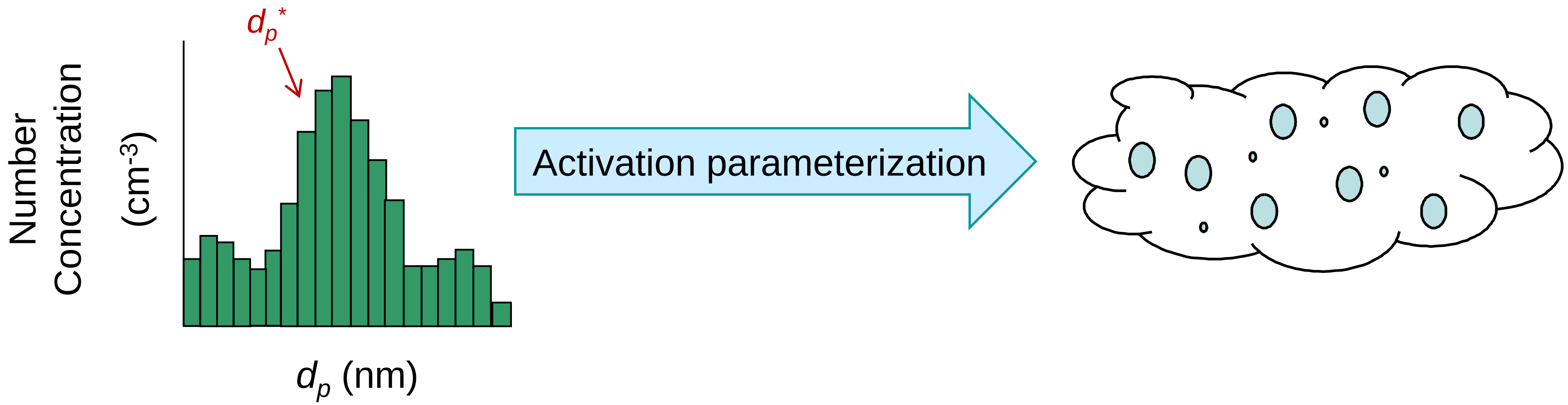
# Now we understand droplet formation



# Describing droplet formation in models…

**Droplet calculation in models then is:**

Calculated size distribution + $\kappa$ + vertical velocity

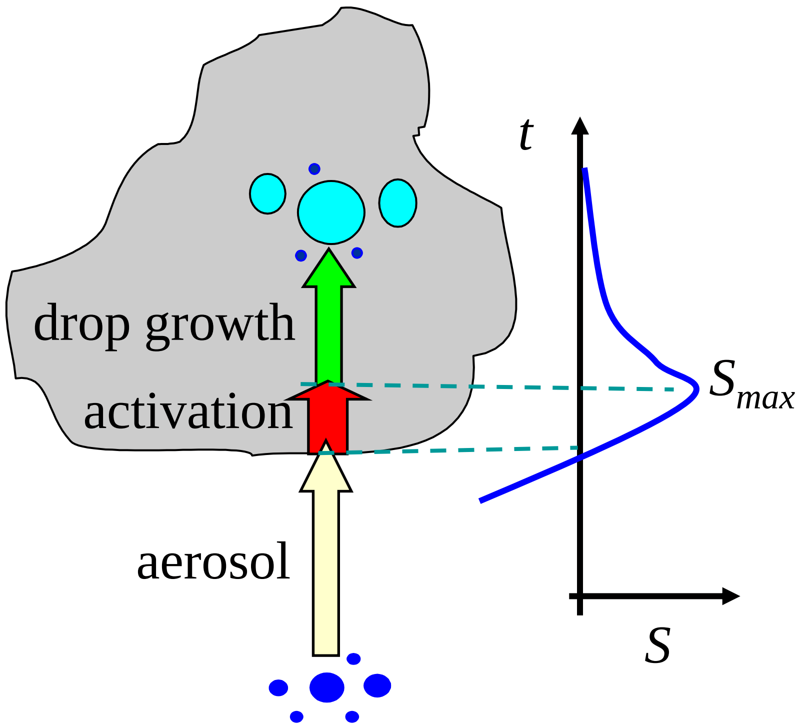



Activation parameterization is either a correlation or a solution to the parcel model equations that describe the activation process in clouds.

# Droplet number needs CCN and max.cloud RH…

**Algorithm for calculating $N_d$ (Mechanistic parameterization):**

1. Calculate $s_{max}$ (approach-dependent)
2. $N_d$ is equal to the CCN with $s_c \leq s_{max}$




**Mechanistic Parameterizations:**
Twomey (1959); Abdul-Razzak et al., (1998); Nenes and Seinfeld, (2003); Fountoukis and Nenes, (2005); Kumar et al. (2009), Morales and Nenes (2014), and others.

**Input:** P,T, vertical wind, particle size distribution,composition.

**Output:** Cloud properties (droplet number, size distribution).

**Comprehensive review & intercomparison:**
Ghan, et al., *JAMES* (2011); Morales and Nenes (2014)

# Is this description of droplet formation real

Evaluate with in-situ data from airborne platforms


Observed Aerosol size distribution & composition

Observed Cloud updraft Velocity (PDF)

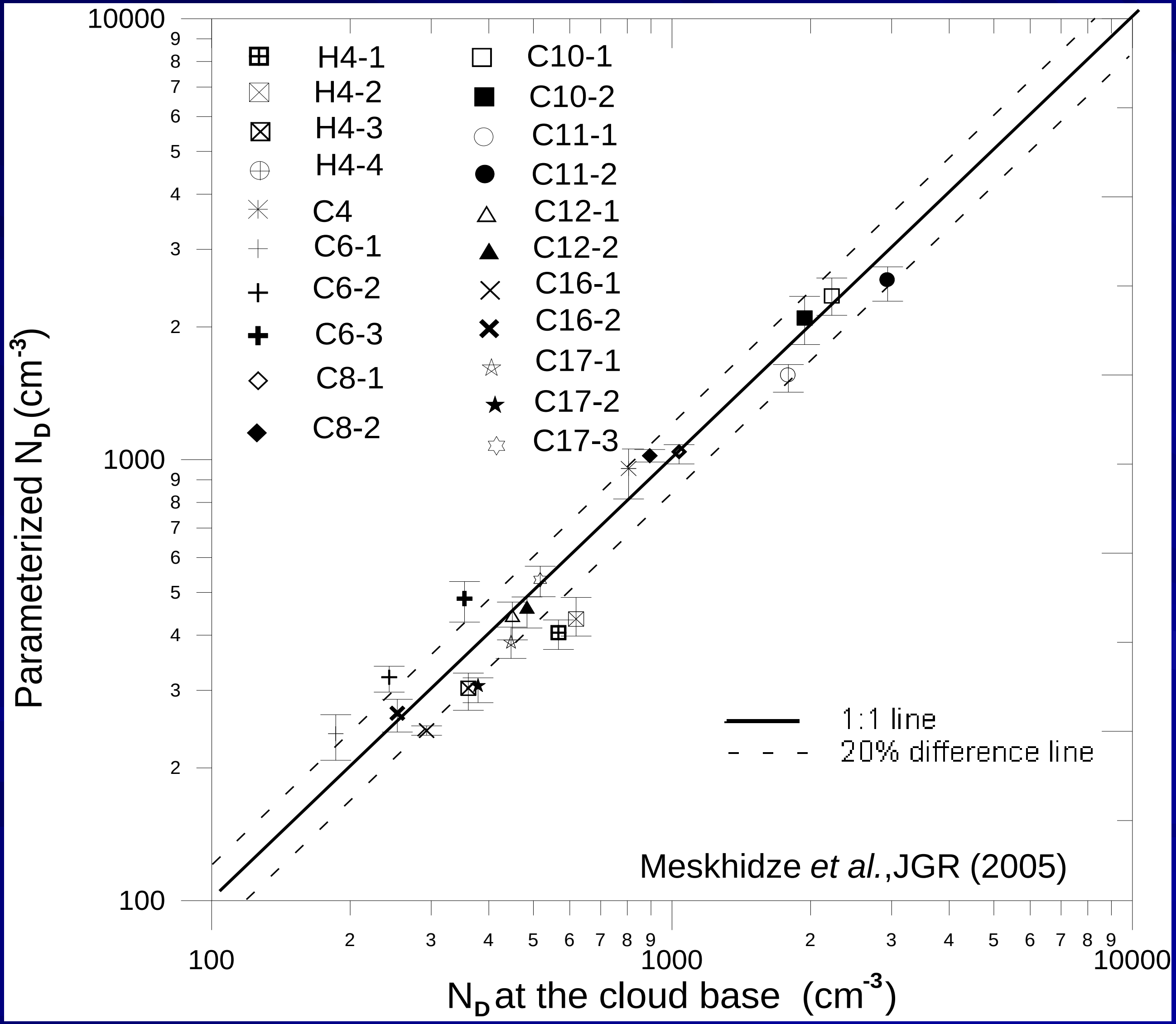
Predicted Drop Number (Parameterization)

Compare

Observed Drop Number Concentration

# CRYSTAL-FACE (2002) Cumulus clouds

CIRPAS Twin Otter




Paramet'n agrees with observed cloud droplet number

Agreement to within a few % (on average)!

...when you know everything about aerosol composition and size

# Issue: aerosols are complex


## Primary emissions

Automobiles, industry, domestic, vegetation, forest fires, seasalt, ...

## Secondary transformations

Oxidation of precursors (by $O_3$, $H_2O_2$, OH, $NO_3$, etc.) generates organic compounds.

Reaction of volatile bases ($NH_3$) with acids, dust and seasalt form salts like $(NH_4)_2SO_4$.

# Parameterizing "characteristic" CCN activity…

Petters and Kreidenweis (2007) expressed the Kohler theory parameter $B$ in terms of a "hygroscopicity parameter", $\kappa$

$$s_c = \left(\frac{4A^3}{27B}\right)^{1/2} = \left(\frac{4A^3}{27\kappa d^3}\right)^{1/2} \Rightarrow s_c = \left(\frac{4A^3}{27\kappa}\right)^{1/2} d^{-3/2}$$

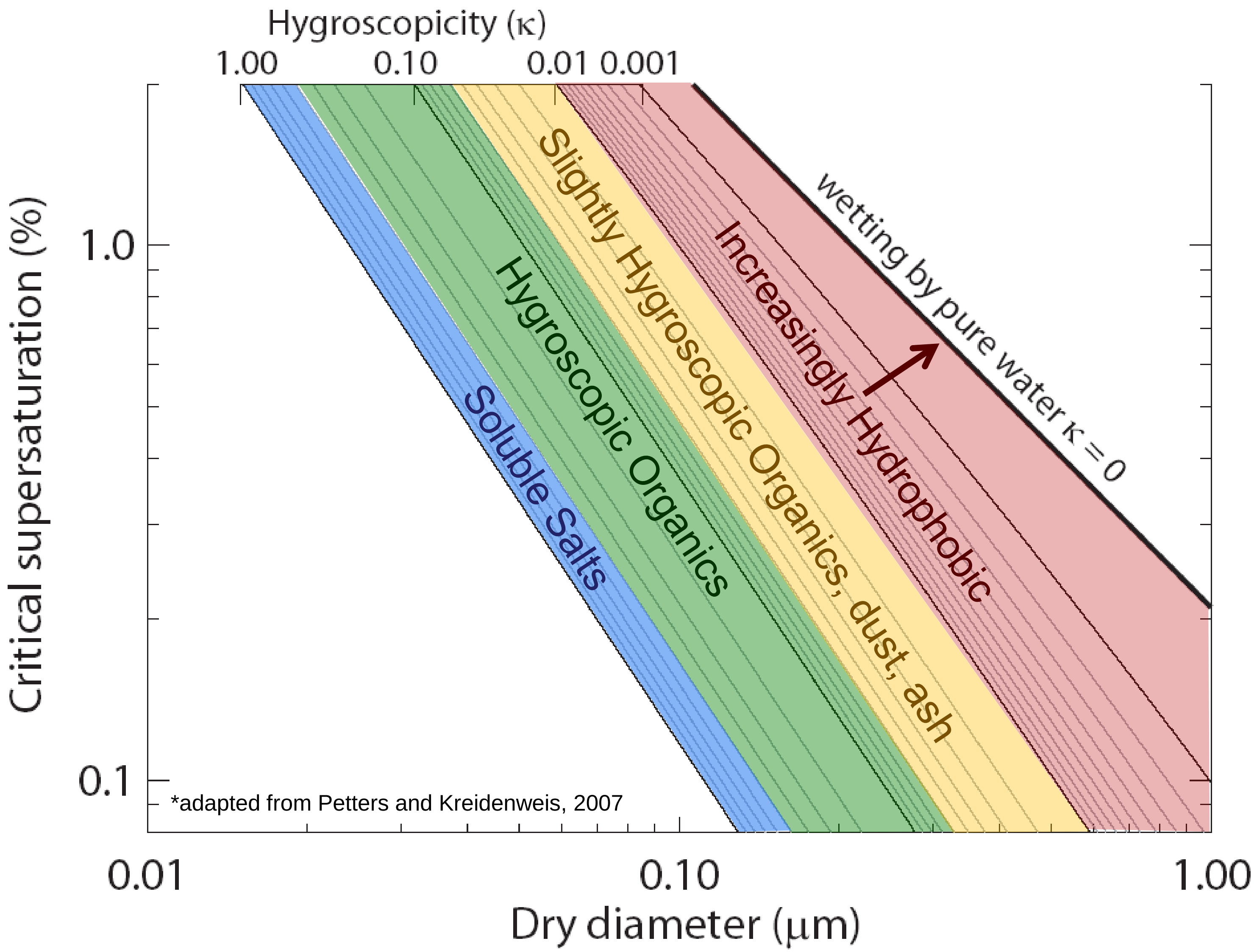
$\kappa \sim 1$ for seasalt, $\sim 0.6$ for $(NH_4)_2SO_4$, $\sim 0$-$0.3$ for organics

$\kappa$ rarely exceeds 1 in atmospheric aerosol

Simple way to think of $\kappa$: the "equivalent" volume fraction of seasalt in the aerosol (the rest being insoluble).

$\kappa \sim 0.6 \Rightarrow$ particle behaves as 60% seasalt, 40% insoluble

# Hygroscopicity Space




- κ is used to parameterize the activation of particles in the atmosphere