Hygroscopic Growth of Aerosols and their Optical Properties

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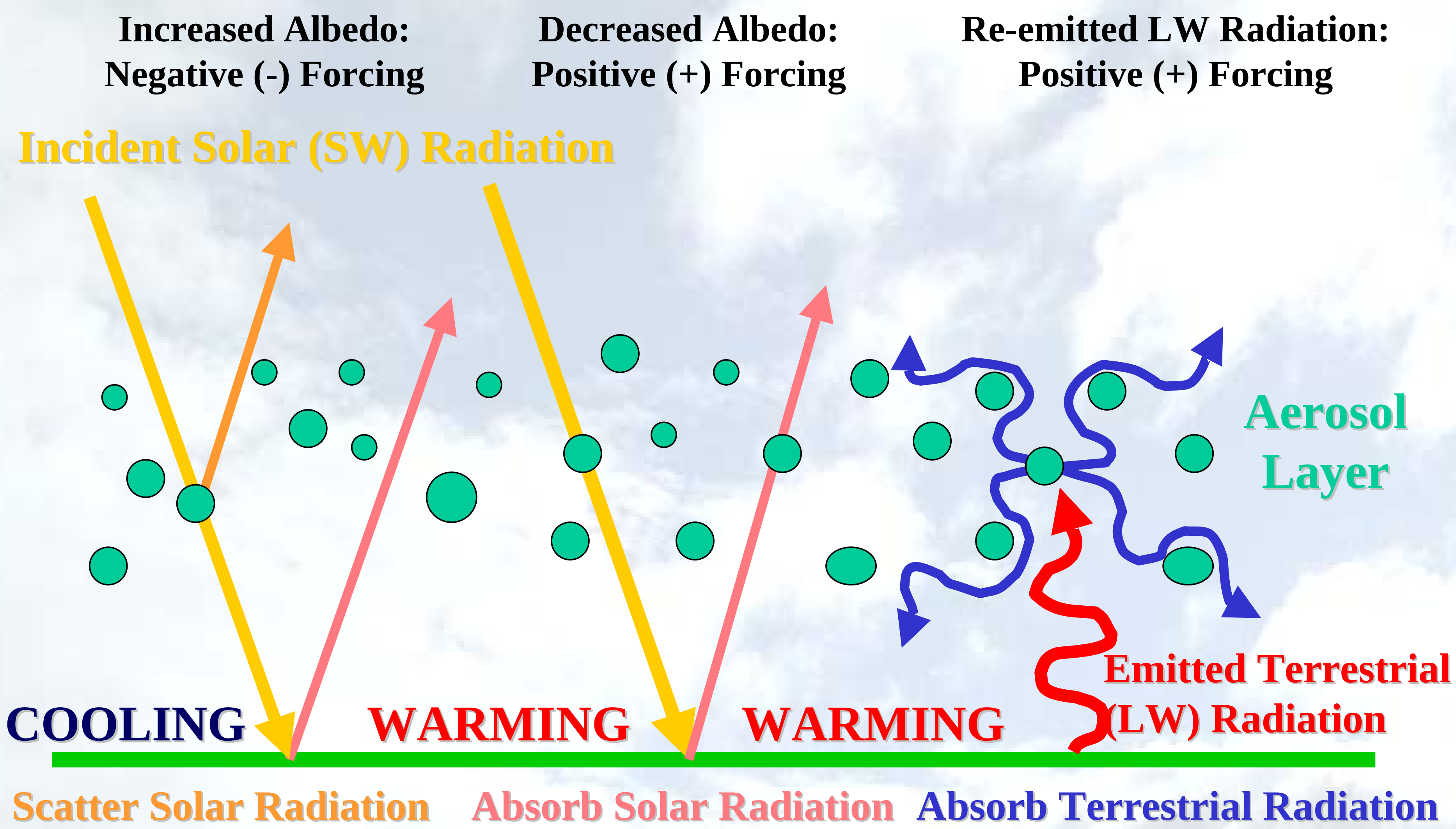
Presentation Overview

- Introduction
  - Aerosol Direct Effect
  - Hygroscopicity , Deliquescence and Efflorescence
  - Mie Scattering
- Organics, Hygroscopicity, and Scattering: Model Results & Comparisons to Measurements
- Summary and Conclusions

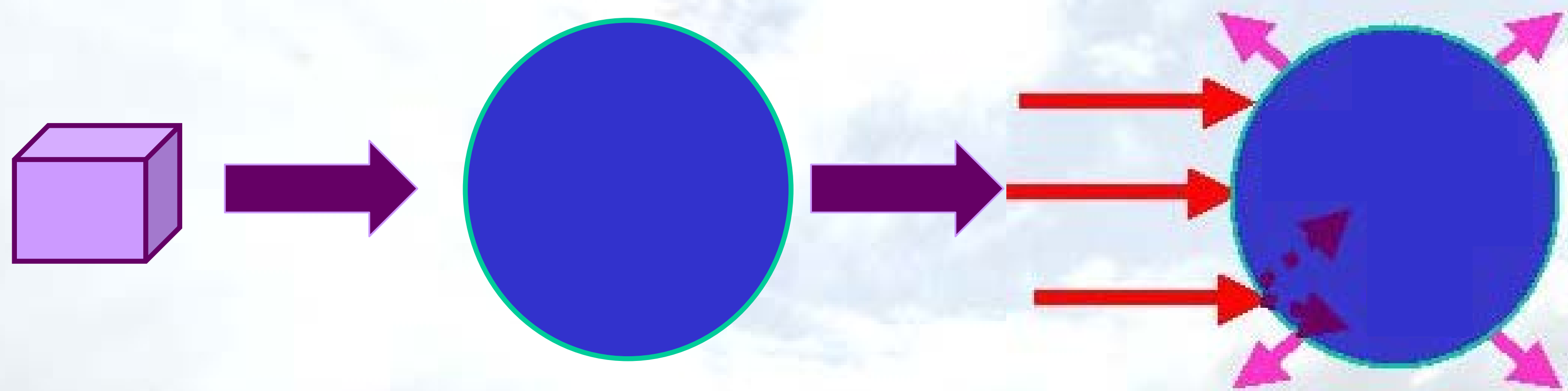
Direct Radiative Forcing by Aerosols



How does water uptake affect scattering?

("Water uptake by aerosols is a key uncertainty factor in the aerosol direct effect (IPCC, 2001)")

- **Water uptake depends on aerosol composition.**
- **Water increases particle size…**
- **Larger particles scatter more light…**
- **Less light reaches the surface…** ⇨ **Less energy**



Example: Sea Salt Aerosol

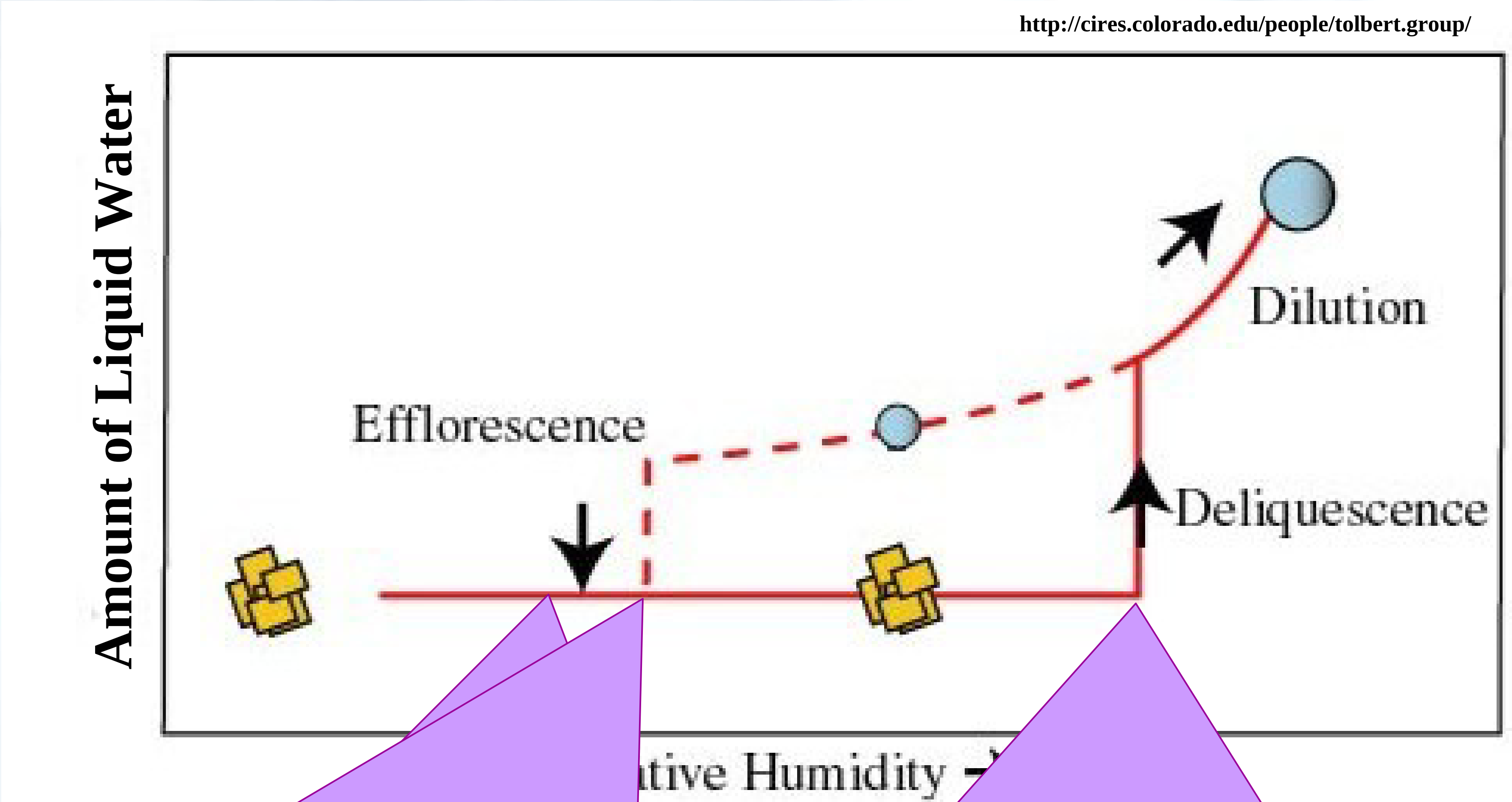
- **Oceans cover 2/3 of the Earth's surface, so production of sea salt is nearly global.**

- **Sea salt accounts for 30 to 75% of all natural aerosols (Blanchard and Woodcock, 1980; Winter and Chýlek, 1997)**

- **Sea salt is the primary contributor to the global-mean clear-sky radiation balance over oceans (Haywood *et. al.*, 1999)**

- **NaCl is the principal constituent of dry sea salt aerosol (O'Dowd and Smith, 1998; Winter and Chýlek, 1997)**

Deliquescence and Efflorescence



As RH over a wet particle decreases, crystallization does not occur at the DRH, but at a much lower *efflorescence* RH.

Hygroscopic Growth of Particles

Hygroscopic Growth Factor (HGF):

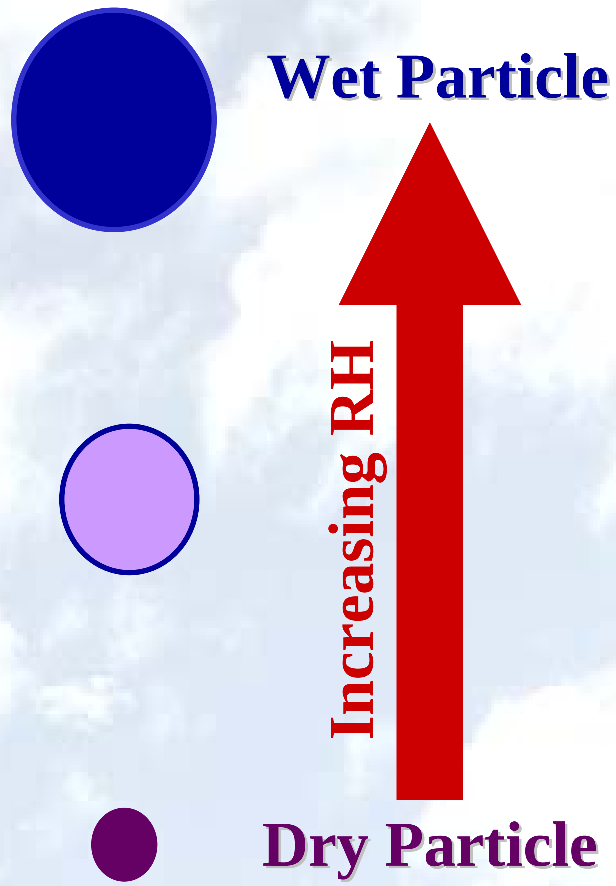
Diameter of Wet Particle

at given RH

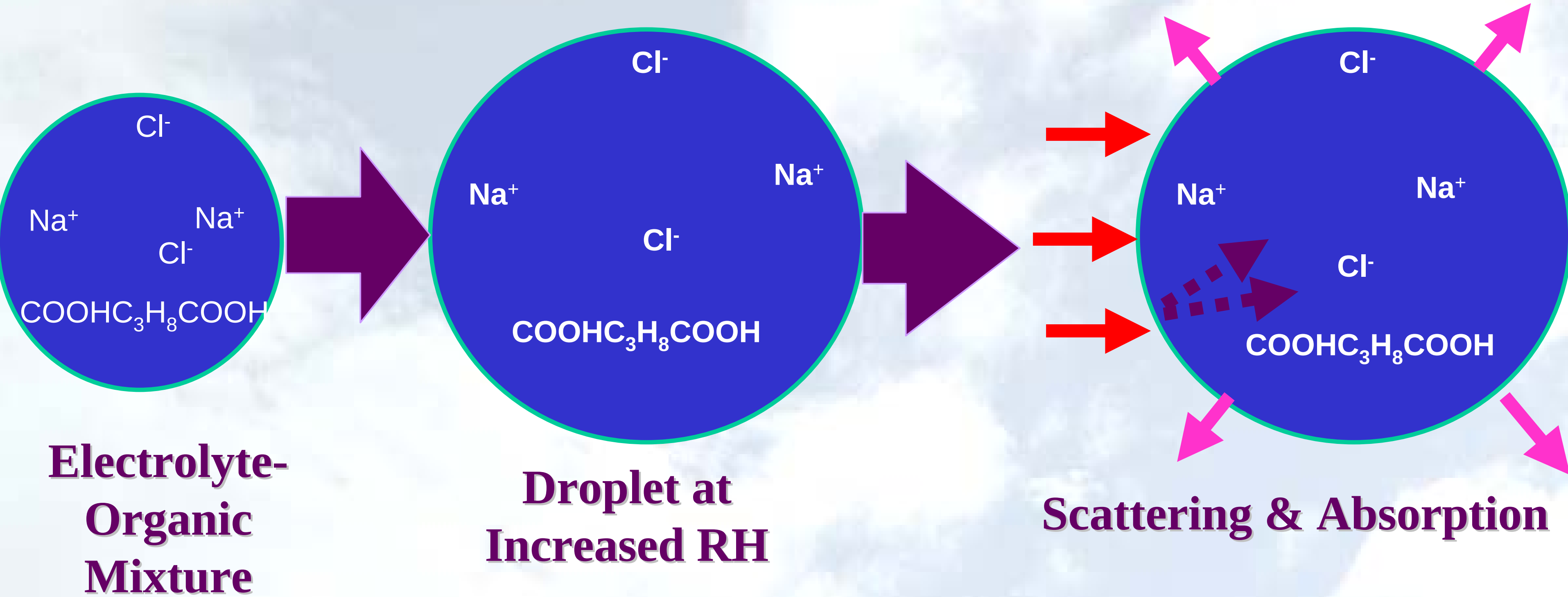
Diameter of Dry Particle

at dry RH (40%)

$$HGF_{RH} = \frac{D_p(RH)}{D_p(RH = 40\%)}$$



Hygroscopicity and Scattering: Organic-Electrolyte Mixtures



- ➢ Organics alter the scattering and absorption of light by aerosols.
- ➢ Up to 50% of total fine aerosol mass is composed of organics.
- ➢ Organics alter the hygroscopicity of aerosols

(Penner *et. al.*, 1998).

(Middlebrook *et al.*, 1998)

(Saxena *et. al.*, 1995).

Mie Scattering

- **Scattering & absorption of light by homogeneous sphere.**
- **Refractive Index ($m = n_r + ik_i$)**
- **Extinction, Scattering, & Absorption Cross-Sections (C_{ext}, C_{scat}, C_{abs}):** Amount of energy removed from the beam of incident radiation by the particle. Analogous to geometrical area of the particle.

$$C_{ext} = C_{scat} + C_{abs}$$

(units are Length^2)

- **Extinction, Scattering, & Absorption Efficiencies (Q_{ext}, Q_{scat}, Q_{abs}):** The extinction cross-section divided by the cross-sectional area of the particle.

$$Q_{ext} = Q_{scat} + Q_{abs} = \frac{C_{ext}}{\pi D_p^2 / 4}$$

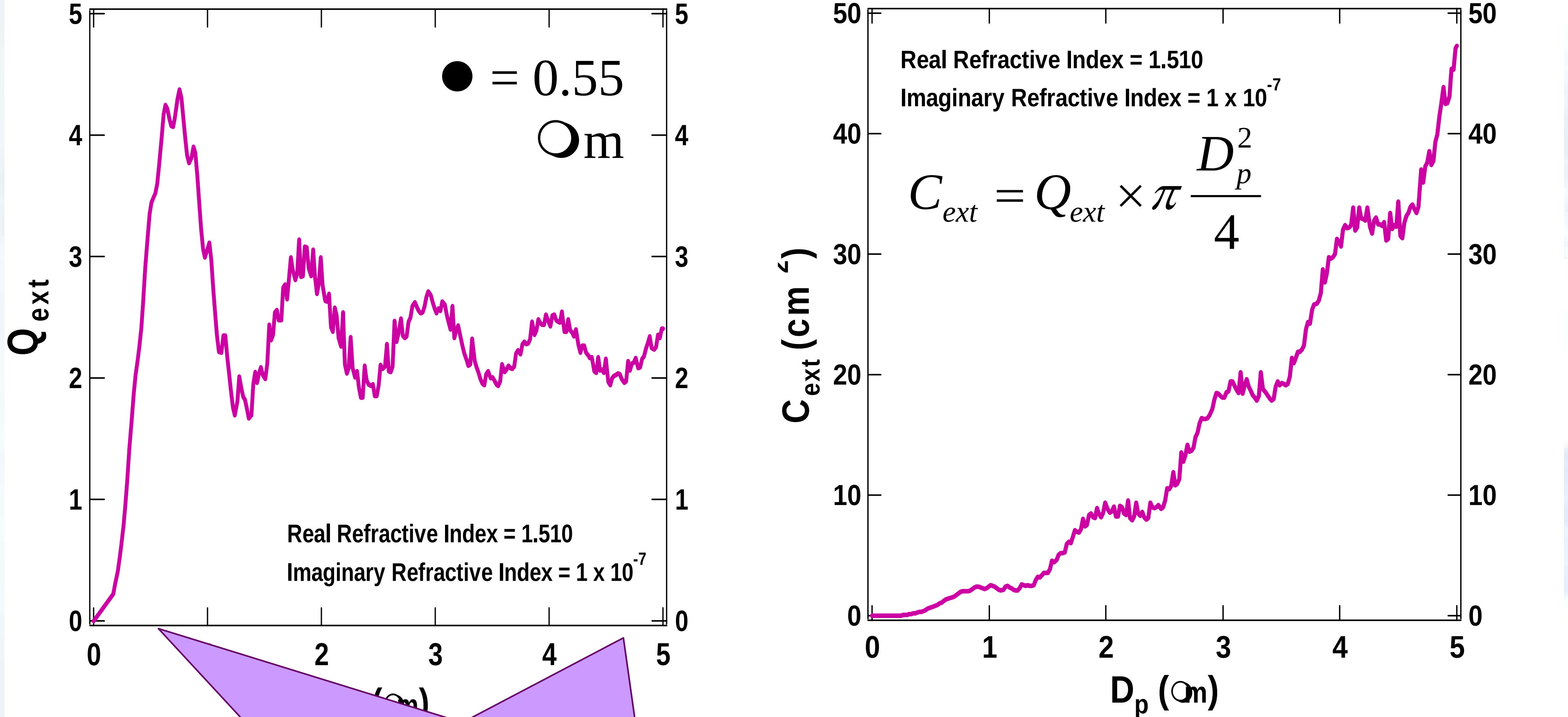
(unitless)

- **Extinction, Scattering & Absorption Coefficients (σ_{ep}, σ_{sp}, σ_{ap}):** The extinction cross section multiplied by a number density N (units Length^{-3}).

$$\sigma_{ep} = \sigma_{sp} + \sigma_{ap} = \int \pi \frac{D_p^2}{4} Q_{ext}(m, D_p) N(D_p) dD_p$$

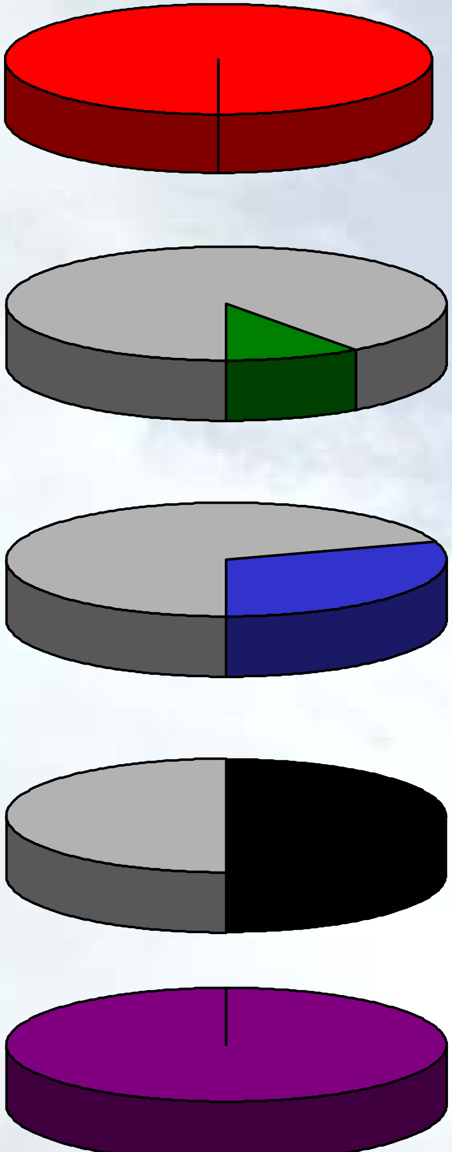
(units Length^{-1})

Larger Particles Scatter More Light



Particles with diameters between about 0.1 and 1 ❍m scatter light most efficiently.

Sensitivity to Organic Fraction



100% NaCl

90% NaCl,
10% Glutaric Acid

70% NaCl,
30% Glutaric Acid

50% NaCl,
50% Glutaric Acid

100% Glutaric Acid

Note: % is % mass dry particle

Clean Marine

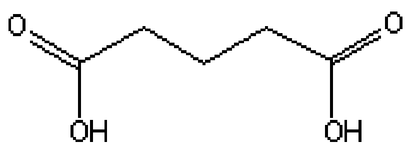
Polluted Marine

(Middlebrook *et. al*., 1998)

Simple "Sea-Salt"-Organic Mixture

Na^+ Cl^-

NaCl



Glutaric Acid ($C_5H_8O_4$)

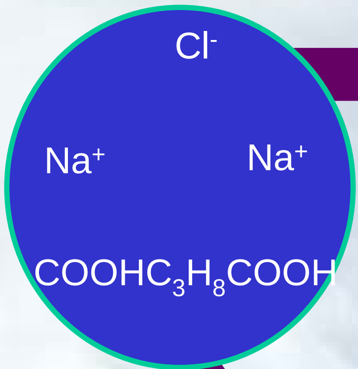
H_2O

Water

- **Aerosol particles in the atmosphere are often complex mixtures of inorganic and organic compounds (Middlebrook *et. al.*, 1998).**
- **NaCl is the major constituent of sea salt (Ming and Russell, 2001).**
- **On average, less than 10% of fine aerosol organic carbon has been attributed to specific compounds (Rogge, 1993).**
- **Di-acids, such as succinic and glutaric acid, have been found in the atmosphere and in marine aerosols (Necessary *et. al.*, 2001; Kawamura and Gagosian, 1990).**

Methodology: Models & Assumptions

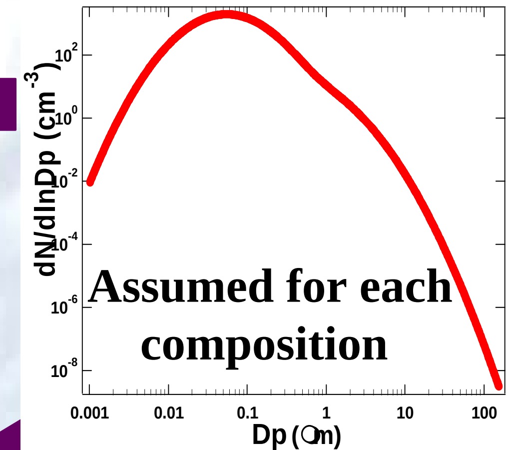
Chemical Composition



Organic-Electrolyte Model

(Ming & Russell, 2002)

Dry Size Distribution



(Shettle & Fenn, 1975)

HGF

Refractive Index

(Erlick *et. al.*, 2000)

Wet Size Distribution

Composite Refractive Index

Refractive Index H_2O

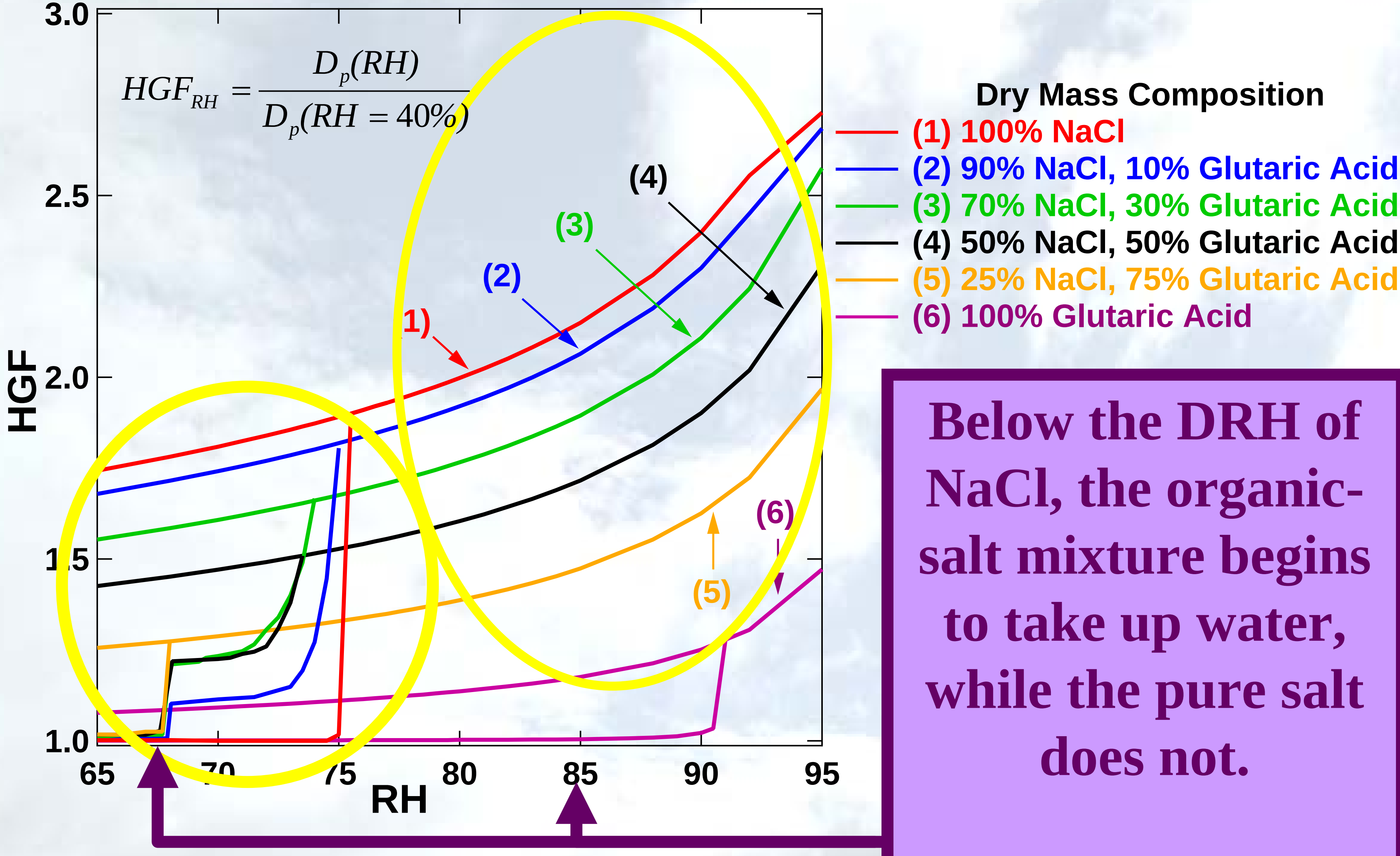
(Erlick *et. al.*, 2000)

Mie Scattering Model

(Bohren & Huffman,1985)

Scattering Coefficient (σ_{scat})

HGF: NaCl & Glutaric Acid

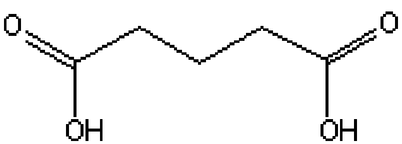


Below the DRH of NaCl, the organic-salt mixture begins to take up water, while the pure salt does not.

Optical Properties

Na^+ Cl^-

NaCl



Glutaric Acid
($C_5H_8O_4$)

H_2O

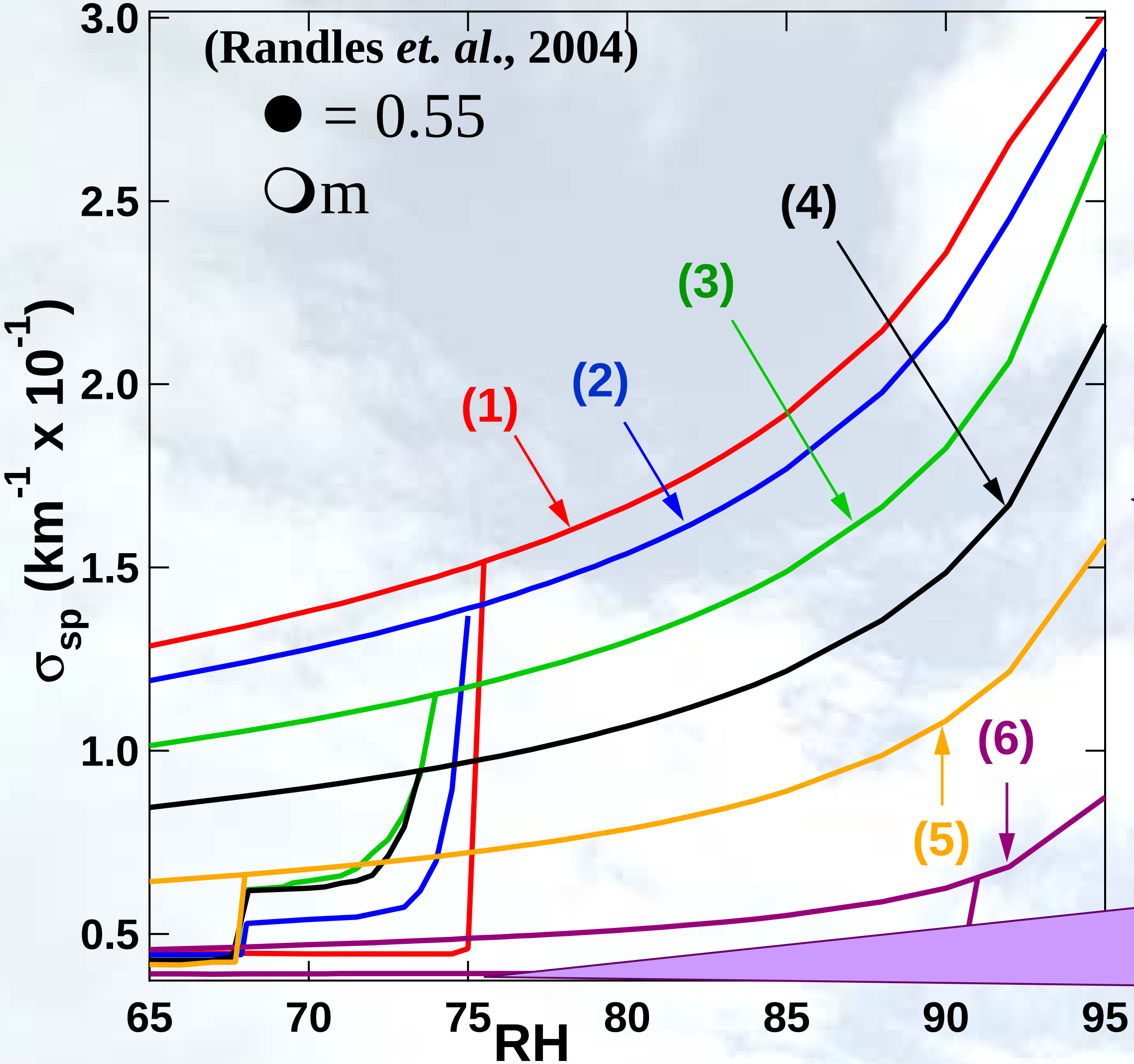
Water

- **Refractive Indices**
  - **NaCl: 1.510 + *i*(1 � 10^{-7})**
  - **Organics: 1.431 + *i*(6 � 10^{-3})**
  - **H_2O: 1.333 + *i*(1.96 � 10^{-9})**

(Erlick *et. al.*, 2001)

- **Sodium Chloride and Water are non-absorbing.**
- **Organics are assumed to be mildly absorbing.**
- **For all calculations ● = 0.55 ❍m (corresponds to peak of solar radiation).**

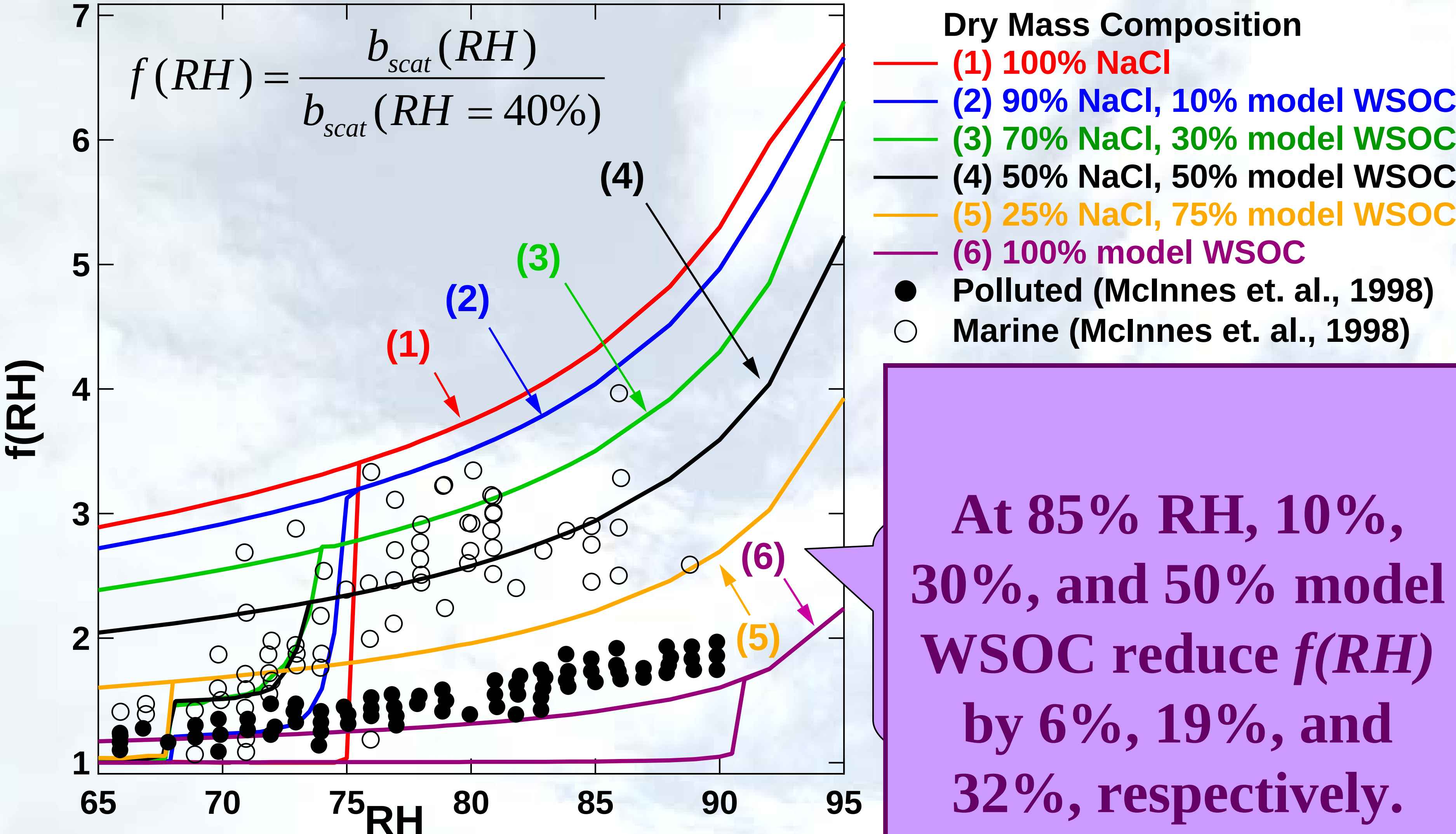
Scattering Varies with Composition



At 85% RH, 10%, 30%, and 50% model WSOC (glutaric acid growth with assumed refractive indices) cause 8%, 22%, and 37% reduction in scattering coefficient. A non-absorbing aerosol causes 7%, 15%, and 21% decrease for these mixtures.

$$\sigma_{sp} = \int \pi \frac{D_p^2}{4} Q_{scat}(m, D_p) N(D_p) dD_p$$

Modeled f(RH) and Observations

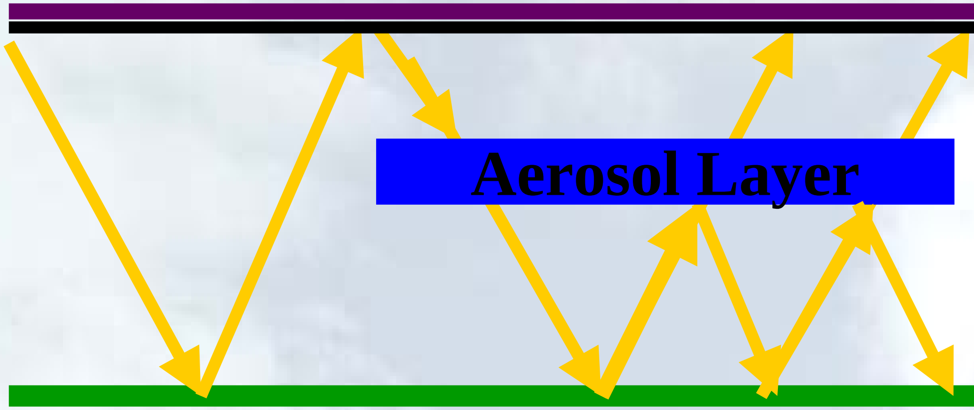


At 85% RH, 10%, 30%, and 50% model WSOC reduce *f(RH)* by 6%, 19%, and 32%, respectively.

(Randles *et. al.*, 2004)

Combined Surface-Aerosol Reflectance

(Chýlek & Coakley, 1974)



Surface Albedo ***a***

(Ignoring other atmospheric constituents)

_a_ = surface albedo or planetary reflectance; fraction of incoming solar radiation reflected to space

R_{as} = total reflectance of the aerosol-surface system

◆$_o$ = σ_{scat}/ σ_{ext} = single scattering albedo.

◆$_o$♌ = fraction scattered into backward hemisphere

$$\Delta R = a - R_{as}$$

➢ **Change in reflectance at top of atmosphere due to presence of aerosol.**

$$\frac{1-\omega_o}{\omega_o\beta} = \frac{(1-a)^2}{2a}$$

➢ **For global average conditions (i.e. integrated over all ❍) , if 🖓_R_ = 0; referred to as "global average critical ratio."**

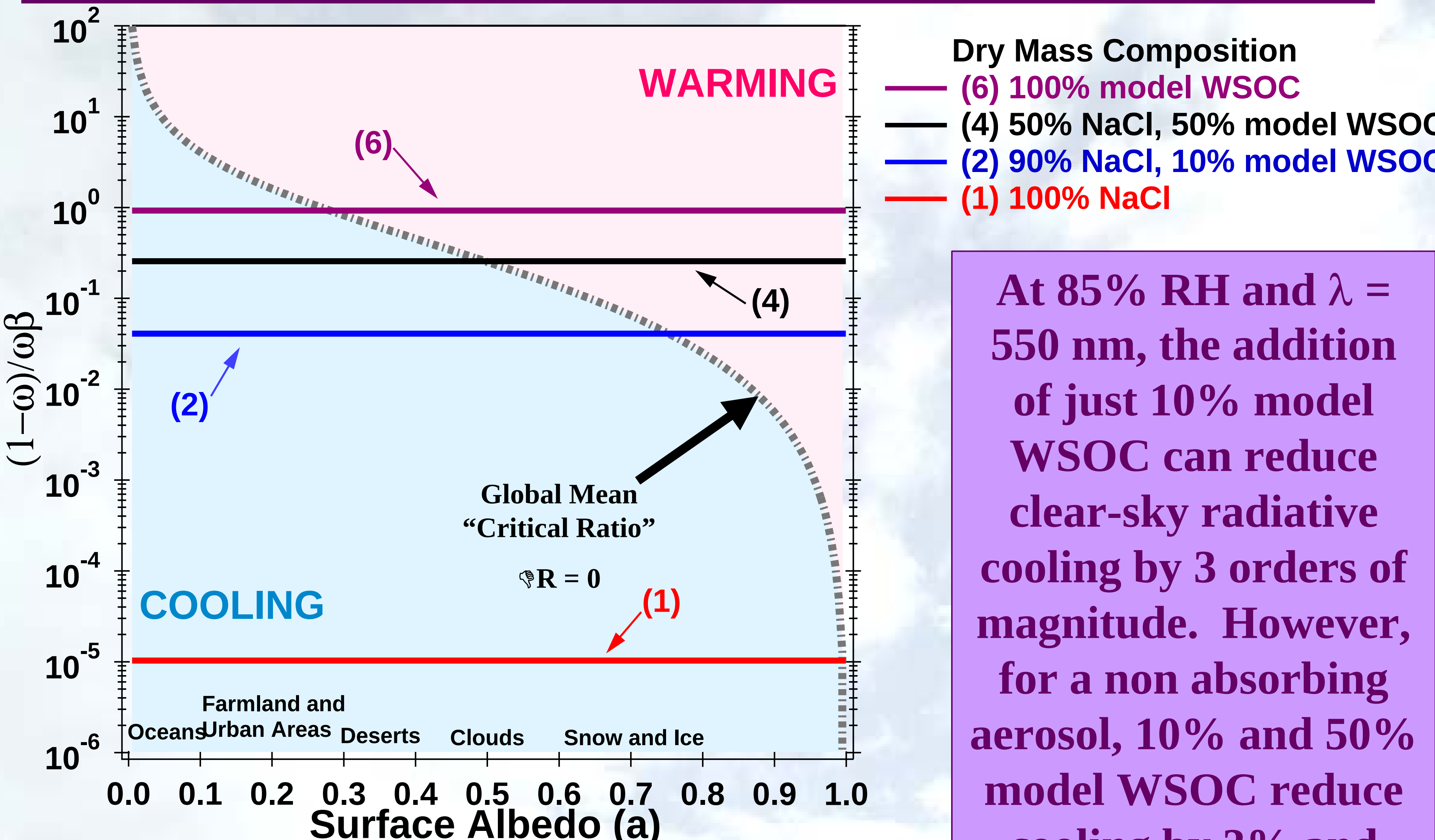
$$\frac{1-\omega_o}{\omega_o\beta} > \frac{(1-a)^2}{2a}$$

➢ **Equivalent to _a_ > R_{as} or 🖓_R_ > 0; aerosol layer decreases total system reflectance of system and causes heating.**

$$\frac{1-\omega_o}{\omega_o\beta} < \frac{(1-a)^2}{2a}$$

➢ **Equivalent to _a_ < R_{as} or 🖓_R_ < 0; aerosol layer increases total system reflectance of system and causes cooling.**

Cooling Decreased by Organics



At 85% RH and λ = 550 nm, the addition of just 10% model WSOC can reduce clear-sky radiative cooling by 3 orders of magnitude. However, for a non absorbing aerosol, 10% and 50% model WSOC reduce cooling by 3% and 25%.

(Randles *et. al.*, 2004) RH = 85%

Summary

- **Organics alter hygroscopic growth factor (HGF):**
  - **Prior to deliquescence of pure salt, slightly enhances growth.**
  - **After deliquescence of pure salt, suppress growth.**
- **Scattering coefficients affected in similar manner as HGF since dependent on particle size.**

Summary

- **Observations of *f(RH)***
  - **Observations of *f(RH)* for polluted air lower than for cleaner marine air.**
  - **Modeled *f(RH)* lowers with increasing organic content as growth is suppressed at higher RH.**
  - **Increasing organic carbon content may contribute to lowering of *f(RH)* in more polluted conditions.**
- **Increased organic content causes less cooling because:**
  - **Organics suppress the size of the aerosol, allowing less of the aerosol size distribution to shift into the optically active range.**
  - **A mildly absorbing organic will have reduced scattering, reducing the amount of cooling.**

Conclusions

- It is important to know the following properties of organic aerosol in order to determine their impact on climate:
  - Mixing state (internal or external)
  - Effects on hygroscopic growth
  - Refractive Indices
- Since WSOC can become associated with both sulfates and sea salt (both of which experience deliquescent behavior), it is likely that the global radiative cooling associated with organic compounds is overestimated because of inadequate accounting of their hygroscopic growth and absorption effects.

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