Surface modification of bioaerosol by physical, chemical, and biological ageing processes

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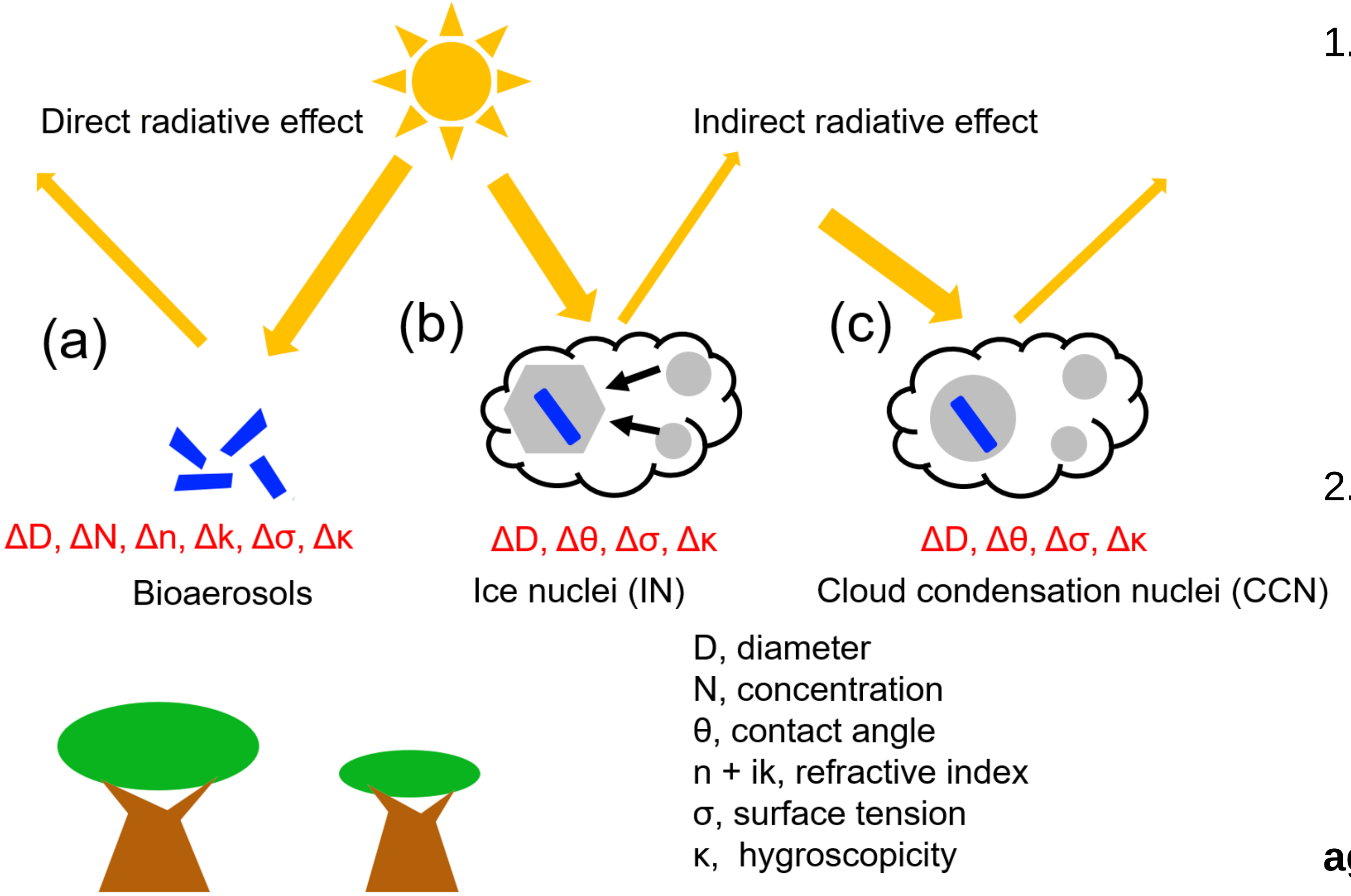
Introduction and Outline



D, diameter
N, concentration
θ, contact angle
n + ik, refractive index
σ, surface tension
κ, hygroscopicity

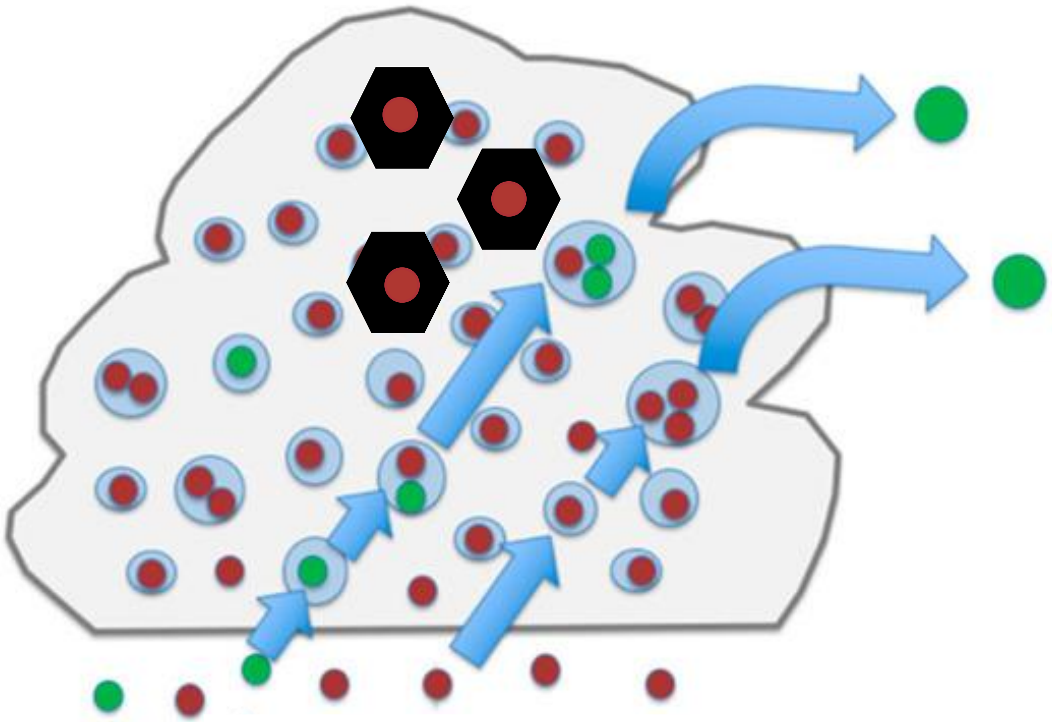
Zhang et al., in preparation

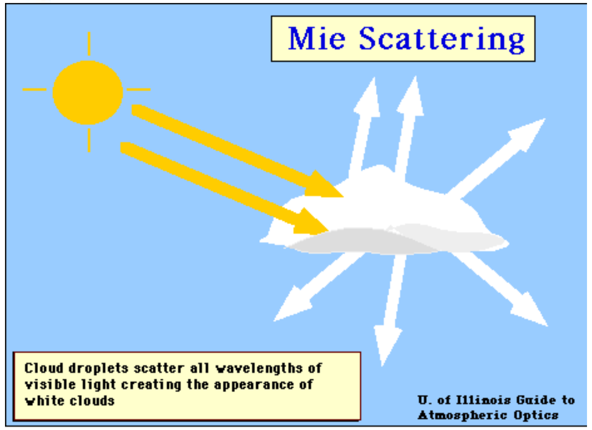
1. What is the sensitivity of the aerosol direct and indirect effects (e.g. IN, CCN, radiative) to the physiocochemical **bioaerosol properties**, such as particle size, concentration, surface properties, refractive index, surface tension, hygroscopicity)?

2. Which
   - physical (e.g. agglomeration or fragmentation, coating with organics),
   - chemical (e.g. oxidation, nitration, degradation),
   - biological (e.g. bacterial growth)

ageing processes are important in influencing properties of bioaerosol?

Model approaches





1. **Adiabatic cloud parcel model (Ervens et al., JGR, 2005, 2011)**

a) Ice nucleation in mixed-phase clouds: Ice nucleation of bacteria by immersion freezing is explored based on classical nucleation theory

b) CCN activation of bacteria is explored based κ-Köhler equation with varying hygroscopicity (κ) and surface tension (σ) for biological aerosol

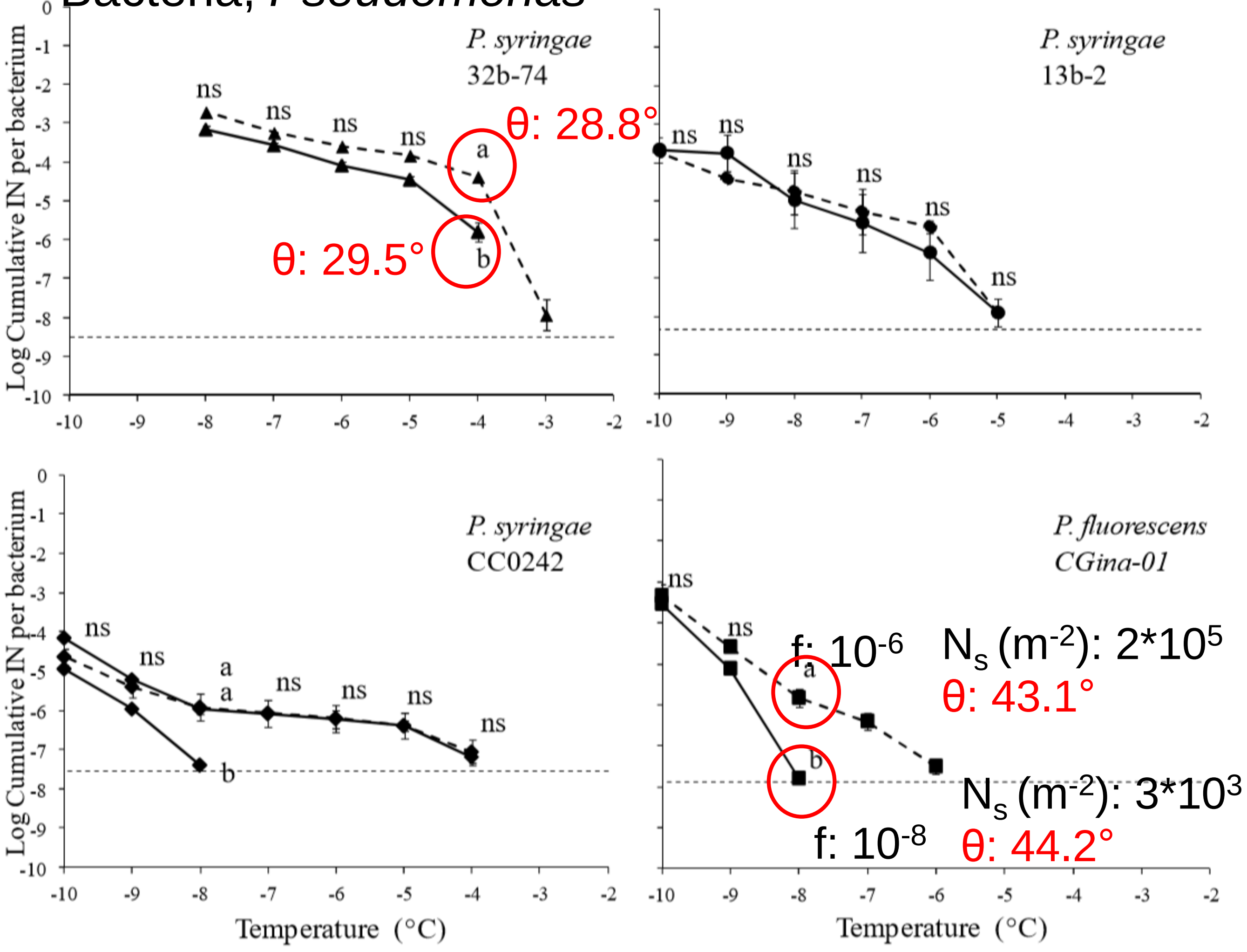
2. Mie theory

The effects of scattering and absorption of biological aerosol are explored based on Mie theory using a range of refractive indices for bacteria

In all model approaches, it is assumed that only one particle size class within an aerosol population (IN: 0.044 μm < D < 2.4 μm, N = 100 cm^{-3}; CCN: 0.005 μm < D < 7.7 μm, N = 902 cm^{-3}; scattering: 0.5 μm < D < 3 μm, N = 1.4 cm^{-3}) contains bacteria (D = 1 μm, N = 0.01 cm^{-3}; base case) that exhibit the various physicochemical parameters explored here.

Example: Protein nitration influences ice nucleation activity

Bacteria, *Pseudomonas*



Attard et al., ACP, 2012

- Experiments by Attard et al., 2012: Nitration (10 h) reduces cumulative IN fraction of bacteria
- The lifetime of aerosol particles in atmosphere is from hours to weeks, which means nitration time of 10 h is within this range.
- We converted the measured 'cumulative IN concentration' into **contact angle θ,** based on classical nucleation theory,

→ Nitration increases θ by ~1° for some bacteria types

Does nitration affect the evolution of mixed-phase cloud to a significant extent?

Simulation of mixed-phase clouds: Effect of contact angle θ

Model simulations

We do not explicitly simulate the nitration process in the model. Instead, we explore the sensitivity of the change in θ inferred by nitration during 10 h in the atmosphere (Δθ ~ 1°).

Output parameters

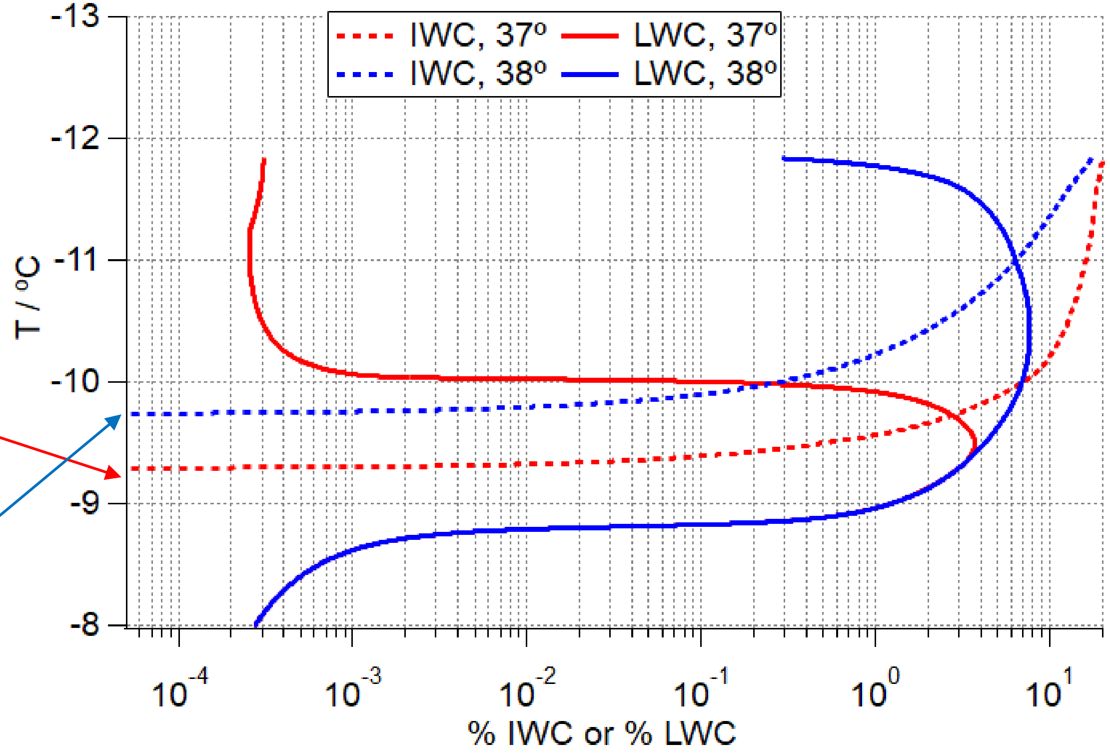
Evolution of ice (IWC) and liquid water content (LWC) [%] in the cloud with decreasing temperature (increasing height)

Results

- Particles with lower θ (non-nitrated): ice forms at higher T (lower heights) in the cloud
- Nitrated IN surfaces are less efficient IN, ice formation starts only at lower T → increase of IWC at the expense of drop evaporation (LWC decrease) (Bergeron-Findeisen process) starts later

ice + water + vapor = constant

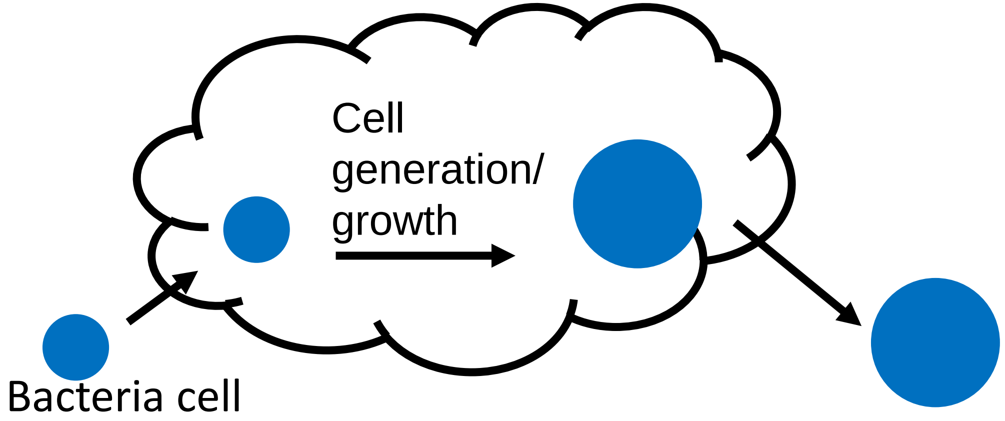
$F_{ice} + F_{water} + F_{vapor} = 100\%$



A small change in the IN surface (Δθ ~ 1) can affect the evolution of mixed-phase clouds (Bergeron-Findeisen process) significantly

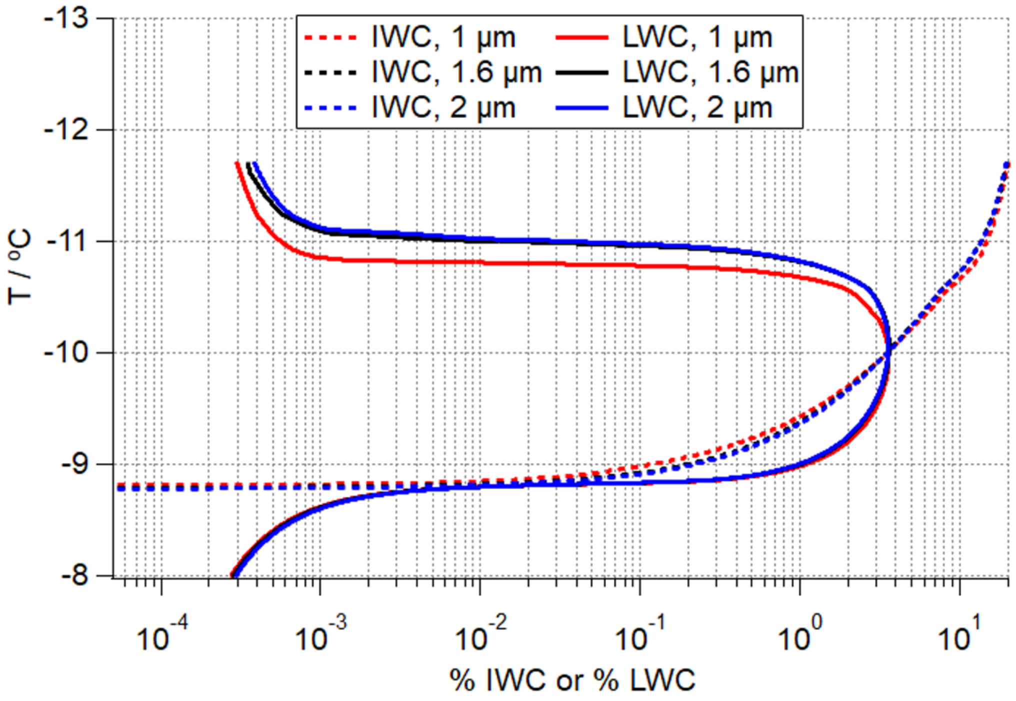
→ Chemical processes that modify the surface of IN should be included in models to account for ageing of IN

Simulation of mixed-phase clouds: Effect of bacteria size



- Ervens & Amato, ACP (2020) suggested that bacteria can efficiently grow in the atmosphere
- Typical cell generation rates are in the range of 0.1 to 0.9 h^{-1}, with an average of ~0.3 h^{-1}.
- Efficient growth is restricted to their time they are exposed to liquid water (in-cloud)
- The lifetime of bioaerosol particles is ~1 week. On average, particles spend ~15% of their time in cloud (~ 20 h)
- Using $D = (1+0.3\ t)^{0.33}$,

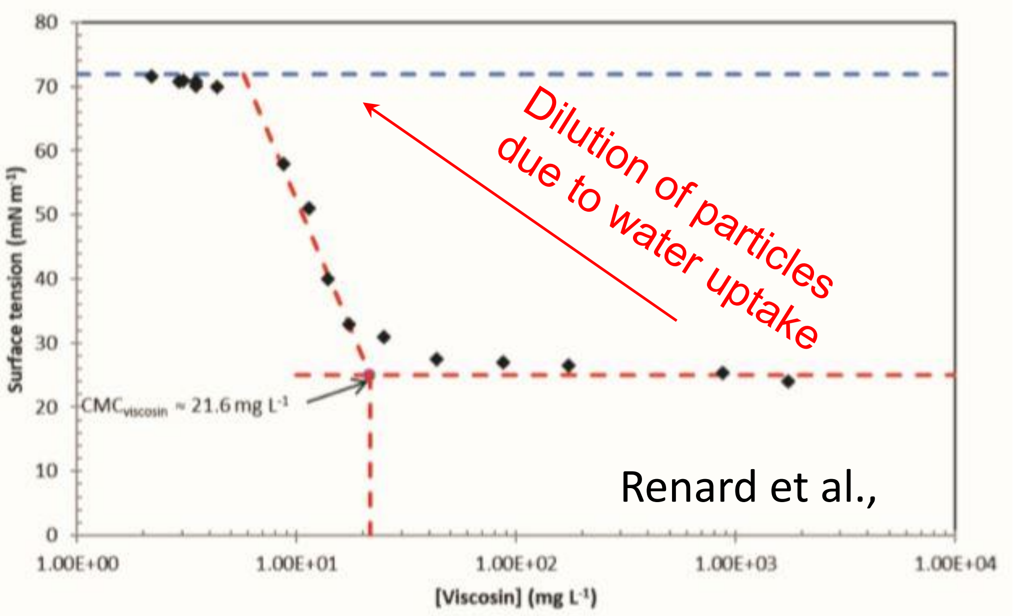
  an initial bacteria cell of 1 μm may double its size after one week in the atmosphere.

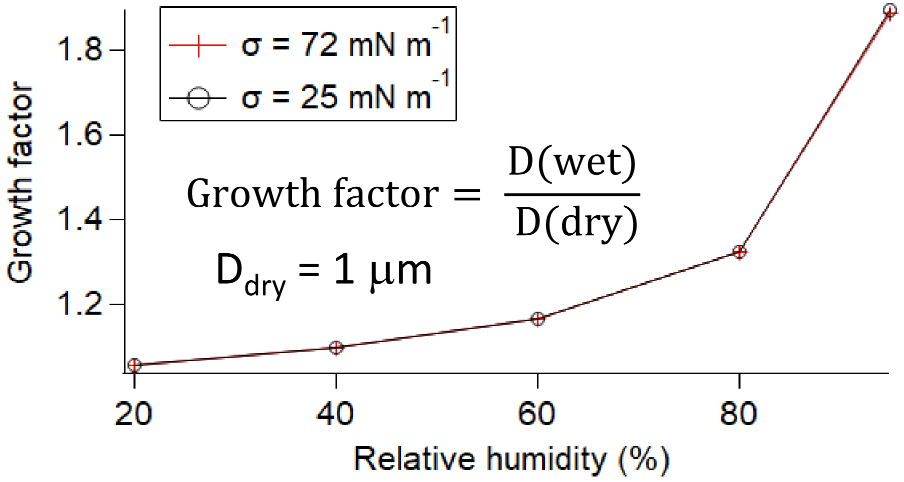


Doubling of cell size by cell growth does not affect IN properties to a significant extent (in agreement with sensitivity studies by Ervens et al., GRL, 2013)

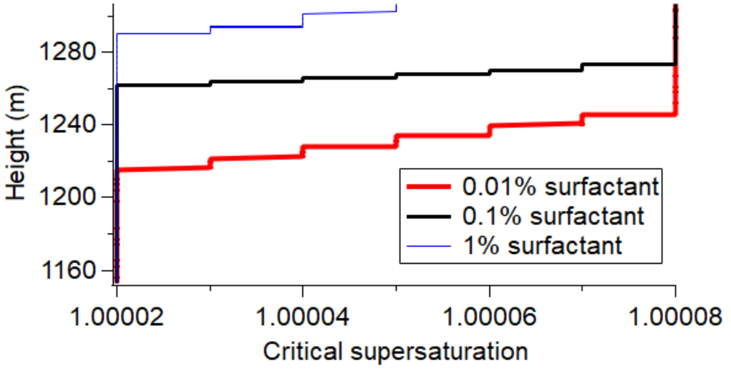
→ Bacteria cell growth can be neglected in determining modification of IN ability of bacteria

Simulation of warm clouds: Effect of biosurfactants





When RH < 100%, surface tension does not affect the growth of particles sufficiently to modify their size

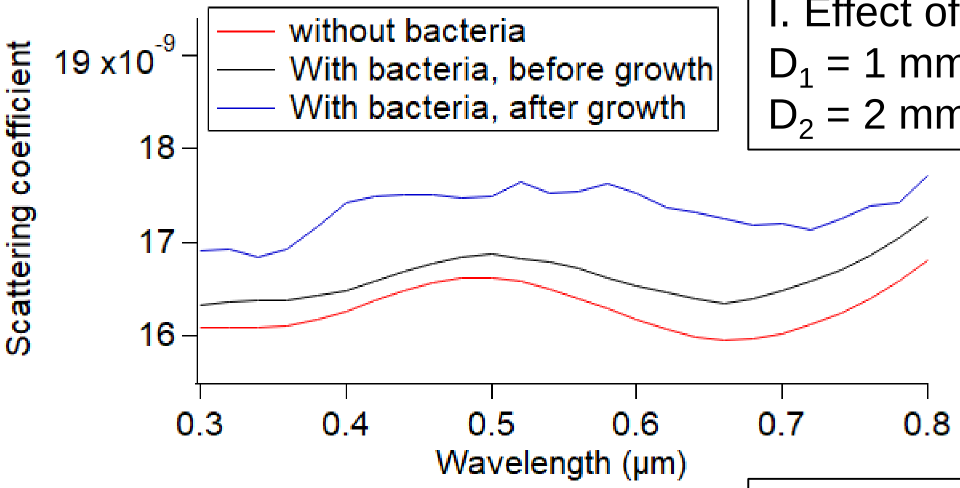


- Bacteria can generate **biosurfactants** which reduce the surface tension of biological particles from $\sigma = 72$ to 25 mN m^{-1} (Renard et al., 2019)
- The particle mass fraction of surfactants is on the order of ~0.1% (Gerard et al., 2019)
- Surface tension reduction enhances water uptake of particles (Kelvin term) and thus affect growth factor and CCN activation

- The presence of biosurfactants affects the critical supersaturation of particles → 'better CCN'
- However, for particles D = μm, S(crit) is sufficiently low to allow activation, independent of σ

Biosurfactants do not significantly affect the growth factors and CCN activation of biological particles (D ~ 1 μm)

Effect of bacteria growth and nitration on scattering coefficient

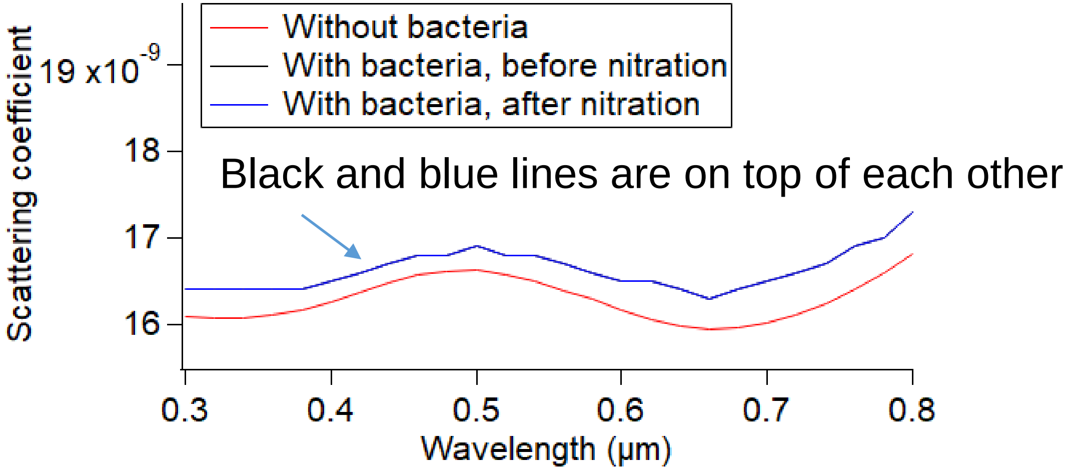


I. Effect of cell growth
D_1 = 1 mm
D_2 = 2 mm

We model the effect of bacteria (N = 0.01 cm^{-3}) on the scattering coefficient of total particles (0.5 µm < D < 3 µm, N = 1.4 cm^{-3})

Due to the lack of data pertinent ot bacteria in terms of refractive indices, we apply values derived from experiments of SOA nitration (Moise et al. 2015).

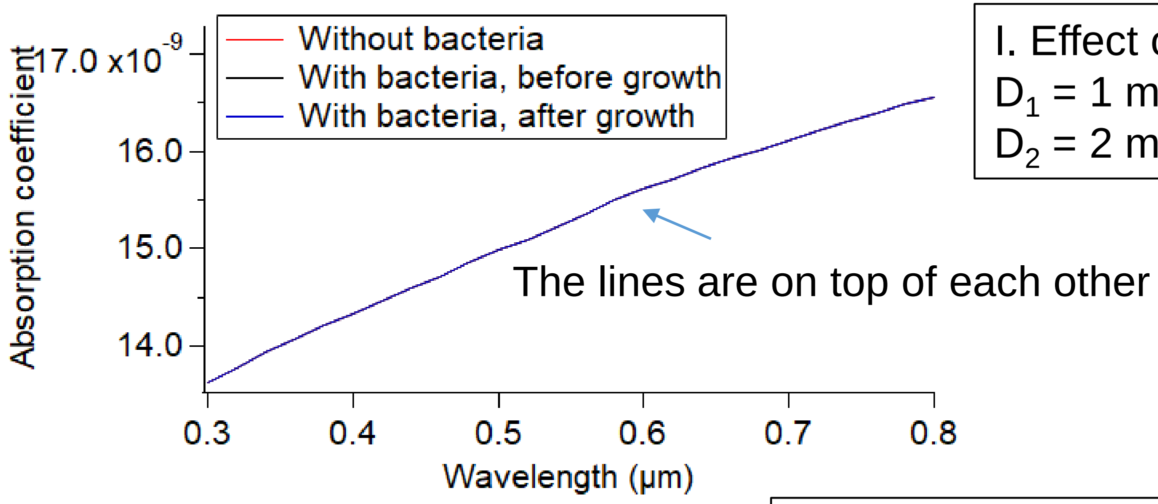
II. Effect of nitration
Real part of refractive index:
1.516 – 1.576 (before nitration)
1.534 – 1.594 (after nitration)



Particle size affects scattering coefficient of total particles significantly.
→ Cell growth needs to be considered in models to account for variability in particle size

Nitration is predicted to change the scattering of total particles to a negligible extent

Effect of bacteria growth and nitration on absorption coefficient

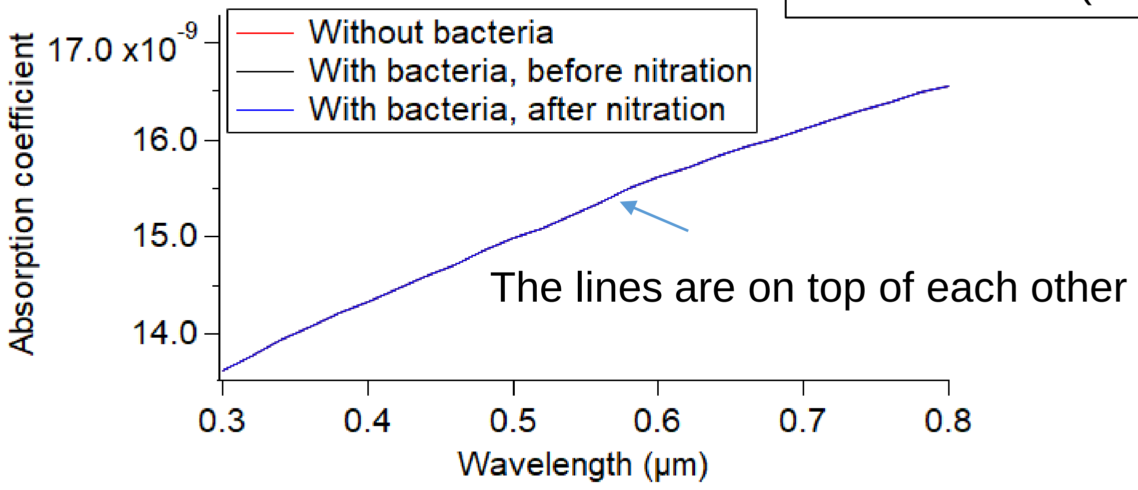


I. Effect of cell growth
D_1 = 1 mm
D_2 = 2 mm

The presence of bacteria, bacteria size and nitration are predicted to change the absorption of total particles to a negligible extent.

Note that we assume that soot accounts for 50% of the other particles, which makes the influence of biological particles on absorption of total particles negligible.

II. Effect of nitration
Imaginary part of refractive index:
0 – 0.013 (before nitration)
0.001 – 0.035 (after nitration)



Conclusions

By means of process model studies, we explored the sensitivity of various aerosol radiative effects (ice nucleation ability, CCN activity, optical properties) to the physicochemical properties of biological particles.

Decrease of importance

Decrease of sensitivity

Ice nucleation (Mixed-phase clouds)		**Scattering/Absorption (aerosol direct effect)**		**CCN activation**	
Fraction of bacteria to total particle number:					
$N_{bio} \sim N_{IN}$ (10%)		$N_{bio} < N_{scattering}$ (1%)		$N_{bio} \ll N_{ccn}$ (0.01%)	
Process	**Property**	**Process**	**Property**	**Process**	**Property**
Chemical ageing, e.g. nitration	Contact angle	Biological ageing, e.g. cell growth	Particle diameter	Biological ageing, e.g. cell growth	Particle diameter
Biological ageing, e.g. cell growth	Particle diameter	Chemical ageing, e.g. nitration	Refractive index	Biological activity, e.g. biosurfactant prod	Surface tension
		Biological activity, e.g. biosurfactant prod	Surface tension		

Properties and processes with high sensitivity should be further investigated in experimental and model studies

References:
Ervens, B., Feingold, G. and Kreidenweis, S. M.: Journal of Geophysical Research D: Atmospheres, 110(18), 1–14, 2005 ; Ervens, B., Feingold, G., Sulia, K. and Harrington, J., Journal of Geophysical Research Atmospheres, 116(17), 2011.; Bohren, C. F.: Absorption and scattering of light by small particles., 1983.; Attard, E., Yang, H., Delort, A. M., Amato, P., Pöschl, U., Glaux, C., Koop, T. and Morris, C. E.Atmospheric Chemistry and Physics, 12(22), 2012.; Moise et al. Chemical Reviews, 2015; Zhang et al., in preparation