The Effects of Secondary Organic Material on the Hygroscopic Properties of Ammonium Sulfate Seed

August 2010

Mackenzie L. Smith, Mikinori Kuwata, and Scot T. Martin
Harvard University

http://www.seas.harvard.edu/environmental-chemistry

Funded by The Department of Energy GCEP Graduate Research Environmental Fellowship and the National Science Foundation

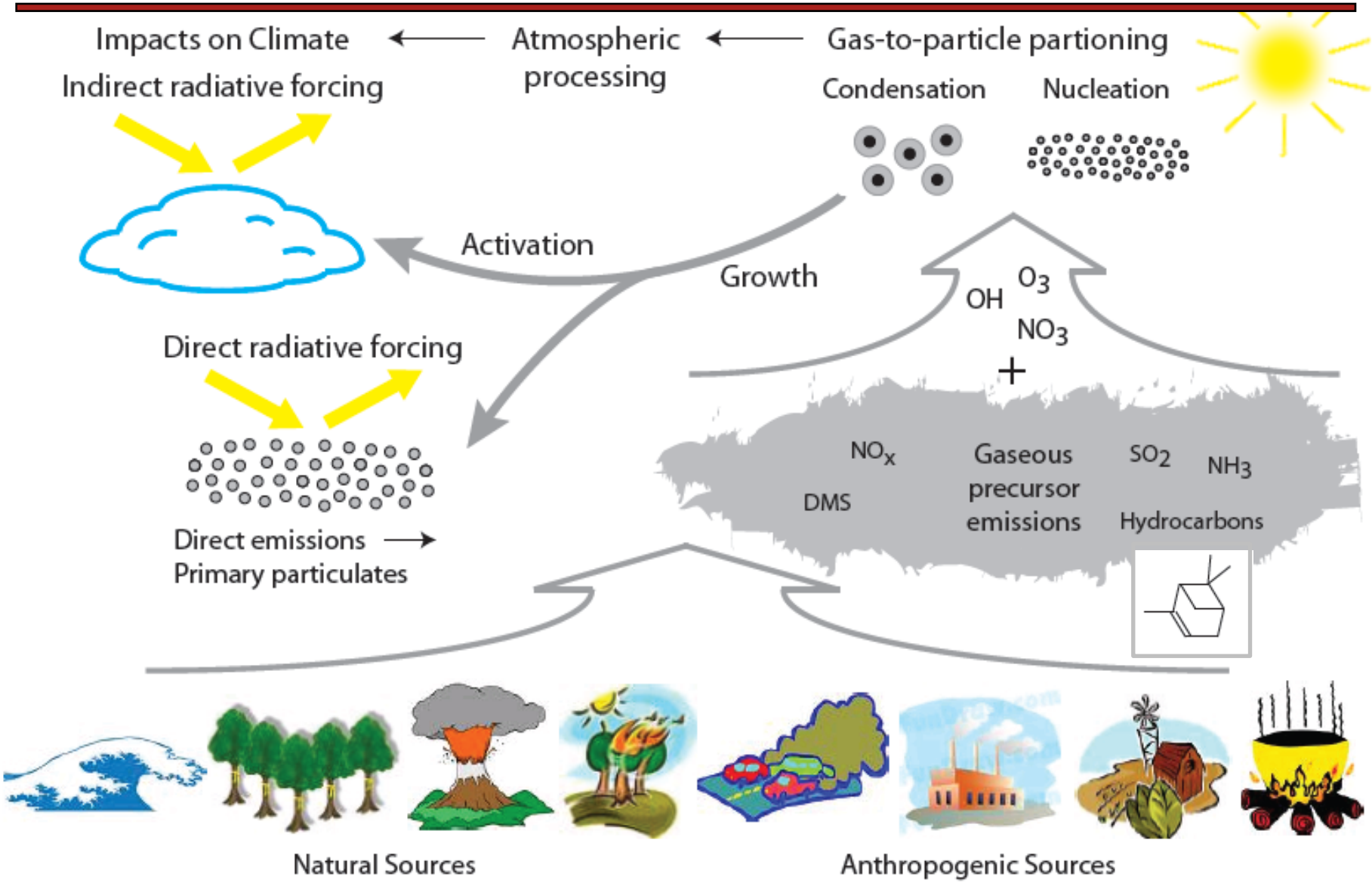
Outline

I. Motivation and Background
II. Previous work
III. Scientific Questions
IV. Experimental Setup
    I. Overall
    II. The 1x3 TDMA

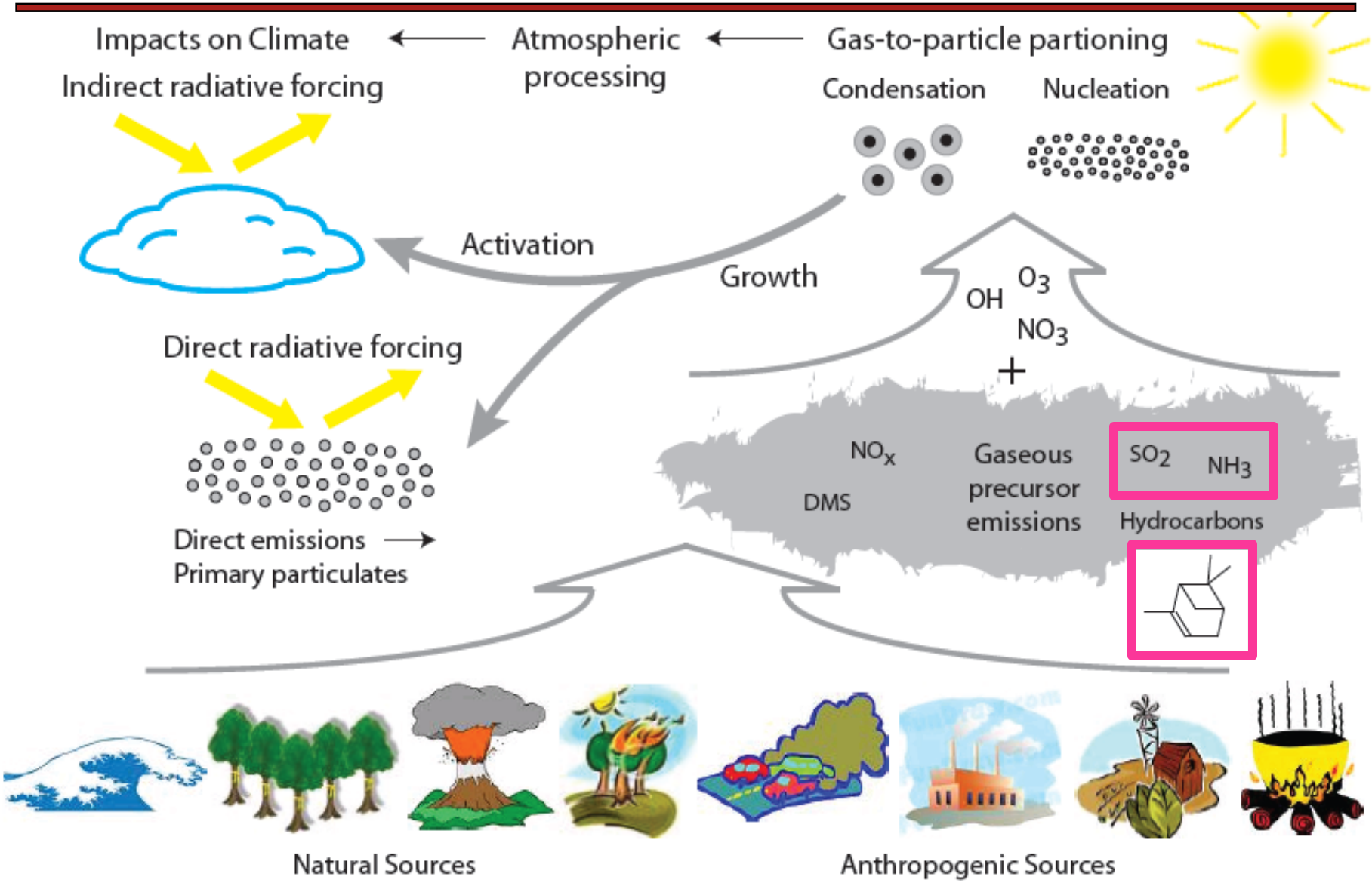
V. Results
    I. Pure Ammonium Sulfate
    II. Phase Transitions of Mixed Organic-Sulfate Particles
    III. Recrystallization of Mixed Organic-Sulfate Particles

VI. Conclusions
VII. Future Work

Atmospheric Significance: Particles



Atmospheric Significance: Particles



Atmospheric Significance: Ammonium Sulfate, Organic Material, and Phase Transitions

Ammonium Sulfate

• Sulfate aerosol is the largest anthropogenic contributor to the global fine-mode aerosol burden and is widely observed in environments around the world

Organic Material

• Organic material can contribute between 20 to 80 % of total particle mass

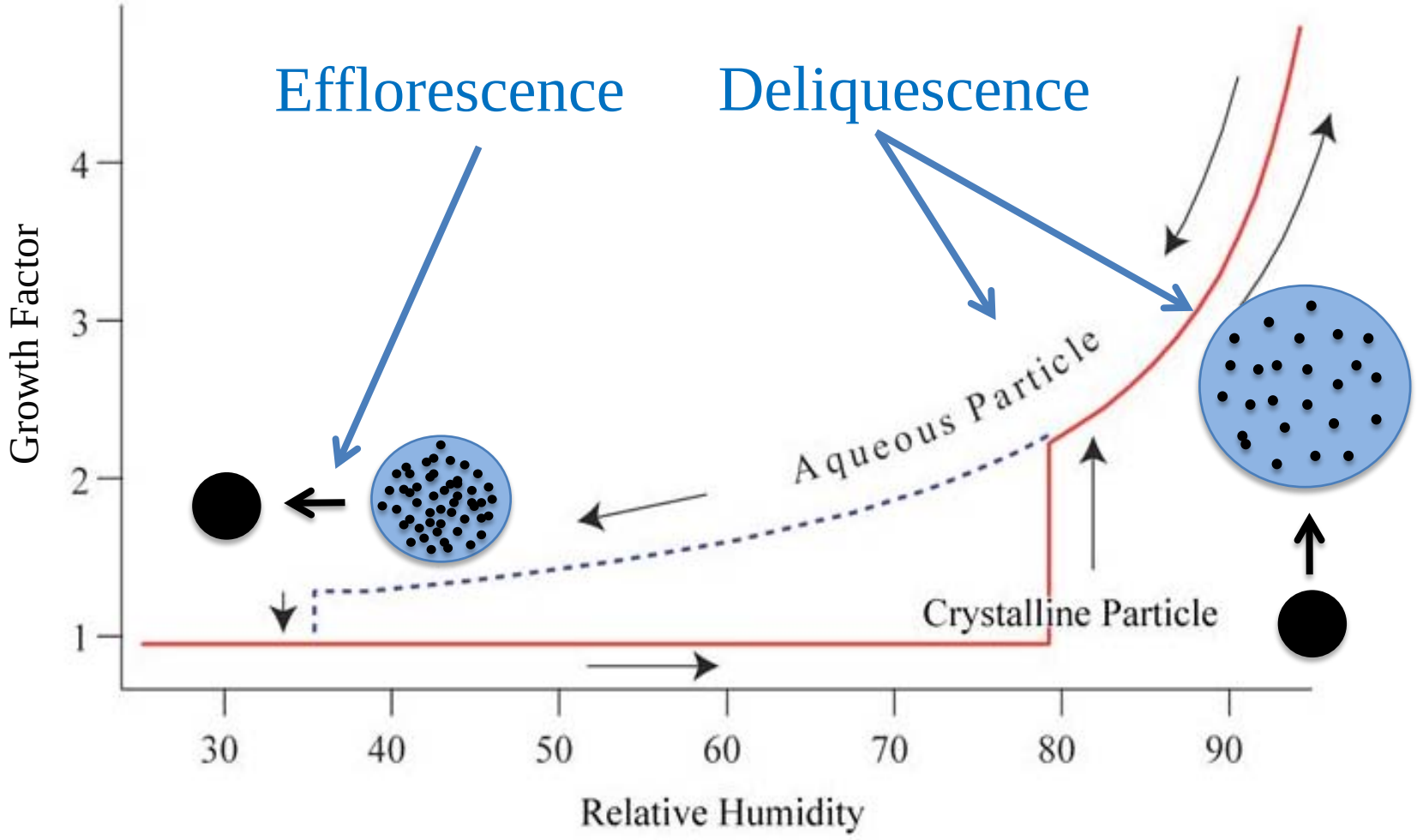
Phase Transitions

• Aqueous particles are larger and can reflect solar radiation more efficiently

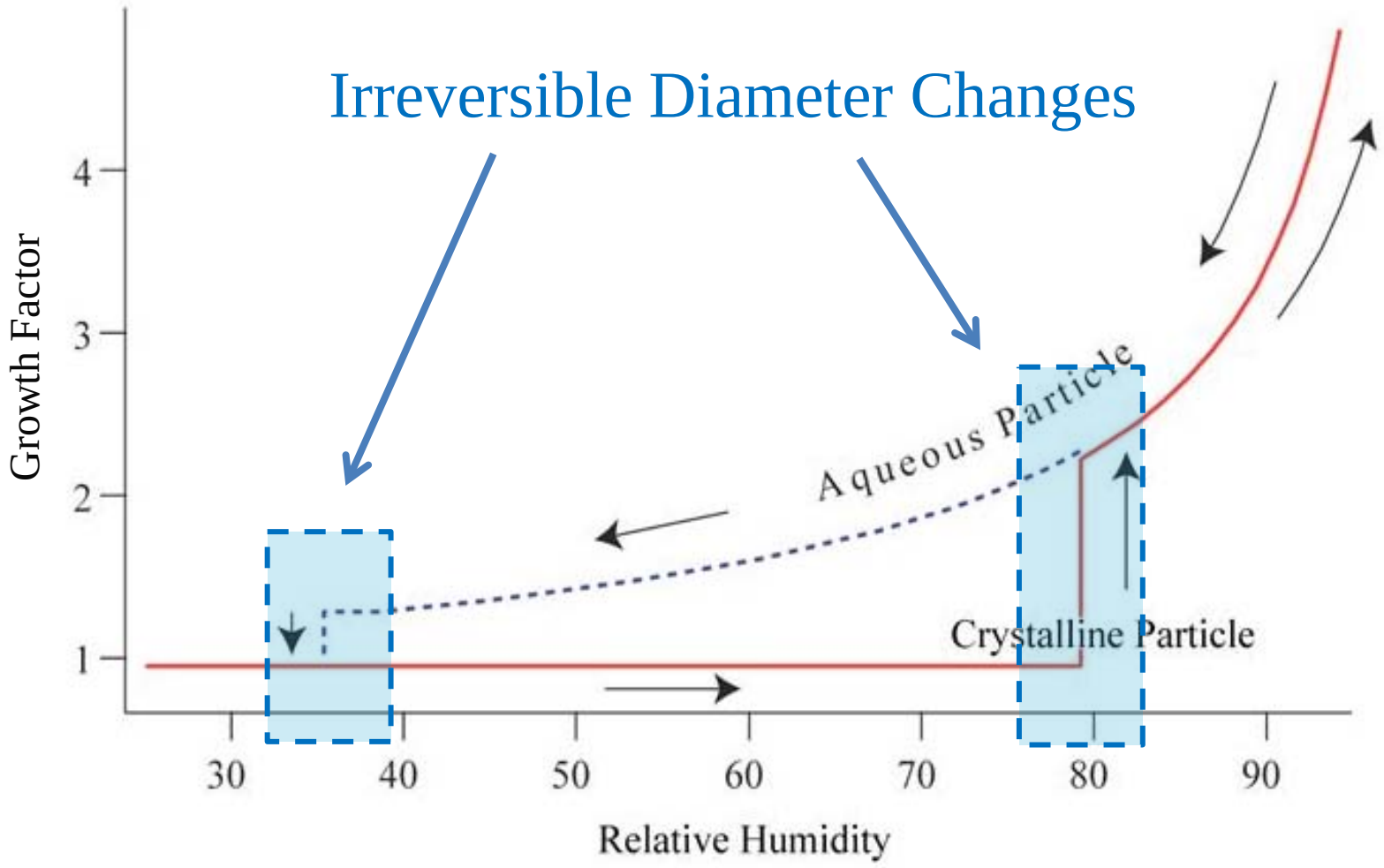
• Some chemical reactions can take placed more readily on the surface or within aqueous particles

Deliquescence and Efflorescence: Detected by Diameter Changes

Hysteresis between DRH and ERH– particle phase is *path dependent*

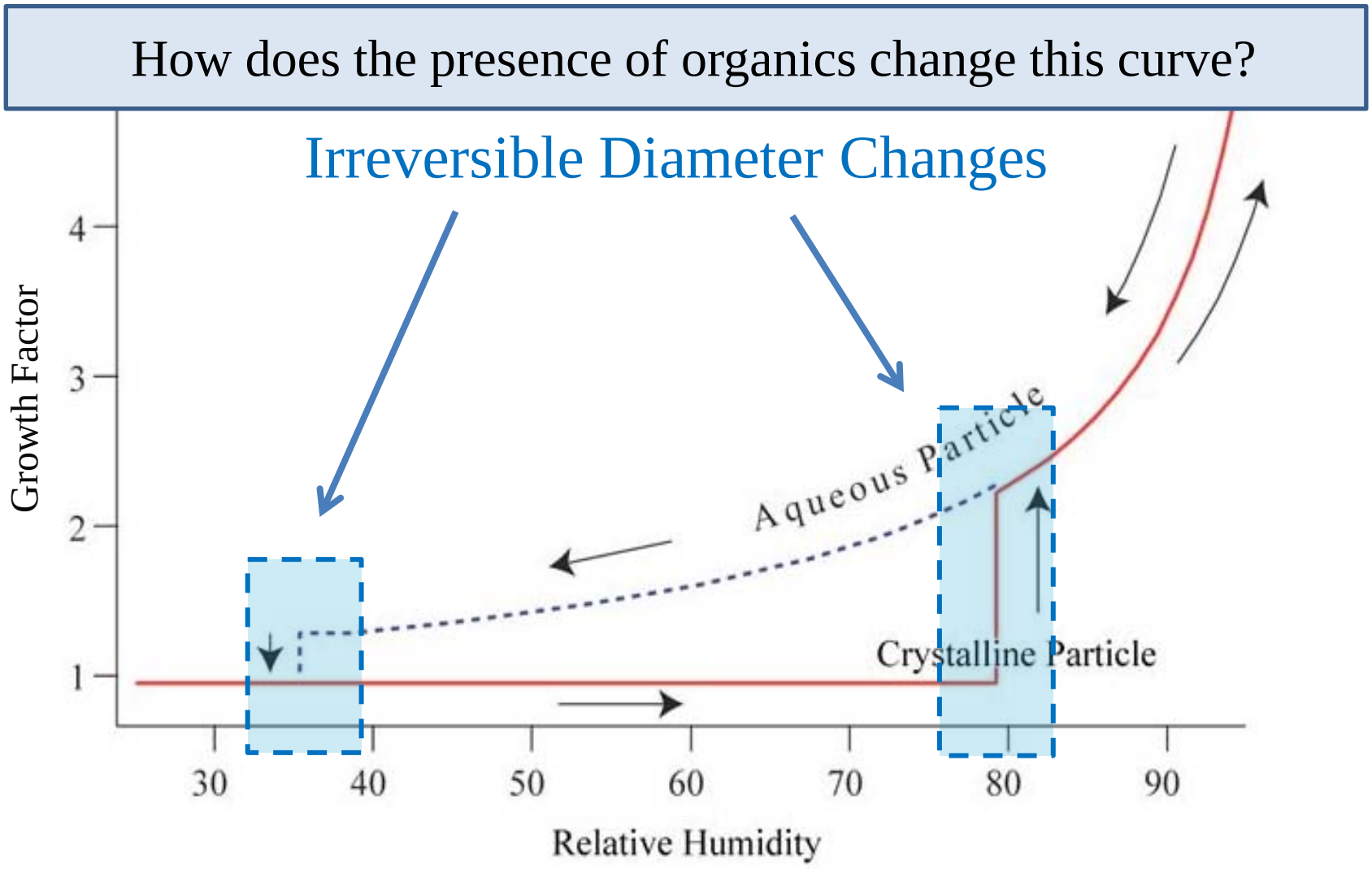


Deliquescence and Efflorescence: Detected by Diameter Changes



Deliquescence and Efflorescence: Detected by Diameter Changes

How does the presence of organics change this curve?



Previous Work: Mixed Organic-Inorganic Particles

Organic	ERH %	DRH %	Organic Fraction	Particle Type
Glycerol	28.2	76-78	0.6	EDB: 5-10 μm^2
Malonic Acid	46	58-73	0.6	EDB: 5-10 μm^2
Succinic Acid	48.3	77-79	0.6	EDB: 5-10 μm^2
Glutaric Acid	56-59	69-77	0.6	EDB: 5-10 μm^2
Dicarboxylic Acid Mix	26-28	75	0.5	EDB: 7-10 μm^3
Glycerol	NA	72	0.4	Bulk solutions[3]
Malonic Acid	None	40	0.4	Atomized[1]
1,4-buntanediol	NA	< 2% change	0-1	Bulk solutions [3]
1,2-hexanediol	NA	< 2% change	0-1	Bulk solutions[3]
Dicarboxylic Acid Mix	35	78	0.2	EDB: 7-10 μm^3
Malonic Acid	30	72	0.1	Atomized[1]

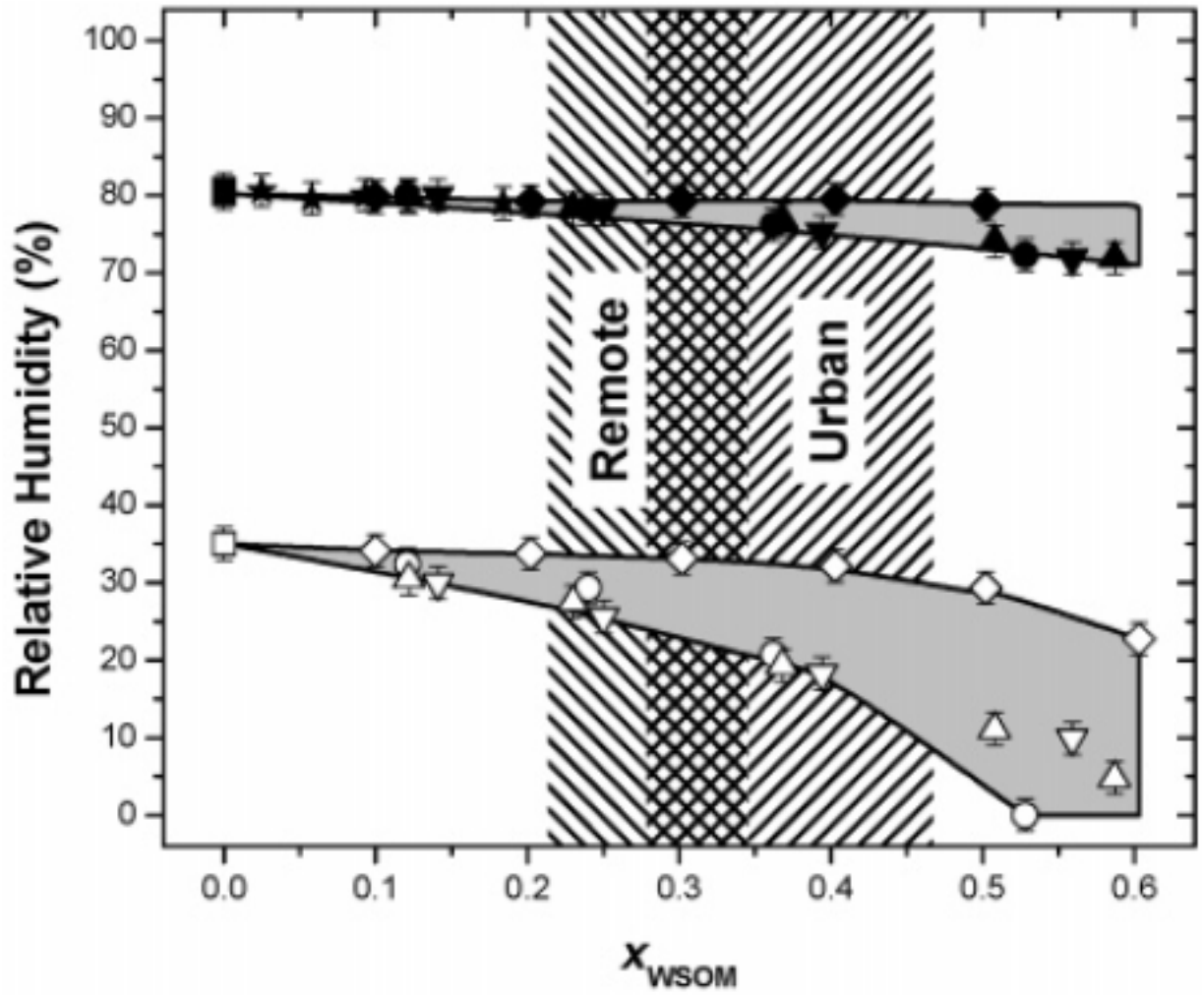
1. Braban and Abbat, 2004
2. Choi and Chan, 2002
3. Marcolli et al., 2006

Previous Work: Mixed Organic-Inorganic Particles

Organic	ERH %	DRH %	Organic Fraction	Particle Type
Glycerol	28.2	76-78	0.6	EDB: 5-10 μm^2
Malonic Acid	46	58-73	0.6	EDB: 5-10 μm^2
Succinic Acid	48.3	77-79	0.6	EDB: 5-10 μm^2
Glutaric Acid	56-59	69-77	0.6	EDB: 5-10 μm^2
Dicarboxylic Acid Mix	26-28	75	0.5	EDB: 7-10 μm^3
Glycerol	NA	72	0.4	Bulk solutions[3]
Malonic Acid	None	40	0.4	Atomized[1]
1,4-buntanediol	NA	< 2% change	0-1	Bulk solutions [3]
1,2-hexanediol	NA	< 2% change	0-1	Bulk solutions[3]
Dicarboxylic Acid Mix	35	78	0.2	EDB: 7-10 μm^3
Malonic Acid	30	72	0.1	Atomized[1]

1. Braban and Abbat, 2004
2. Choi and Chan, 2002
3. Marcolli et al., 2006

Previous Work: Mixed Organic-Inorganic Particles



Parsons et al., 2004

Inorganic
Ammonium Sulfate

Organics
Glutaric Acid
Glycerol
Levoglucosan
Malonic Acid

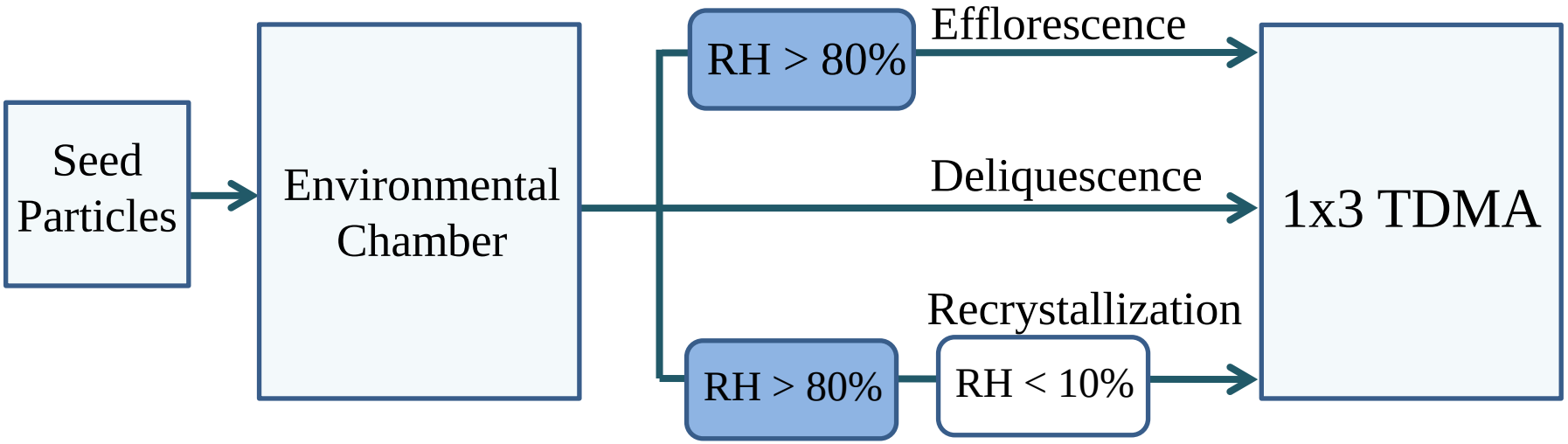
Previous Work: Laboratory Generated SOA

VOC precursor	Oxidation Pathway	Organic Fraction	DRH (%)	ERH (%)	Reference
toluene *p*-xylene 1,3,5-TMB	photo-oxidation	0.16 0.13 0.05	80 80 80	30 30 30	Kleindienst et al. (1999)
α-pinene	dark ozonolysis	0.18	Between 70 and 80*	NA	Saathoff et al. (2003)
α-pinene limonene	dark ozonolysis	0.54-0.72 0.59-0.94	NA	28-34 ± 2.5 28-34 ± 2.5	Takahama et al. (2007)
α-pinene	photo-oxidation	0.0-0.2 0.2-0.9	Between 75 and 85* < 75*	NA	Meyer et al. (2009)

Scientific Questions

- How does the presence of secondary organic material influence the hygroscopic properties of ammonium sulfate?
  - Do the deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) shift from pure ammonium sulfate values? Is this dependent on organic volume fraction?
  - Does the DRH of recrystallized mixed organic-sulfate particles differ from the DRH of particles sampled directly from the chamber?

Overall Experimental Setup



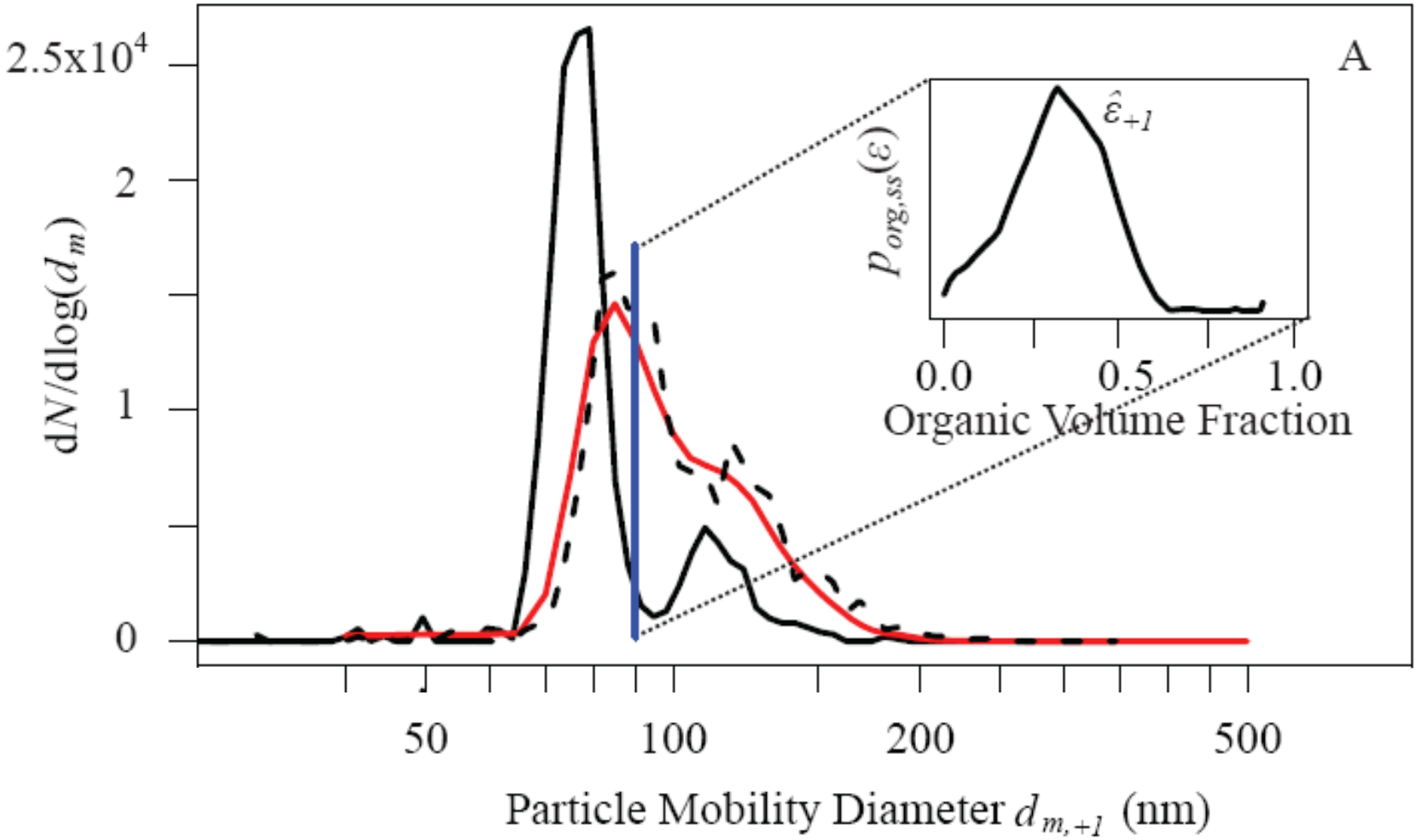
Chamber Conditions

- RH: 40%
- Seed: 80 or 50 nm solid ammonium sulfate
- α-pinene: 2 or 20 ppb (1.63 or 12.2 μg m^{-3})
- Ozone: 50 ppb

1x3 TDMA

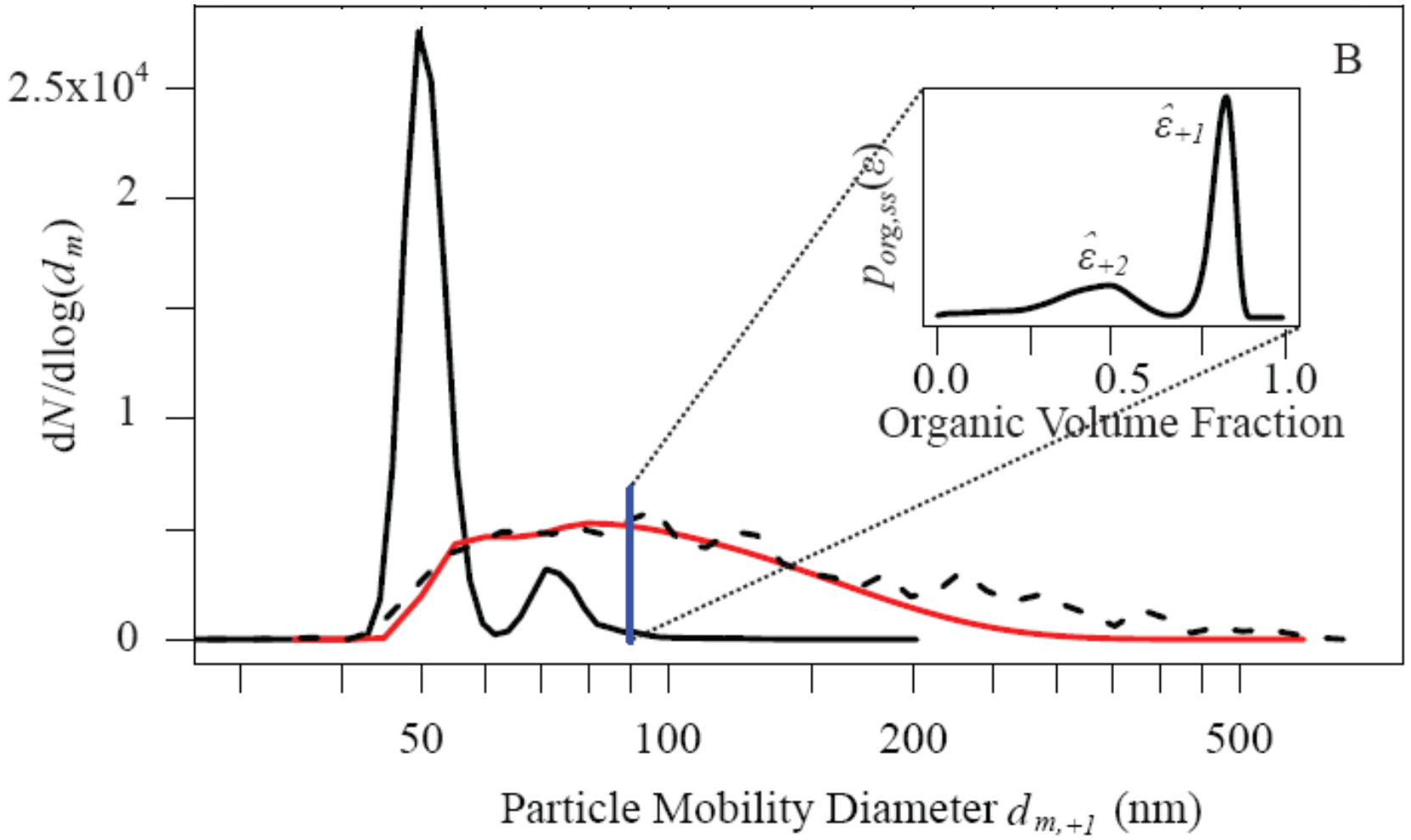
- Vary selected diameter
  → Vary organic volume fraction
- Measure DRH and ERH
- Measure growth factor

Varying Organic Volume Fraction



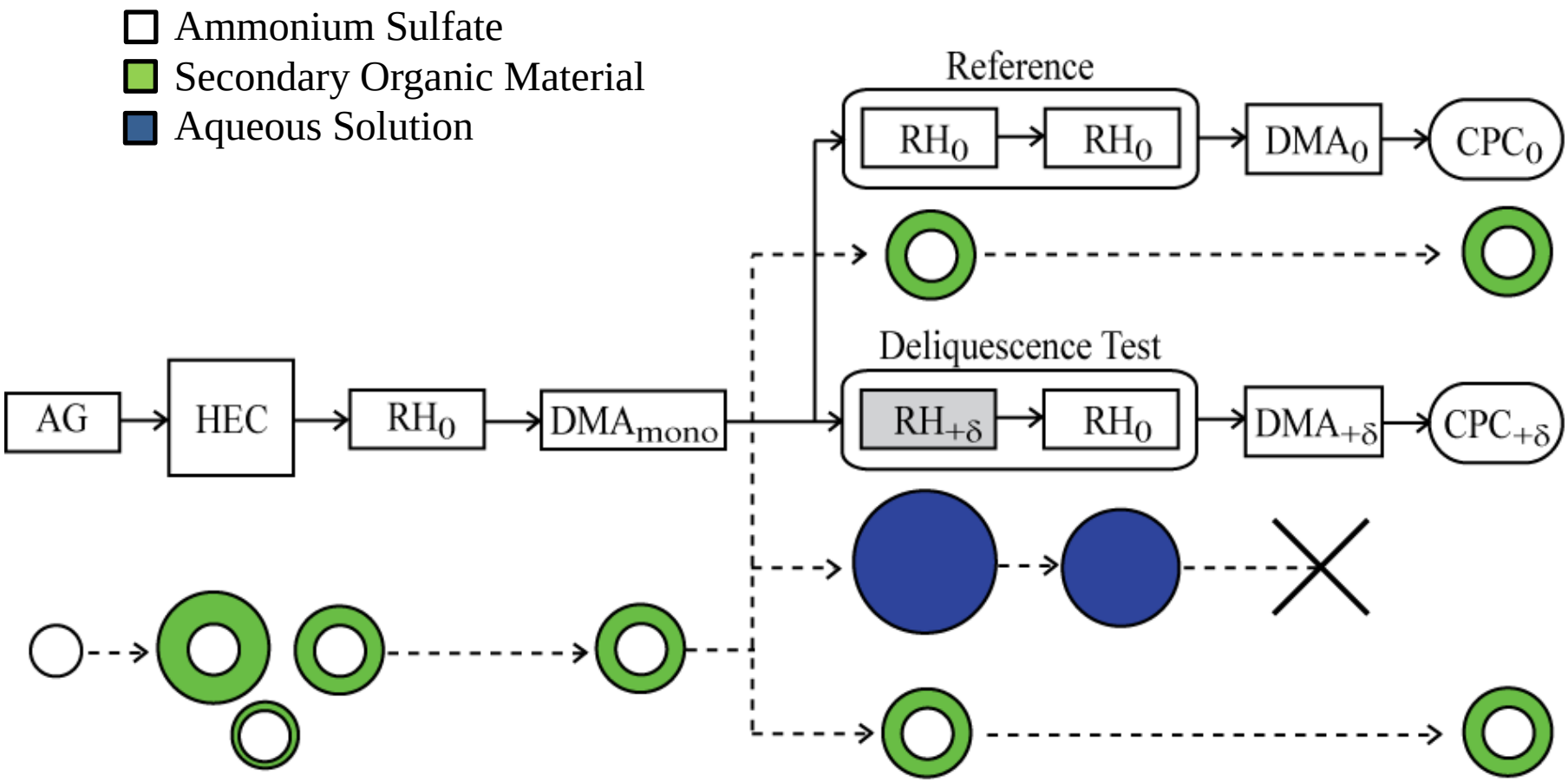
Seinfeld et al. (2003)

Varying Organic Volume Fraction

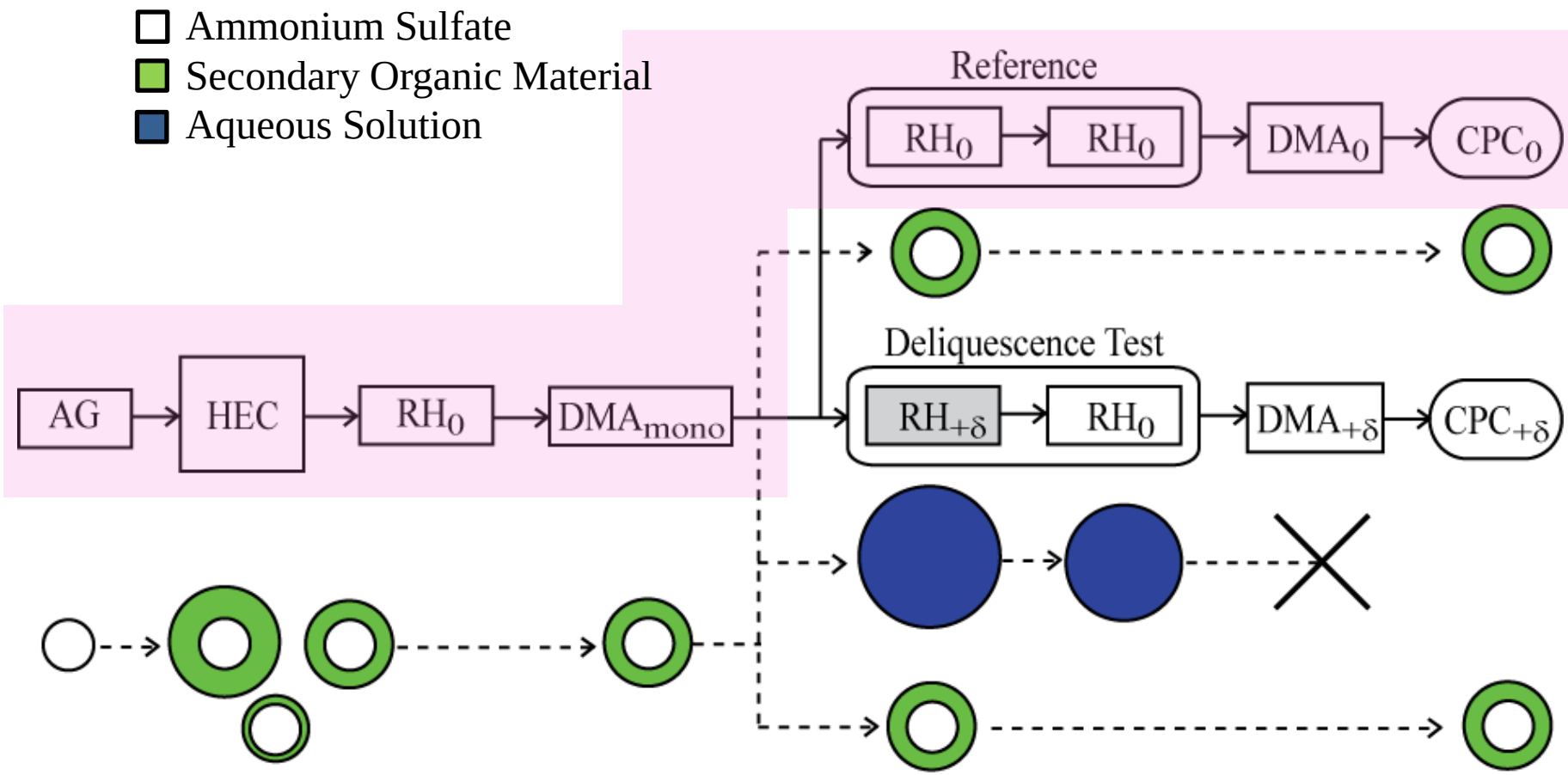


Seinfeld et al. (2003)

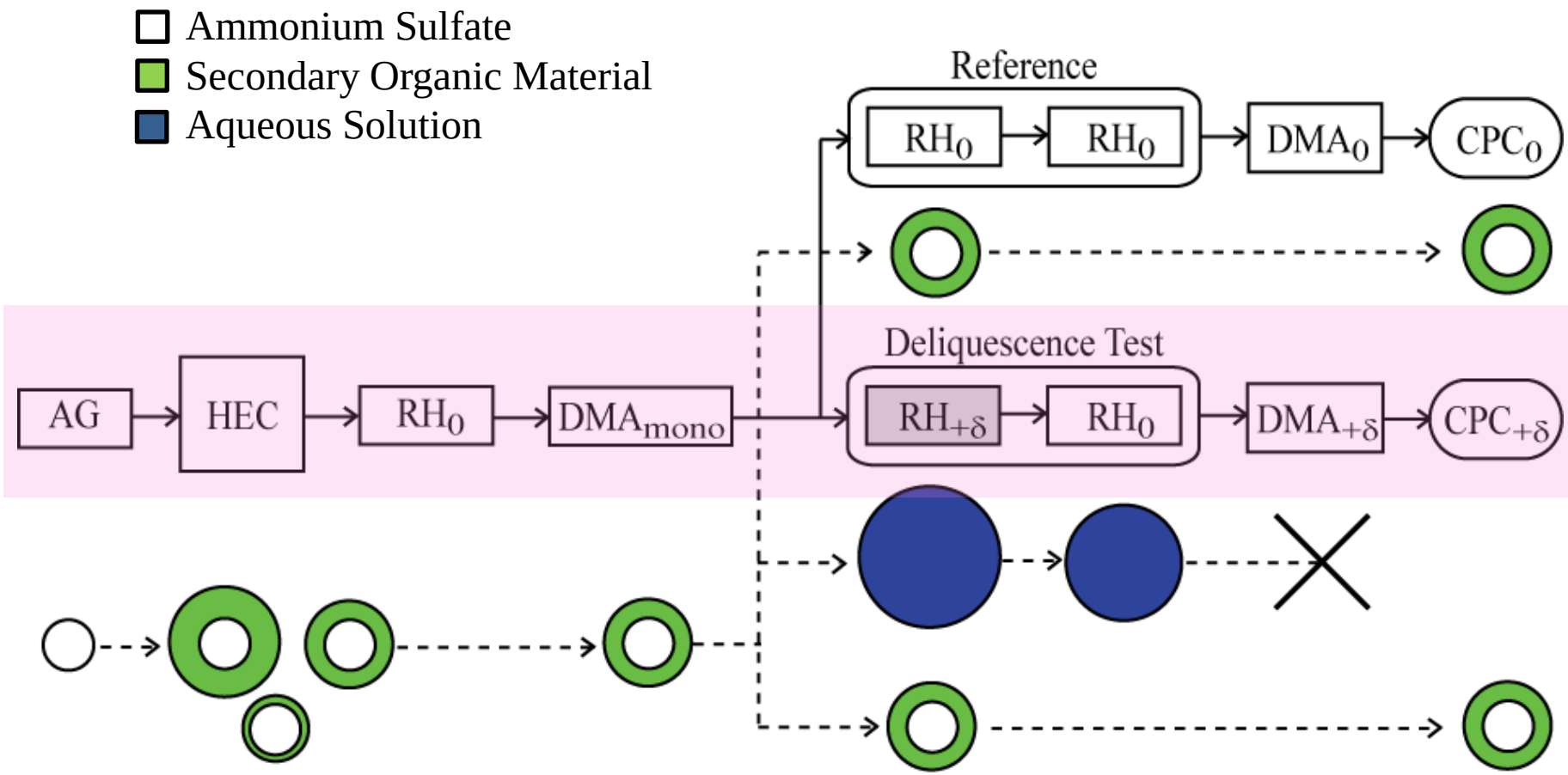
The 1x3 TDMA: Deliquescence Test



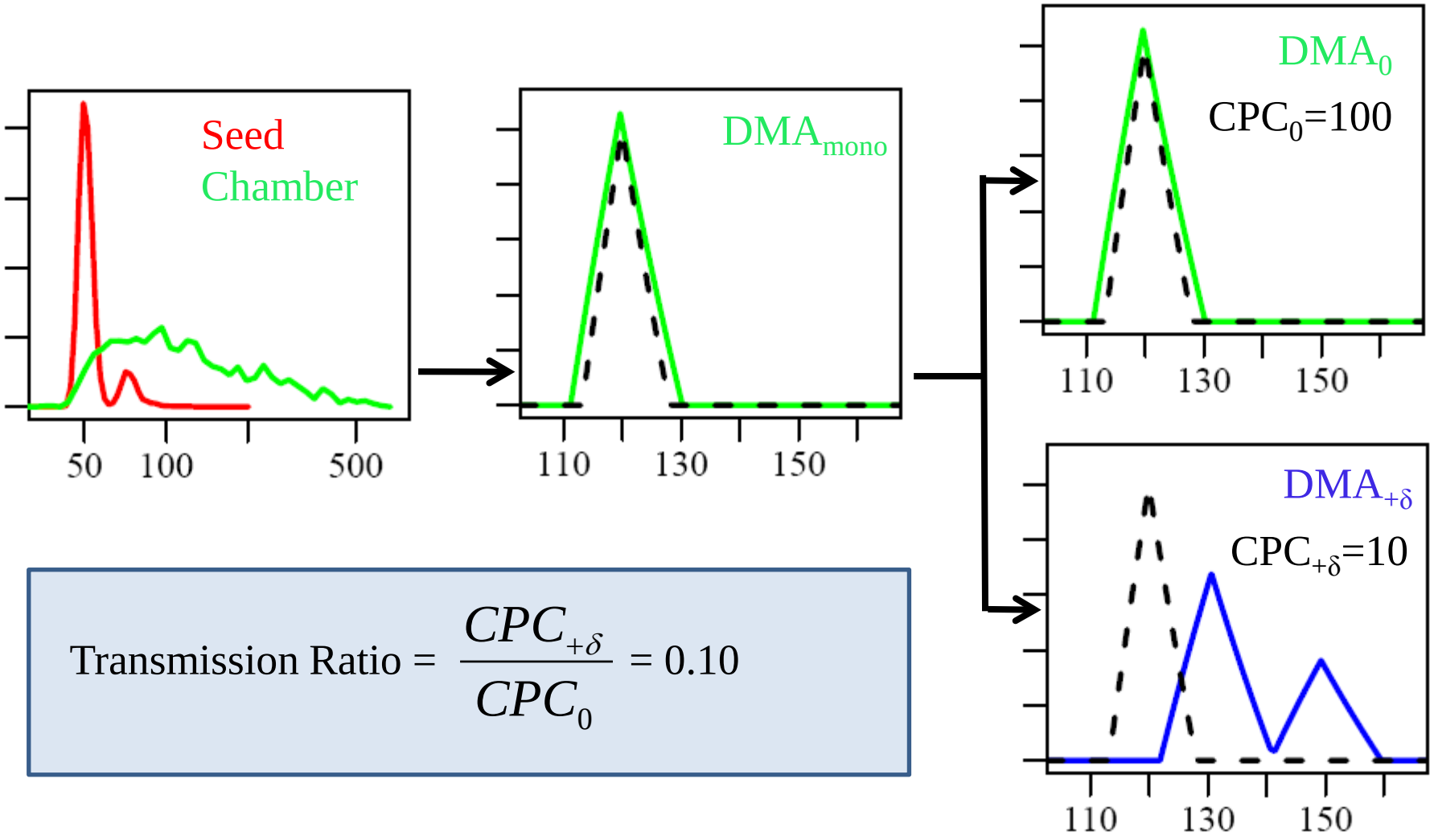
The 1x3 TDMA: Deliquescence Test



The 1x3 TDMA: Deliquescence Test

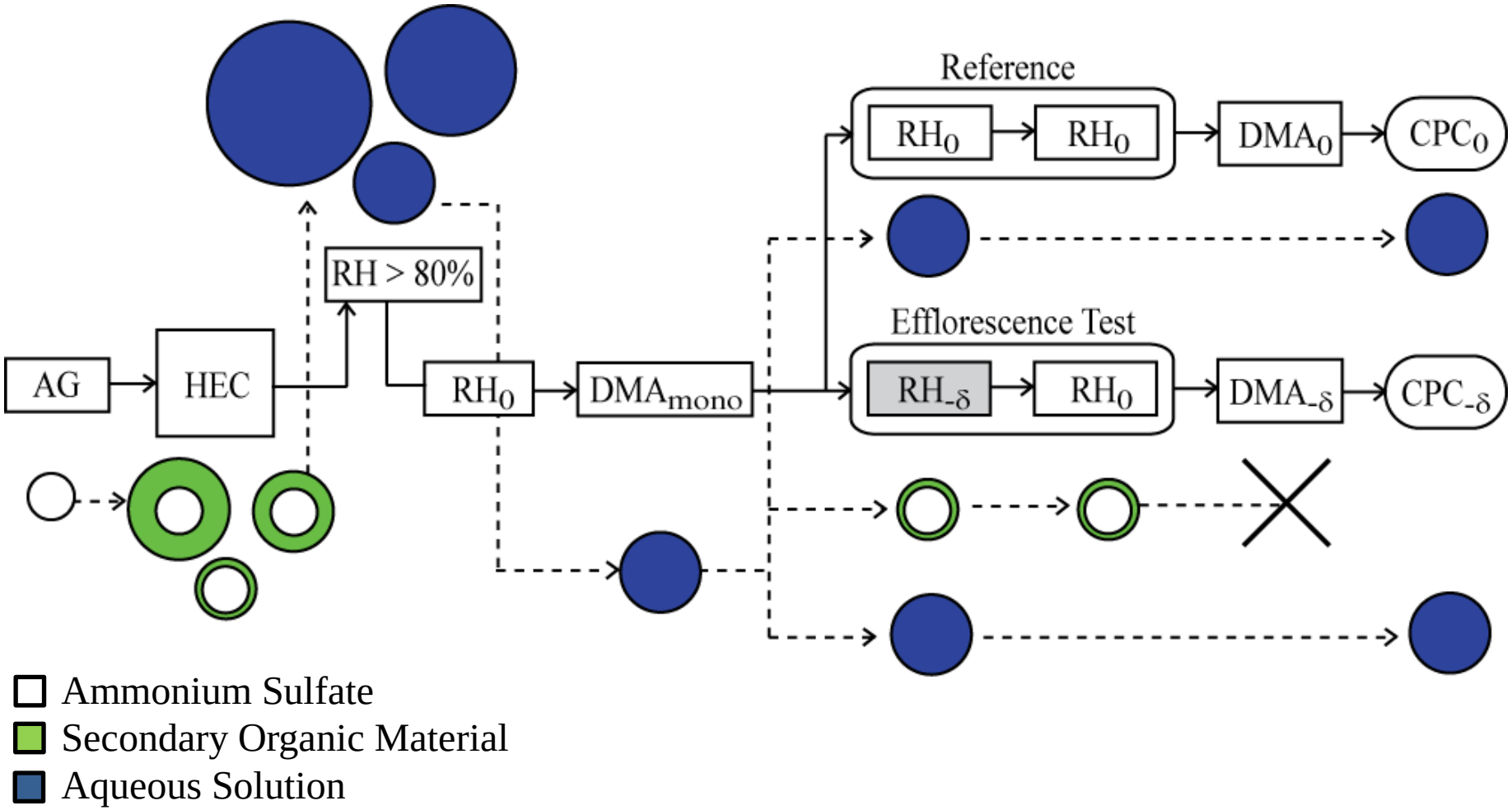


The 1x3 TDMA: Deliquescence Test

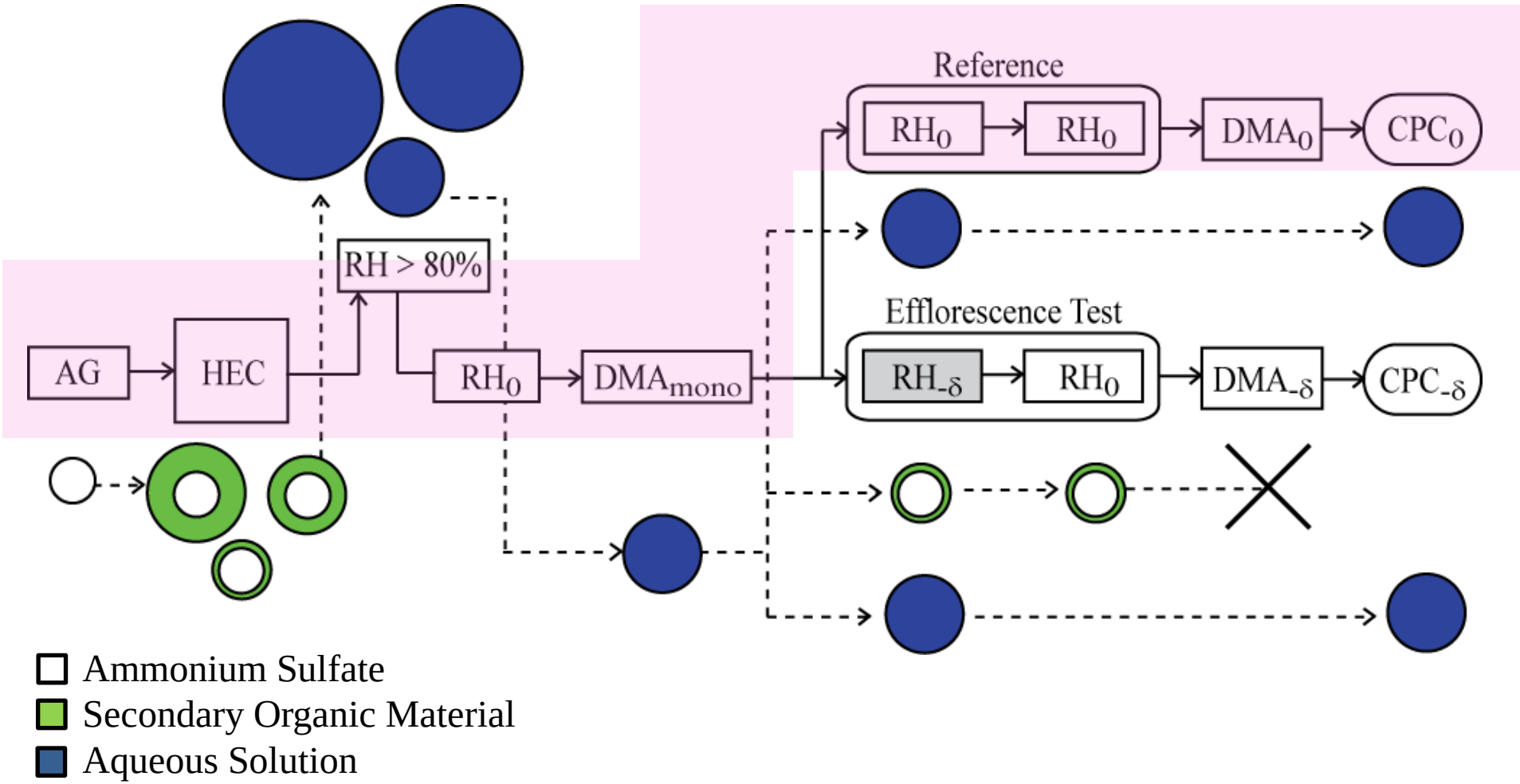


$$\text{Transmission Ratio} = \frac{CPC_{+\delta}}{CPC_0} = 0.10$$

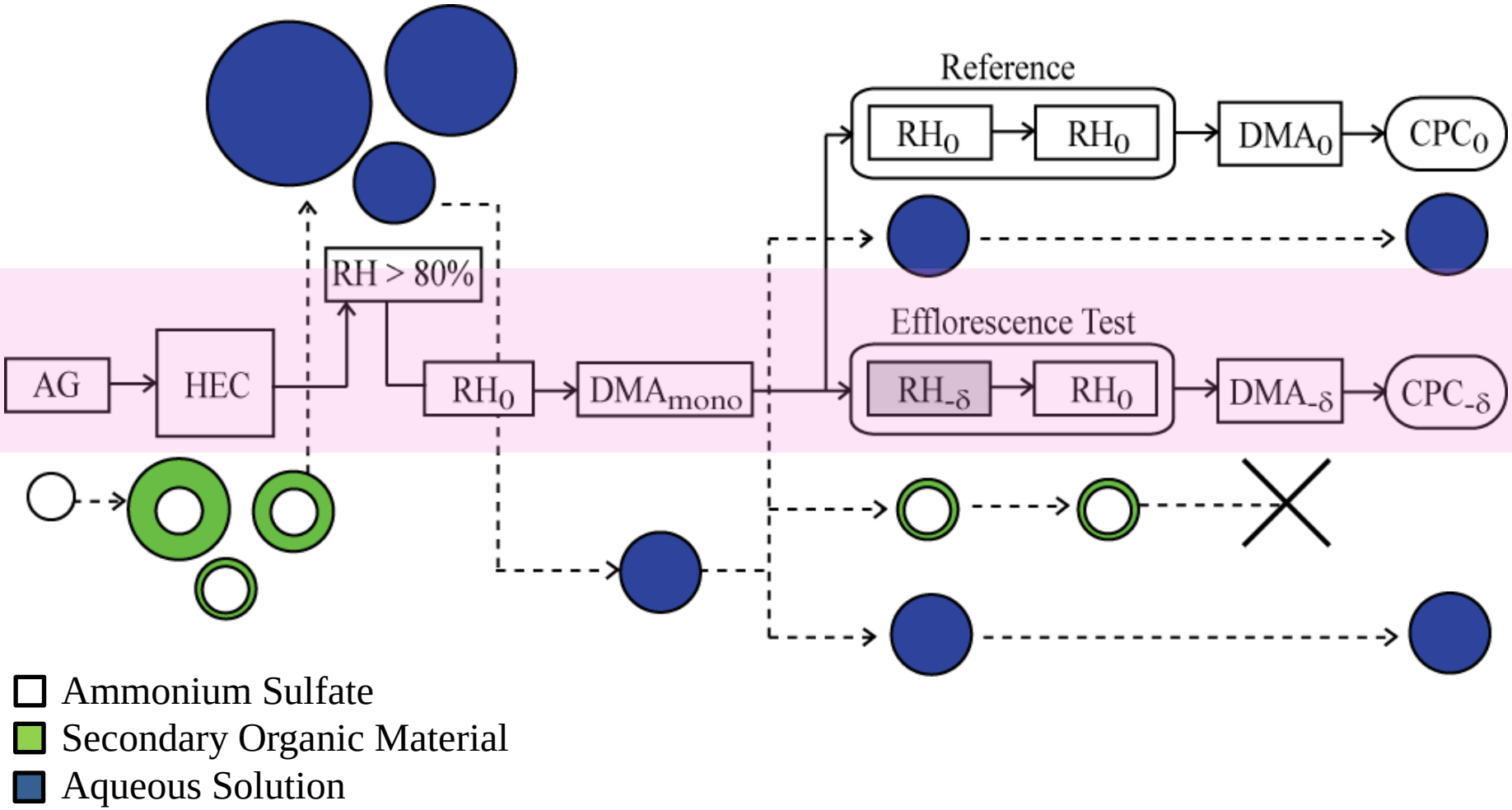
The 1x3 TDMA: Efflorescence Test



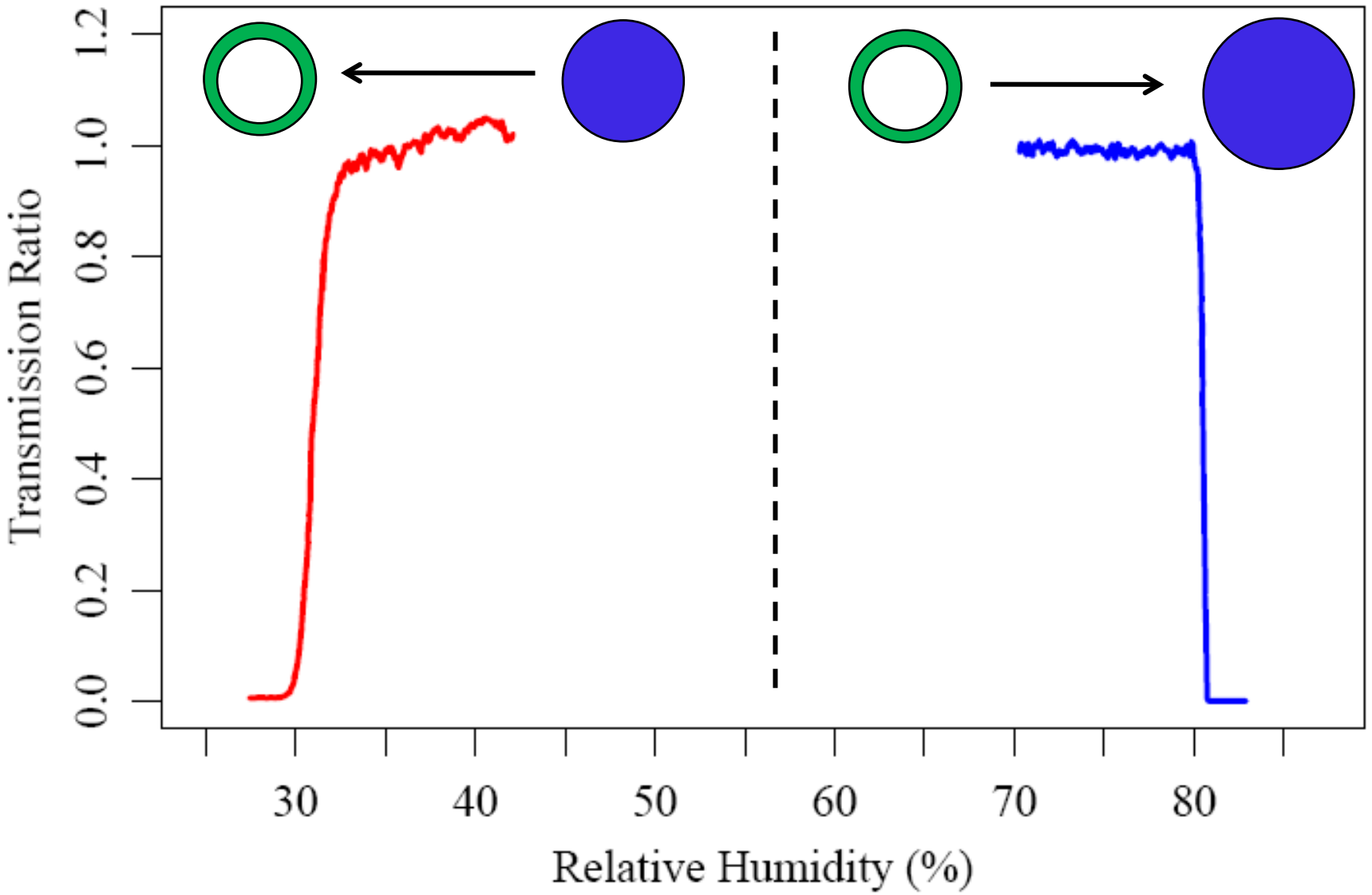
The 1x3 TDMA: Efflorescence Test



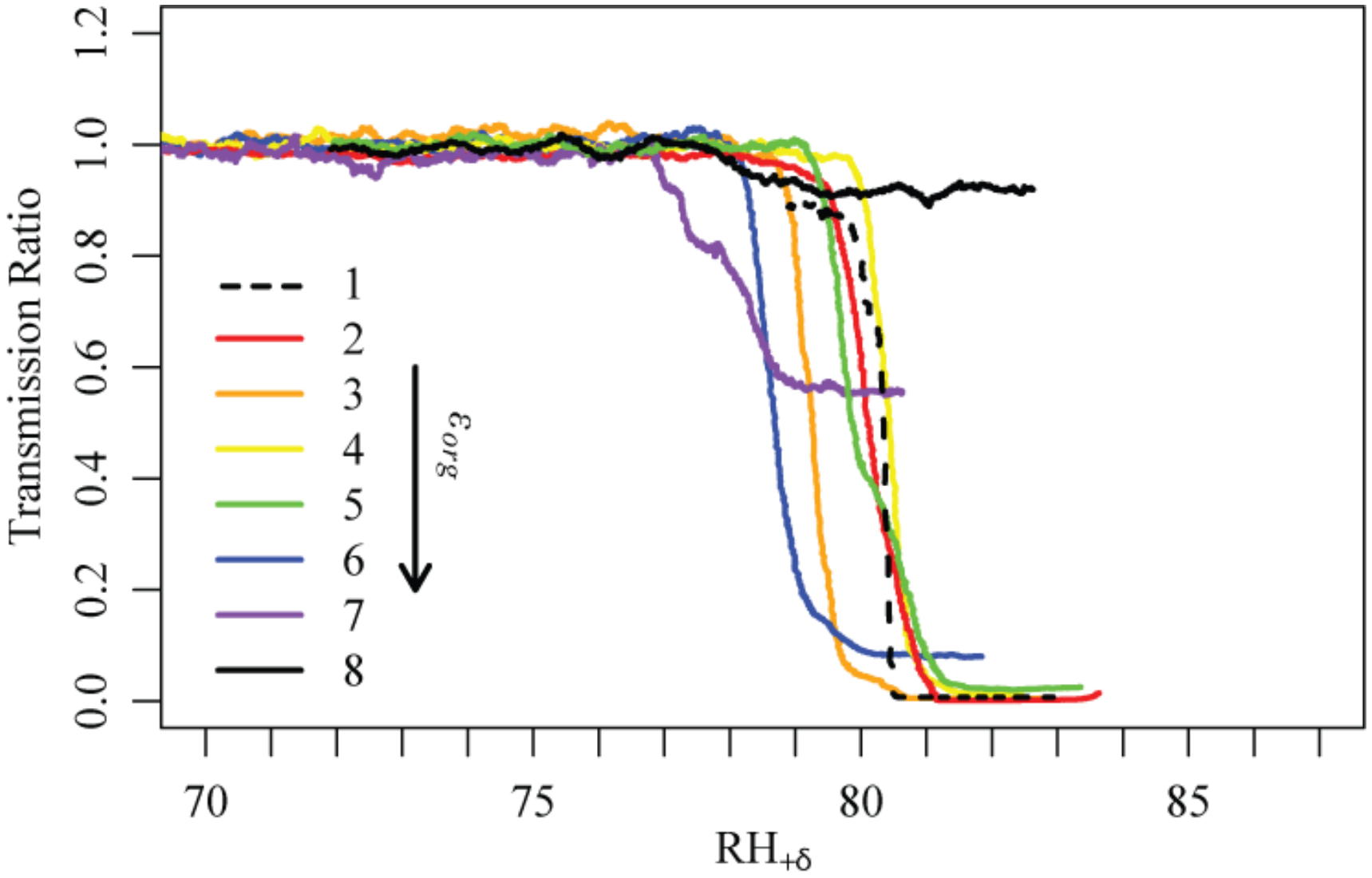
The 1x3 TDMA: Efflorescence Test



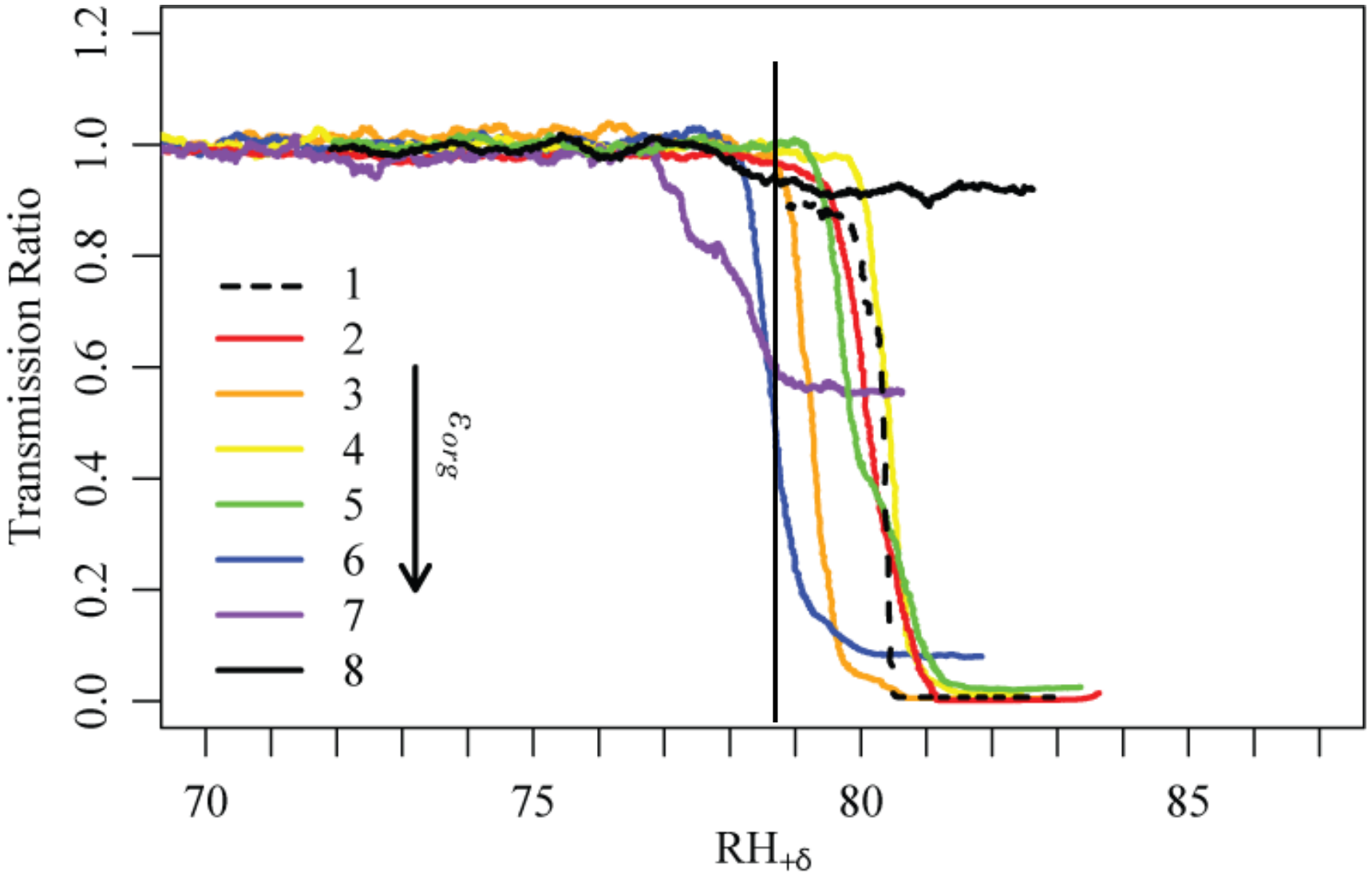
Results: Pure Ammonium Sulfate



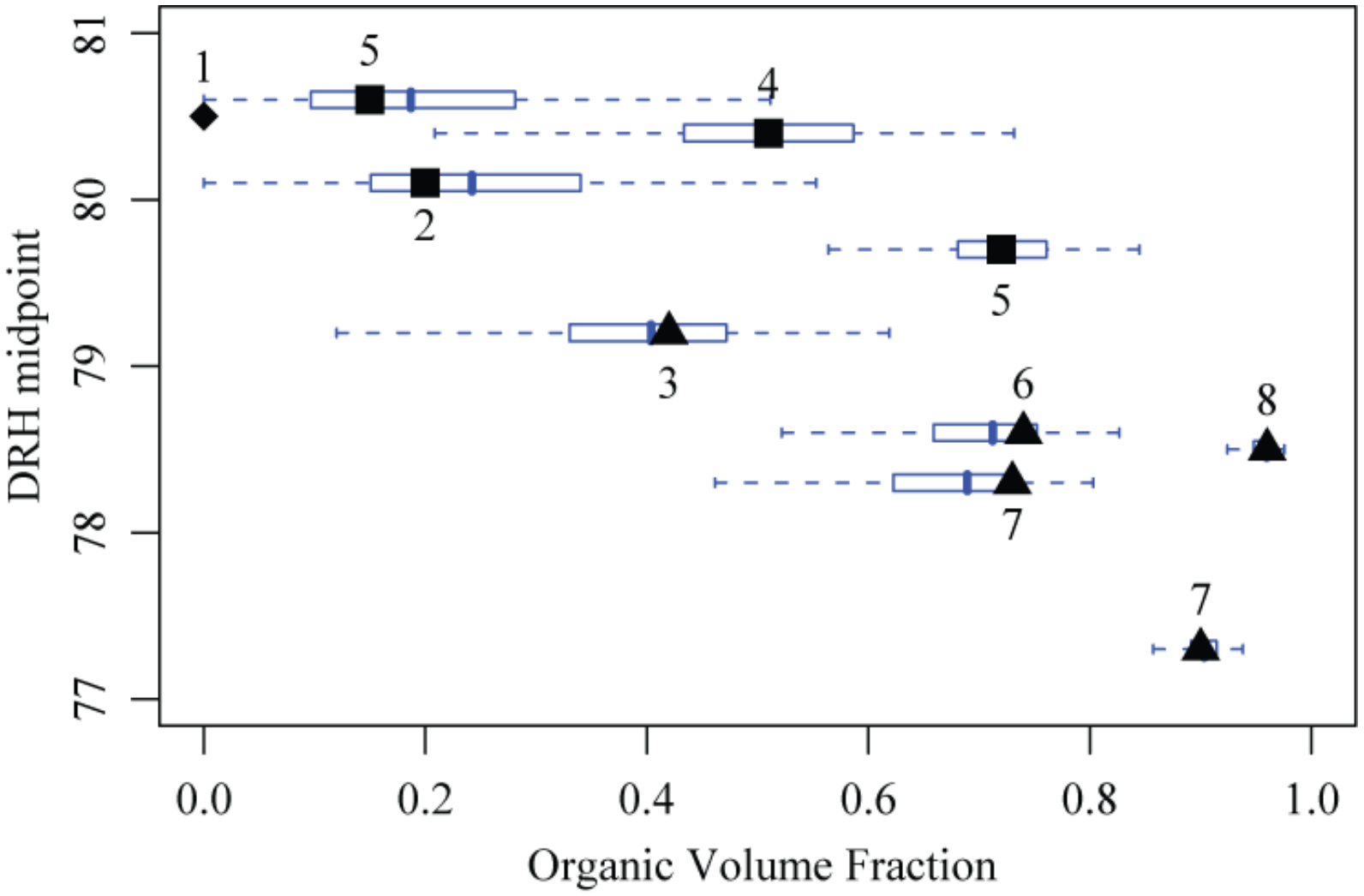
Results: Deliquescence of Mixed Particles



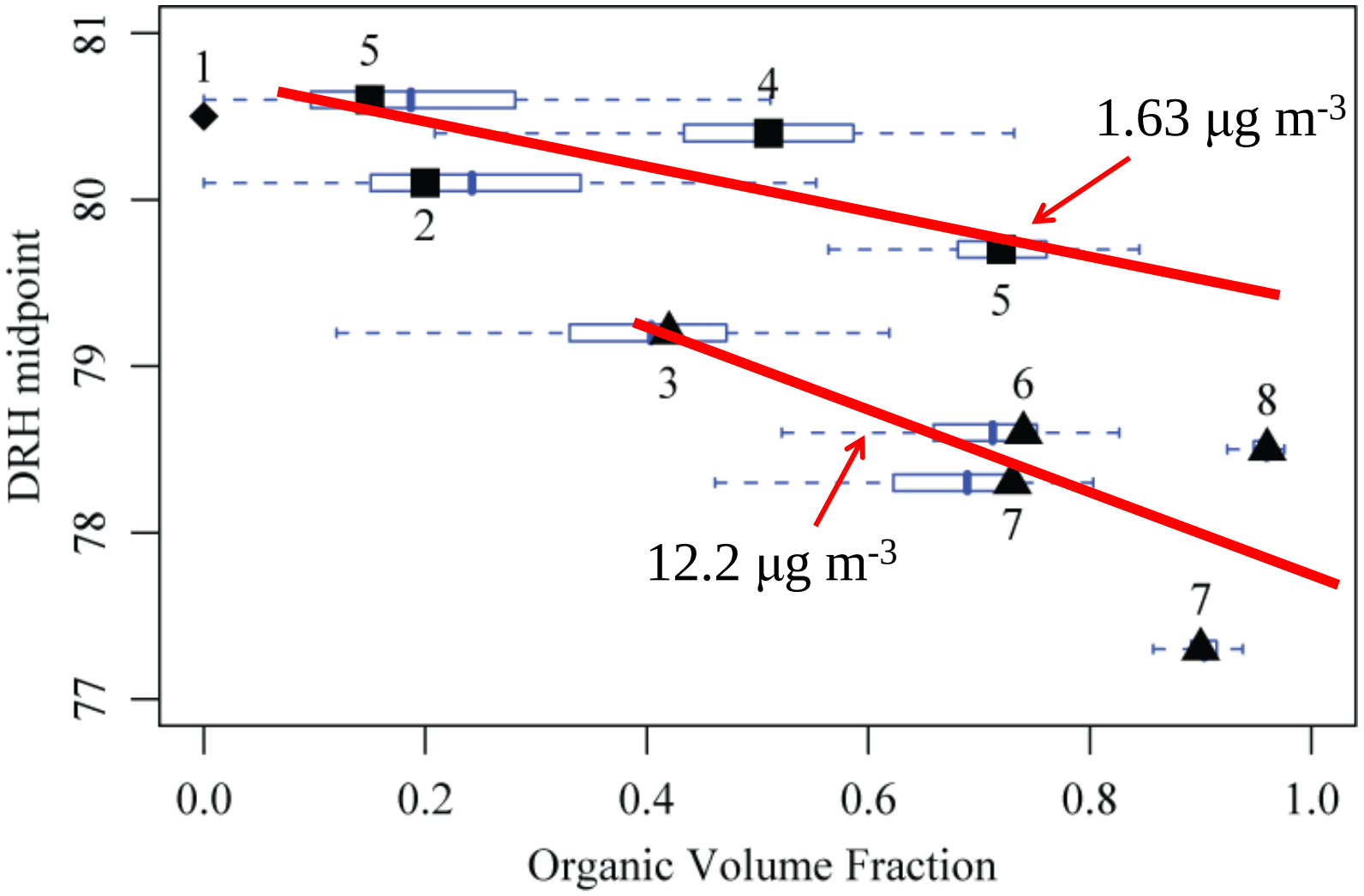
Results: Deliquescence of Mixed Particles



Results: Deliquescence of Mixed Particles



Results: Deliquescence of Mixed Particles

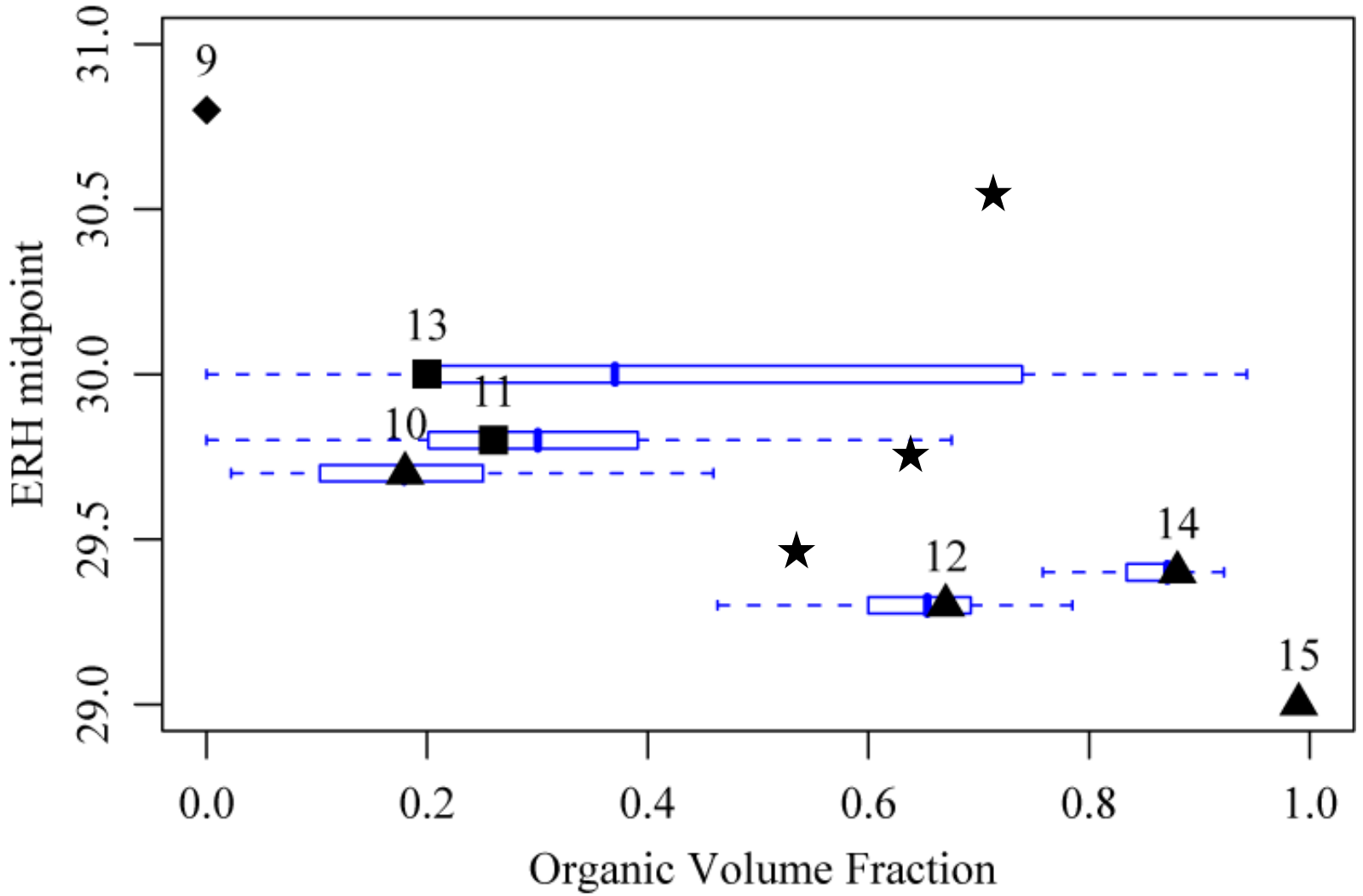


◆ This work: pure AS

■ This work: 1.63 µg m^{-3}

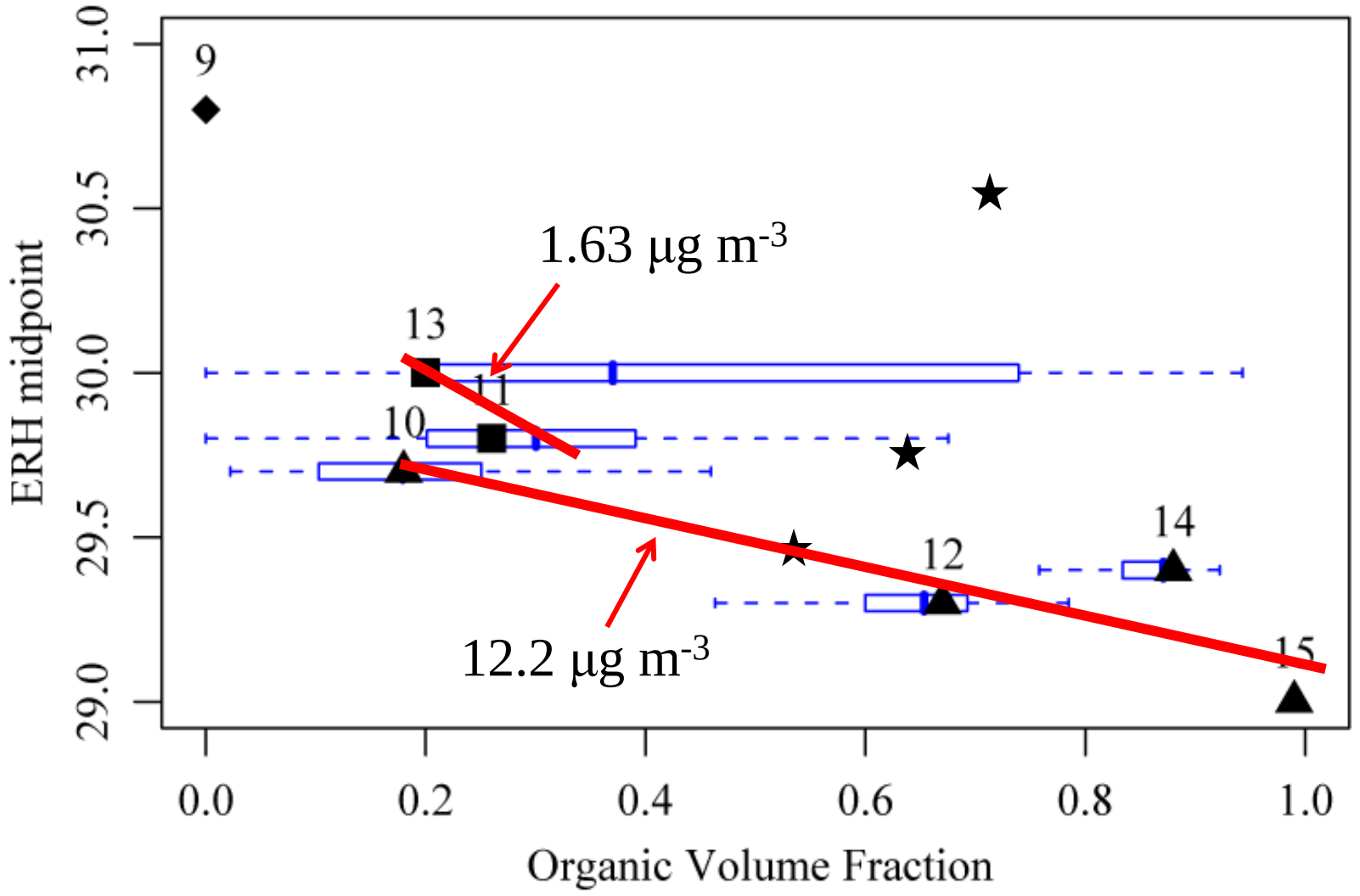
▲ This work: 12.2 µg m^{-3}

Results: Efflorescence of Mixed Particles



★Takahama et al. (2007)
◆This work: pure AS
■This work: 1.7 μg m^{-3}
▲This work: 13.9 μg m^{-3}

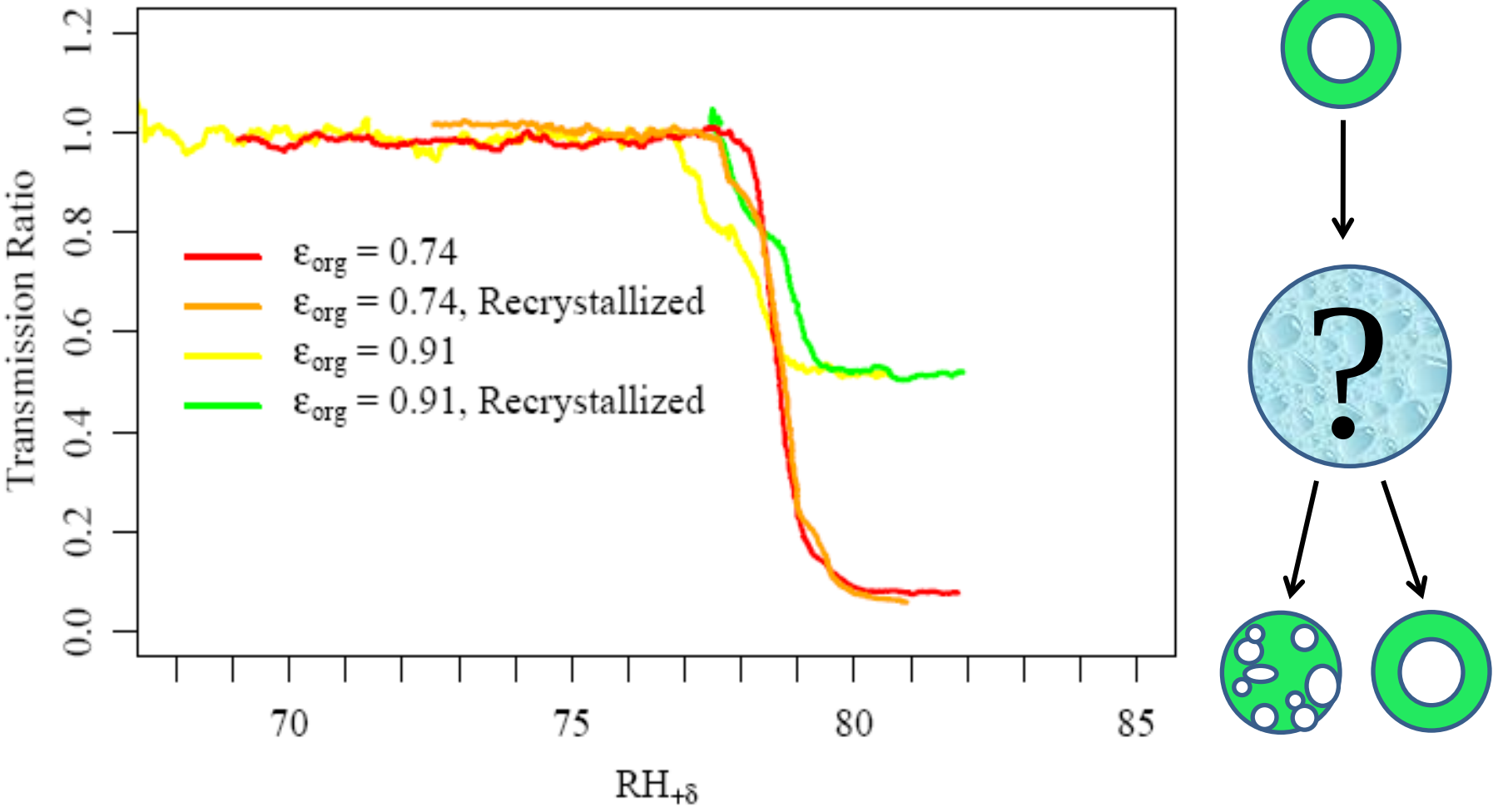
Results: Efflorescence of Mixed Particles



★Takahama et al. (2007)
■This work: 1.7 µg m^{-3}
◆This work: pure AS
▲This work: 13.9 µg m^{-3}

Results: Recrystallization of Mixed Particles

- **Deliquescence behavior not dependent on recrystallization**



Summary and Conclusions

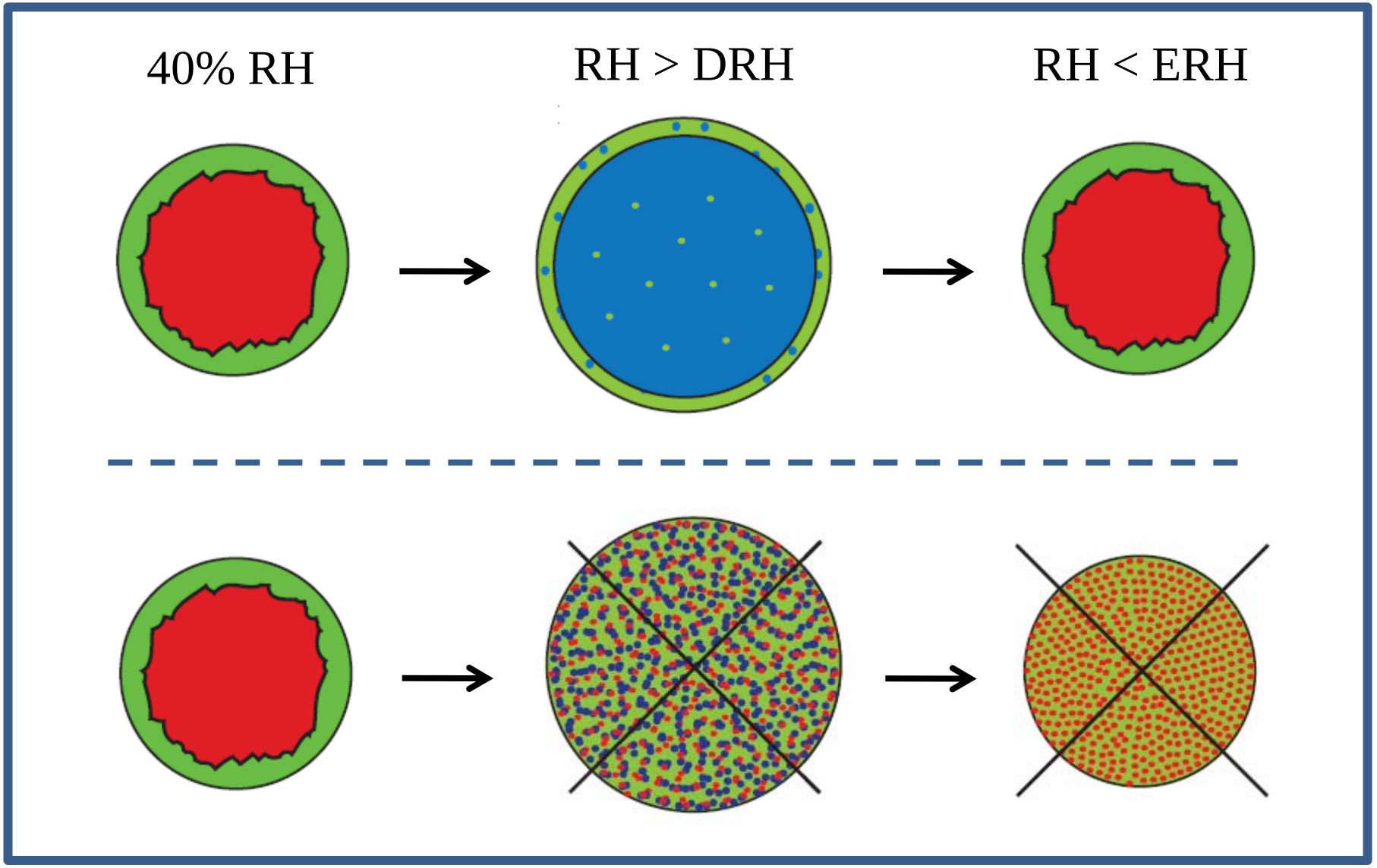
1. Model SOA compounds are not necessarily good predictors of chamber-generated SOA behavior

2. The DRH and ERH of mixed organic-sulfate particles decrease less than 4% from the DRH and ERH of pure ammonium sulfate
   - *Holds for organic volume fractions between 0.0 and 0.96*
   - *DRH and ERH decreased slightly as organic volume fraction and mass loading were increased*

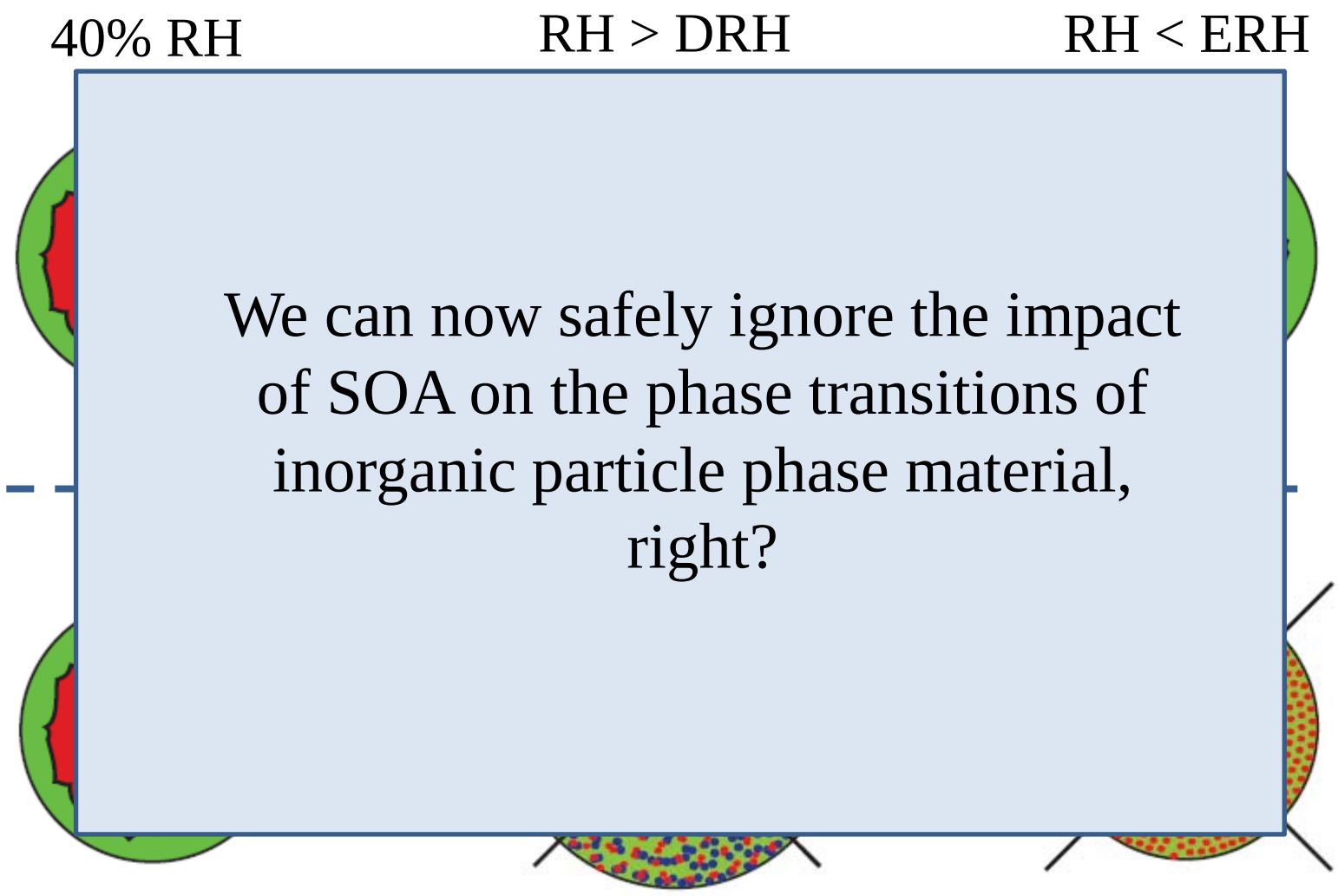
3. Recrystallization of mixed organic-sulfate particles did not affect the DRH.

4. **Results 2 and 3 imply phase separation between (1) aqueous ammonium sulfate and (2) aqueous organic material.**

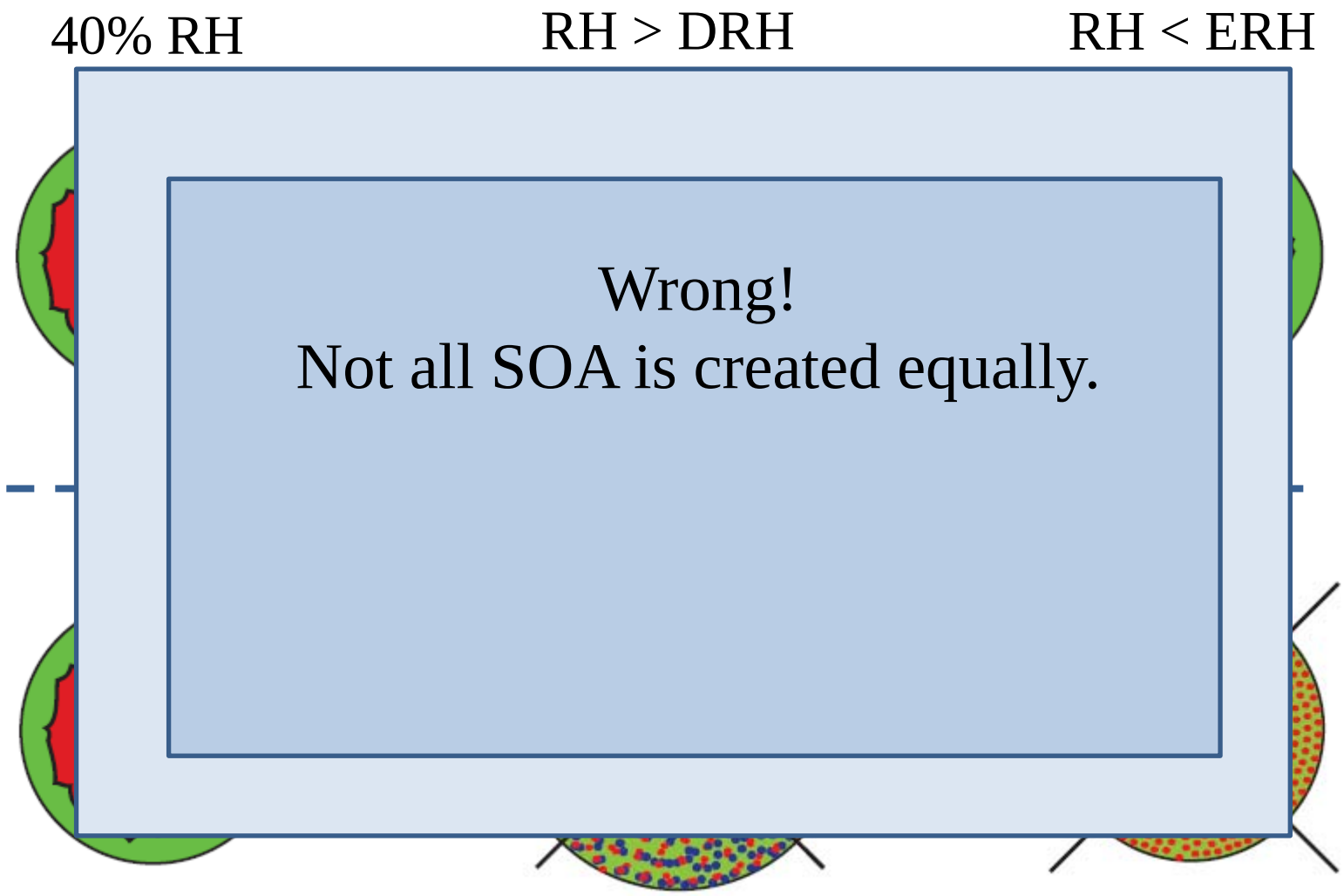
Summary and Conclusions



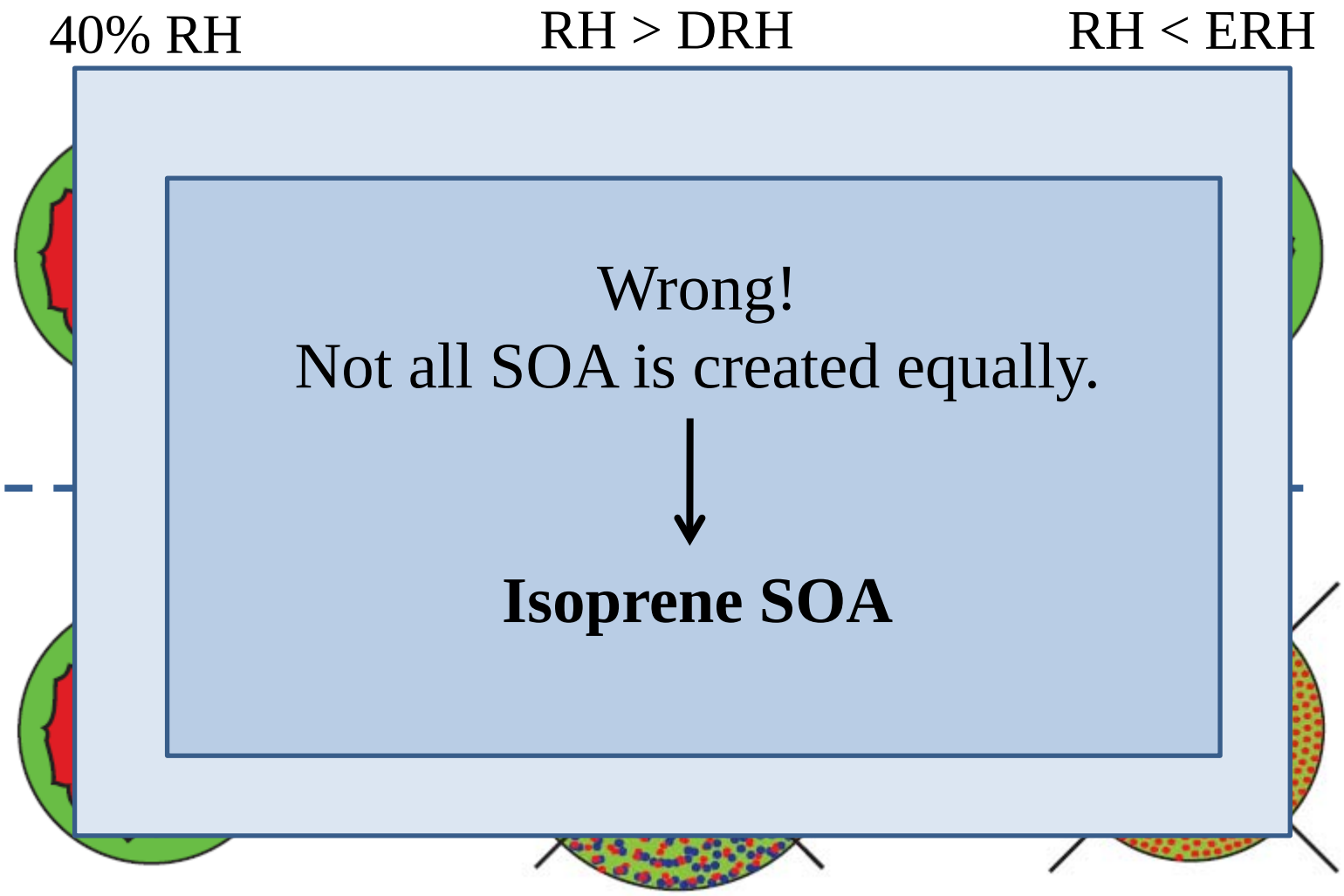
Summary and Conclusions



Summary and Conclusions



Summary and Conclusions



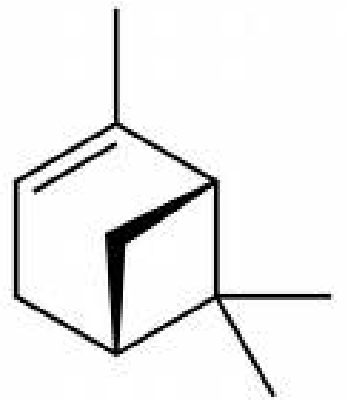
Future Work

→ Isoprene photo-oxidation

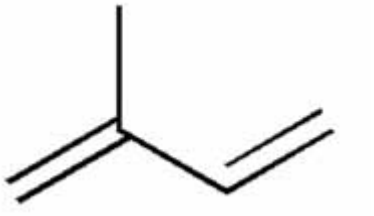
→ Much smaller than α-pinene (MW = 68.12 g mol^{-1} vs. 136.23 g mol^{-1} for α-pinene)

→ Smaller, more soluble oxidation products?

α-pinene: $C_{10}H_{16}$



Isoprene: C_5H_8



Acknowledgments

- Martin Group, Harvard University

    - Professor Scot Martin
    - Dr. Mikinori Kuwata

- National Science Foundation

- Robert McGraw and Ernie Lewis, Brookhaven National Laboratory

- DOE GCEP Graduate Research Environmental Fellowship