Initial steps of aerosol nucleation and growth: field observation in Nanjing and laboratory experiments

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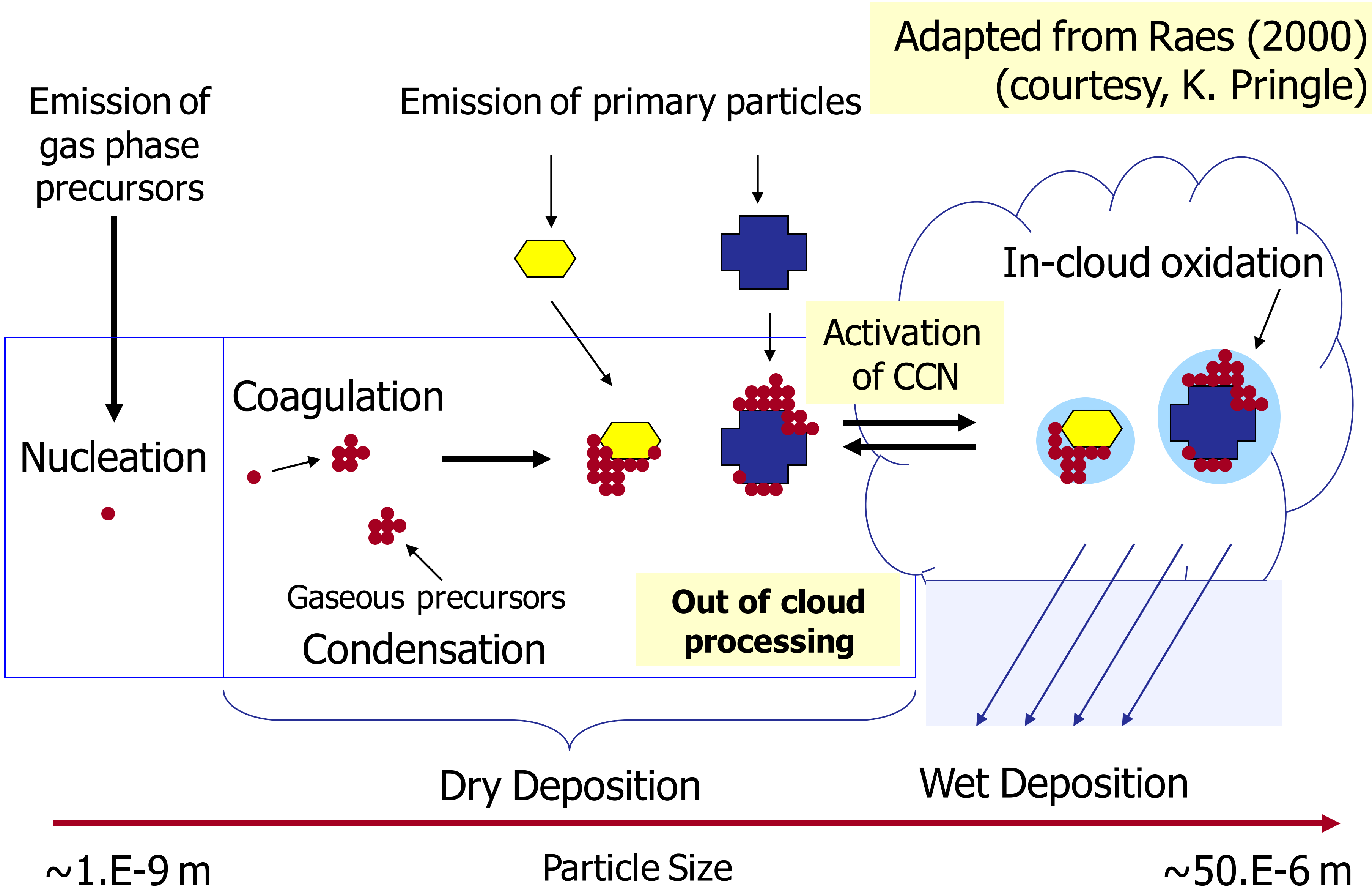
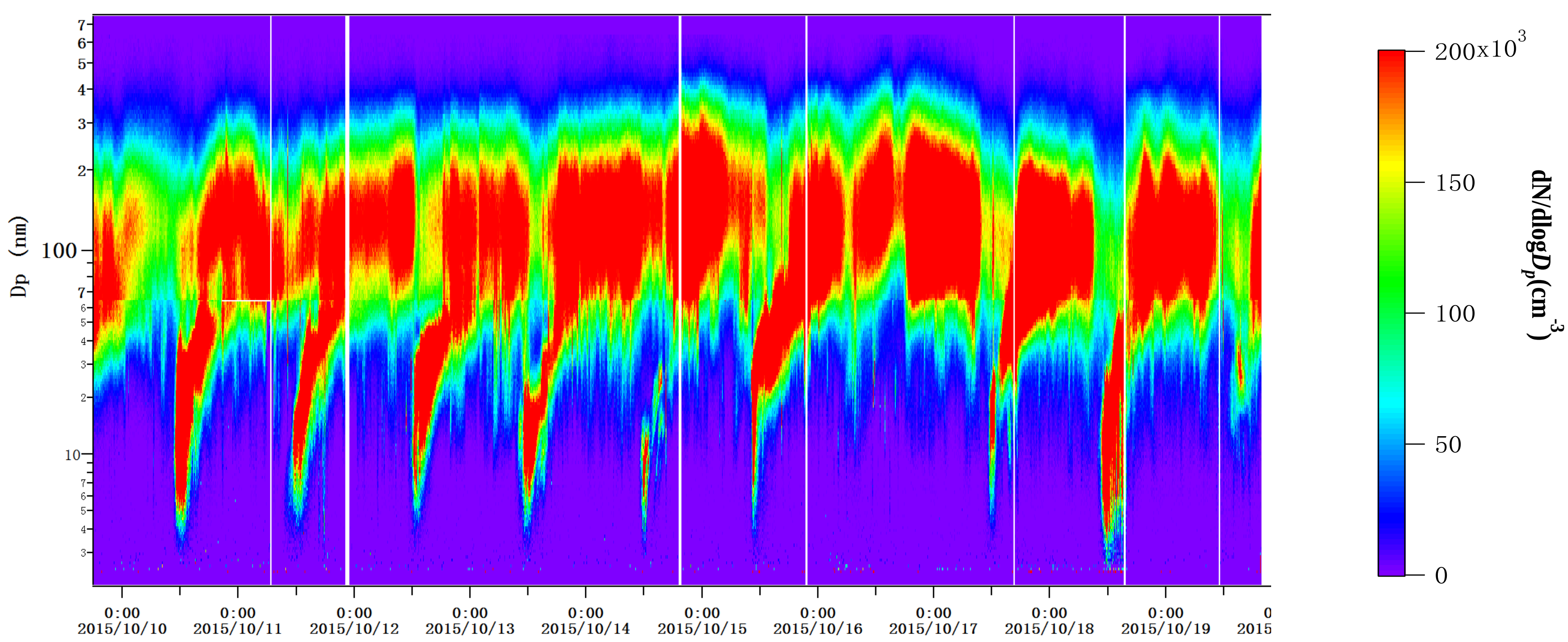
Nov 12, 2015

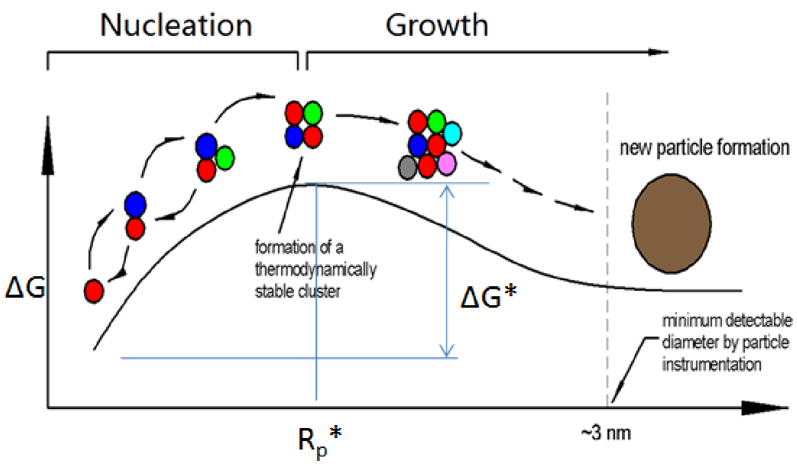


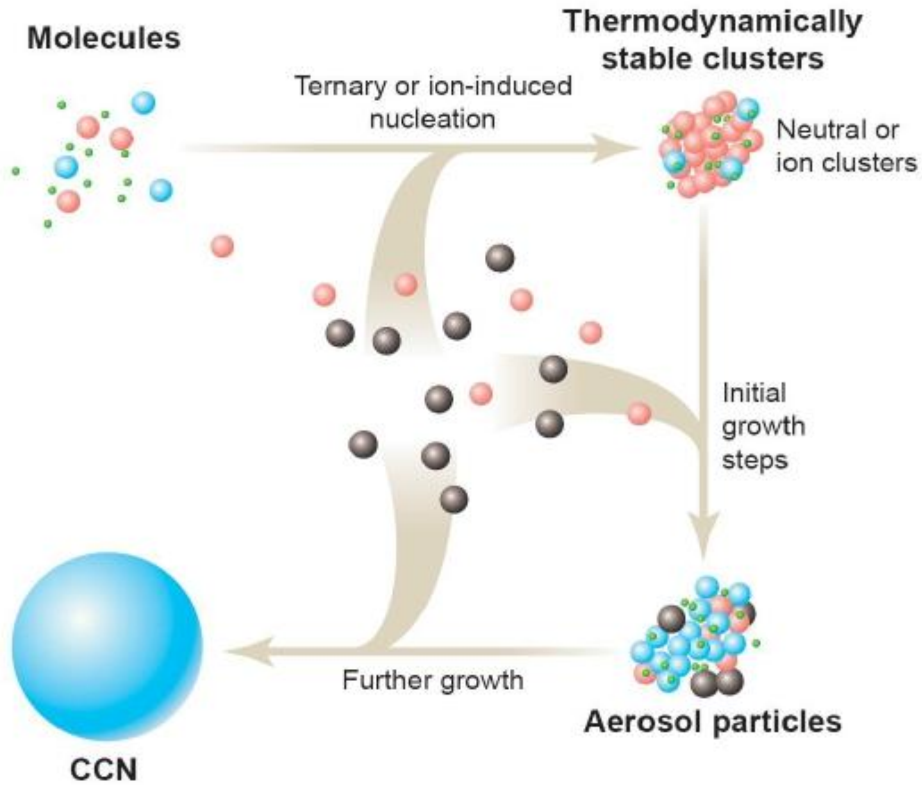
Adapted from Raes (2000)
(courtesy, K. Pringle)
Emission of gas phase precursors
Emission of primary particles
In-cloud oxidation
Activation of CCN
Nucleation
Coagulation
Gaseous precursors
Condensation
Out of cloud processing
Dry Deposition
Wet Deposition
~1.E-9 m
Particle Size
~50.E-6 m

Typical new particle formation events



Two critical steps in New Particle Formation

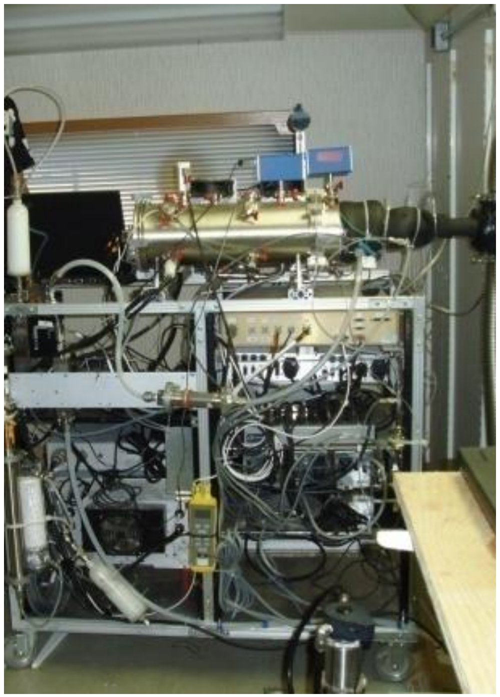




Source: Kulmala, *Science*, 2003

Particle Sizers scanning 1 nm-1000 nm

Aerosol Lifecycle IOP campaign 2011



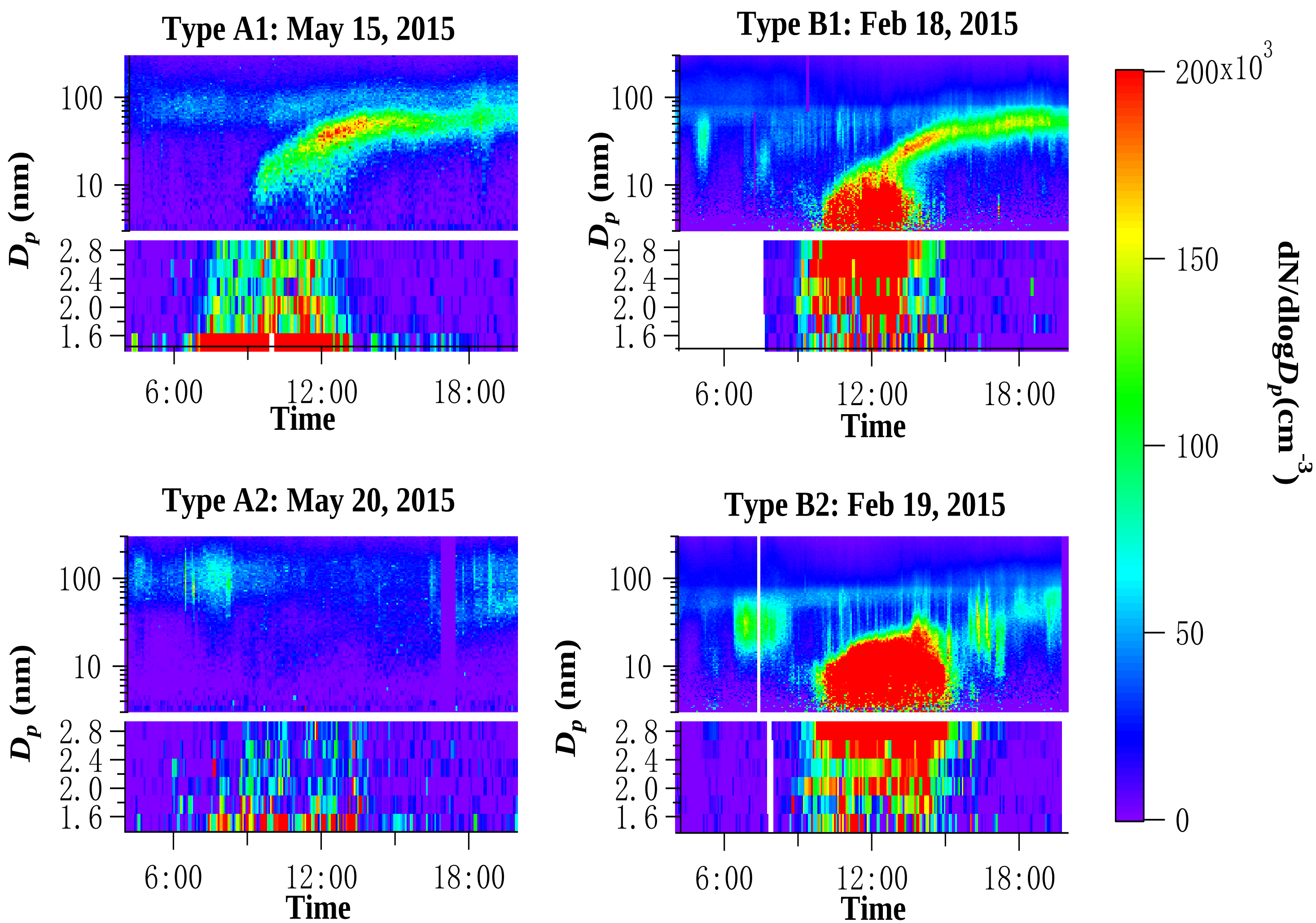
PSM	>1 nm particles
Nano-SMPS	3-64 nm particles
Long-SMPS	10 - 478 nm particles
NO3-CIMS	H_2SO_4
PTR-TOF-MS	VOCs
Gas analyzer	SO_2, O_3, NO_x/NO_y, CO

Yu H., et al., JGR-Atmosphere, 119(2), 2014.

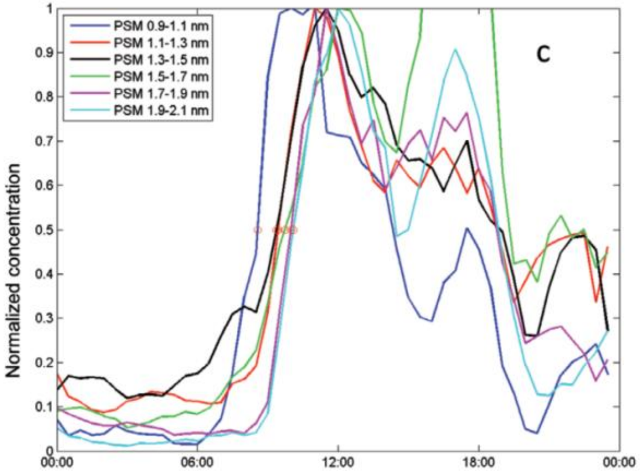
PINOT NOIR campaign (2012)

Yu, H.* et al., ***Aerosol Science and Technology***, 2014.

field observation in Nanjing (urban atmosphere)

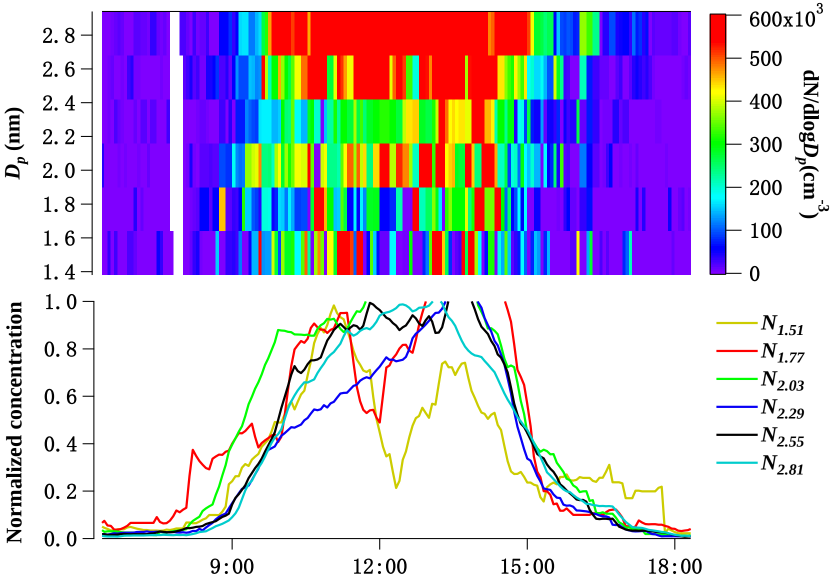


How to get Growth Rate and Nucleation Rate ?
---conventional method



Appearance **T**ime method

Kulmala, *Science*, 2013
Lehtipalo et al. 2014



Problematic for rapid growth of particles (Feb 18 2015, Nanjing)

Size- and time dependent nucleation rate calculation
--- **A**erosol **D**ynamic **B**alance method

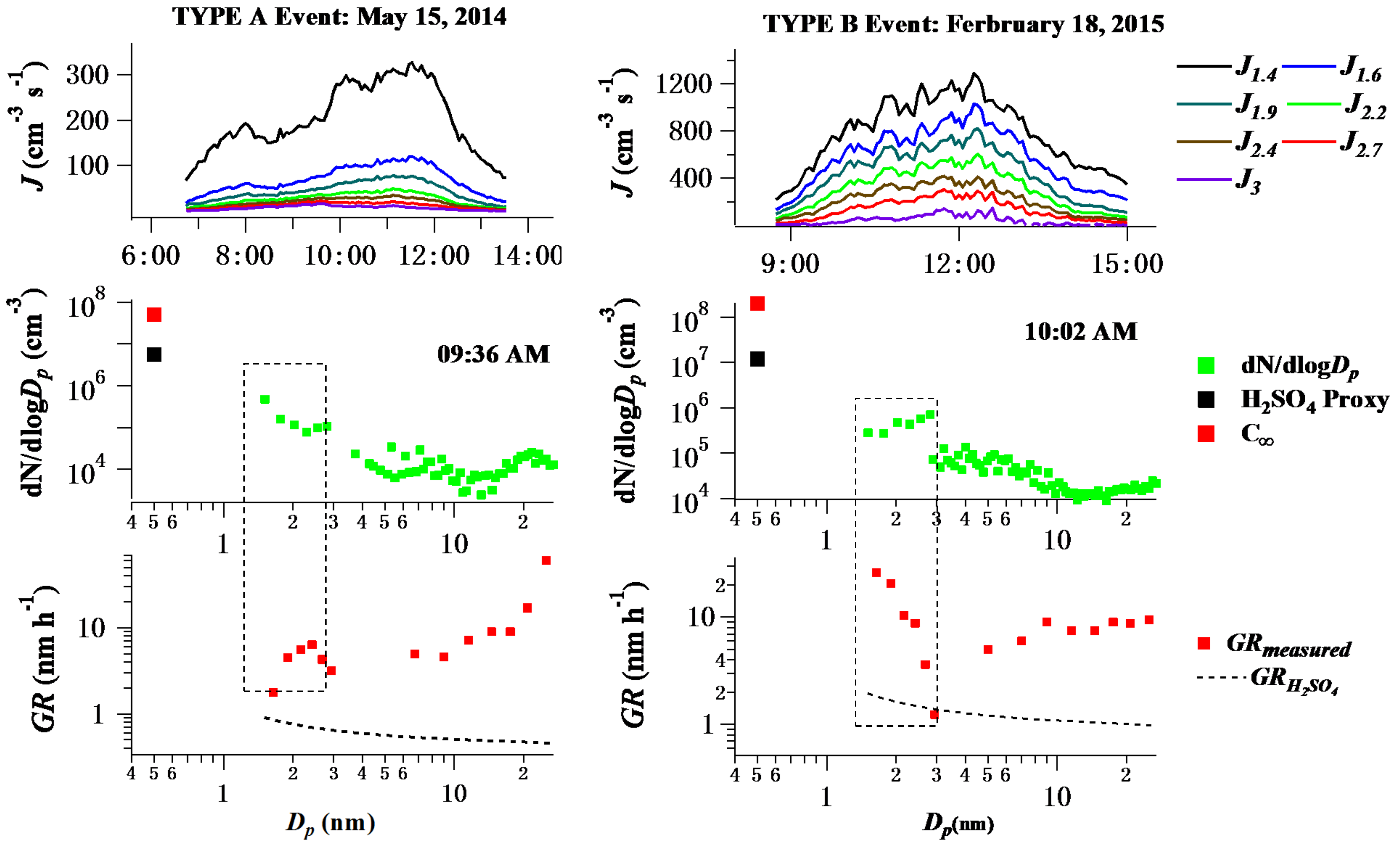
General Dynamic Equation

$$\frac{\partial N_c(r_c)}{\partial t} = \int_{r_c}^{r_\infty} \left(\frac{\partial n(r)}{\partial t}\right) dr = -\int_{r_c}^{r_\infty} (k_L(r) n(r)) dr + g(r_c) n(r_c) +$$

$$\int_{r_c}^{r_\infty} \left(\int_{r_0}^{r_c} \left(k_C(r_1, r_2) n(r_1) n(r_2) \left(\frac{r}{r_2}\right)^2 \right) dr_1 \right) dr -$$

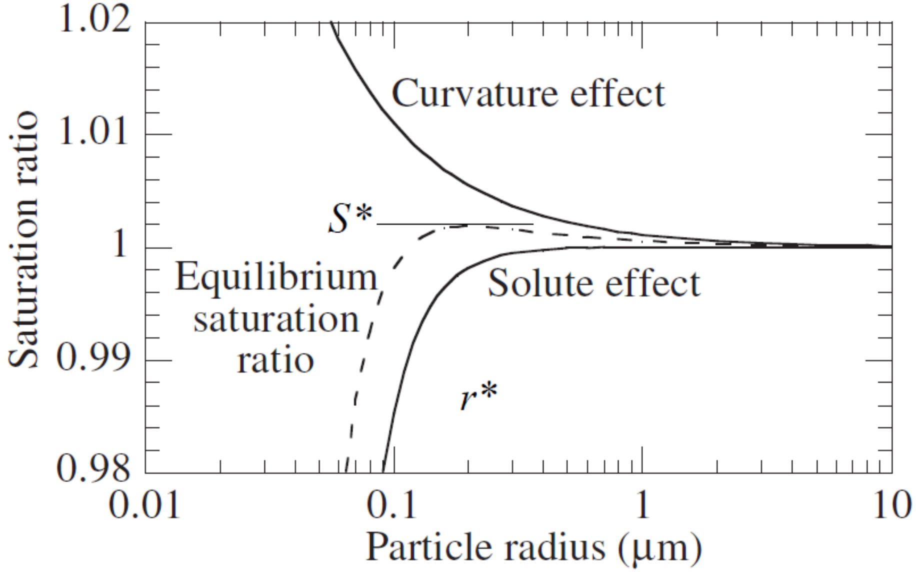
$$2 \int_{r_c}^{r_\infty} \left(n(r) \int_{r_0}^{r_\infty} (k_C(r, r_1) n(r_1)) \, dr_1 \right) dr$$

Fast and non-monotonically increasing growth rate with size



Köhler curve

nano-Köhler curve



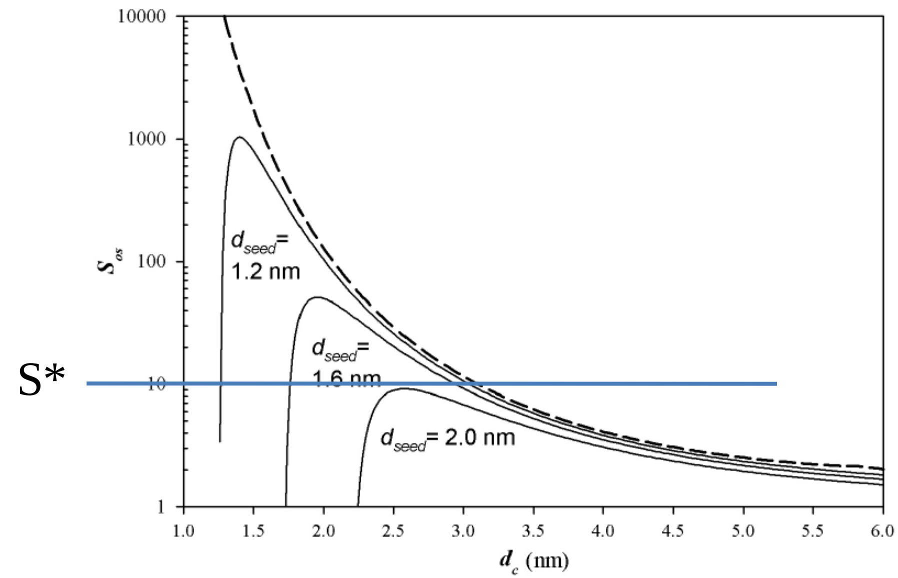
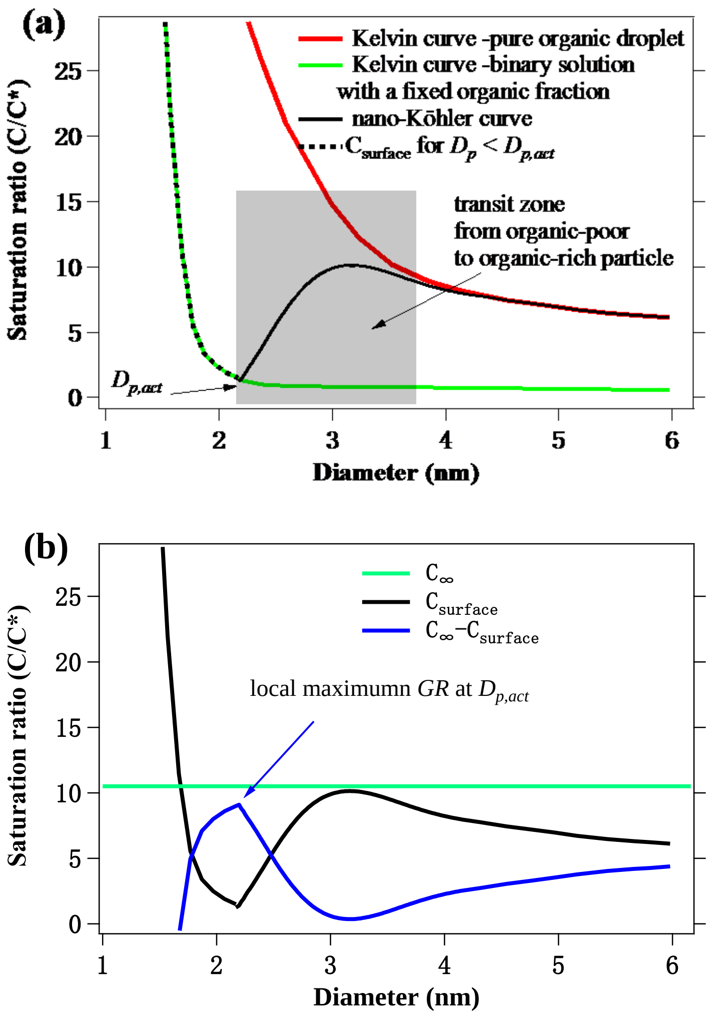


Table 1. Primary Differences Between the Traditional Köhler Theory [*Köhler*, 1936; *Laaksonen et al.*, 1998] and the Nano-Köhler Theory[a]

Theory	Binary Köhler	Nano-Köhler
Activating particles		
Identity	Cloud condensation nuclei	Inorganic clusters
Size (diameter)	>50 nm	1–3 nm
Activating vapor		
Identity	water	soluble organic compound
Gaseous concentration	10^{16}–10^{17} molecules cm^{-3}	10^{6}–10^{8} molecules cm^{-3}
Saturation ratio (*S*)	<1.01	not limited
Factors influencing *S*	*CS*, air cooling rate, fluctuations in cooling rate	*CS*, *Q*, P_0, fluctuations in *Q*, *CS*, and P_0
Secondary vapor		
Identity	e.g., HNO_3, HCl, NH_3	water
Gaseous concentration	10^{9}–10^{11} molecules cm^{-3}	10^{16}–10^{17} molecules cm^{-3}

[a]Here *Q* is the production rate of condensing vapour, P_0 is its saturation pressure and *CS* is the condensation sink.

A modified nano-Köhler curve to explain GR behavior



GR due to organic condensing vapor (LVOC):

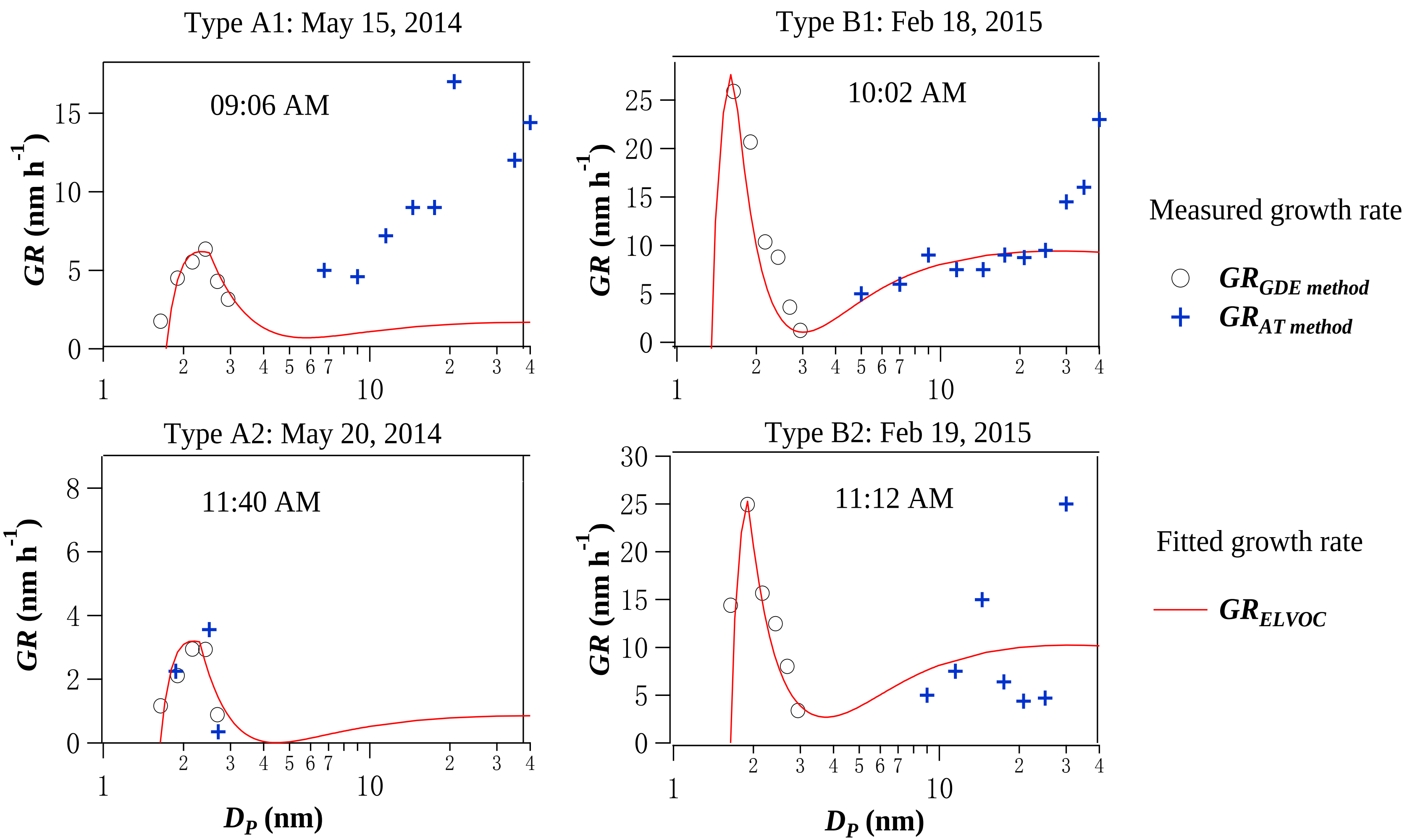
$$GR_{ELVOC} = \frac{\gamma}{2\rho_v}\left(1+\frac{d_v}{d_p}\right)^2\left(\frac{8kT}{\pi}\right)^{\frac{1}{2}}\left(\frac{1}{m_p}+\frac{1}{m_v}\right)^{\frac{1}{2}} m_v\left(C_\infty - C_{surface}\right)$$

kinetic prefactor (Nieminen et al. 2012)

$$C_{surface} = C^* \exp\left(\frac{4\sigma v}{kTD_p}\right)\left(x_{D_p} + \exp\left(-\varphi\left(D_p/D_{p0}\right)^3\right)\right)$$

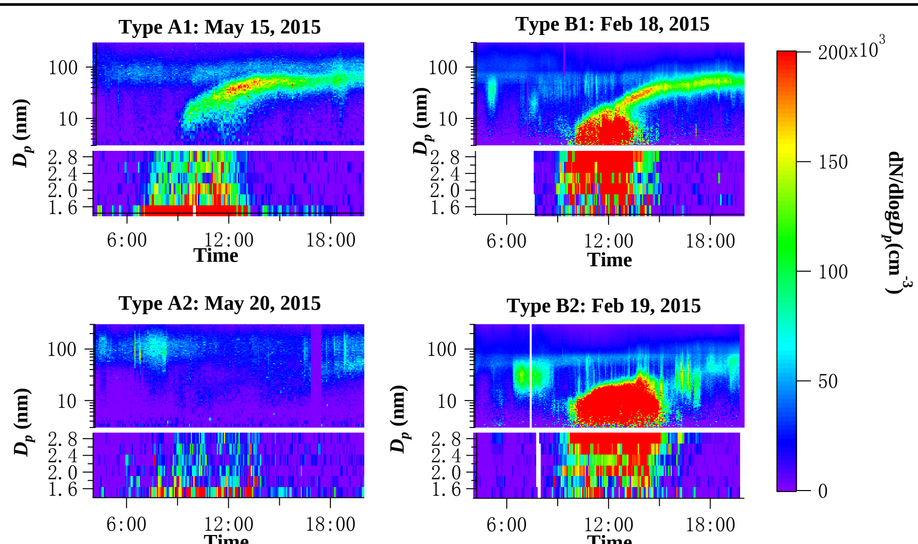
Kelvin effect Raoult effect empirical correction

Measured GR vs. fitted GR at an instance in time



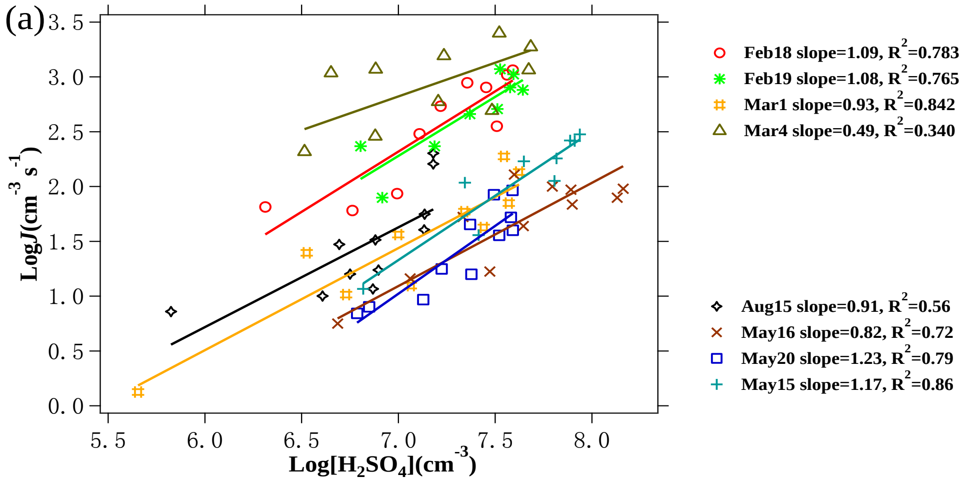
Low Volatility OC (ELVOC) concentration may be the key factor of growth patterns

Type	Date	$D_{p,act}$ (nm)	$GR_{max,1.4\text{-}3}$ (nm h^{-1})	$GR_{1.4\text{-}3}$ (nm h^{-1})	$GR_{3\text{-}20}$ (nm h^{-1})	$J_{1.4}$ ($cm^{-3}s^{-1}$)	T (°C)	CS ($10^{-2}s^{-1}$)	Mikkonen H_2SO_4 proxy (cm^{-3})	C_{∞} (cm^{-3})	C^* (cm^{-3})
A1	May 15, 2014	2.4	6.4	3.6	7.7	3.0×10^2	20.8	1.6	8.7×10^7	5.1×10^7	6.3×10^6
A1	Aug 15, 2014	2.4	14.5	7.1	7.7	2.0×10^2	26.1	1.8	9.3×10^7	1.1×10^8	2.5×10^7
A2	May 16, 2014	2.4	3.8	1.9	0	95	25.3	1.9	1.4×10^8	3.0×10^7	4.0×10^6
A2	May 20, 2014	2.2	2.9	1.6	0	92	24.1	1.9	3.8×10^7	2.3×10^7	2.5×10^6
B1	Feb 18, 2015	1.6	25.9	4.4	6.0	1.1×10^3	8.2	3.3	3.9×10^7	1.7×10^8	3.5×10^7
B1	Dec 27, 2014	1.6	17.7	4.2	5.5	1.9×10^2	7.6	2.8	3.5×10^7	1.2×10^8	2.8×10^7
B2	Feb 19, 2015	1.9	25.0	8.9	10.1	8.0×10^2	7.4	3.2	3.7×10^7	2.0×10^8	5.7×10^7
B2	Mar 4, 2015	1.9	18.0	5.8	8.7	2.5×10^3	3.9	2.2	4.8×10^7	1.4×10^8	2.0×10^7



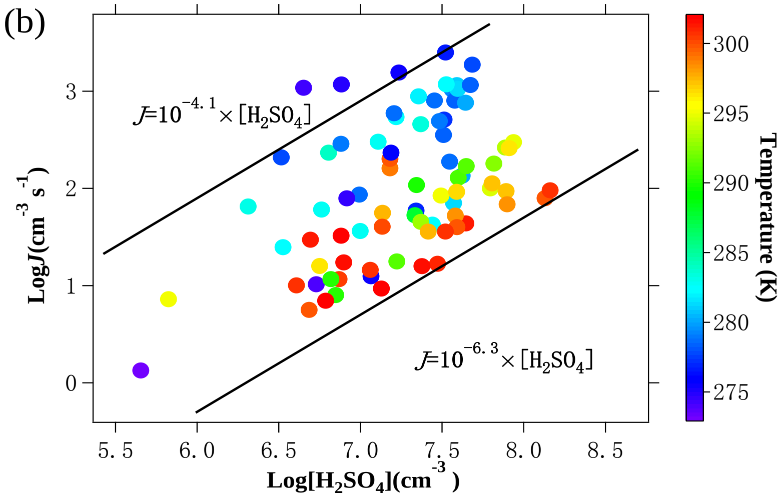
H. Yu* et al., ***ACPD***, 15, 18653–18690, 2015

$J_{1.4}$ vs. H_2SO_4 proxy in the urban atmosphere



$$[H_2SO_4]=8.21\times10^{-3}\cdot k\cdot \text{Radiation}\cdot[SO_2]^{0.62}\cdot(\text{CS}\cdot\text{RH})^{-0.13}$$

Mikkonen et al. 2011



1. Lowed predictive ability of H_2SO_4 proxy in heavily urban atmosphere
2. Temperature dependence of nucleation rate
3. The enhancement of nucleation by organics

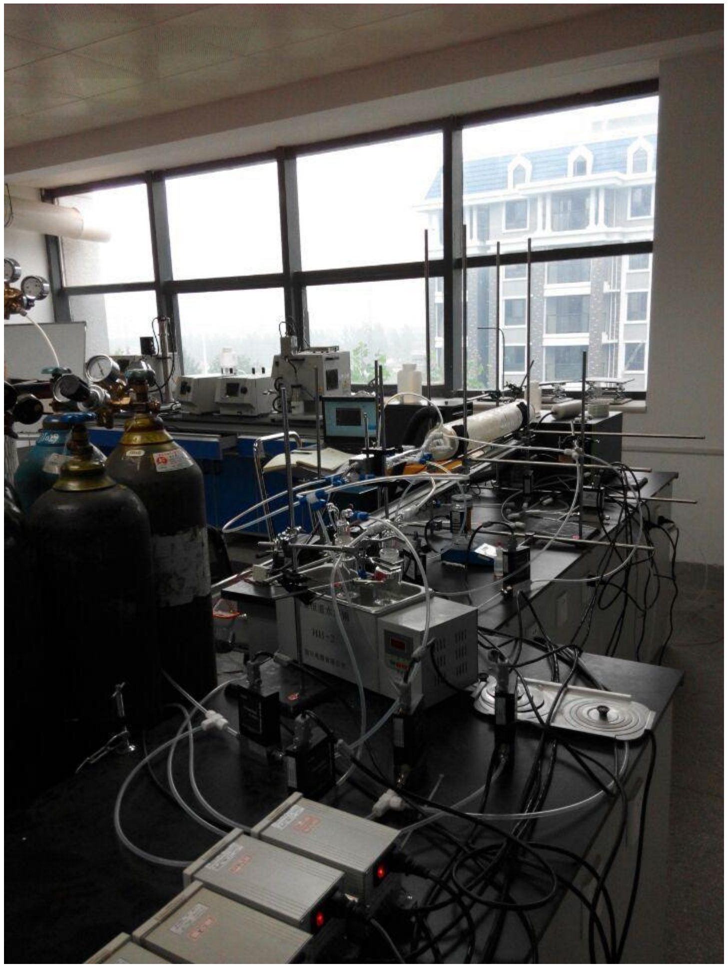
Summary

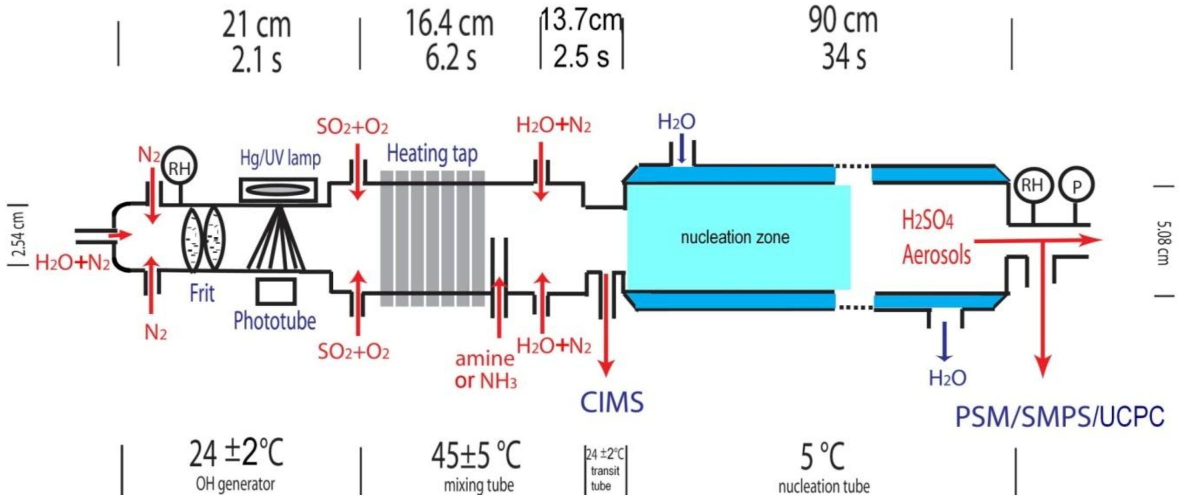
1. Size- and time- dependent growth rate and nucleation rate using ADB method
2. Strong temperature dependence of J vs. [H_2SO_4] correlation
3. Growth rate is fast and not monotonically increasing in 1-10 size range
4. A modified nano-Köhler theory framework is proposed to explain ELVOC condensation

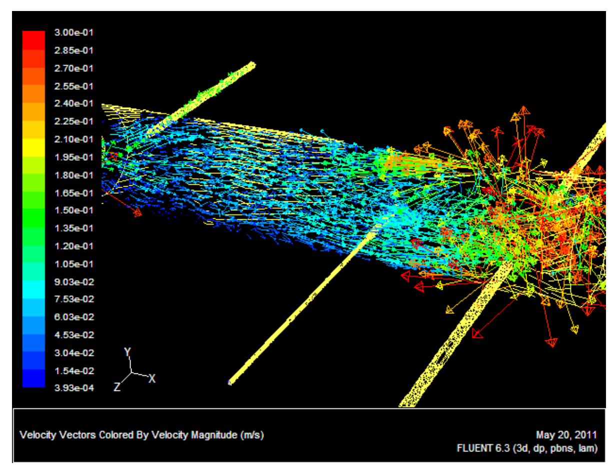
Future work

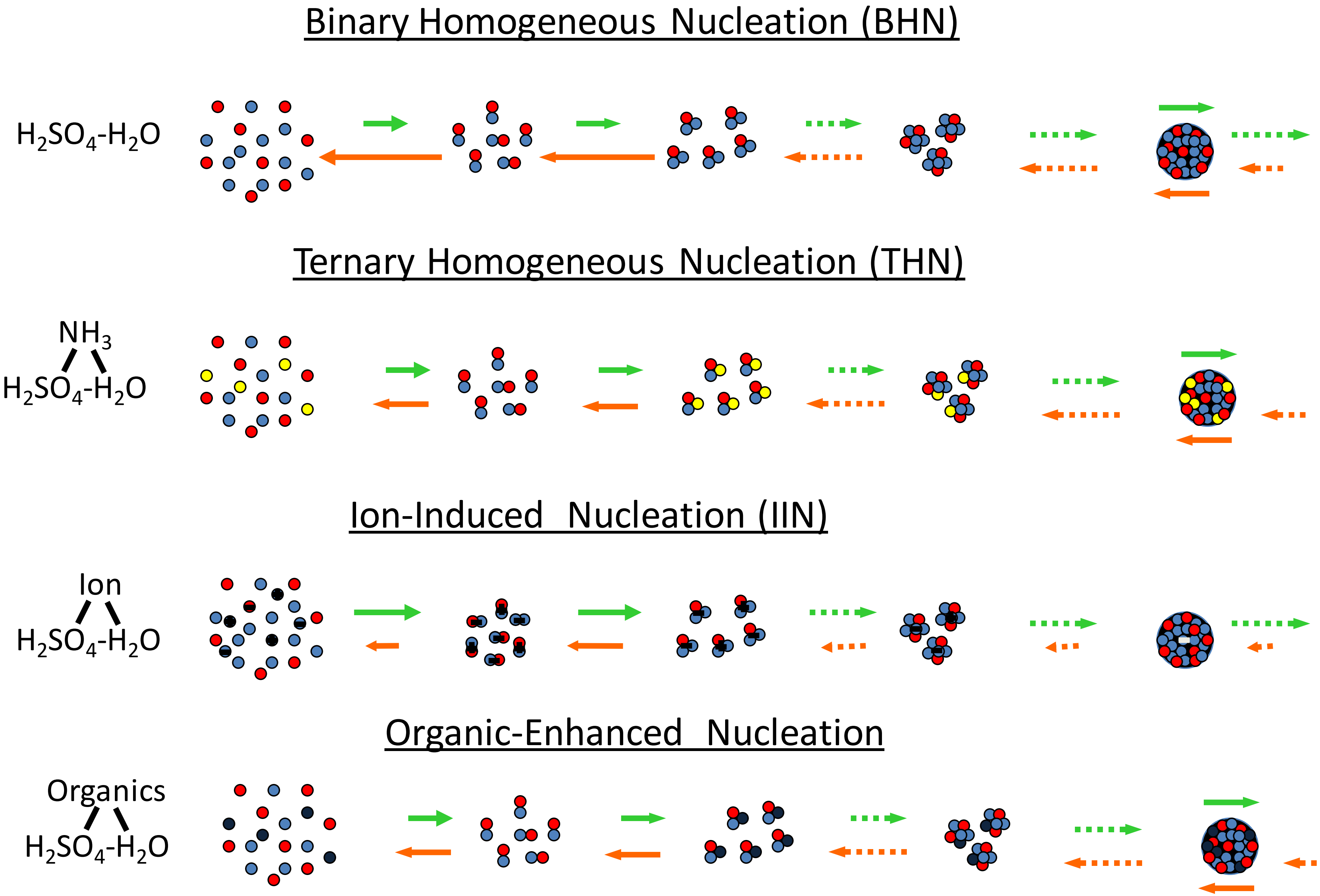
More observations on NPF characteristics and the influences of VOCs

Multicomponent Nucleation Setup @ *NUIST*

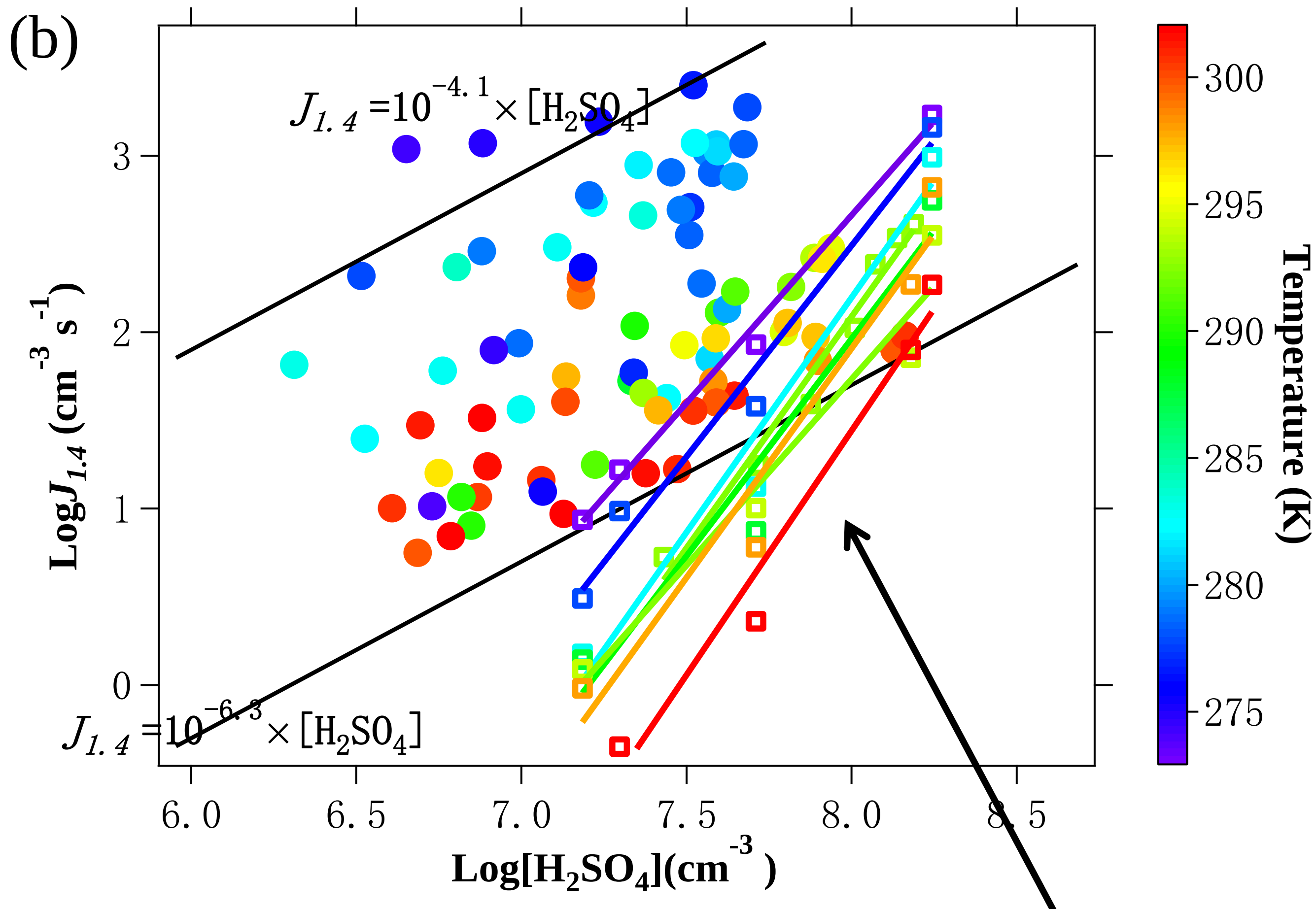







Binary Homogeneous Nucleation (BHN)
H_2SO_4-H_2O
Ternary Homogeneous Nucleation (THN)
NH_3
H_2SO_4-H_2O
Ion-Induced Nucleation (IIN)
Ion
H_2SO_4-H_2O
Organic-Enhanced Nucleation
Organics
H_2SO_4-H_2O

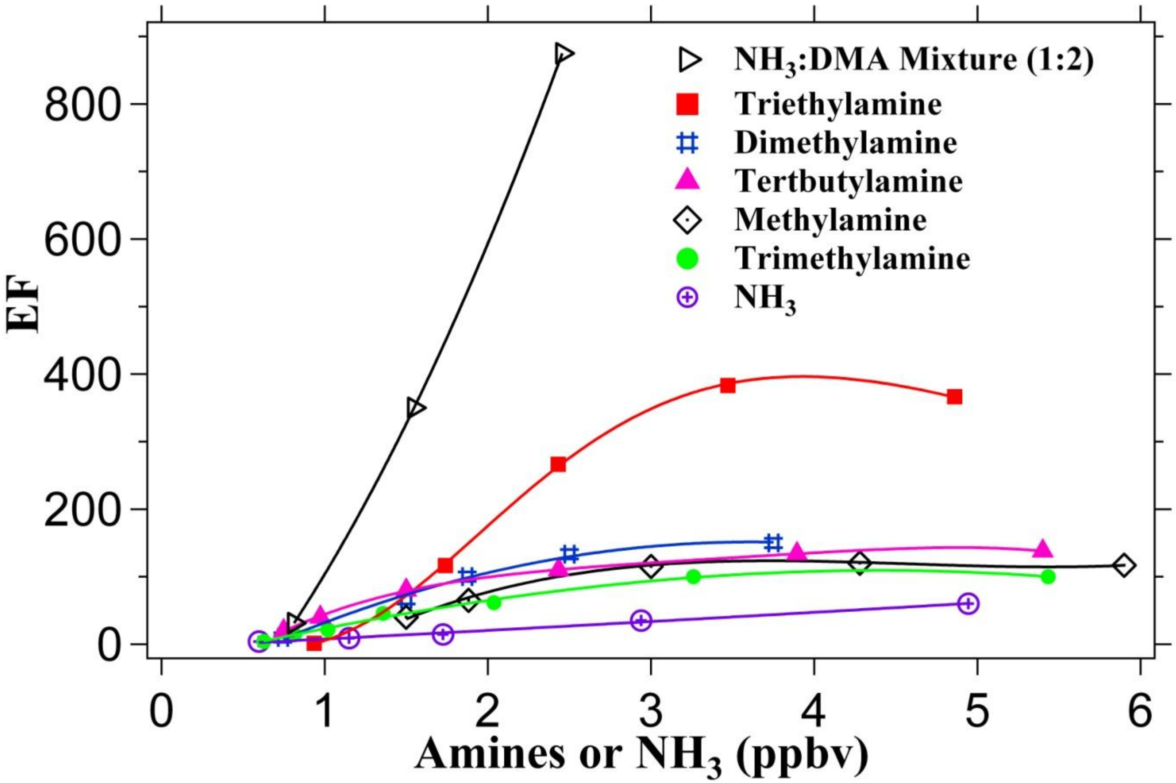
Seasonal variation of $J_{1.4}$ vs. H_2SO_4 can not be simply explained as temperature change



Flow tube simulation of binary H_2SO_4-H_2O nucleation

unpublished data, Yu et al. under preparation, 2015

Enhancement factors (EF) of amines in particle formation rate



$[H_2SO_4] = 7 \times 10^6$ cm^{-3}
RH = 32%
residence time = 34 s.

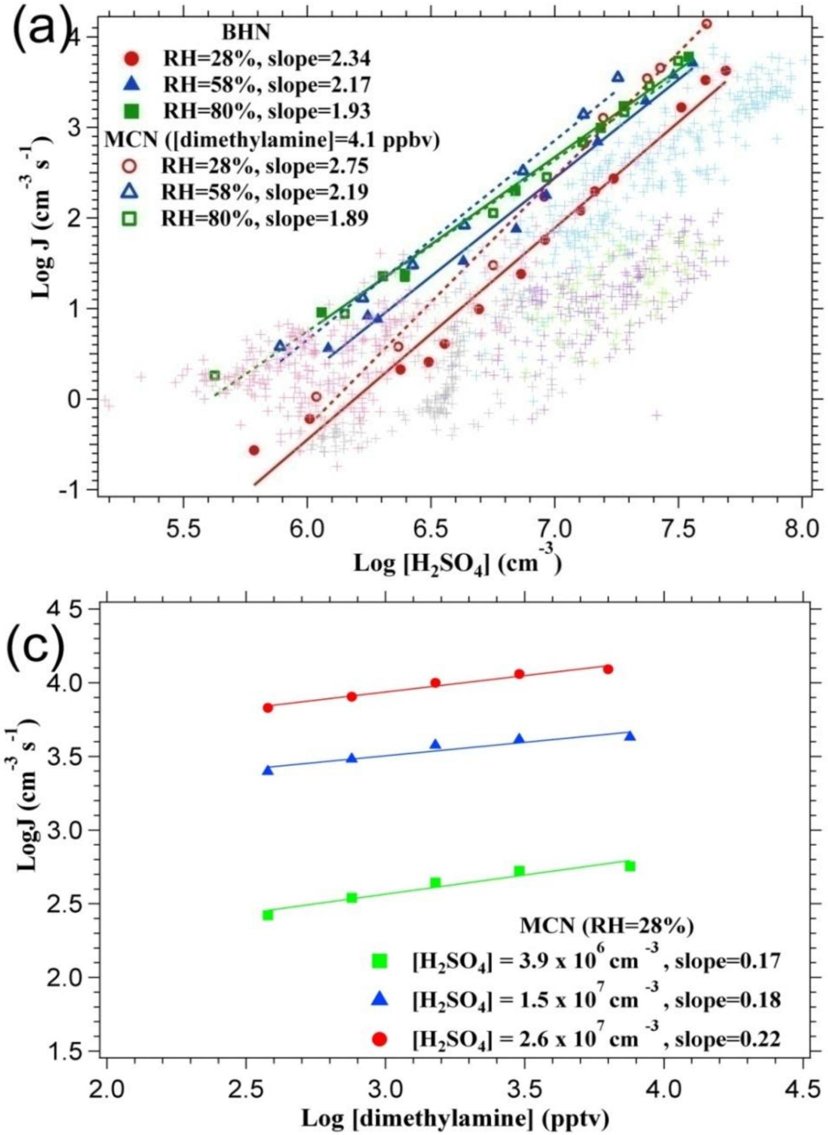
Amine/NH_3	pK_b	*PA(kcal/mol)*
triethylamine	3.25	235.5
dimethylamine	3.27	224.8
tert-butylamine	3.32	223.3
methylamine	3.35	218.4
trimethylamine	4.22	228.6
ammonnia	4.75	207.0

1. Amines promote nucleation more effectively than ammonia.
2. EF is related to basicity (not proton affinity)
3. Amine-ammonia mixture has highest enhancement.

Yu et al. GRL 2012, EC 2012

J vs. [H_2SO_4], RH, and [dimethylamine]

(PSM results, residence time = 35 s, 278 K)



1. Our lab quasi-BHN particle formation rate reproduced boundary layer nucleation rate observations.

2. Slopes do not vary between BHN and multicomponent nucleation.

Yu et al. GRL 2012, EC 2012

Summary

1. Temperature and H_2SO_4 alone can not explain seasonal variations of new particle formation
2. Evaporation must be considered to evaluate particle growth
3. Strong enhancement from 5 different amines and synergistic effect for ammonia and amines.
4. Isoprene suppression effect on NPF from α-pinene ozonolysis was observed in a flow tube system