

# 스모그챔버와 흐름반응기를 이용한 미세먼지의 실험실 연구

임호진

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동북아초미세먼지사업단, 온라인

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- 대기오염과 광화학 반응
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## 2. 광화학 반응을 이용한 유기 미세먼지 연구

- 반응 메커니즘 연구
- 확산모델 모수 : 생성수율
- 물리적 성질 규명 : 상 상태, 점도, 휘발도
- 독성

## 3. 요약 및 제언

# 스모그 현상으로 대표되는 대기오염

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Mexico City, Mexico



New Delhi, India



Harbin, China, Oct. 21, 2013



Seoul, Korea



**미세먼지(PM10)** : 공기 중에 부유한  
공기역학적 직경이  $10\ \mu\text{m}$  이하인 입자

**초미세먼지(PM2.5)** : 공기 중에 부유한  
공기역학적 직경이  $2.5\ \mu\text{m}$  이하인 입자

**황사(Asian Dust, Yellow Dust)** :  
공기 중에 부유한 모래먼지/흙먼지

**에어로졸(Aerosol)** : 공기 중에 부유한  
모든 액체/고체 입자

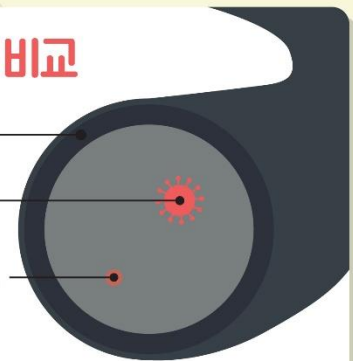
## 미세먼지란?

미세먼지란 대기 중에 떠다니거나 흩날려 내려오는 입자상 물질로  
미세먼지는 사람의 머리카락 지름( $50\sim 70\ \mu\text{m}$ )의 약  $1/5\sim 1/7$  정도이며,  
초미세먼지는 머리카락의 약  $1/20\sim 1/30$ 에 불과할 정도로 매우 작음.

세계보건기구 산하 국제암연구소  
발암이 확인된 1군 발암물질(Group 1)로 지정

### 미세먼지 크기 비교

- 머리카락 단면
- 미세먼지 PM10
- 초미세먼지 PM2.5



산림청 (2019)

# 현재 우리나라의 심각한 사회문제로 대두된 미세먼지

## 1 미세먼지 심각성

### 1급 발암물질

WHO는 담배연기, 술·석면, 벤젠 등과 함께  
미세먼지를 1급 발암물질로 규정

미세먼지 주의보 및 경보  
약 **200%** 증가

2018년 1월 1일~4월 26일까지 발생횟수는 425회,  
전년동기 148회보다 187% 증가

국민들이 우려하는 건강  
**1, 2위** 이슈

2017 환경영향 미세먼지 선다 조사결과

전세계  
**최악** 수준

지난 25년 동안 OECD 국가들의  
연평균 미세먼지 농도는  
15 $\mu\text{g}/\text{m}^3$ 로 낮아진 반면,  
한국은 23 $\mu\text{g}/\text{m}^3$ 로 높아져,  
OECD 회원국 중에서  
가장 나쁜 수준으로 악화  
(미국 제외)

OECD, WHO, UNEP 자료

## 2 미세먼지와 호흡기 질환



미세먼지, 폐 속 폐포,  
**혈관**안까지 침투

미세먼지는 작은 입자로 폐포, 혈관까지 침투하고  
기관지염부터 천식, 폐렴, 폐암의 발생 위험을 높이는 직접적 위험요소

WHO, UNEP, OECD 자료, KEDC 연구결과



대기오염 조기 사망률  
**세계 1위**

OECD는 2000년 대기오염으로 인한 한국의 초기 사망률이  
OECD 회원국 중 1위가 될 것이라고 경고  
34개 OECD 회원국 중 유일하게 한국이 1,000명을 넘어설 것으로 전망

OECD, The Economic and Environmental Cooperation Development

## 3 만성폐쇄성폐질환 COPD

미세먼지(PM10) 농도가 10 $\mu\text{g}/\text{m}^3$  증가 시

**사망률** 증가  
1.1% 증가

**입원율** 증가  
2.7% 증가

1인 사회경제적  
연간 비용  
당뇨약 **5배**



**330만명**

COPD 환자수

**13%**

40세 이상 인구 COPD 유병률

**2.8%**

COPD 진단율

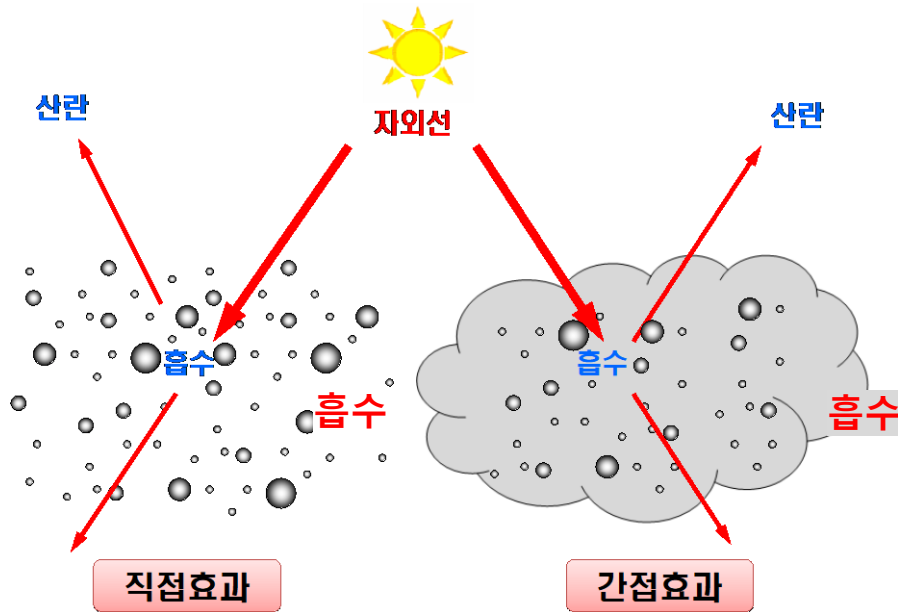
**5위**

한국인 10대 만성 질환 질병 부담



# 미세먼지의 환경 문제 : 기후 변화 및 시정 감소

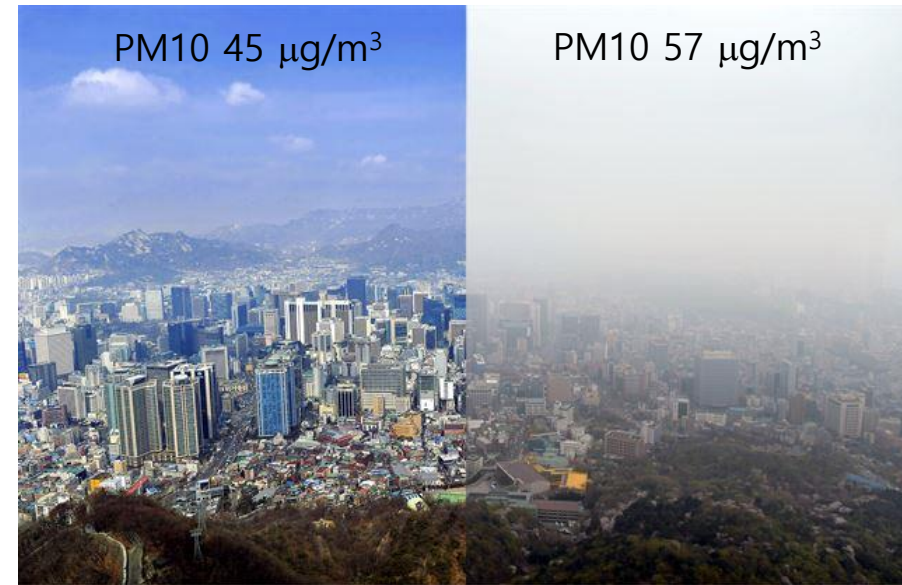
- ▶ 먼지의 태양 빛(자외선)에 대한 간접 현상
  - 국지적 복사강제력 및 기후 변화 야기함
  - 농작물 생산성도 감소시킴



산란 → 냉각효과  
(Parasol effect)

흡수 → 온난화효과  
(Greenhouse effect)

- ▶ 먼지의 태양 빛(가시광선)에 대한 간접 현상
  - 가시거리 감소
  - 심미적 불쾌감 유발시킴

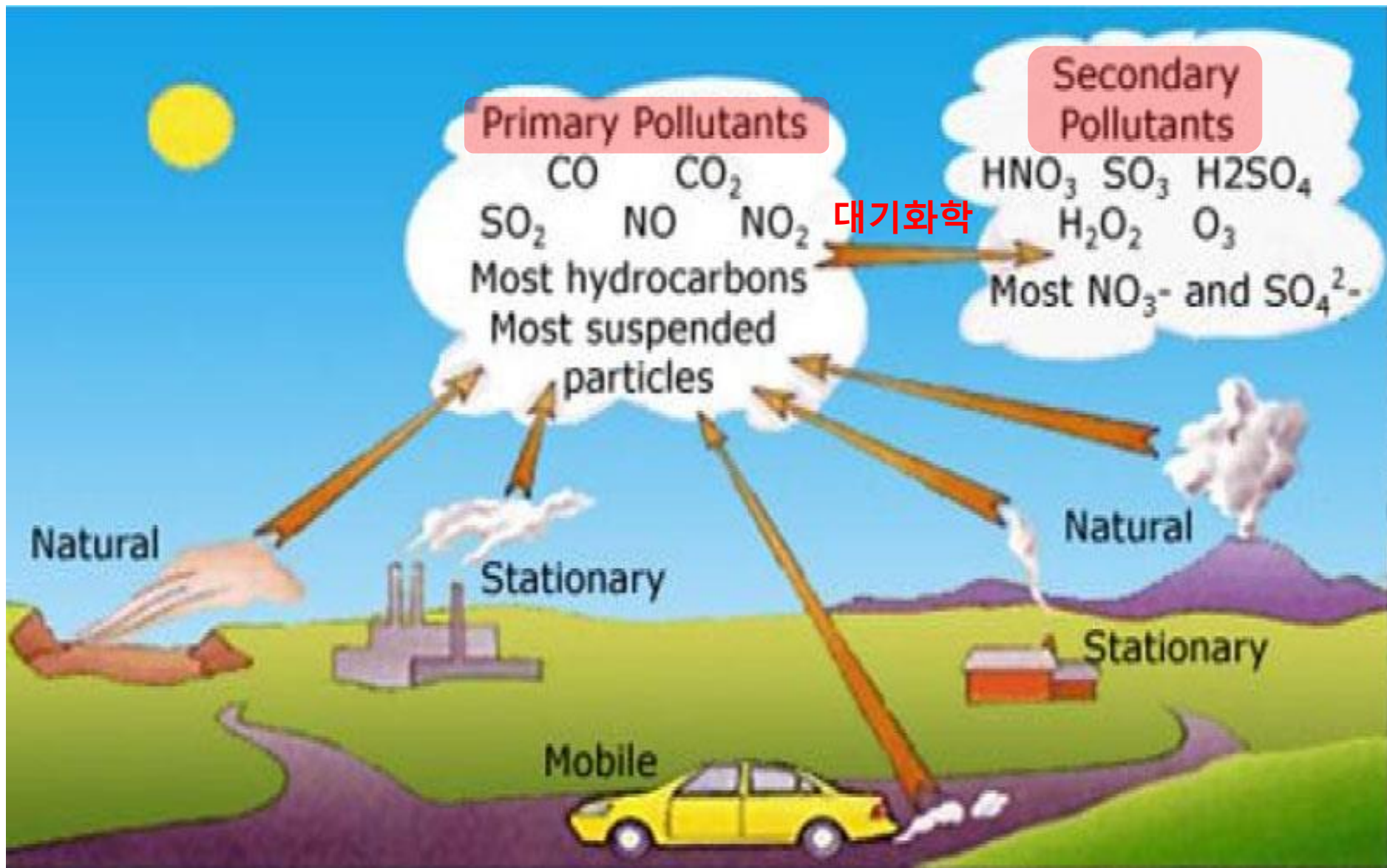


한국일보 (2014.4.15)

- Twomey 효과(1차 효과) : 구름 응결핵의 수농도 증가에 의해 광학 두께가 증가하고 이에 따른 냉각효과 증가.
- Albrecht 효과(2차 효과) : 구름 응결핵의 수농도 증가는 강우를 감소시키고 구름의 체류시간 증가.

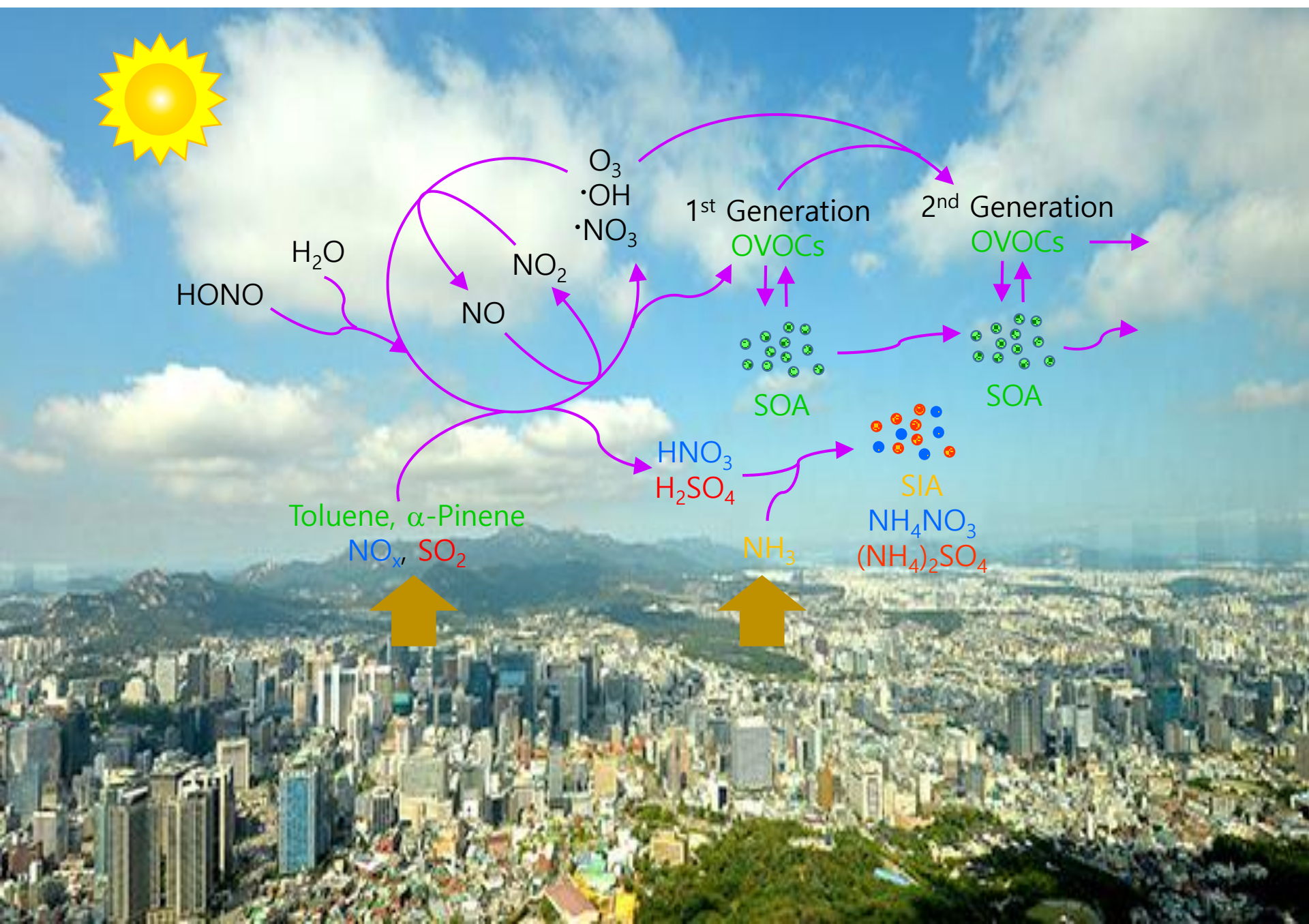
# 스모그 현상과 대기화학

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# 대기화학 및 이차에어로졸 생성



# 이차 에어로졸 생성 관련 대기화학반응

Phase	Species	 Daytime Reaction	 Nighttime Reaction	$P^{\circ}_{\text{sat}}$ (torr)
Homo-	$\text{SO}_2$	$\text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4$ $\rightarrow (\text{NH}_4)_2\text{SO}_4$	No reaction	$2.5 \times 10^{-5}$ $5.1 \times 10^{-13}$
	$\text{NO}_x$	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ $\rightarrow \text{NH}_4\text{NO}_3$	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$ $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ $\rightarrow \text{NH}_4\text{NO}_3$	60 $1.1 \times 10^{-5}$
	ROG	$\text{C}_c\text{H}_h + \text{OH} \rightarrow \text{C}_c\text{H}_h\text{O}_o$ $\text{C}_c\text{H}_h + \text{O}_3 \rightarrow \text{C}_c\text{H}_h\text{O}_o$	$\text{C}_c\text{H}_h + \text{O}_3 \rightarrow \text{C}_c\text{H}_h\text{O}_o$ $\text{C}_c\text{H}_h + \text{NO}_3 \rightarrow \text{C}_c\text{H}_h\text{O}_o\text{N}_n$	$1.0 \times 10^{-11}$ $-1.0 \times 10^{-5}$
Hetero-	$\text{SO}_2$	$\text{SO}_2 + \text{OH}^- \rightarrow \text{SO}_3^{2-}$ $\text{SO}_3^{2-} + \text{O}_x \rightarrow \text{SO}_4^{2-}$ $(\text{H}_2\text{O}_2, \text{O}_3, \text{Fe}^{2+}, \text{Mn}^{2+} \text{ @ pH})$ $\rightarrow (\text{NH}_4)_2\text{SO}_4$	$\text{SO}_2 + \text{OH}^- \rightarrow \text{SO}_3^{2-}$ $\text{SO}_3^{2-} + \text{O}_x \rightarrow \text{SO}_4^{2-}$ $(\text{H}_2\text{O}_2, \text{O}_3, \text{Fe}^{2+}, \text{Mn}^{2+})$ $\rightarrow (\text{NH}_4)_2\text{SO}_4$	$< 2.5 \times 10^{-5}$ $< 5.1 \times 10^{-13}$
	$\text{NO}_x$	$\text{NO}_2 + \text{OH}^- \rightarrow \text{HNO}_3$ $\rightarrow \text{NH}_4\text{NO}_3$	$\text{NO}_2 + \text{OH}^- \rightarrow \text{HNO}_3$ $\rightarrow \text{NH}_4\text{NO}_3$	$< 60$ $< 1.1 \times 10^{-5}$
	ROG	$\text{C}_x\text{H}_y\text{O}_z + \text{OH} \rightarrow \text{C}_x\text{H}_y\text{O}_{z+}$	No reaction	$< 1.0 \times 10^{-11}$ $-1.0 \times 10^{-5}$

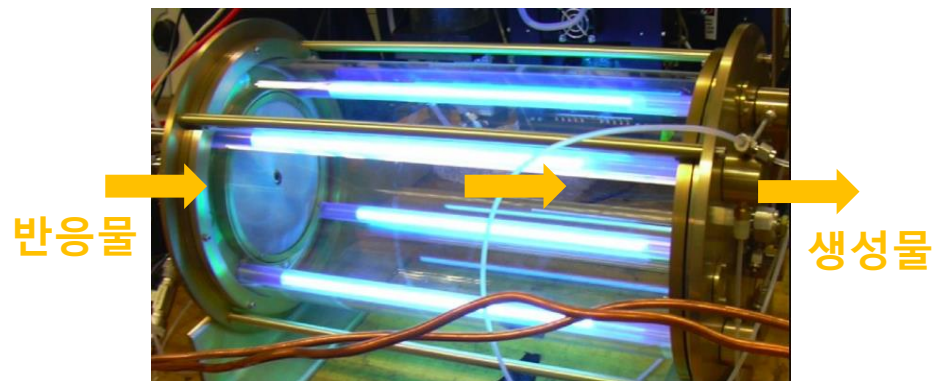
# 대기화학 및 이차입자 연구용 반응기

반회분식 반응기 : 스모그 챔버



- 반응물을 밀폐된 공간에 주입 후 반응
- 반응 개시 후 반응기 내부의 화학물질 및 물리화학적 성질 측정
- 반응기 성질
  - 광투과성
  - 내화학적성
  - 재질 : 테플론
- 광원 : 태양광/UVA 램프

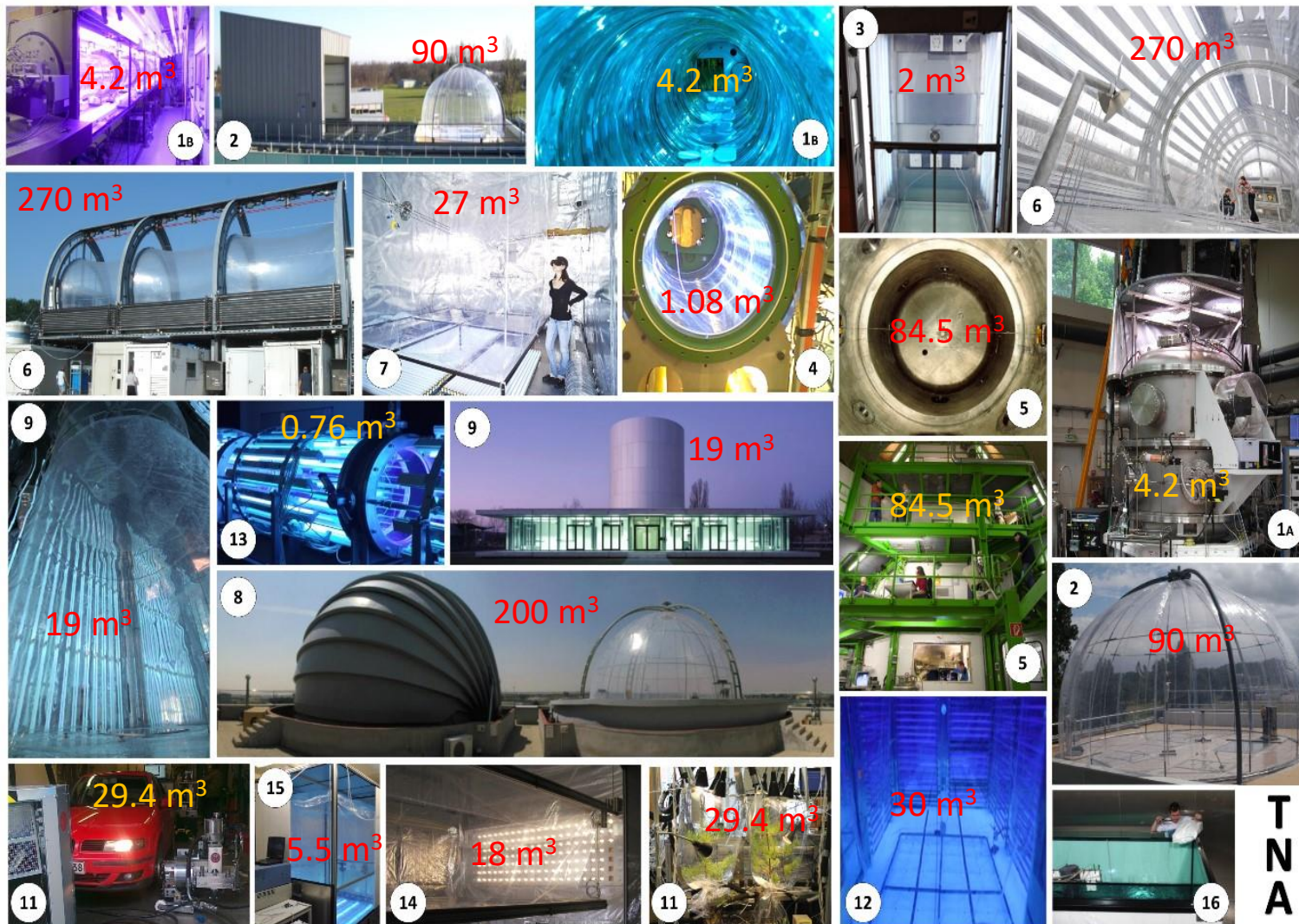
흐름 반응기



- 반응물을 일정 속도로 유입 및 유출시키면서 반응
- 반응기에서 유출되는 화학물질 및 물리화학적 성질 측정
- 반응기 재질
  - 내화학적성
  - 재질 : 테플론, 유리, 석영, 알루미늄
- 광원 : UVC 램프



# 스모그챔버 시설 : EUROCHAMP 2020



T  
N  
A

- |                     |                      |                           |
|---------------------|----------------------|---------------------------|
| 1 CESAM (CNRS, FR)  | 5 AIDA (KIT, DE)     | 9 LEAK-LACIS (TROPOS, DE) |
| 2 HELIOS (CNRS, FR) | 6 SAPHIR (FZJ, DE)   | 10 IASC (UCC, IE)         |
| 3 ISAC (CNRS, FR)   | 7 PACS-C3 (PSI, CH)  | 11 ILMARI (UEF, FI)       |
| 4 QUAREC (BUW, DE)  | 8 EUPHORE (CEAM, ES) | 12 FORTH-SC (FORTH, GR)   |
|                     |                      | 13 CERNESIM (UAIC, RO)    |
|                     |                      | 14 MAC-MICC (NCAS, UK)    |
|                     |                      | 15 CASC (NCAS, UK)        |
|                     |                      | 16 ASIBIA (NCAS, UK)      |

EUROCHAMP  
2020

# 동아시아 스모그 챔버 시설

Country	Institute	Size (m <sup>3</sup> )	Material	Location	Refs
Japan	National Institute for Environmental Studies	6.07	PFA/SUS	Indoor	Akimoto et al. (1979)
	National Institute for Environmental Studies	4.28	FEP	Mobile	Shibuya et al. (1981)
	National Institute for Environmental Studies	0.7	FEP	Indoor	Deng et al. (2021)
China	RCEES-CAS	0.1	Teflon	Indoor	Wu (2001)
	AIOFM-CAS	0.023	Quartz	Indoor	Nie et al. (2002)
	Tsinghua Univ.	23 x 2	Teflon	Indoor	Ren et al. (2005)
	Tsinghua Univ.	2	FEP	Indoor	Wu et al. (2007)
	IAP-CAS	0.07	Teflon	Indoor	Du et al. (2007)
	IC-CAS	0.1	FEP	Indoor	Gai et al. (2009)
	IC-CAS	0.15	Teflon	Indoor	Gai et al. (2011)
	GIG-CAS	5 x 2	FEP	Indoor	Wang et al. (2014)
	GIG-CAS	30	FEP	Indoor	Wang et al. (2014)
	RCEEES-CAS	30	FEP	Indoor	Chen et al. (2019)
	CESE/CEH-Peking Univ.	0.3	Teflon	Indoor	Kuang & Shang (2020)
	IEHPC-Guangdong Univ. of Technology	2 x 2	FEP	Indoor	Luo et al. (2020)
	CRAES	56	FEP	Outdoor	Li et al. (2021)
Hong Kong	Aerosol and Haze Laboratory, Beijing Univ.	10	Quartz	Indoor	Ma et al. (2022)
	Hong Kong Polytechnic University	2.38	SUS	Indoor	Lee et al. (2001)
	Hong Kong Polytechnic University	18.16	SUS	Indoor	Lee & Wang (2006)
	Hong Kong Polytechnic University	6	PFA	Indoor	Tan et al. (2020)
Korea	Korea Institute of Science and Technology	6	FEP	Indoor	Bae et al. (2003)
	National Institute of Environmental Research	0.8	FEP	Indoor	Hong et al. (2003)
	Kyungpook National University	8	FEP	Indoor	Barbar et al. (2017)
	Korea Institute of Science and Technology	27	FEP	Indoor	Lee (2021)
	Korea Institute of Construction Technology	13.8 x 2	ETFE	Outdoor	Park et al. (2020)
	Korea Institute of Construction Technology	1163	ETFE	Outdoor	Kim et al. (2021)

# 전형적인 스모그 챔버 구성

## 스모그 챔버

제한된 공간 내에 대기 성분을  
주입하여 대기화학반응 및  
프로세스를 모사하는 장치

- 광원 : 태양광 / 인공
- 위치 : 실외 / 실내
- 이동성 : 고정 / 이동
- 크기 : 초소형 - 초대형

반응기(백)

광원

### 공조장치

- 반응기가 설치된 공간
- 온도/습도
- 공기정화

### 공기공급장치

- 반응기 내부
- 컴프레셔
- 공기정화장치

### 반응물 공급장치

- 전구체 : ROG, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub>
- 산화제 : HONO, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>
- 핵 입자

### 측정장치

- 가스
- 입자
- 입자 특성
- 환경 (온/습도, 광)



# KNU 실내 스모그 챔버 : FEP 반응기-자외선 형광등

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FEP bag  
(8 m<sup>3</sup>)

Double layered sealing  
(2" Teflon/Kapton tapes)

UV-A lamps 40W x 60  
UV-B lamps 40W x 12

Moving  
lamp panel

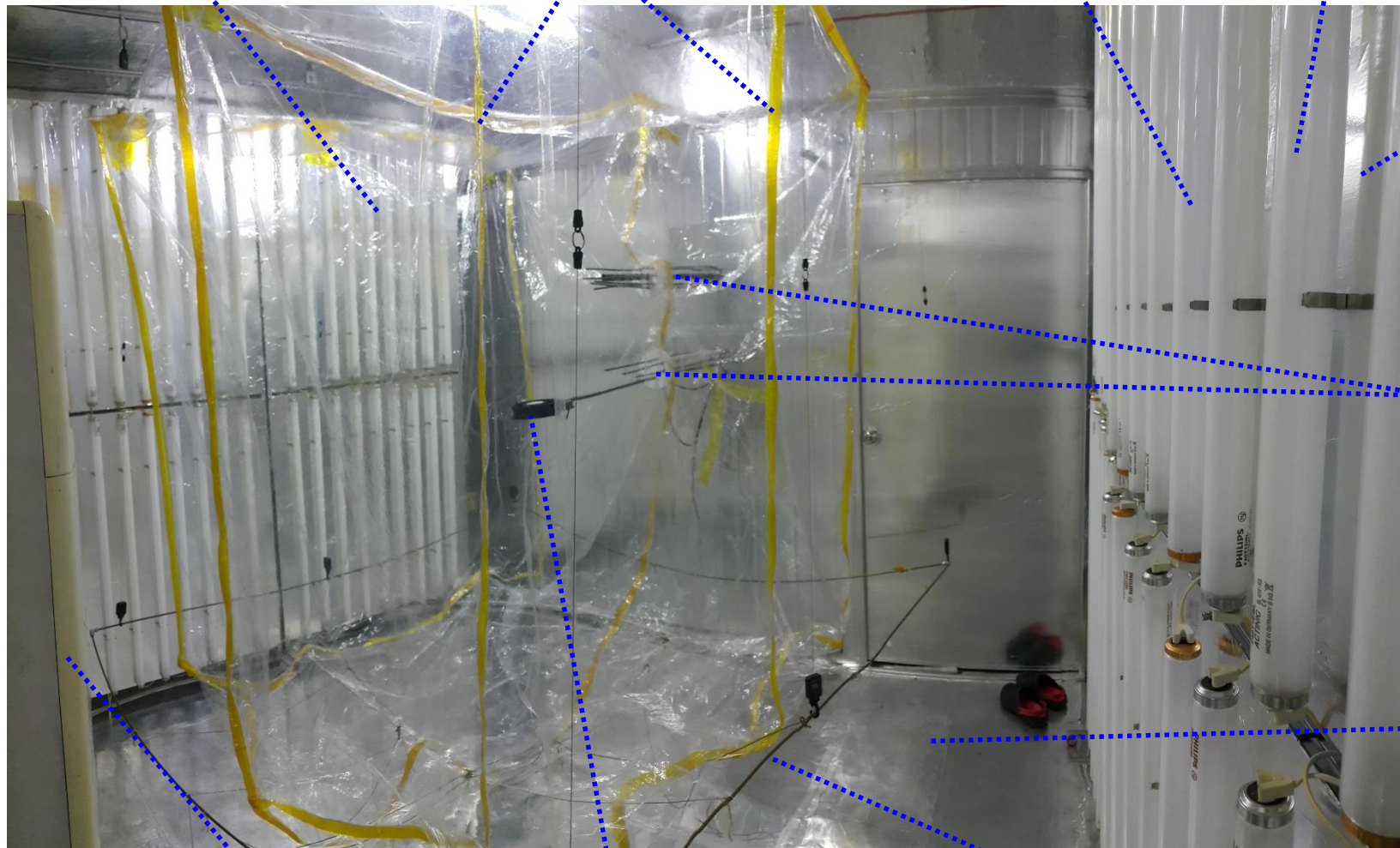
Teflon  
manifolds  
for tubing  
insertions

UV  
reflective  
Al sheets

Air conditioner

Mixing  
fan

Elastic  
string net



# KNU 스모그 챔버 : FEP 반응기 제작 및 설치

14

## ➤ 치수 측정



## ➤ 재단



## ➤ 열 밀봉



## ➤ 밀봉 검사



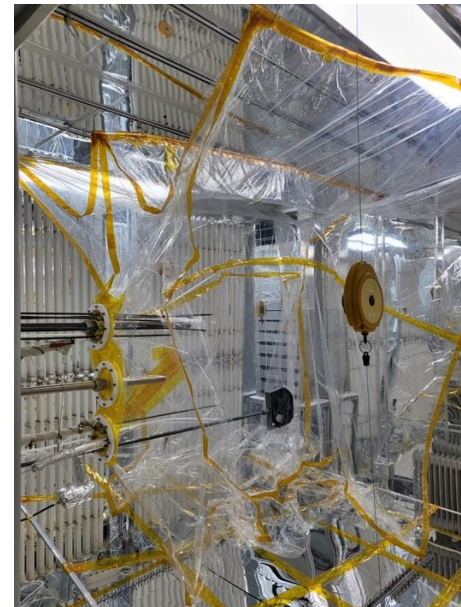
## ➤ 테프론 접착 테이프 보강



## ➤ 캡톤 접착 테이프 보강



## ➤ 설치





# KNU 스모그 챔버 : 공기 정화 장치



# KNU 스모그 챔버 : 공기 정화 장치

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Oil-free scroll air  
compressor



Ambient  
air



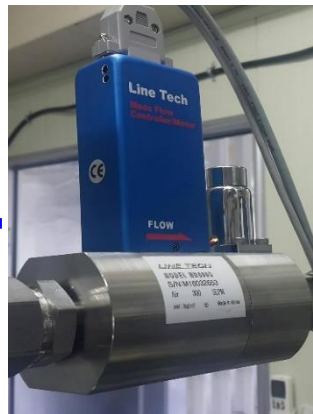
Pure air generator  
(Pressure Swing Adsorption)



FEP bag



Mass flow  
controller



HEPA filters



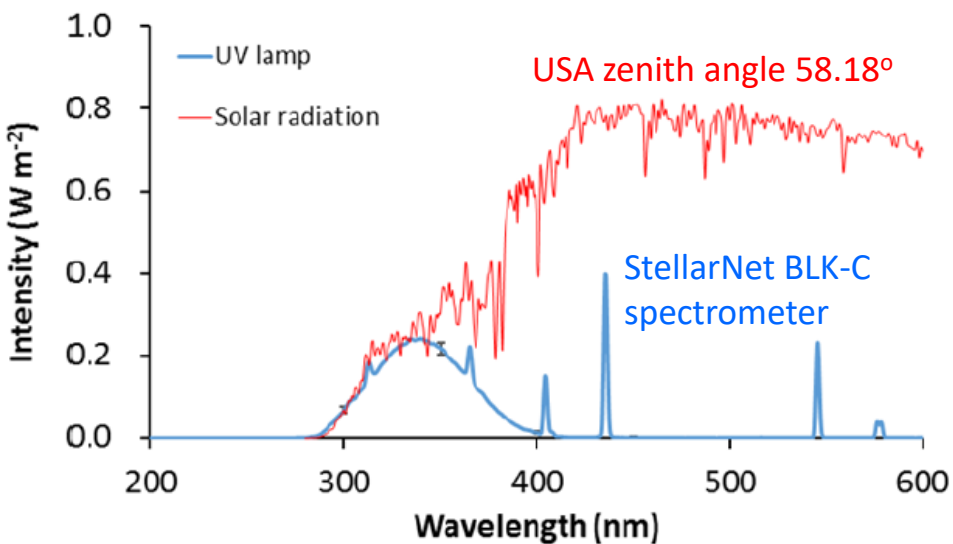
Dry gas  
meter



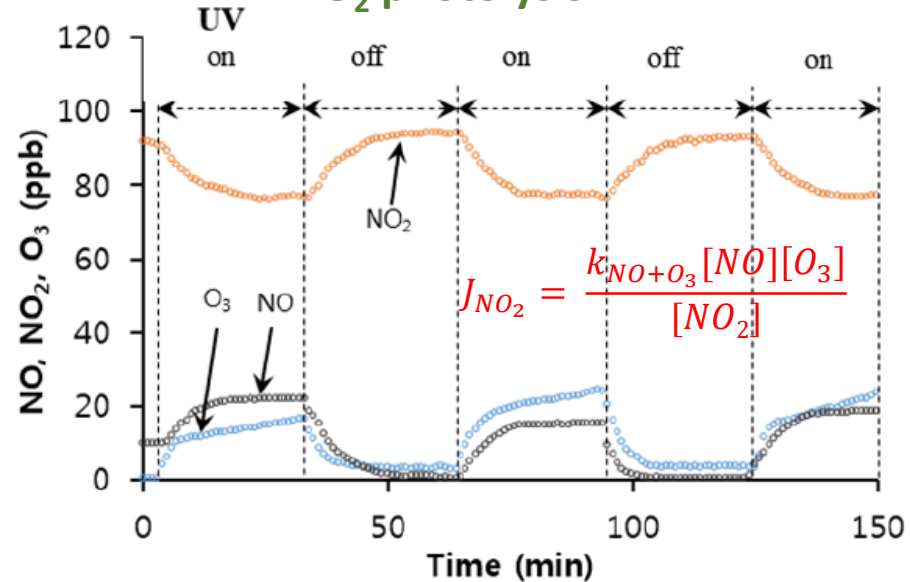
# KNU 스모그 챔버 : 특성 평가

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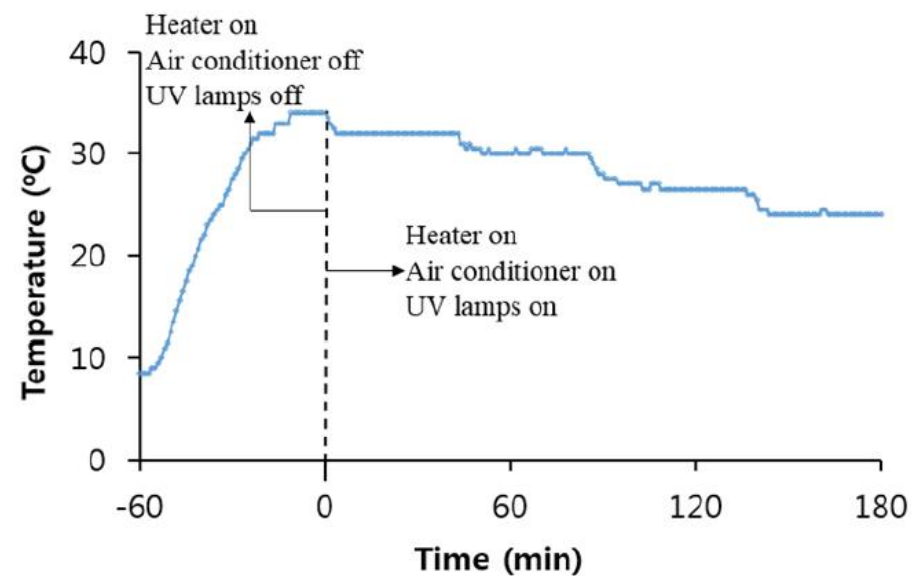
## UV lamp radiation spectrum



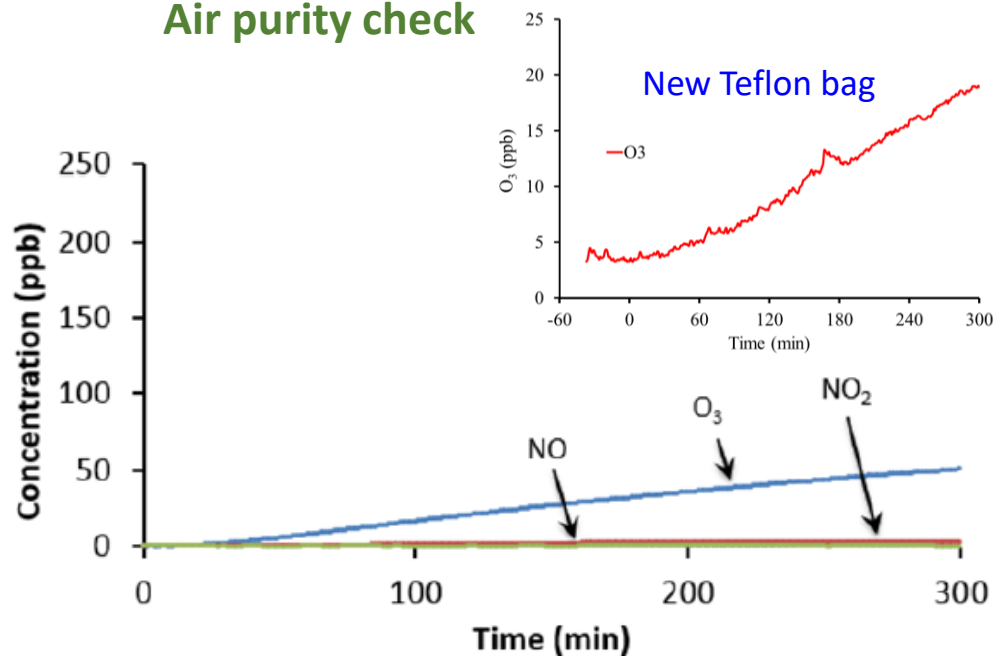
## $\text{NO}_2$ photolysis



## Temperature control

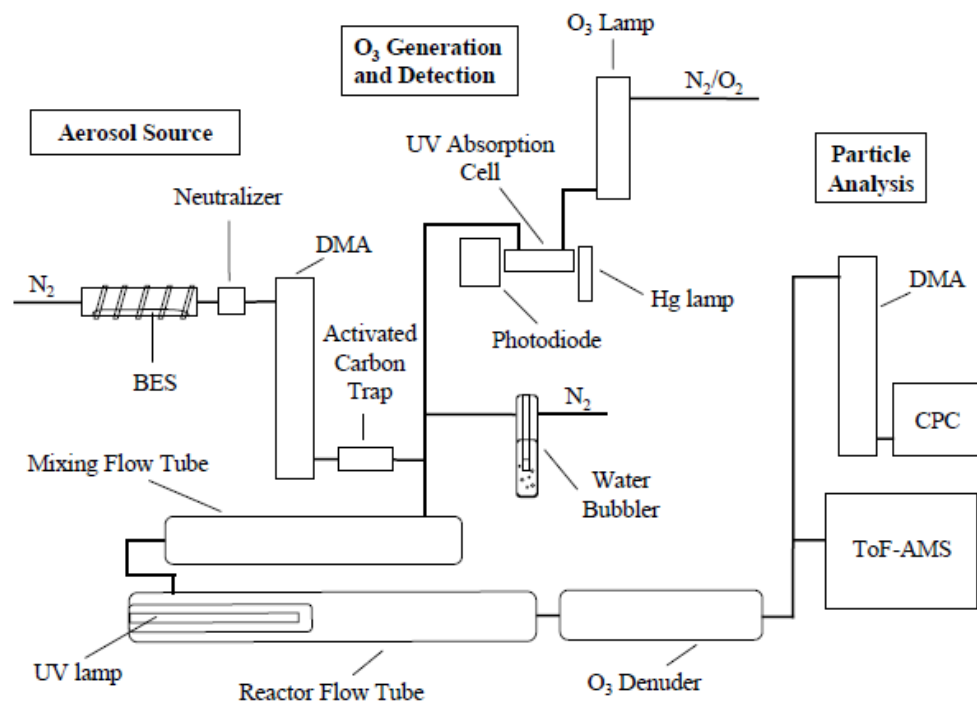


## Air purity check



# 대기화학 연구용 흐름 반응기의 전환점

## ➤ Toronto Photo-Oxidation Tube (TPOT) reactor

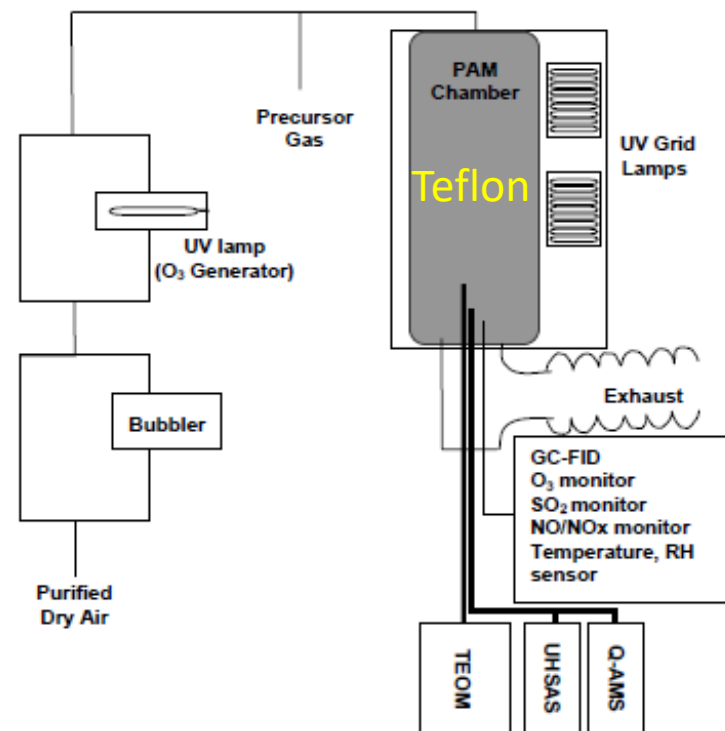


- Reactor: Glass, ID 7.3 cm x L 34 cm
- OH generation : single lamps (254 nm)



George et al., ACP (2007)

## ➤ Potential Aerosol Mass (PAM) flow reactor



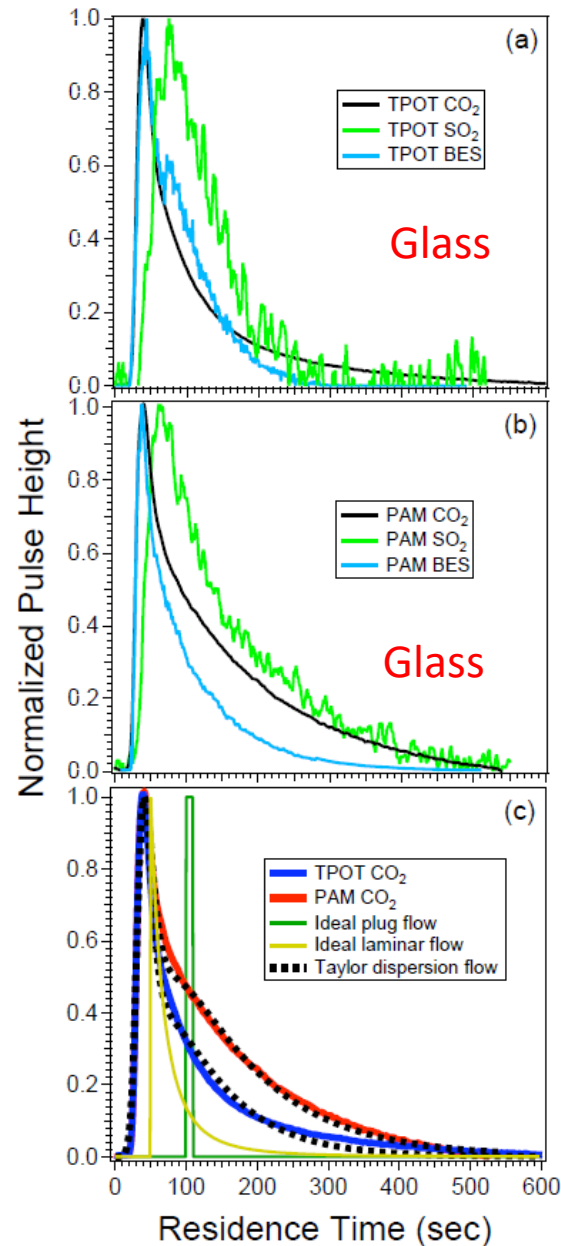
- Reactor: FEP, ID 20 cm x L 60 cm
- OH generation : dual lamps (185 nm, 254 nm)



Kang et al., ACP (2007)

# 흐름 반응기 상용화

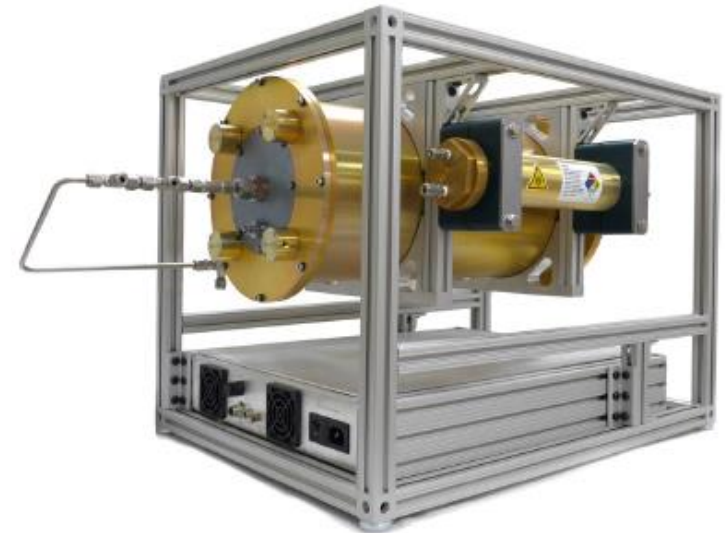
## ➤ Retention time distribution



Glass tube showed

- Long tailed retention time distribution much different from plug and laminar flow
- Delay of SO<sub>2</sub> due to adsorption

## ➤ Aerodyne PAM oxidation flow reactor



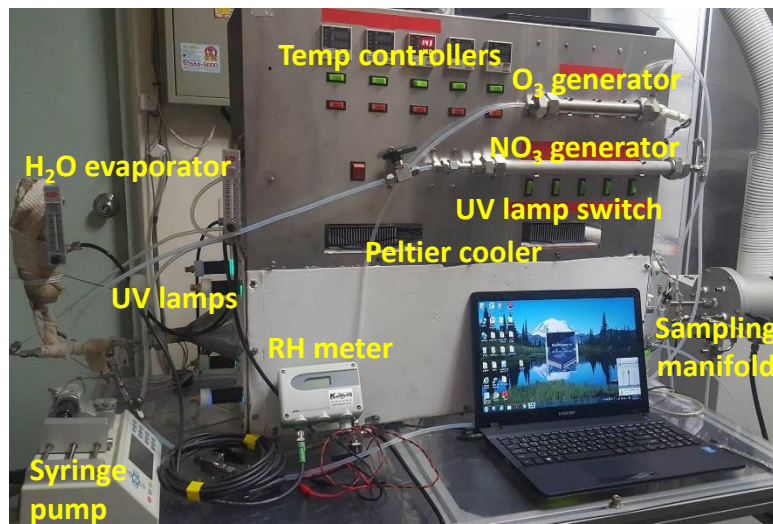
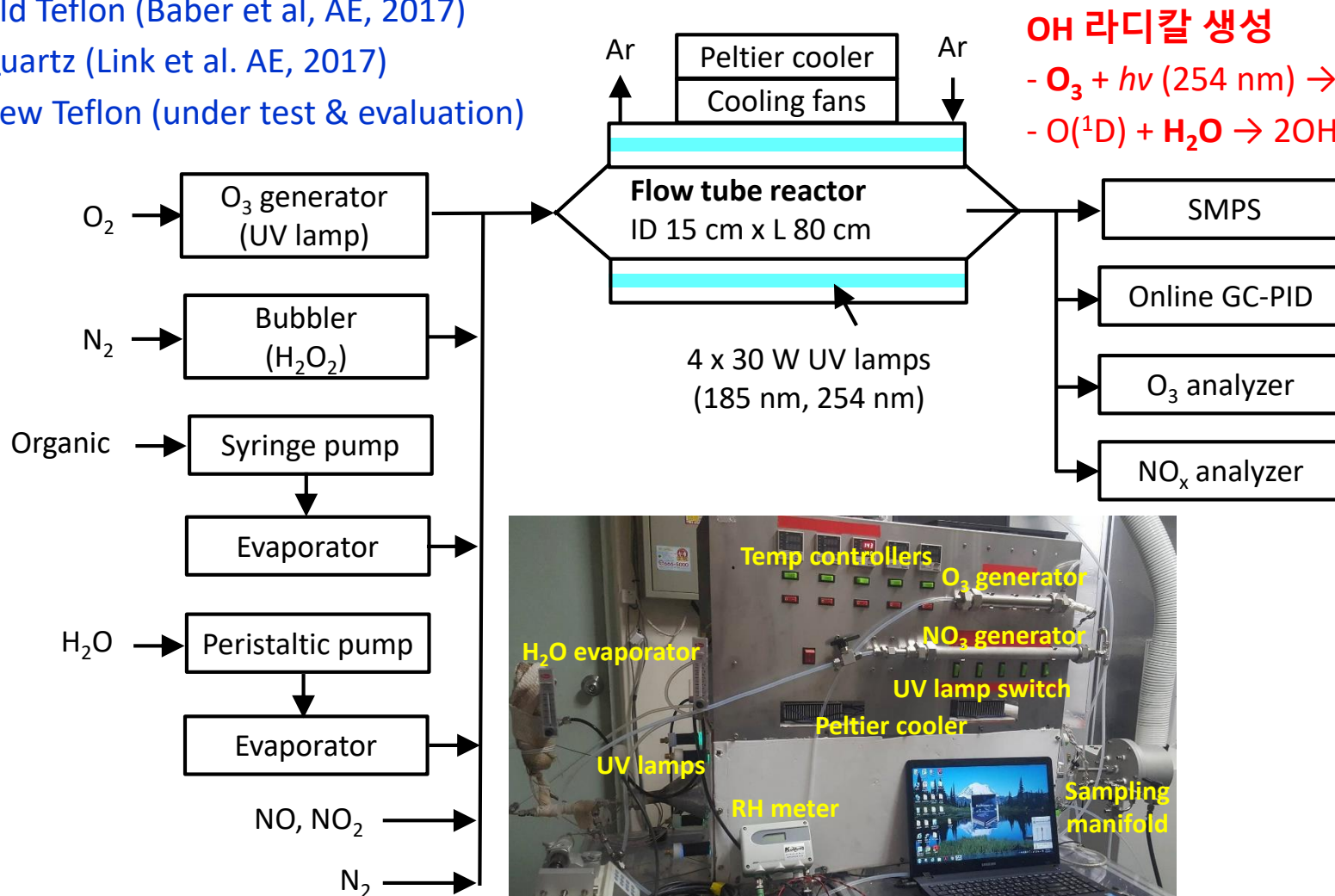
- Reactor
  - Aluminum tube with chrome plated inner surface to reduce adsorption
  - ID 22 cm x L 46 cm
- Dual lamps (185 nm, 254 nm)
  - $\text{H}_2\text{O} + h\nu (185 \text{ nm}) \rightarrow \text{OH} + \text{H}$
  - $\text{O}_2 + h\nu (185 \text{ nm}) \rightarrow 2\text{O}(^3\text{P})$
  - $2\text{O}(^3\text{P}) + \text{O}_2 \rightarrow \text{O}_3$
  - $\text{O}_3 + h\nu (254 \text{ nm}) \rightarrow \text{O}(^1\text{D}) + \text{O}_2$
  - $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$



# KNU Old Teflon Flow Tube Reactors

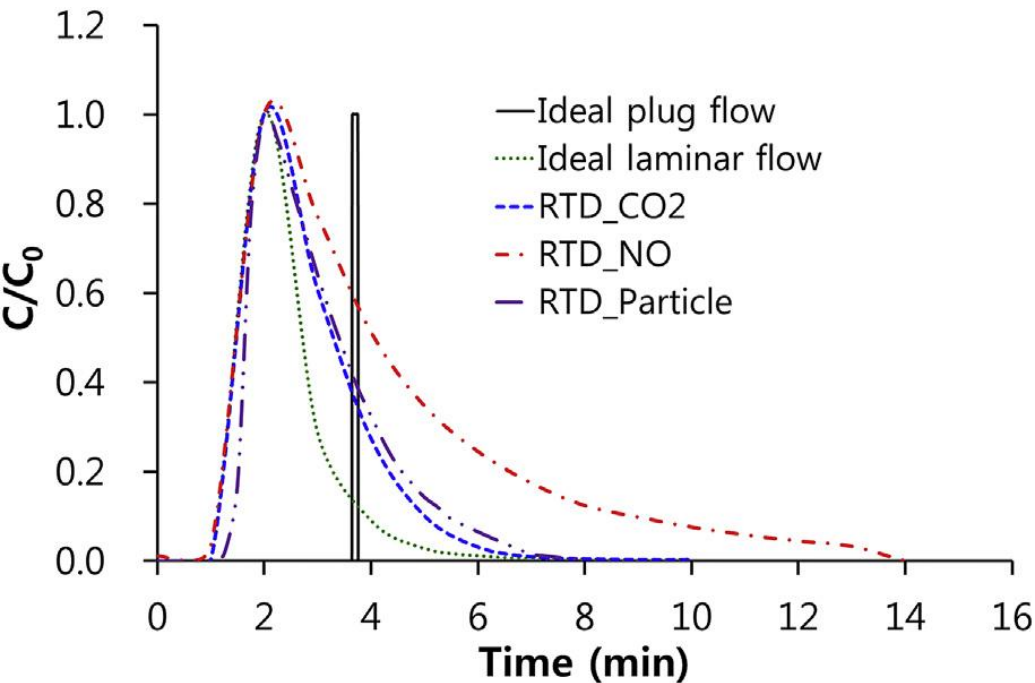
## Reactor material

- Old Teflon (Baber et al, AE, 2017)
- Quartz (Link et al. AE, 2017)
- New Teflon (under test & evaluation)



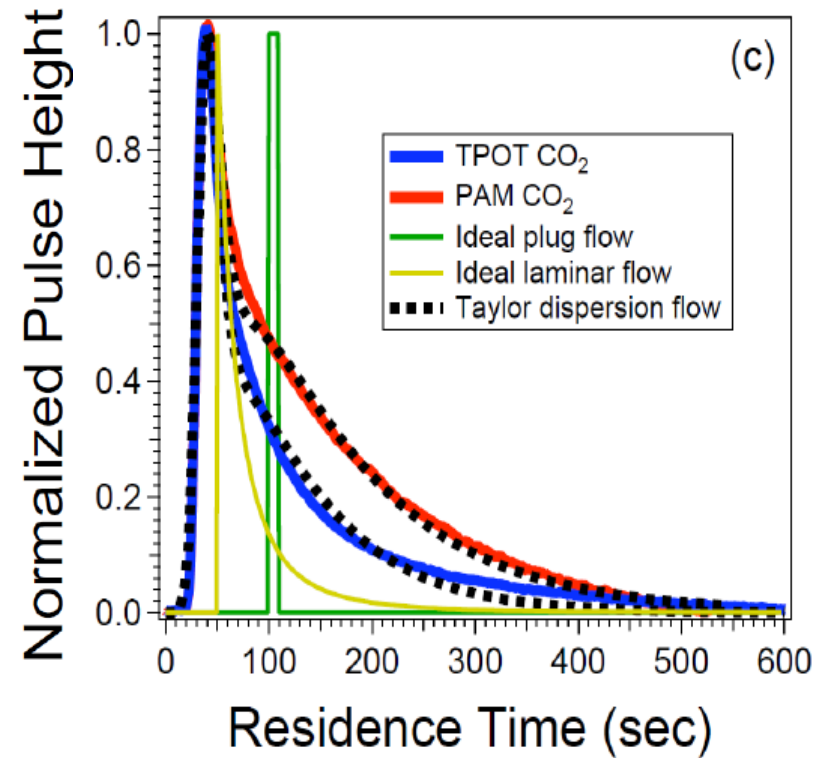
# Residence Time Distribution: KNU Old Teflon Flow Reactor <sup>21</sup>

## ➤ KNU old Teflon flow reactor



Babar et al., AE, 2017

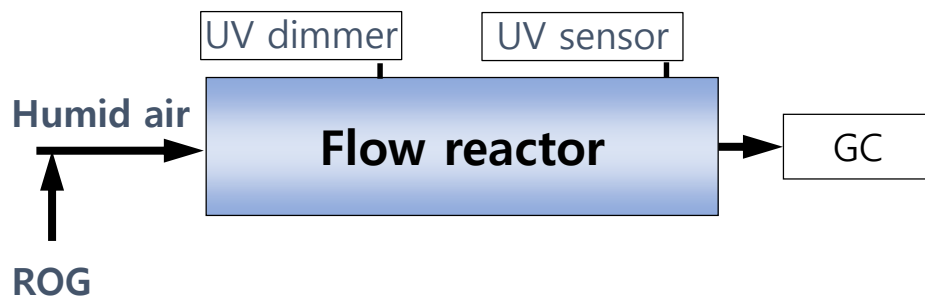
## ➤ PAM & TPOT



Lambe et al., AMT, 2011

# OH Exposure Calibration: KNU Quartz Flow Reactor

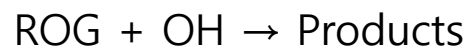
22



## ➤ Calibration setup

- Set UV intensity and RH
  - UV intensity adjusted by the voltage of UV lamp dimmer (UV dimmer)
  - RH adjusted by water vapor injection rate
- Measure consumption of ROG by GC
- Estimate OH concentration and atmospheric aging time of the reactor

## ➤ Estimation of OH radical concentration



$$d[\text{ROG}]/dt = -k_{\text{OH}+\text{ROG}}[\text{OH}][\text{ROG}]$$

$$= -k_{\text{OH}+\text{ROG,pseudo}}[\text{ROG}]$$

$$k_{\text{OH}+\text{ROG,pseudo}} = \ln([\text{ROG}]_0/[\text{ROG}]_{\text{tFR}})/t_{\text{FR}}$$

$$[\text{OH}] = k_{\text{OH}+\text{ROG,pseudo}} / k_{\text{OH}+\text{ROG}}$$

## ➤ Estimation of atmospheric aging time

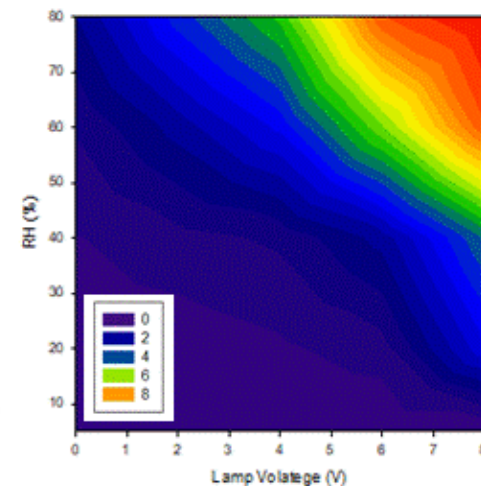
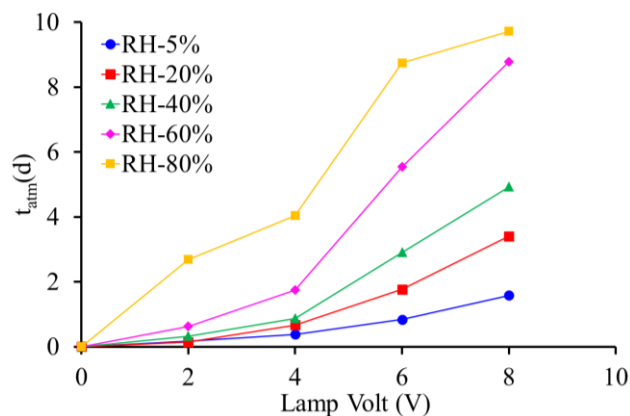
$$t_{\text{atm}} = \frac{[\text{OH}]_{\text{FR}} t_{\text{FR}}}{[\text{OH}]_{\text{atm}}}$$

$t_{\text{atm}}$  = atmospheric aging time (d)

$t_{\text{FR}}$  = residence time of flow reactor (d)

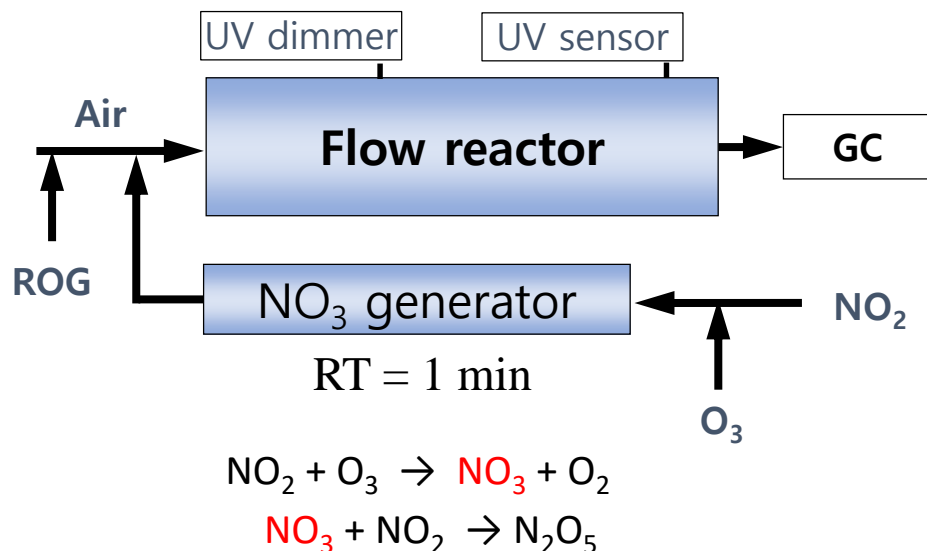
$[\text{OH}]_{\text{FR}}$  = [OH] of reactor (molecules  $\text{cm}^{-3}$ )

$[\text{OH}]_{\text{atm}}$  = [OH] of atmosphere (molecules  $\text{cm}^{-3}$ )  
 $= 1.5 \times 10^{-5}$  molecules  $\text{cm}^{-3}$

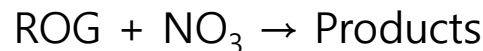


# NO<sub>3</sub> Exposure Calibration: KNU Quartz Flow Reactor

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- Estimation of NO<sub>3</sub> radical concentration



$$d[\text{ROG}]/dt = -k_{\text{NO}_3+\text{ROG}}[\text{NO}_3][\text{ROG}]$$

$$= -k_{\text{NO}_3+\text{ROG,pseudo}}[\text{ROG}]$$

$$k_{\text{NO}_3+\text{ROG,pseudo}} = \ln([\text{ROG}]_0/[\text{ROG}]_{\text{tFR}})/t_{\text{FR}}$$

$$[\text{NO}_3] = k_{\text{NO}_3+\text{ROG,pseudo}} / k_{\text{OH}+\text{ROG}}$$

- Estimation of atmospheric aging time

$$t_{\text{atm}} = \frac{[\text{NO}_3]_{\text{FR}} t_{\text{FR}}}{[\text{NO}_3]_{\text{atm}}}$$

$t_{\text{atm}}$  = atmospheric aging time (d)

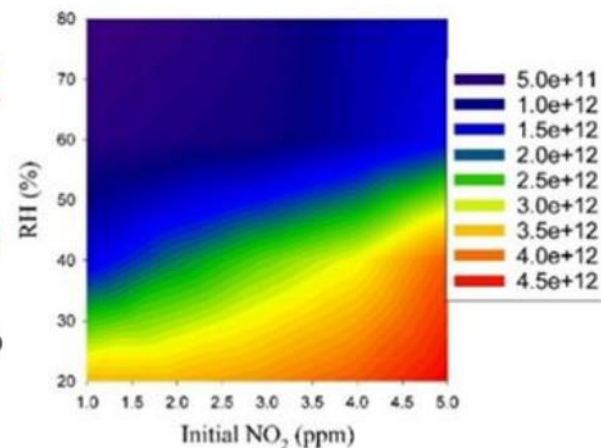
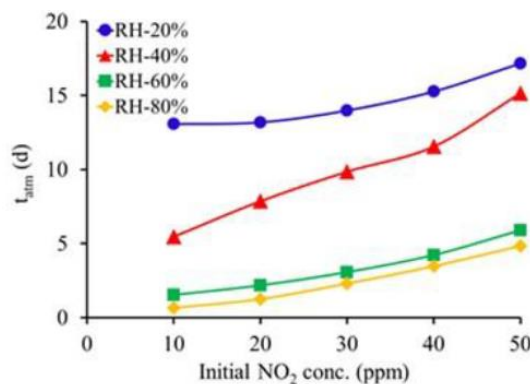
$t_{\text{FR}}$  = residence time of flow reactor (d)

$[\text{OH}]_{\text{FR}}$  = [OH] of reactor (molecules cm<sup>-3</sup>)

$[\text{OH}]_{\text{atm}}$  = [OH] of atmosphere (molecules cm<sup>-3</sup>)  
= 1.5x10<sup>-5</sup> molecules cm<sup>-3</sup>

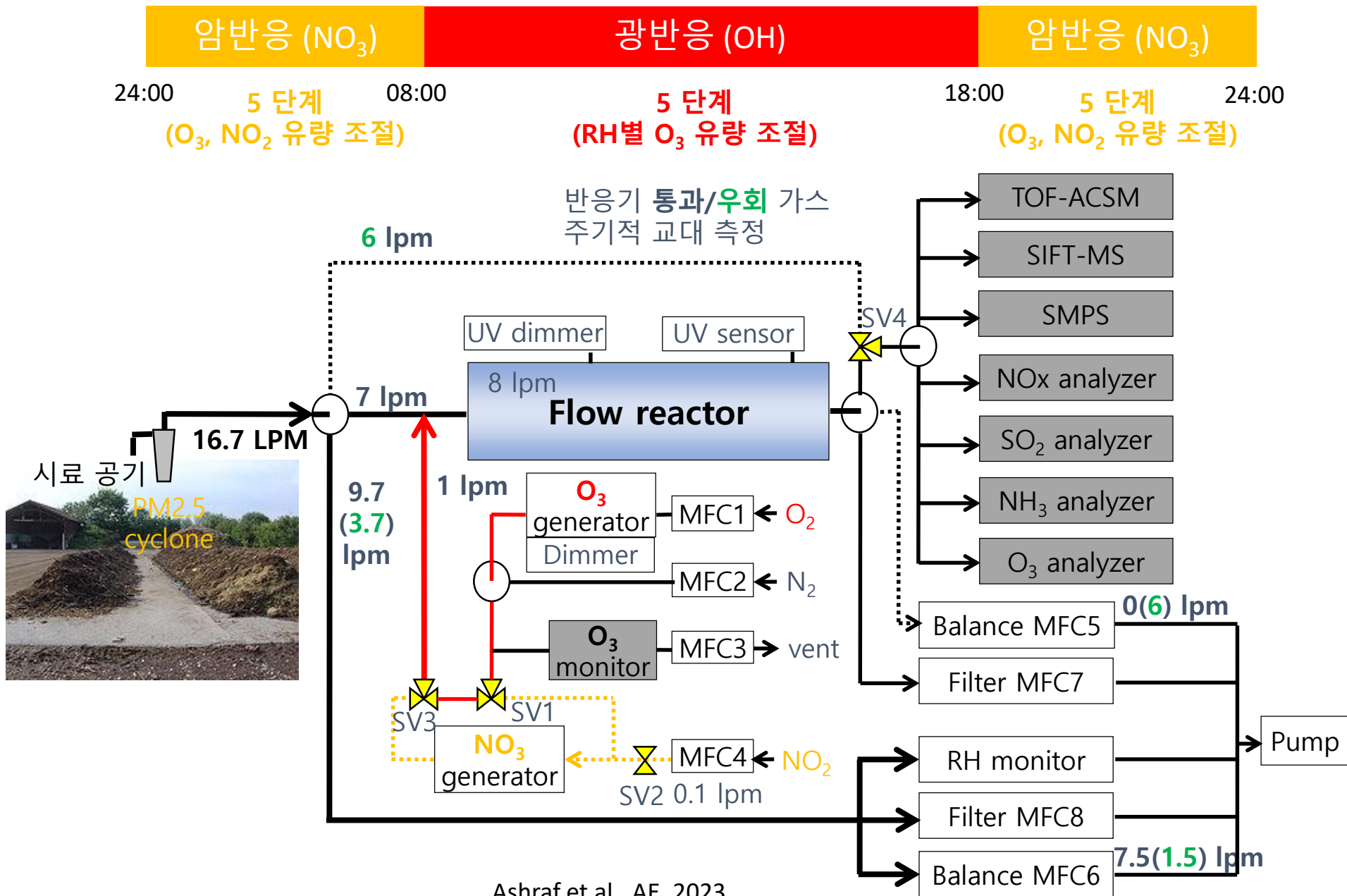
- Calibration setup

- Set NO<sub>2</sub> and O<sub>3</sub> concentration
- Measure consumption of ROG by GC
- Estimate NO<sub>3</sub> concentration and atmospheric aging time of the reactor



# Automated Operation of KNU Quartz Flow Reactor

24



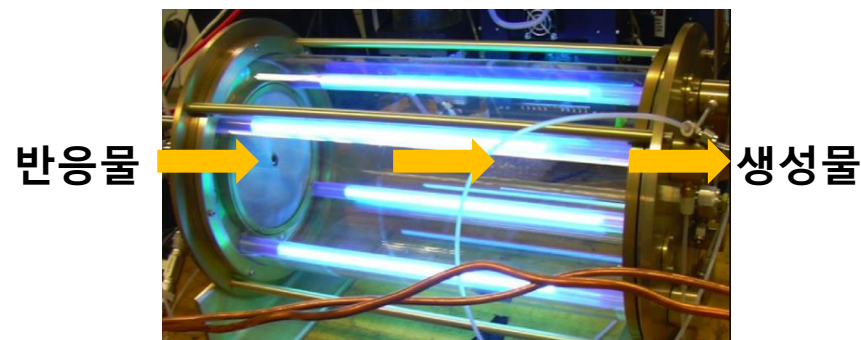


# Comparison of Reactor Systems for SOA Formation

## Semi-Batch reactor: Smog chamber



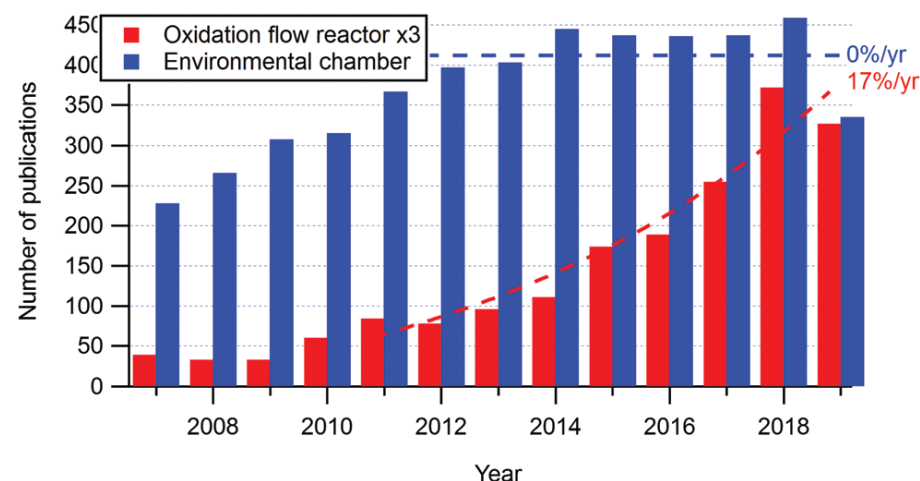
## Flow reactor



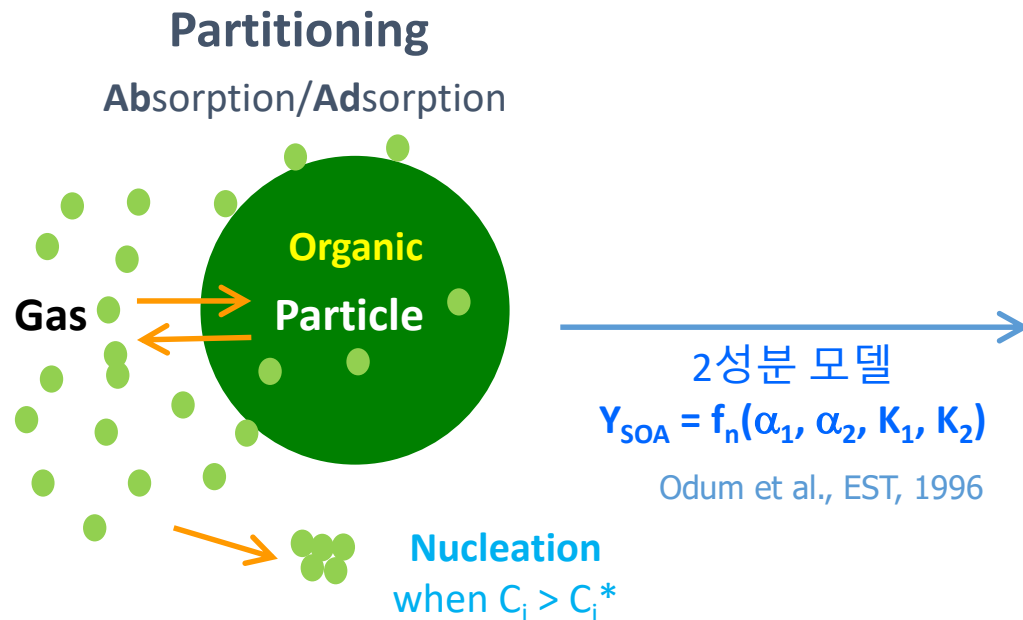
### 스모그 챔버와 흐름반응기 비교

	Smog chamber	Flow reactor
Oxidant	<b>OH, O<sub>3</sub>, NO<sub>3</sub></b>	<b>OH, O<sub>3</sub>, NO<sub>3</sub></b>
UV radiation	UVA (>300 nm)	UVC (254 nm, 185 nm)
OH radical conc.	10 <sup>6</sup> - 10 <sup>7</sup> #/cm <sup>3</sup>	10 <sup>8</sup> - 10 <sup>10</sup> #/cm <sup>3</sup>
Experimental time	~ hr	~ min
Atmospheric aging time	1 d	1 - 30 d
O <sub>3</sub> conc.	<~ ppm	~ 1000 ppm
Setup time	> 1 d	~ min
Mobility	immobile	mobile
Uncertainty in aging time	none	Very large
Surface effect	large	Very large

### 연구논문 발표 수



Peng & Jimenez, Chem SOC Rev, 2020



$$K_p = \frac{P_i/TSP}{G_i} = \frac{f_{om} 760RT}{p_{Li}^0 \zeta_i MW_{om} 10^6}$$

$K_{p,i}$  ( $m^3/\mu g$ ) = particle/gas partition constant of species  $i$

$P_i$  ( $\mu g/m^3$ ) = particle phase concentration of organic  $i$

TSP ( $\mu g/m^3$ ) = total suspended particle concentration

$G_i$  ( $\mu g/m^3$ ) = gas phase concentration of organic  $i$

$f_{om}$  = fraction of organic matter

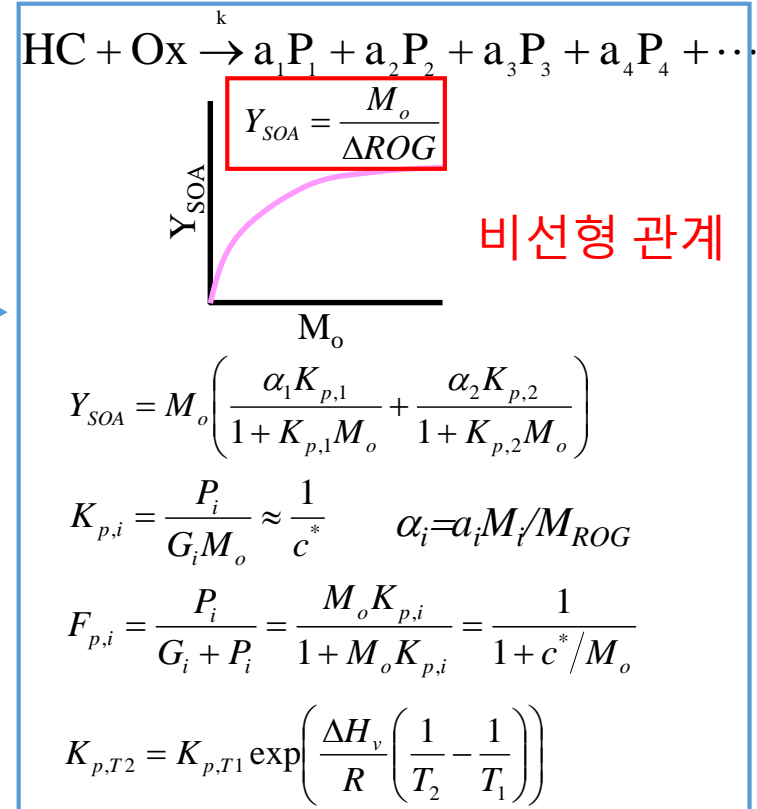
$R$  (atm-L/mol-K) = ideal gas constant

$T$  (K) = temperature

$p_{L,i}^0$  (atm) = vapor pressure

$\zeta_i^*$  = activity coefficient of organic  $i$

$MW_{om}$  (g/mol) = molecular weight of organic matter



$Y_{SOA}$  = SOA yield =  $M_o / \Delta ROG$

$F_p$  = fraction of organic in particle

$C_i^*$  ( $\mu g/m^3$ ) = effective saturation concentration

$M_o$  ( $\mu g/m^3$ ) = organic aerosol mass concentration

$\alpha_i$  = mass stoichiometric coefficient of species  $i$

$K_{p,i}$  ( $m^3/\mu g$ ) = particle/gas partitioning constant of species  $i$

$T$  (K) = temperature

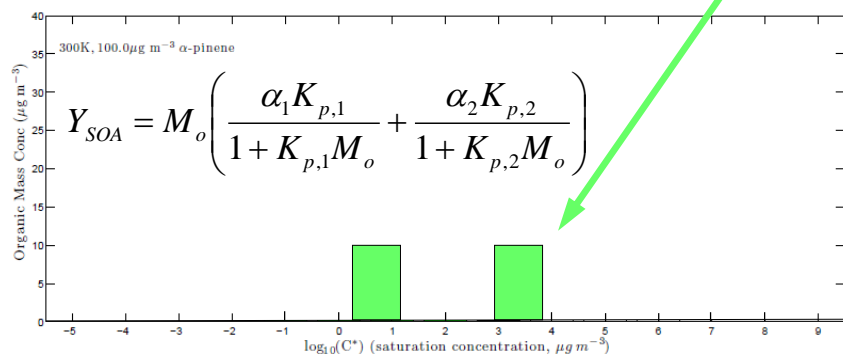
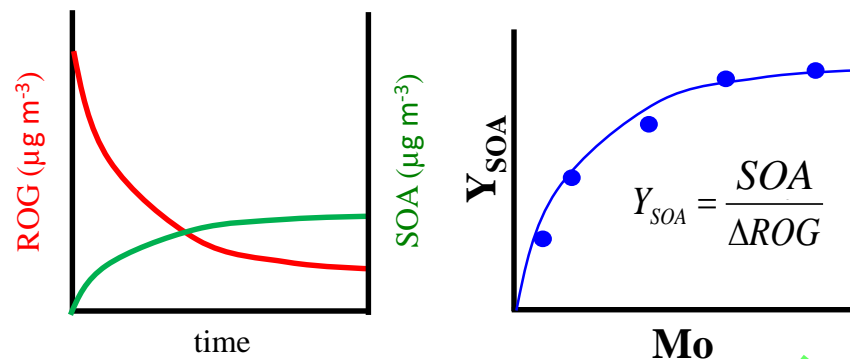
$1000 \alpha_i \Delta ROG = P_i + G_i$

# SOA 생성수율 모수화 : 2 생성물 모델 vs. VBS

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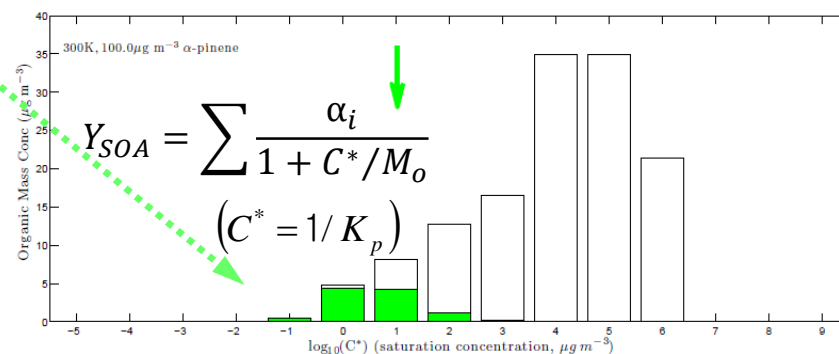
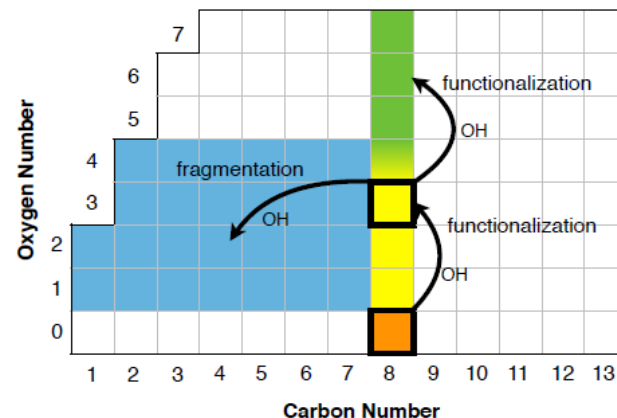
2 Product model  
(Odum et al, ES&T, 1996)



$$N_i = 2 (\alpha_i, K_{pi})$$

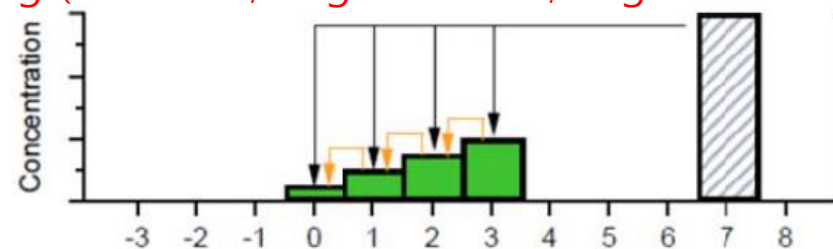
No aging

Volatility Basis Set (VBS)  
(Donahue et al, ACP, 2012)

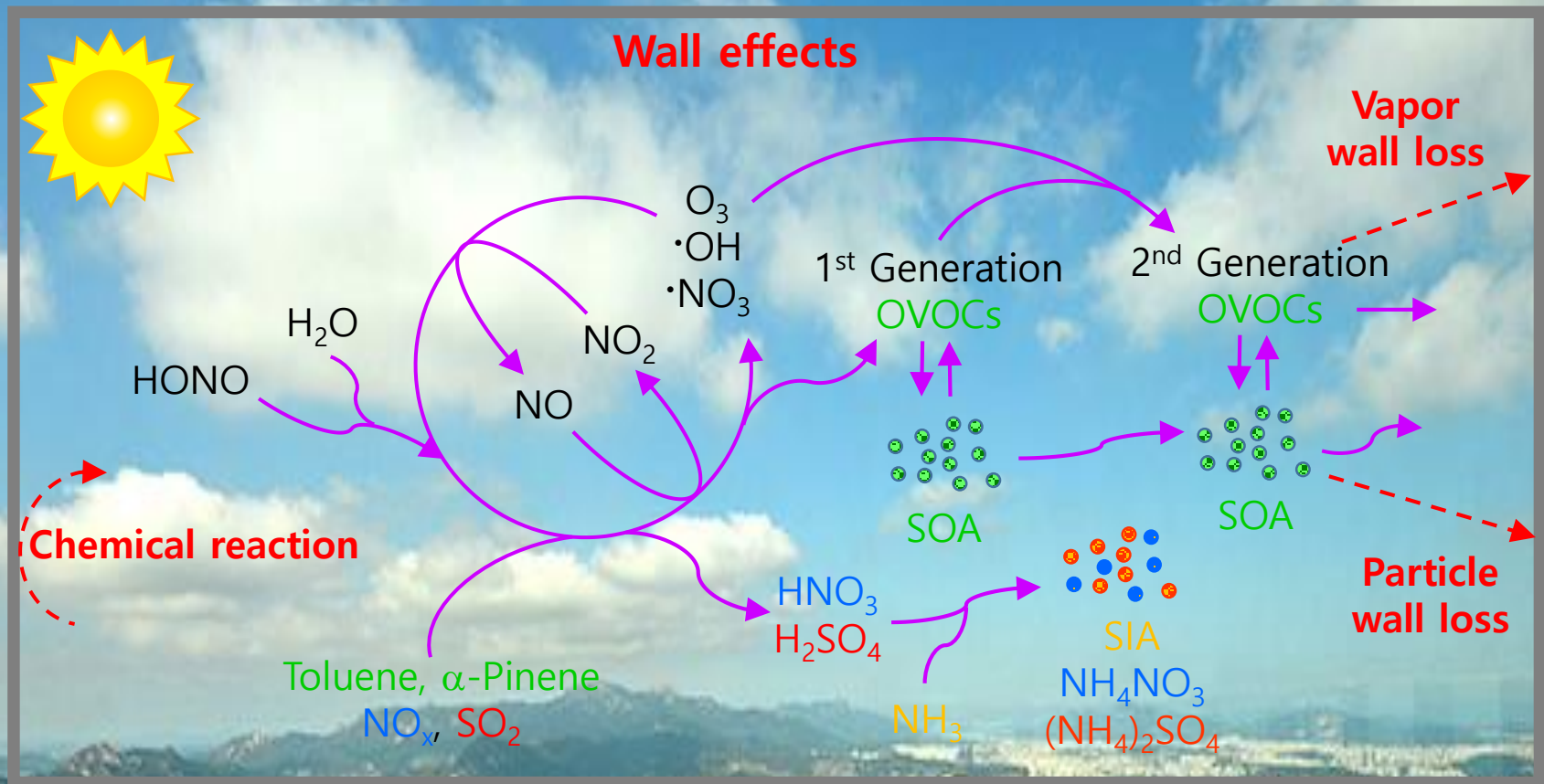


$$N_i \geq 2 (\alpha_i, C_i^*)$$

Aging (oxidation, fragmentation, oligomerization)



# 스모그 챔버의 벽면 효과



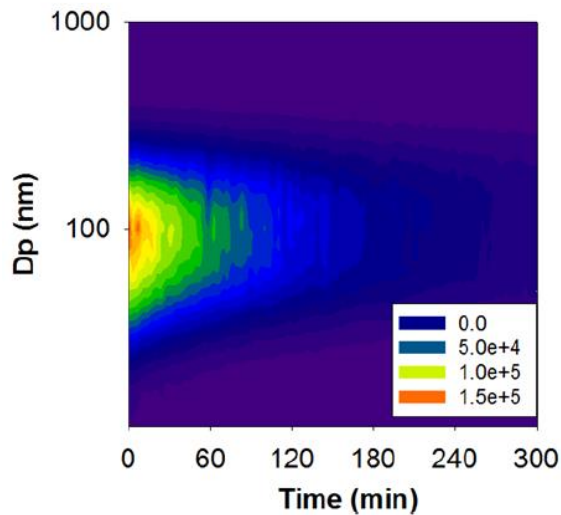


# 스모그 챔버의 벽면 효과 : 입자 벽 손실 및 보정

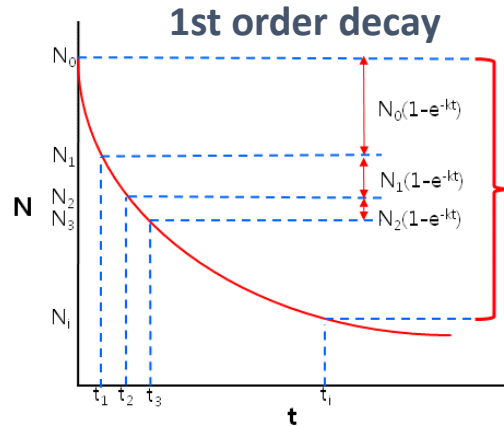
## ➤ 침적 손실

- 입자의 브라운 운동, 정전기적 인력, 중력에 의한 침적 손실
- 입경별 수농도 손실 속도상수, 부피/질량농도의 손실 속도상수를 이용하여 보정 가능
- 입경별 수농도 손실 속도상수를 이용한 보정이 가장 적절

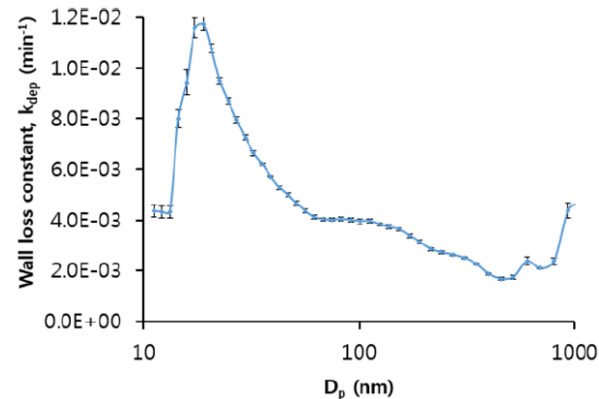
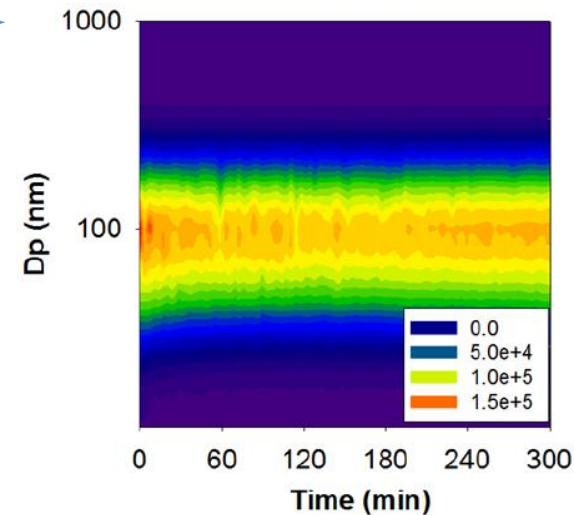
**Before correction**



**Size-dependent wall loss correction**

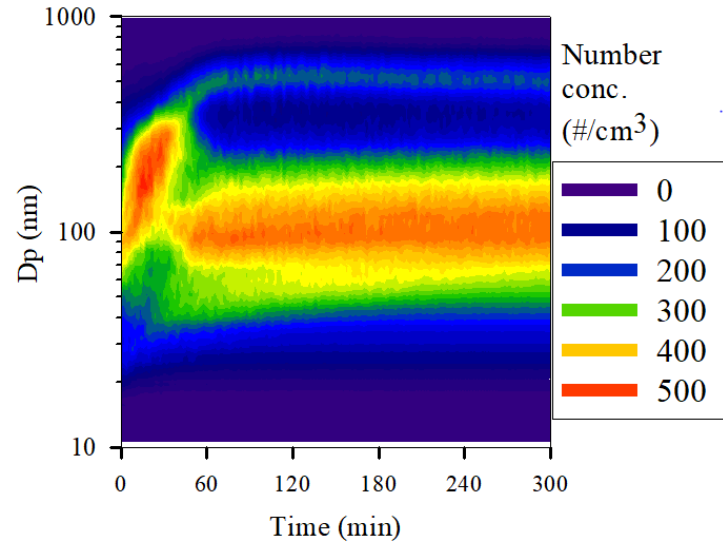


**After correction**

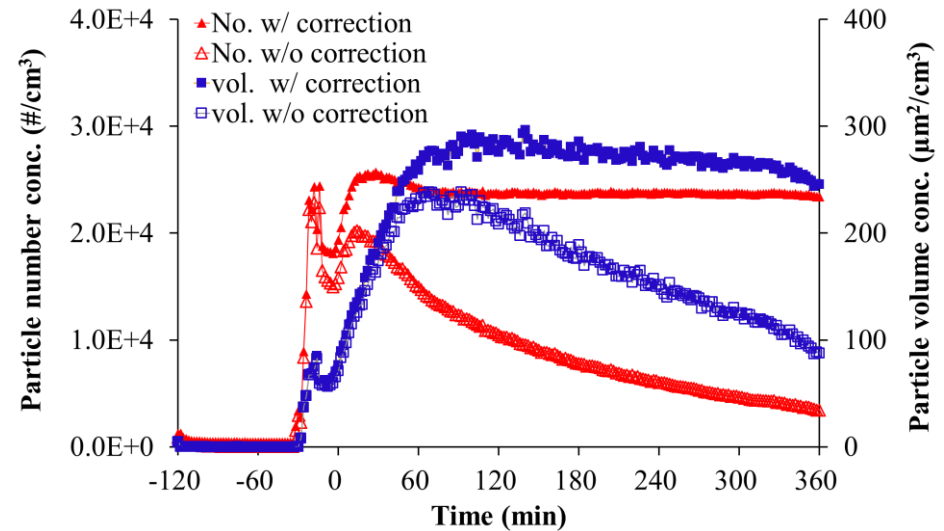


# SOA 생성시 에어로졸, 가스, 온도, 습도 측정 : 1,2,4-TMB

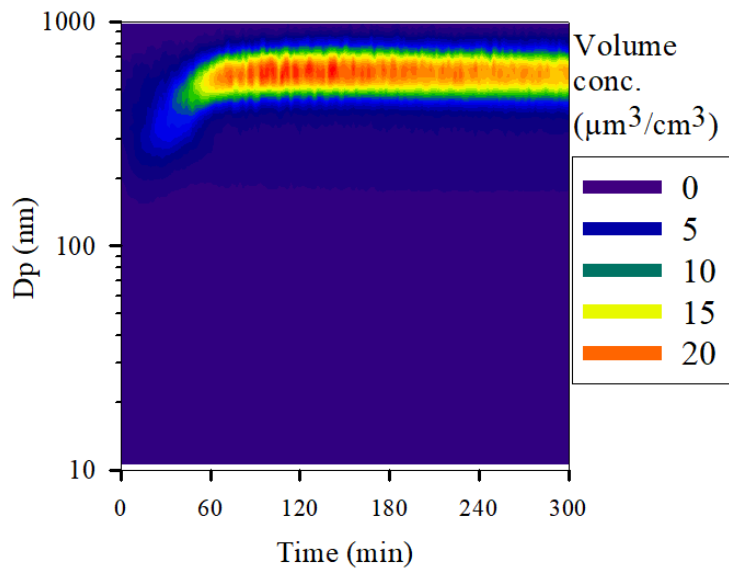
## 입자 수농도의 입도 분포



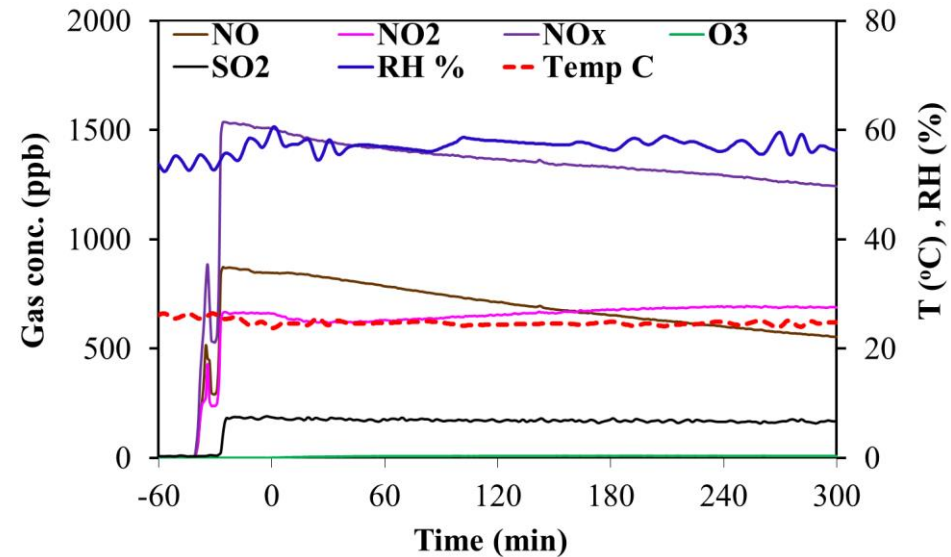
## 입자의 벽 손실 보정



## 입자 부피농도의 입도분포



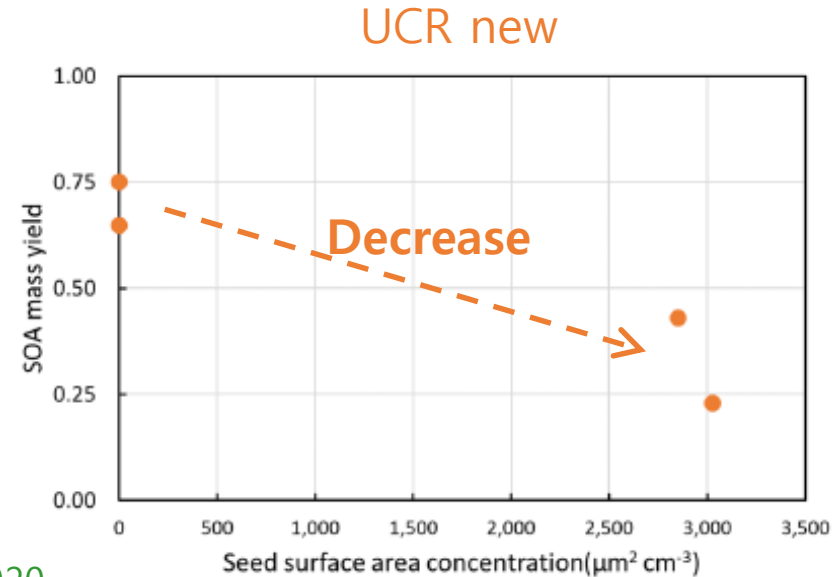
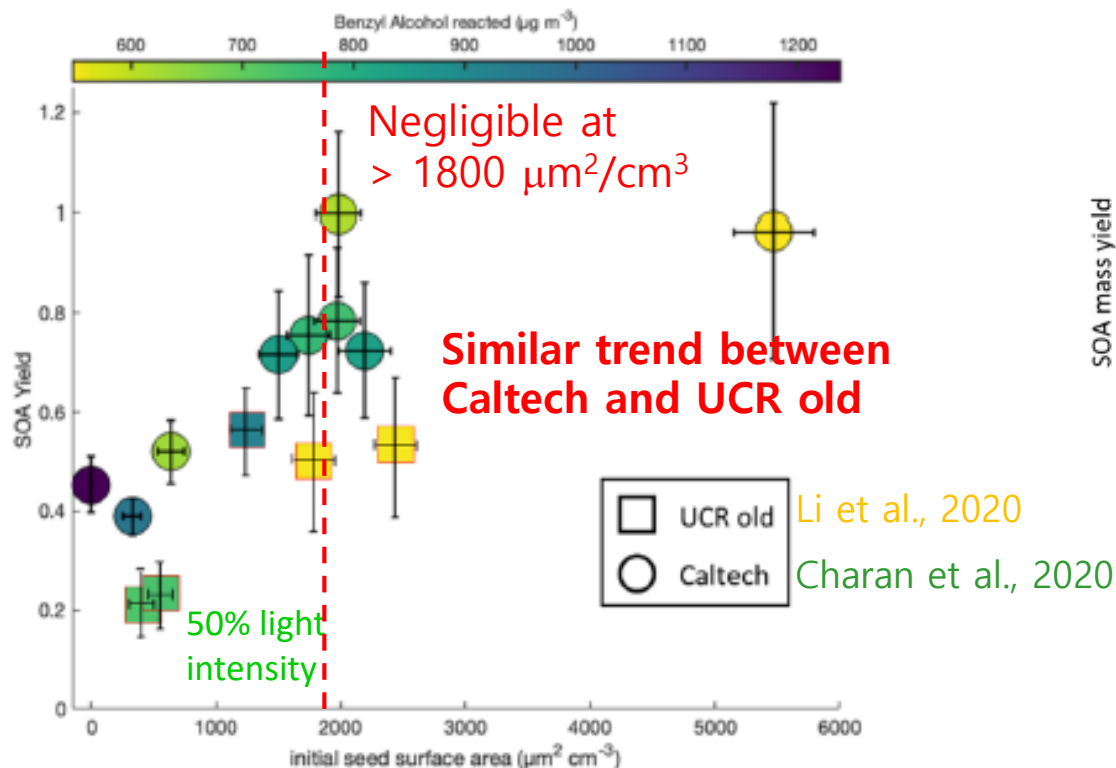
## 가스 농도, 온도, 습도



# 스모그 챔버의 벽면 효과 : 증기 벽 손실

## ➤ 흡착 손실

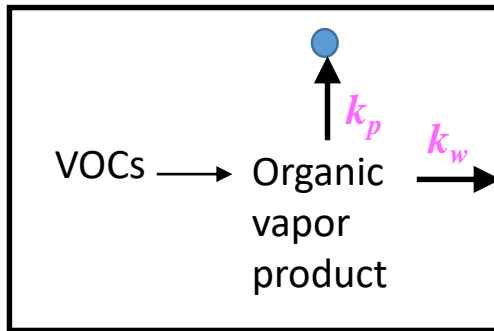
- 휘발도가 낮은 유기성분의 흡착 손실로써 특히 입자의 표면적 농도가 낮을수록 증가하며, SOA 생성수율의 감소로 이어짐
- 핵 입자 표면적 농도가 SOA 생성수율에 미치는 영향에서 상당한 편차가 보고됨 (Zhang et al., 2014, Nah et al., 2016, Charan et al., 2019, 2020, Li et al., 2022)
- 속도 모델을 이용한 증기 흡착 손실의 보정 가능



“further investigation is definitely required before any speculations being given”

# 스모그 챔버의 벽면 효과 : 입자 벽 손실 및 보정

- Kinetic theory of vapor loss: competition between particle and wall surface (Zhang et al., 2014; Li et al., 2021)



- Loss rate coefficient

$$k_p = 2\pi N_p \bar{D}_p D_{\text{gas}} \bar{F}_{FS}$$

$$k_w = \left(\frac{A}{V}\right) \frac{\alpha_w \bar{c}}{1.0 + \frac{\pi}{2} \left[ \frac{\alpha_w \bar{c}}{4(k_e D_{\text{gas}})^{0.5}} \right]}$$

- Life time

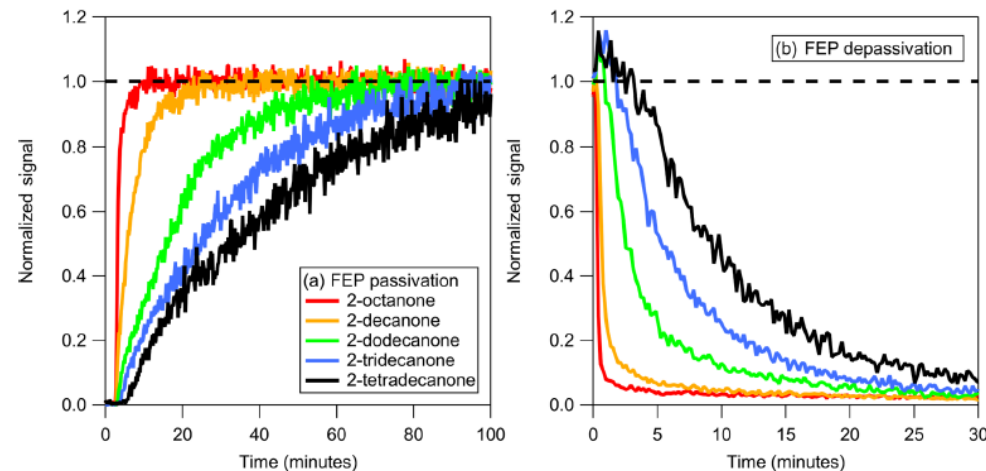
$$\tau_{g-p} = 1/k_p$$

$$\tau_{g-w} = 1/k_w$$

- Vapor wall loss correction factor

$$R_{\text{wall}} = \frac{k_p + k_w}{k_p} = \frac{\tau_{g-p} + \tau_{g-w}}{\tau_{g-w}}$$

- Vapor wall loss depends on both the characteristics of chamber and vapor



Deming et al., 2019

$N_p$  = particle number concentration

$\bar{D}_p$  = particle mean diameter

$D_{\text{gas}}$  = gas phase diffusion coefficient

$\bar{F}_{FS}$  = Fuchs–Sutugin correction term

$A/V$  = surface (A) / volume (V) of chamber

$\alpha_w$  = mass accommodation coefficient of vapor onto the chamber wall

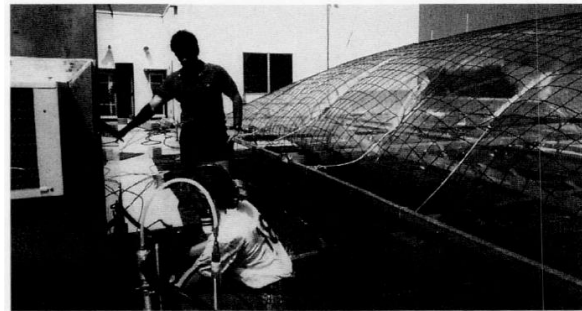
$\bar{c}$  = mean thermal velocity of vapor

$k_e$  = coefficient of eddy diffusion

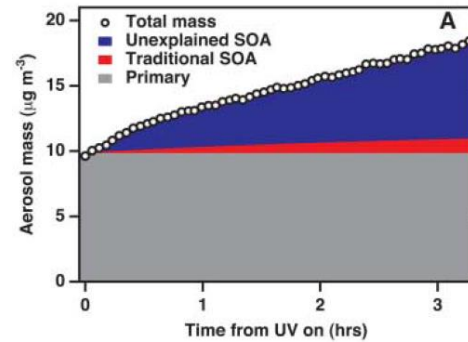
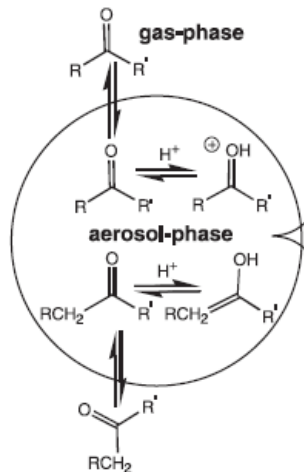
$D_{\text{gas}}$  = diffusion coefficient of vapor



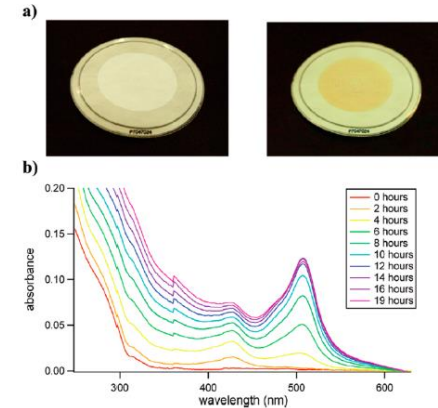
# 이차유기입자 생성 연구의 중요한 성과



Gas phase chemistry



Multigeneration aging



Brown carbon

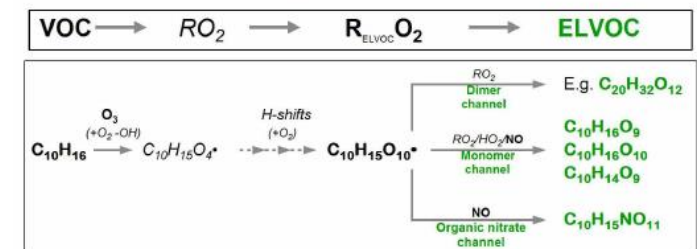
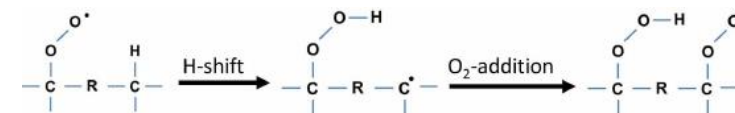
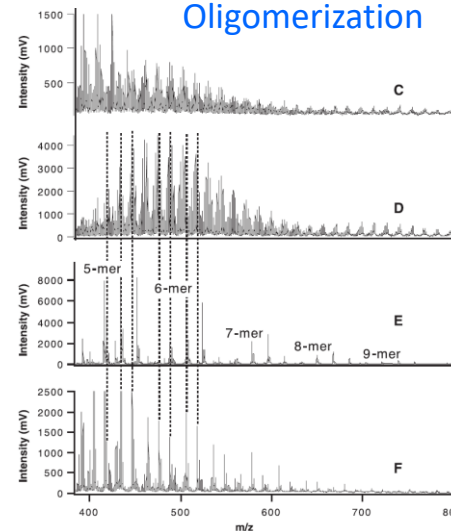
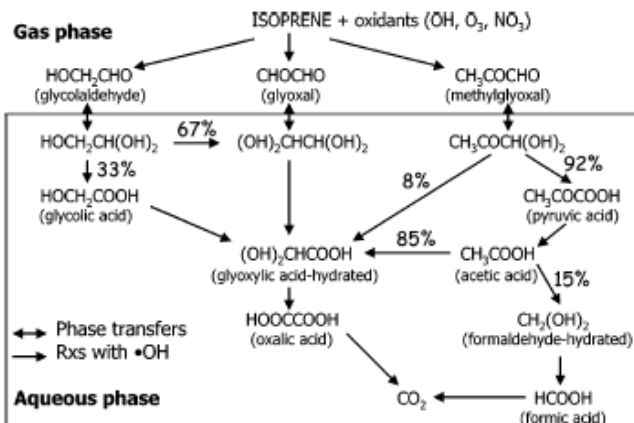
1970 1980 1990 2000 2010 2020

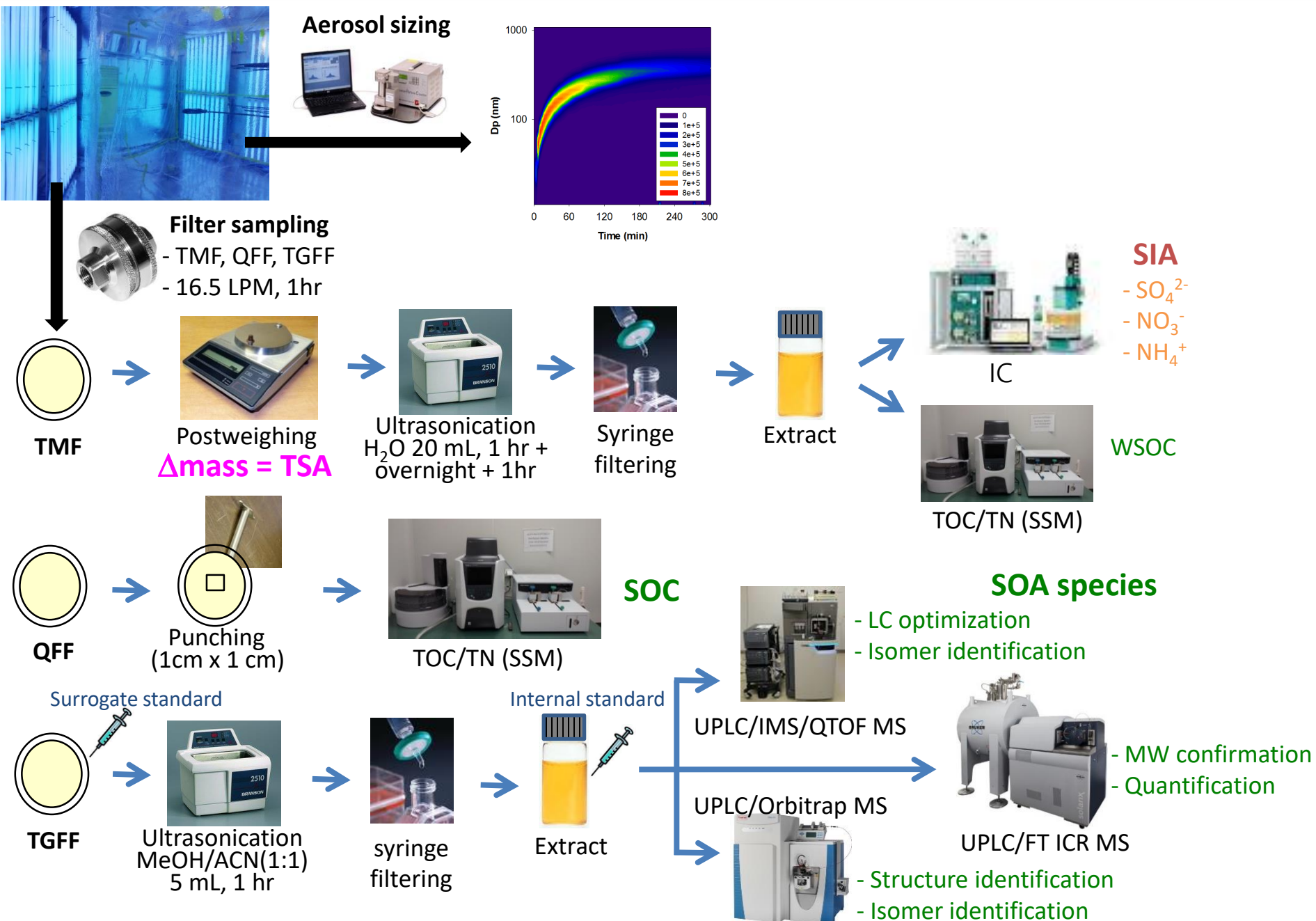
Aqueous chemistry

Acid catalyzed surface chemistry

Autooxidation forming ELVOC

Oligomerization

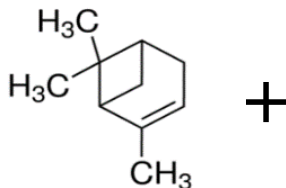




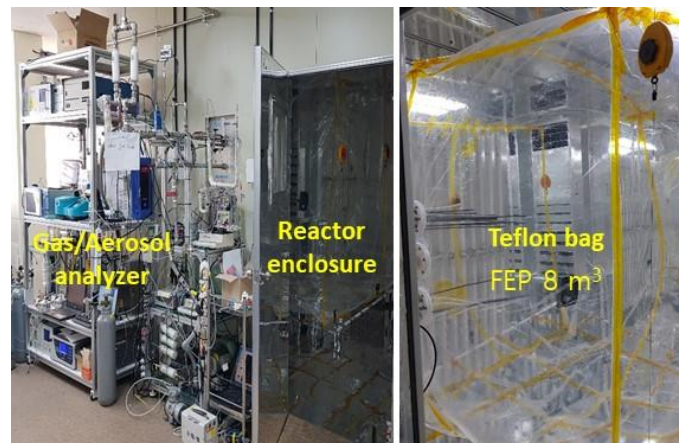
# $\alpha$ -피넨 SOA의 $\text{NO}_x$ 영향 : 화학조성 – 질소 함유 성분 (CHON)

## SOA 생성 및 시료 채취

### 스모그챔버



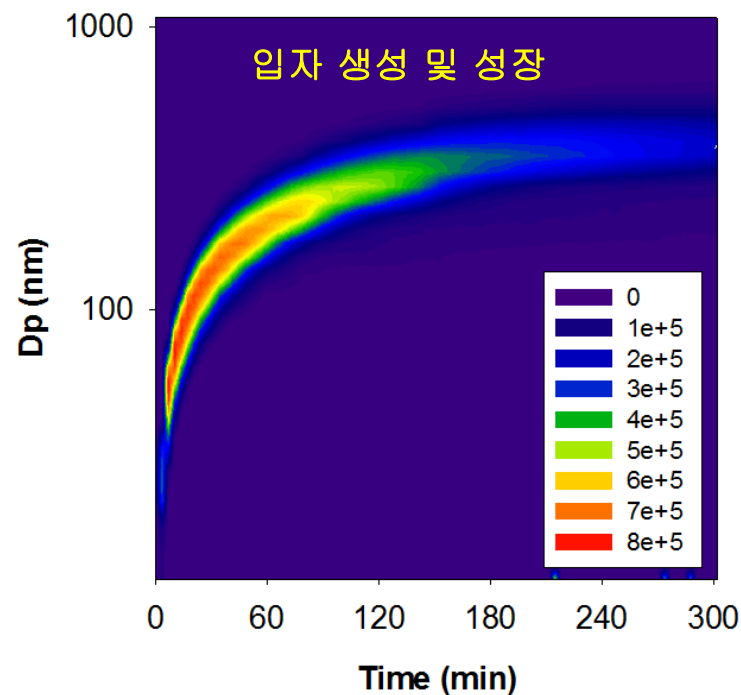
1.  $\text{O}_3$  ( $\text{O}_3$ )
2.  $\text{O}_3$  + n-hexane ( $\text{O}_3 + \text{HX}$ )
3.  $\text{H}_2\text{O}_2$  +  $h\nu$  ( $\text{OH}$ )
4.  $\text{H}_2\text{O}_2$  +  $\text{NO}$  +  $h\nu$  ( $\text{OH} + \text{NO}$ )
5.  $\text{H}_2\text{O}_2$  +  $\text{NO}$  +  $\text{NO}_2$  +  $h\nu$  ( $\text{OH} + \text{NO}_x$ )



5시간 반응



시료채취 (TMF, TGF, QFF)  
1시간 @ 20 L/min



# $\alpha$ -피넨 SOA의 $\text{NO}_x$ 영향 : SOA 생성

## SOA 생성 실험 결과 요약 (5시간 반응)

Park et al, AE, 2017

Exp ID	$\text{Pin}_{\text{ini}}$	$\Delta\text{PIN}$	$\text{H}_2\text{O}_2$	$\text{NO}_{\text{ini}}$	$\text{NO}_{2\text{ini}}$	$\text{O}_{3\text{ini}}$	Hexane	$\text{SOA}_{\text{SMPS}}^a$	$\text{SOA}_{\text{GA}}$	WSOC	WSON	WSON/WSOC
	ppb	ppb	ppb	ppb	ppb	ppb	ppm	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	%
$\text{O}_3$	1033.9	1033.9	0	0	2	1175	-	3504	1831	695	6.09	0.88
$\text{O}_3+\text{HX}$	1017.6	1015.4	0	0	3	1242	100	3133	1305	700	5.49	0.78
OH	1028.6	330.2	1000	0	2	0	-	1248	772	179	1.87	1.04
OH+NO	1126.4	1126.0	1000	1064	37	0	-	579	491	131	8.40	6.41
OH+ $\text{NO}_x$	1022.4	1021.6	1000	1008	1072	0	-	2129	1200	441	18.57	4.21

HX : hexane (OH 제거제); WSOC : water soluble organic carbon; WSON : water soluble organic nitrogen.  
WSOC, WSON : Shimadzu TOC/TN 분석기

## 질량 분석기를 이용한 성분 분석

- 시료채취 : 20 L/min 1 시간, 테프론 코팅된 유리섬유필터
- 시료전처리 : HPLC용 acetonitrile 4 mL로 20 분간 초음파 추출
- 분석 : **직접주입**-ESI-FT ICR MS (기초과학지원연구원)



Advion  
ESI chip



Nano spray  
400 nL/min

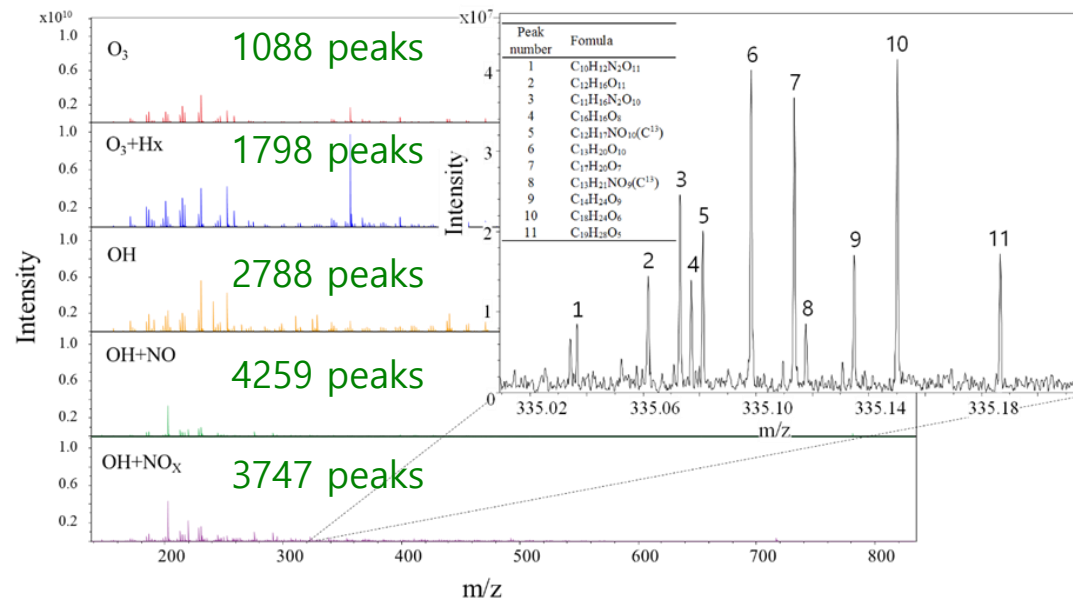
- Detection mode : broadband
- Acquisition size : 4 M point
- Mass range: 160 – 1,000 m/z
- Spectra averaging : 2,000 scans
- Collision cell accumulation : 0.1 s
- TOF : 0.5 s



15 T FT-ICR-MS  
(기초과학지원연구원)



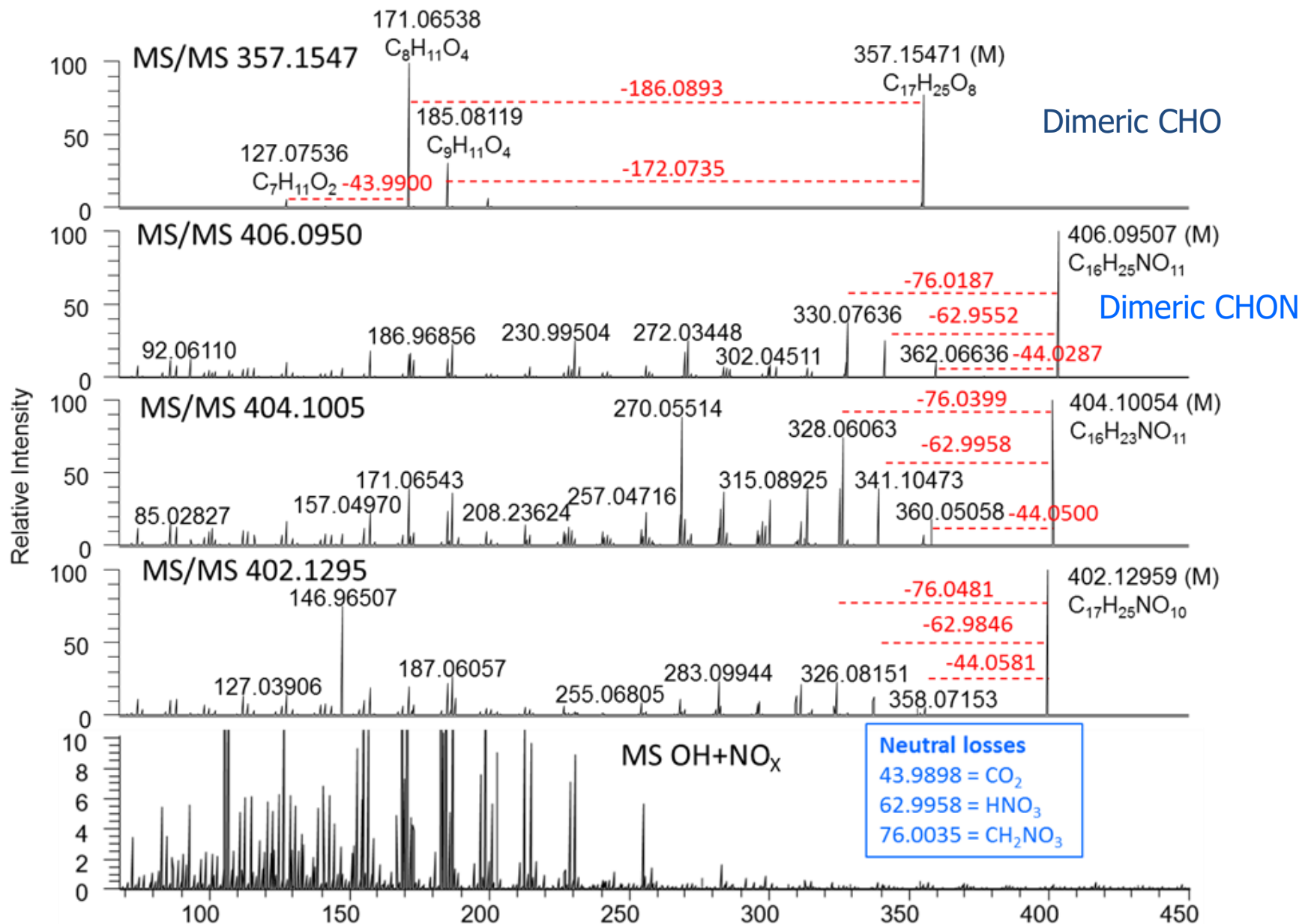
# $\alpha$ -피넨 SOA의 $\text{NO}_x$ 영향 : 다이머 & CHON



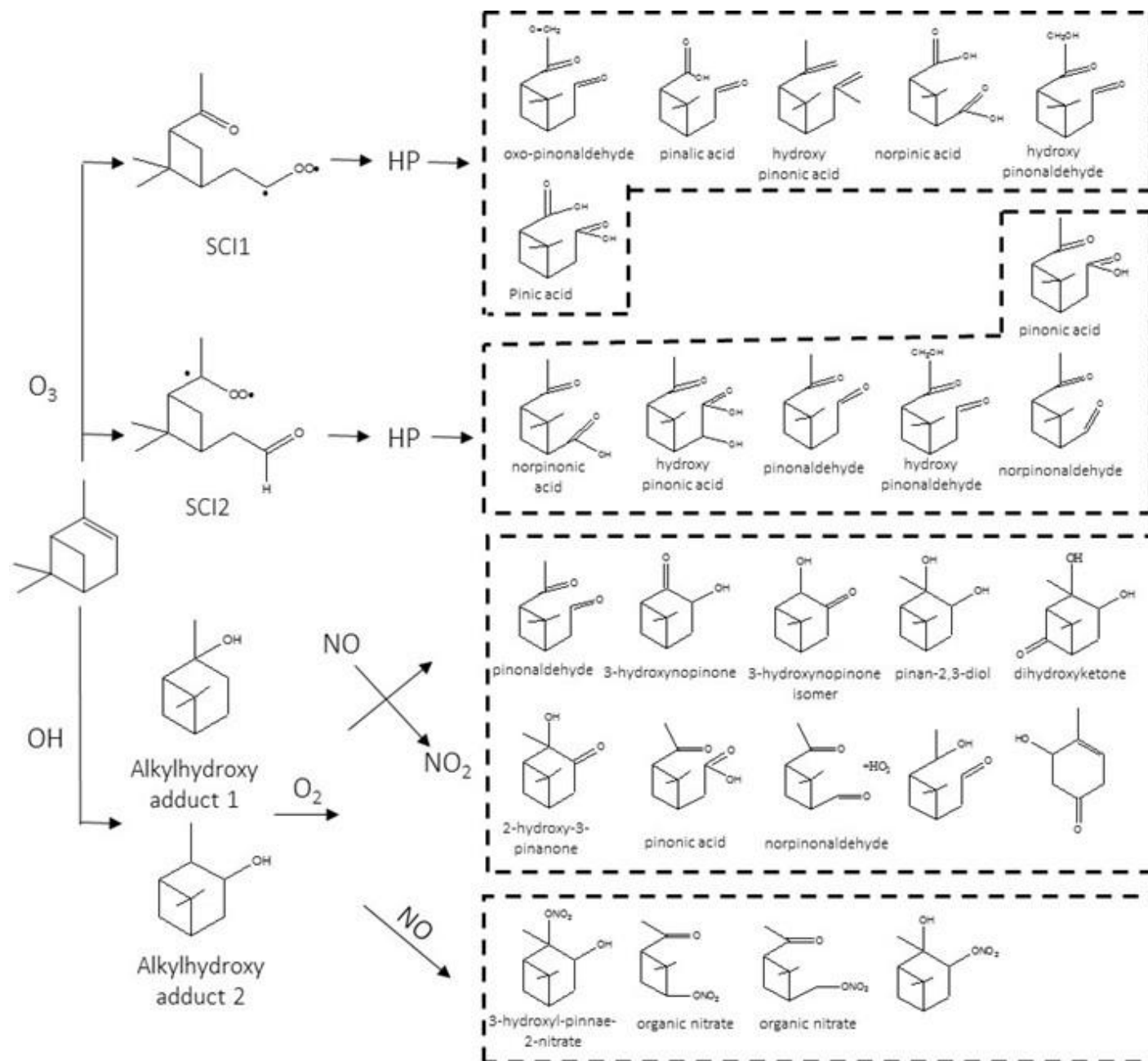
- 오차가  $\pm 0.5$  ppm ( $\pm 0.0005$  m/e) 이내에서 가장 작은 화학식
- 탄소 동위원소 패턴 ( $^{13}\text{C}/^{12}\text{C} = 1.11\%$ )
- 원소 수 제한 ( $\text{C} \leq 100$ ,  $\text{H} \leq 200$ ,  $\text{O} \leq 100$ ,  $\text{N} \leq 3$ ,  $\text{S} \leq 2$ )
- 원소비 제한 ( $0.3 \leq \text{H}/\text{C} \leq 2.25$ ,  $0 \leq \text{O}/\text{C} \leq 2$ ,  $0 \leq \text{C}/\text{N} \leq 0.5$ )
- 질소 법칙 (N 홀수  $\rightarrow$  m/e 짝수)
- Double bond equivalent (DBE)  $\geq 0$  (DBE = 1 -  $\text{H}/2 + \text{N}/2 + \text{C}$ )

Int.	$\text{O}_3$	$\text{O}_3+\text{HX}$	OH	OH+NO	OH+NO <sub>x</sub>
1	$\text{C}_{17}\text{H}_{26}\text{O}_8$ (100)	$\text{C}_{17}\text{H}_{26}\text{O}_8$ (100)	$\text{C}_{10}\text{H}_{16}\text{O}_6$ (100)	$\text{C}_8\text{H}_{12}\text{O}_6$ (100)	$\text{C}_8\text{H}_{12}\text{O}_6$ (100)
2	$\text{C}_{10}\text{H}_{16}\text{O}_6$ (75.0)	$\text{C}_{10}\text{H}_{16}\text{O}_6$ (20.9)	$\text{C}_{17}\text{H}_{26}\text{O}_8$ (40.5)	$\text{C}_{10}\text{H}_{16}\text{O}_6$ (92.2)	$\text{C}_{10}\text{H}_{16}\text{O}_6$ (97.7)
3	$\text{C}_{10}\text{H}_{16}\text{O}_5$ (39.2)	$\text{C}_{10}\text{H}_{16}\text{O}_5$ (13.3)	$\text{C}_{17}\text{H}_{26}\text{O}_7$ (38.8)	$\text{C}_{10}\text{H}_{14}\text{O}_6$ (64.1)	$\text{C}_{10}\text{H}_{14}\text{O}_6$ (65.9)
4	$\text{C}_{10}\text{H}_{14}\text{O}_6$ (39.1)	$\text{C}_{10}\text{H}_{14}\text{O}_6$ (12.9)	$\text{C}_{10}\text{H}_{14}\text{O}_6$ (31.1)	$\text{C}_{10}\text{H}_{15}\text{NO}_8$ (54.6)	$\text{C}_{10}\text{H}_{15}\text{NO}_8$ (50.2)
5	$\text{C}_{19}\text{H}_{28}\text{O}_9$ (38.5)	$\text{C}_9\text{H}_{14}\text{O}_6$ (12.2)	$\text{C}_{19}\text{H}_{28}\text{O}_9$ (24.7)	$\text{C}_{10}\text{H}_{15}\text{NO}_9$ (46.6)	$\text{C}_{10}\text{H}_{15}\text{NO}_9$ (42.3)
6	$\text{C}_9\text{H}_{14}\text{O}_6$ (31.3)	$\text{C}_{17}\text{H}_{26}\text{O}_7$ (11.6)	$\text{C}_8\text{H}_{12}\text{O}_6$ (18.4)	$\text{C}_7\text{H}_{11}\text{NO}_7$ (38.4)	$\text{C}_{10}\text{H}_{14}\text{O}_5$ (41.0)
7	$\text{C}_8\text{H}_{12}\text{O}_6$ (29.4)	$\text{C}_{19}\text{H}_{28}\text{O}_9$ (11.0)	$\text{C}_{19}\text{H}_{28}\text{O}_8$ (18.2)	$\text{C}_{10}\text{H}_{14}\text{O}_5$ (36.6)	$\text{C}_7\text{H}_{11}\text{NO}_7$ (35.9)
8	$\text{C}_{17}\text{H}_{26}\text{O}_7$ (26.4)	$\text{C}_{11}\text{H}_{16}\text{O}_7$ (10.9)	$\text{C}_{10}\text{H}_{16}\text{O}_7$ (17.3)	$\text{C}_{10}\text{H}_{14}\text{O}_7$ (30.7)	$\text{C}_{10}\text{H}_{14}\text{O}_7$ (32.5)
9	$\text{C}_{11}\text{H}_{16}\text{O}_7$ (25.8)	$\text{C}_{16}\text{H}_{24}\text{O}_8$ (10.9)	$\text{C}_{18}\text{H}_{26}\text{O}_8$ (16.5)	$\text{C}_8\text{H}_{13}\text{NO}_8$ (23.7)	$\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_{15}$ (23.4)
10	$\text{C}_{10}\text{H}_{16}\text{O}_7$ (25.5)	$\text{C}_{19}\text{H}_{28}\text{O}_7$ (10.3)	$\text{C}_{18}\text{H}_{28}\text{O}_8$ (15.5)	$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_{10}$ (23.0)	$\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_{14}$ (23.3)

# $\alpha$ -피넨 SOA의 $\text{NO}_x$ 영향 : 다이머

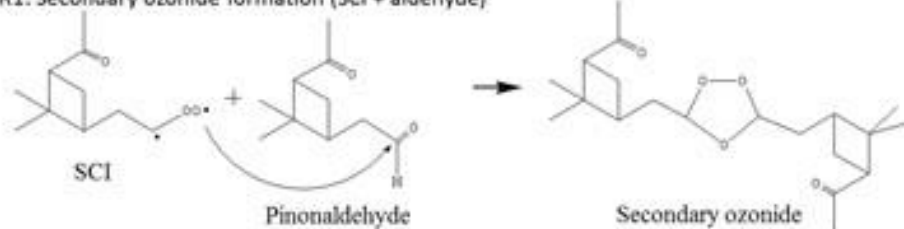


# SOA 생성 반응 경로 및 생성물 : $\alpha$ -Pinene SOA

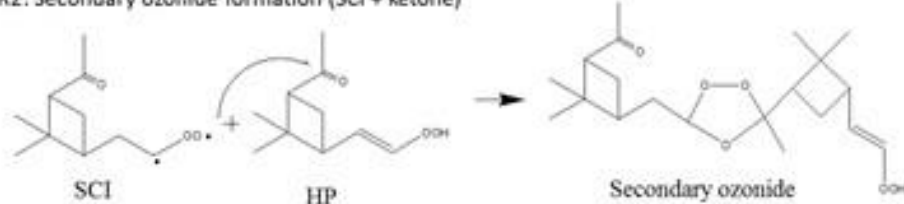


# 다이어 생성 메커니즘: $\alpha$ -Pinene SOA

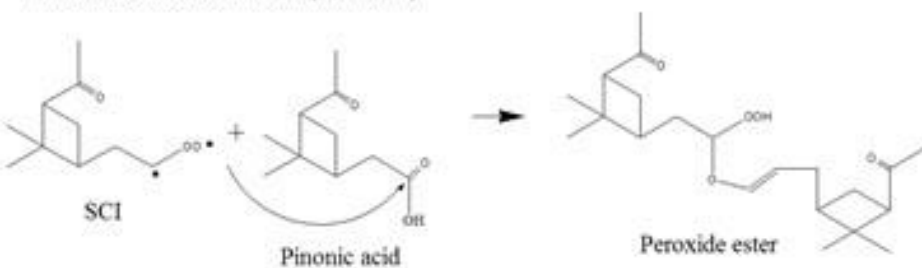
R1: Secondary ozonide formation (SCI + aldehyde)



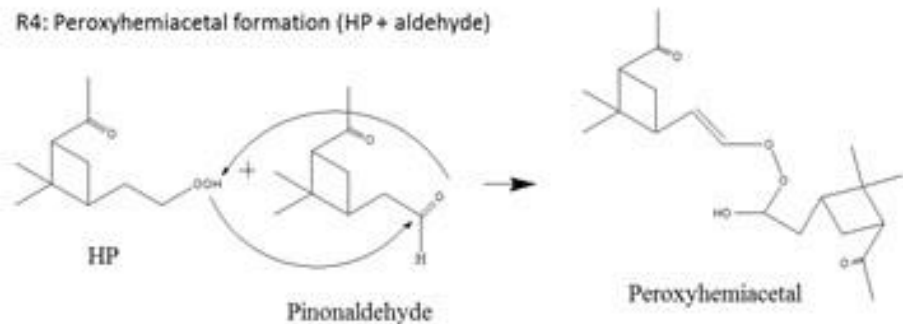
R2: Secondary ozonide formation (SCI + ketone)



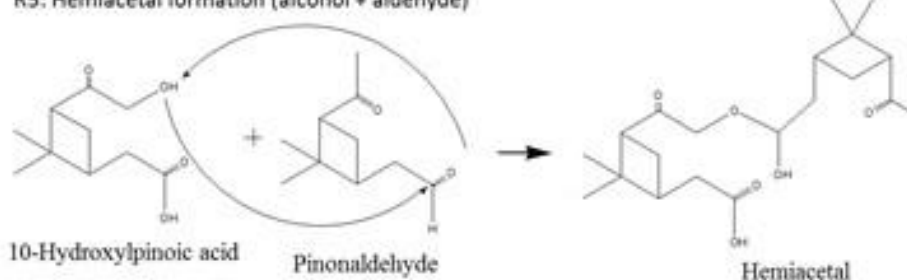
R3: Peroxide ester formation (SCI + acid)



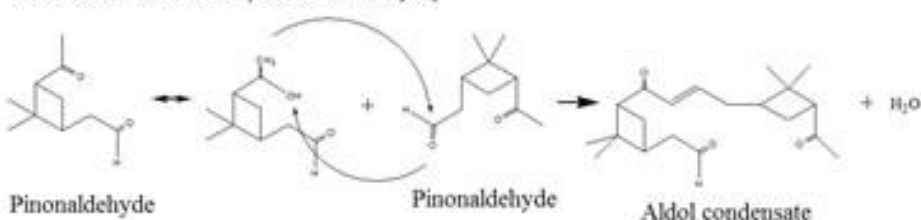
R4: Peroxyhemiacetal formation (HP + aldehyde)



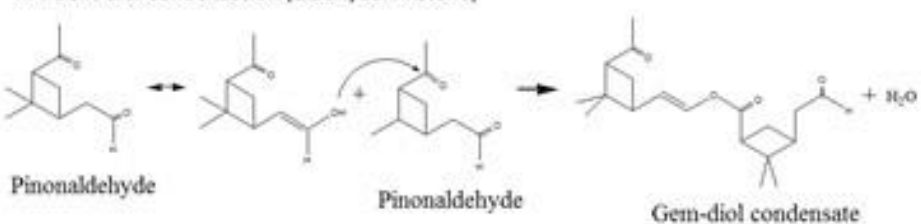
R5: Hemiacetal formation (alcohol + aldehyde)



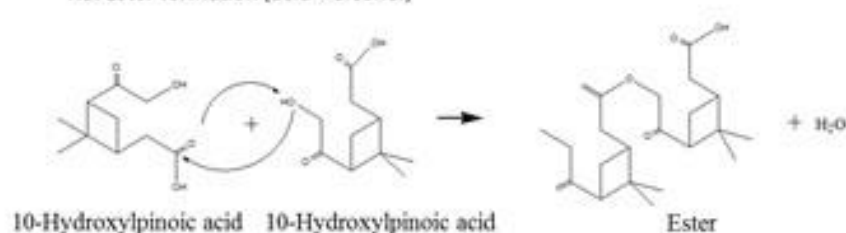
R6: Aldol condensation (ketone + aldehyde)



R7: Gem-diol condensation (aldehyde + ketone)

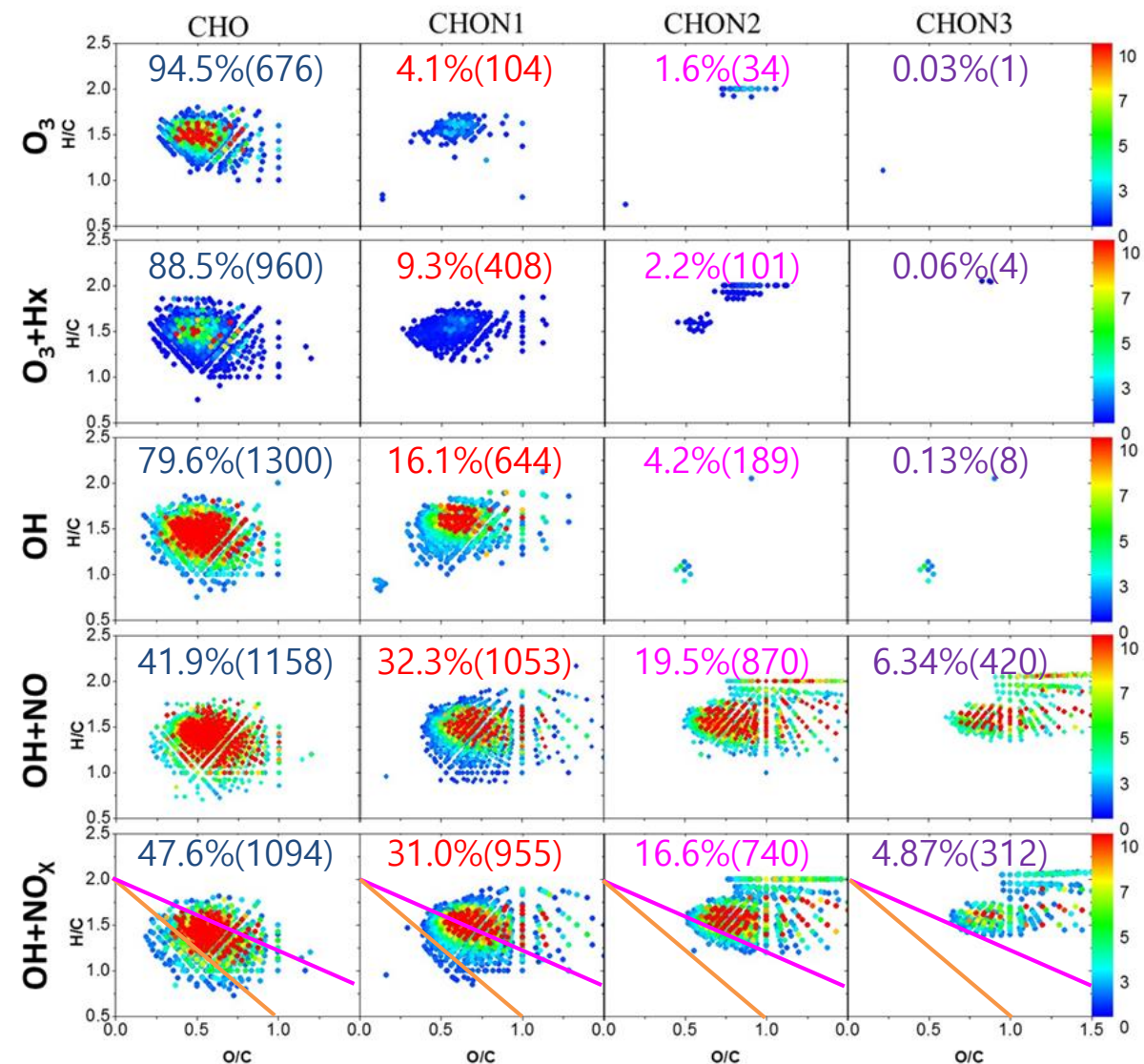


R8: Ester formation (acid + alcohol)

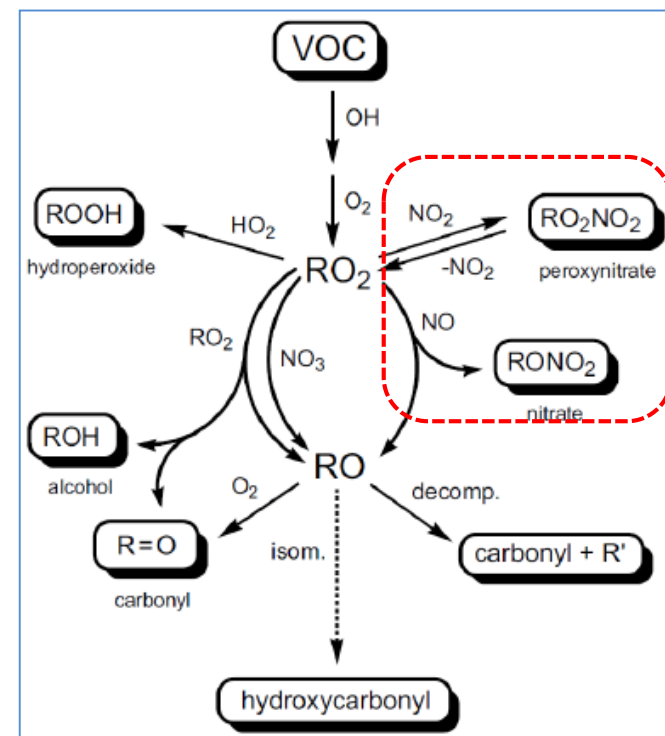




# CHON 탄소의 산화상태



- 고 NO<sub>x</sub> 조건에서 질소 화합물이 생성이 뚜렷함.
- 저 NO<sub>x</sub> 조건에서 CHON의 생성은 잔류된 미량의 NO<sub>x</sub>에 의한 것으로 추정됨 (Krechmer et al., 2015)
- CHON의 **겉보기 탄소 산화상태**가 CHO보다 큼. 산소 중 일부는 질소와 결합된 형태(-NO<sub>2</sub>, -ONO<sub>2</sub>)일 수 있음.

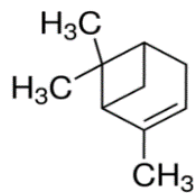


기울기 = -1 → 카복실산

기울기 = -2 → 카보닐

# $\alpha$ -피넨 SOA에 대한 $\text{NH}_3$ 영향 : SOA 생성실험

## SOA 생성



50-400 ppb

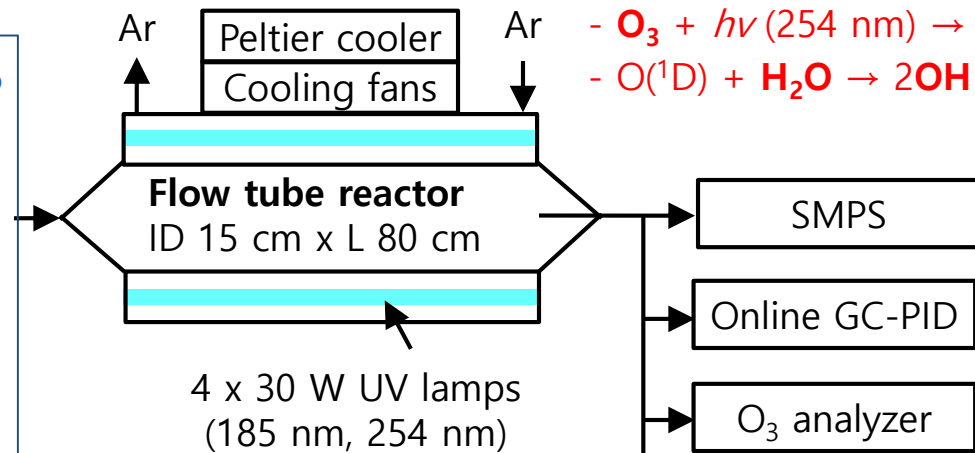
RH 50%

+

1.  $\text{O}_3$ :  $\text{O}_3$ \_w/o  $\text{NH}_3$
2.  $\text{O}_3 + \text{NH}_3$ :  $\text{O}_3$ \_w/  $\text{NH}_3$
3.  $\text{O}_3 + \text{H}_2\text{O} + h\nu$ 
  - OH\_0.5d\_w/o  $\text{NH}_3$
  - OH\_1.0d\_w/o  $\text{NH}_3$
  - OH\_3.0d\_w/o  $\text{NH}_3$
4.  $\text{O}_3 + \text{H}_2\text{O} + \text{NH}_3 + h\nu$ 
  - OH\_0.5d\_w/  $\text{NH}_3$
  - OH\_1.0d\_w/  $\text{NH}_3$
  - OH\_3.0d\_w/  $\text{NH}_3$

## OH radical formation

- $\text{O}_3 + h\nu (254 \text{ nm}) \rightarrow \text{O}(^1\text{D}) + \text{O}_2$
- $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$



## HPLC-MS 분석

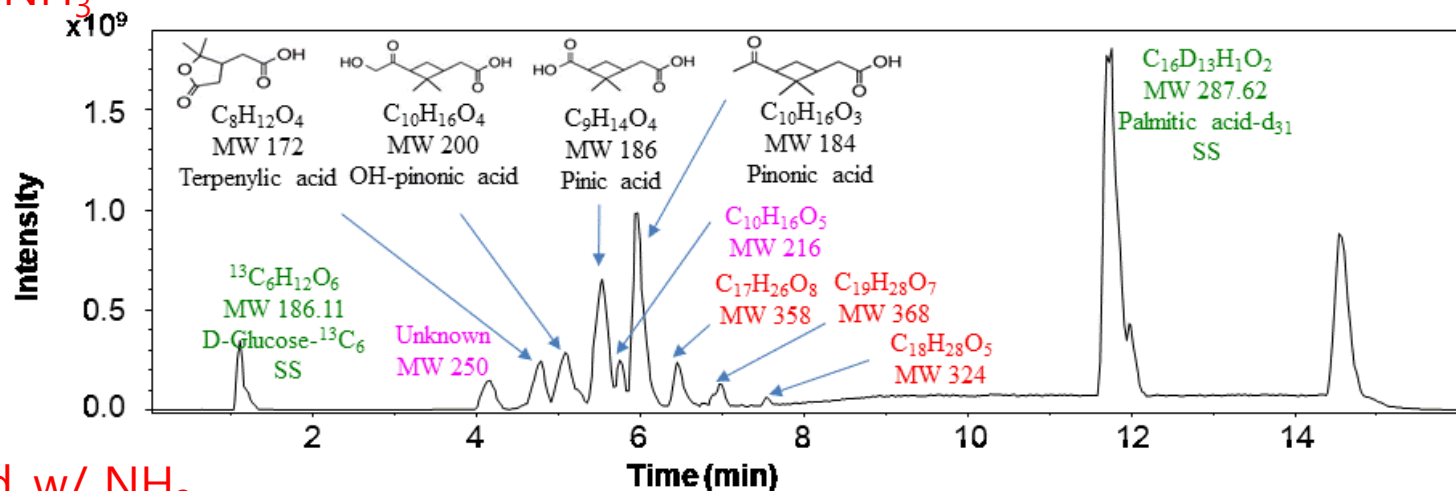
- System: Bruker 7T FT-ICR MS
- Column: Waters ACQUITY HSS T3 (2.1 × 100 mm, 1.8  $\mu\text{m}$ ) at 45 °C.
- Eluent A:  $\text{H}_2\text{O}$  (0.1% acetic acid)
- Eluent B: MeOH (0.1% acetic acid)

- Gradient: 0-1 min (B 0%)  
1-3.5 min (B 0% → 50%)  
3.5-7 min (B 50% → 90%)  
7-15 min (B 90%)  
15-16 min (B 90% → 0%)

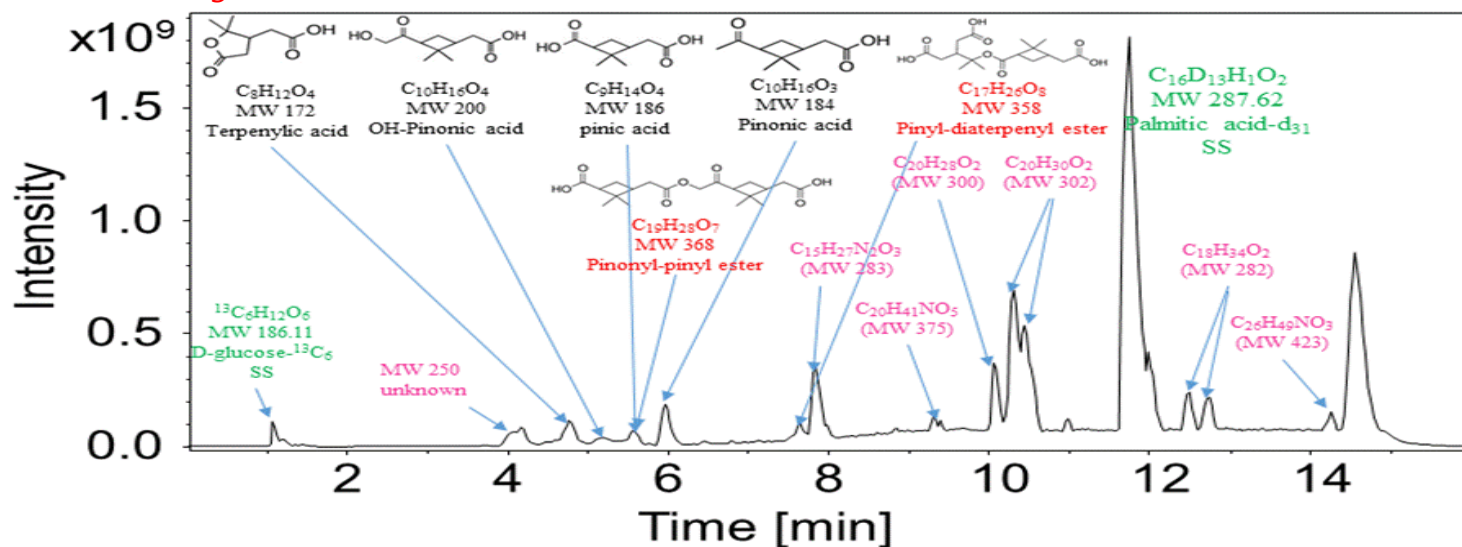
- Flow rate: 0.3 mL/min
- Injection volume: 1  $\mu\text{L}$

# $\alpha$ -피넨 SOA에 대한 $\text{NH}_3$ 영향 : 화학조성

$\text{O}_3$ \_w/o  $\text{NH}_3$

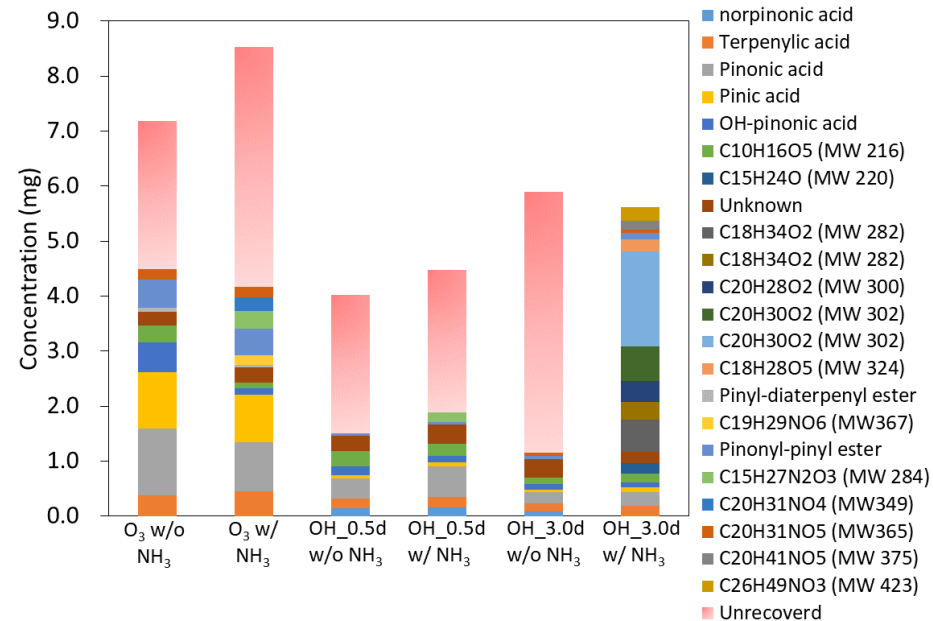
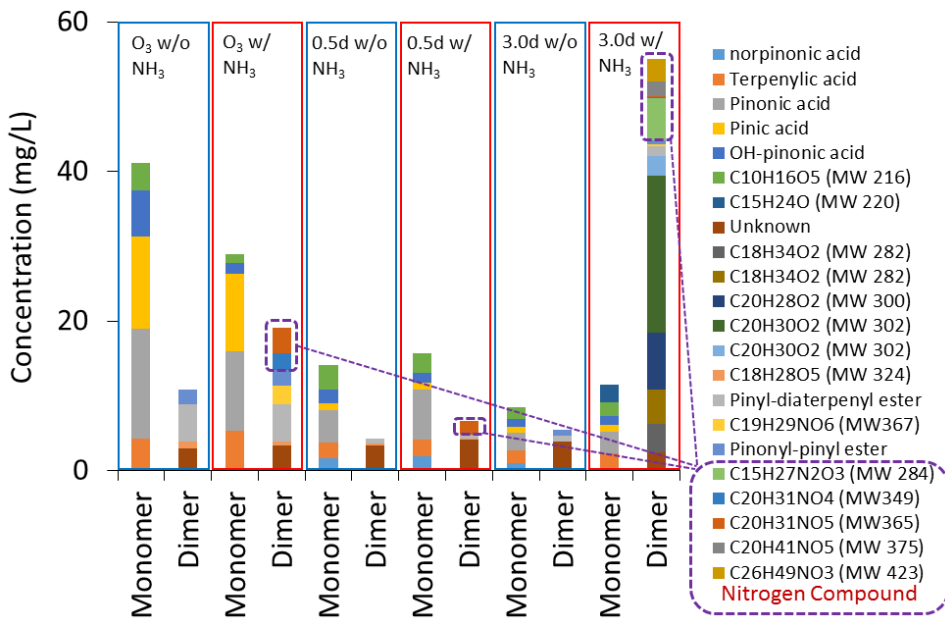


$\text{OH}_{3.0\text{d}}$ \_w/  $\text{NH}_3$



- CHO 다имер가  $\text{NH}_3$ 에 상관없이 확인됨.
- $\text{NH}_3$ 가 있을 때 CHON 다имер가 상당히 많이 생성됨.
- 향후 CHON 다имер의 구조와 생성 메커니즘이 규명되어야 함.

# $\alpha$ -피넨 SOA에 대한 $\text{NH}_3$ 영향 : 화학조성



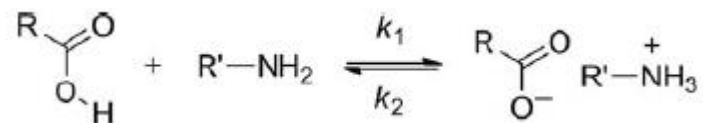
- $\text{NH}_3$ 가 있는 경우 다이머의 함량 증가.
- $\text{NH}_3$ 가 있는 조건에서 3일 광화학반응에서 CHON 생성이 상당히 활발함.
- SOA 성분의  $\sim 52 \pm 28\%$ 가 확인되었음. 대체 표준물질을 사용하여 추출과정을 포함한 전처리 회수율을 보정하면 향상될 것으로 기대함.



# NH<sub>3</sub>에 의한 CHON 생성 메커니즘 제안

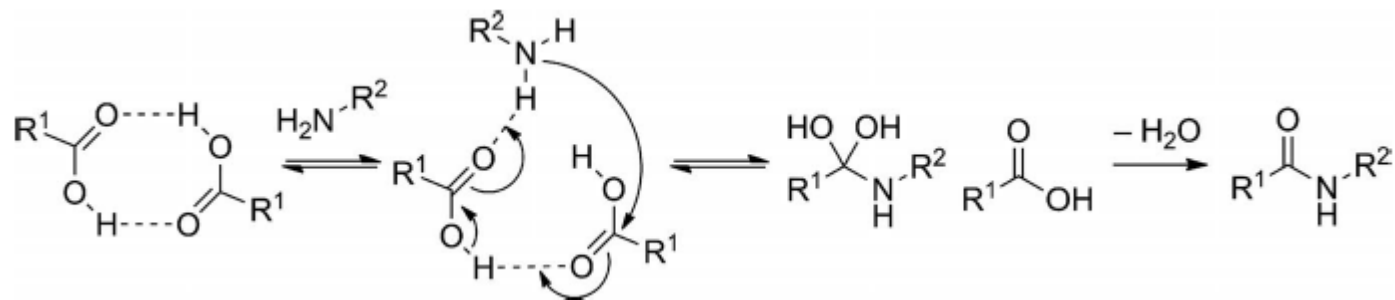
## 카복실산 암모늄 염의 생성 - SOA

Na et al. (2007)



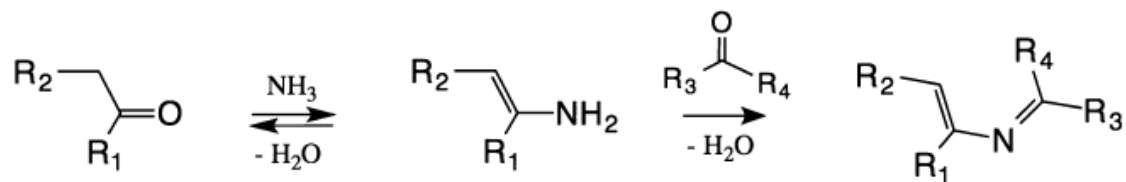
## 카복실산의 아미드화 반응 - 유기합성

Charville et al. (2011)



## Schiff 염기 반응 - SOA

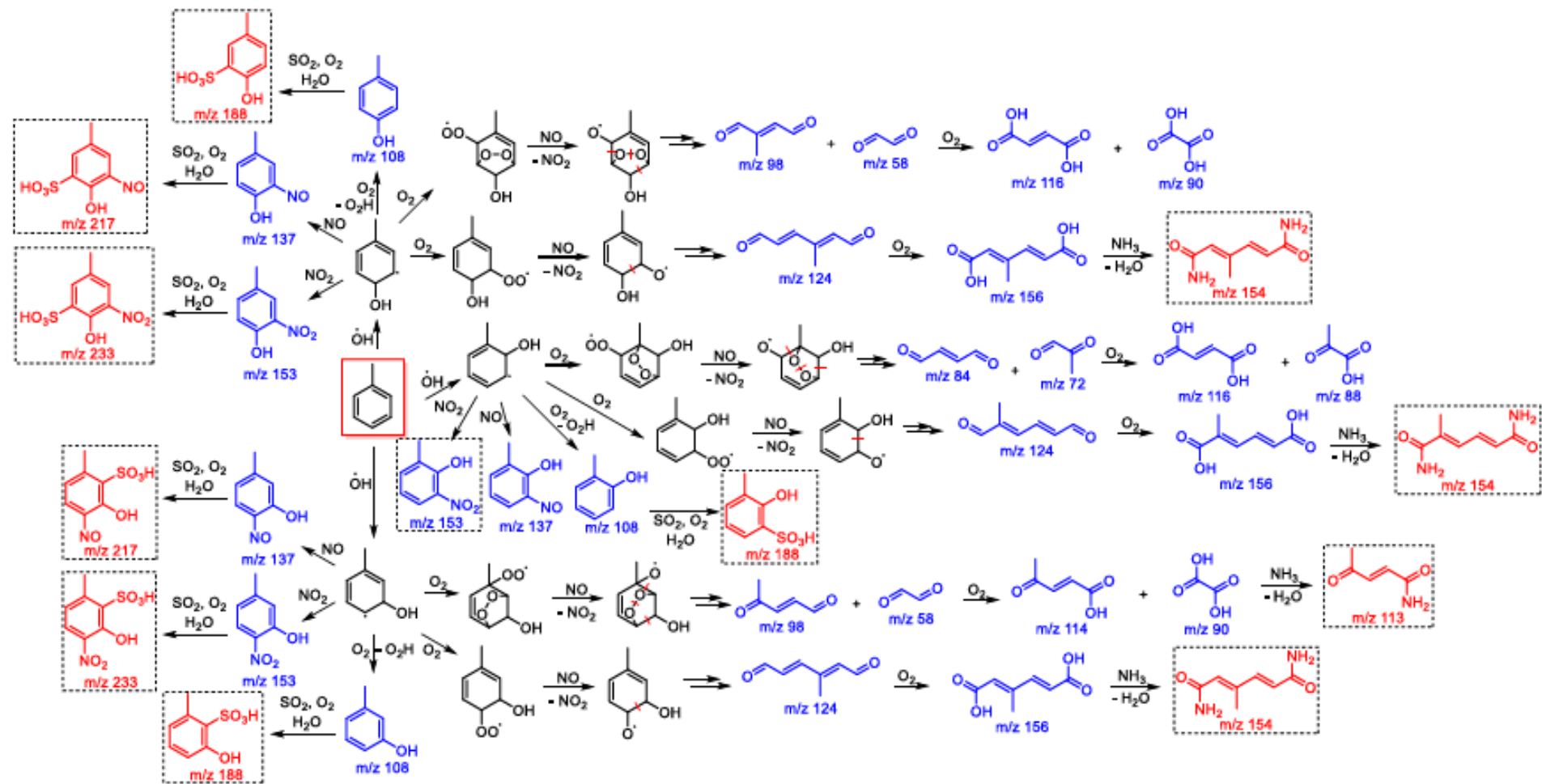
Laskin et al. (2013)



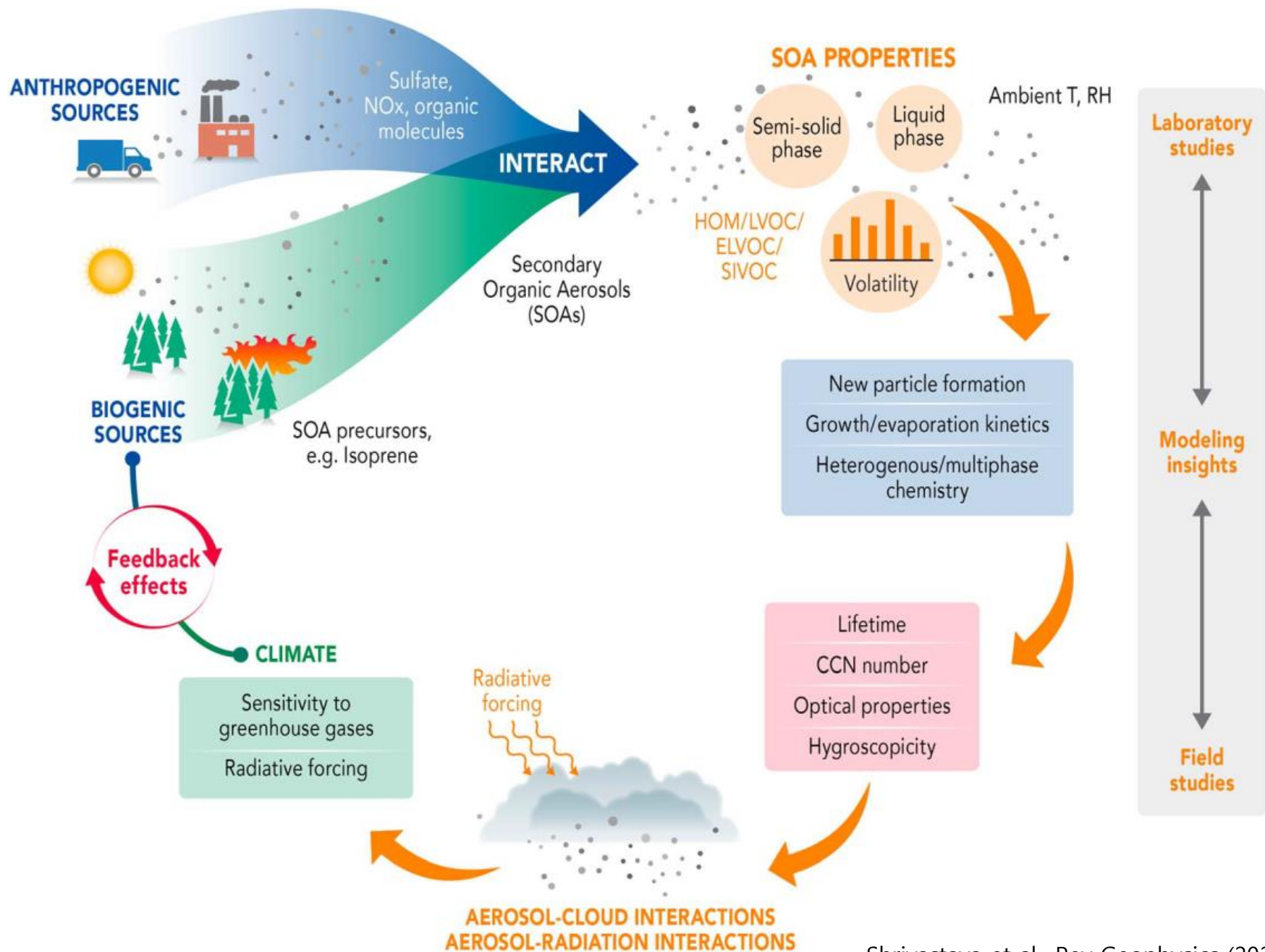
# 톨루엔 SOA 생성 메커니즘 해석

➤ 톨루엔/ $\text{NO}_x$ / $\text{SO}_2$ / $\text{NH}_3$  혼합물 : Cresol and bicyclic intermediate pathways

## Organosulfates와 Amines 확인

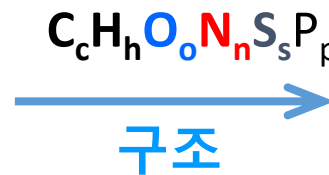
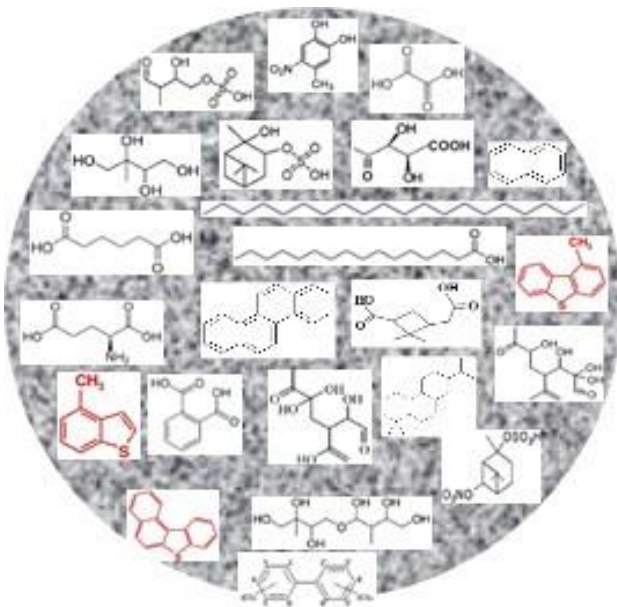


# SOA 생성과 환경영향에서 에어로졸 물성의 영향



# 미세먼지의 화학 조성, 물리화학적 성질, 환경영향 사이 연관성

- 미세먼지의 환경 영향은 화학조성에 의해 결정되는 물리화학적 성질에 영향을 받음.
- 따라서, 화학조성과 물리화학적 성질 간의 관련성을 제대로 이해하는 것이 중요함.



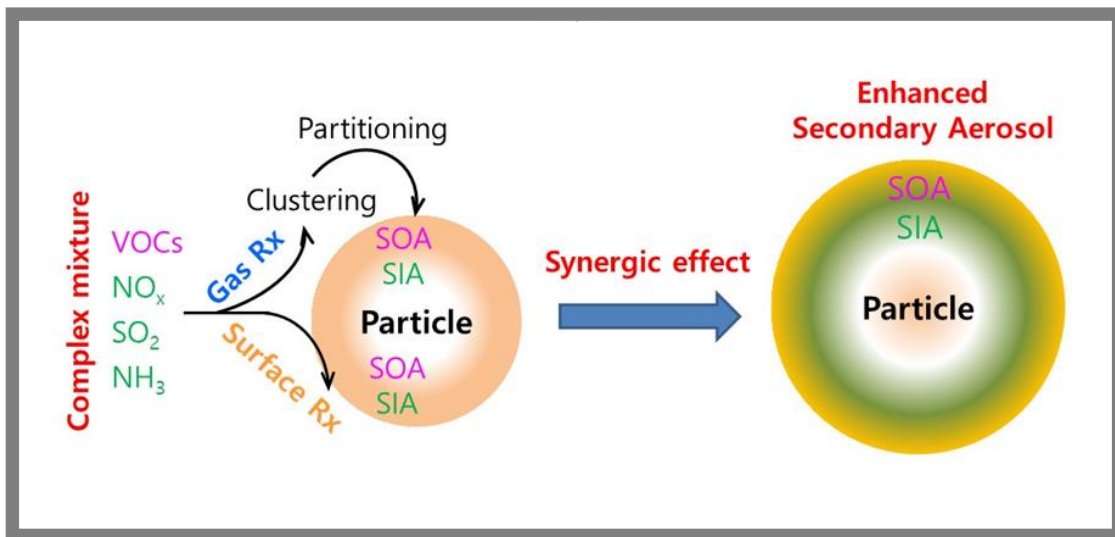
Properties	O/C		N/C	
	high	low	high	low
Hygroscopicity	high	low	high	low
Volatility	low	high	high	low
Density	high	low	high	low
Light absorption			high	low
Processing	aged	fresh	high NOx	low NOx
Oxidation	high	low	high	low
Toxicity	high	low	high	low



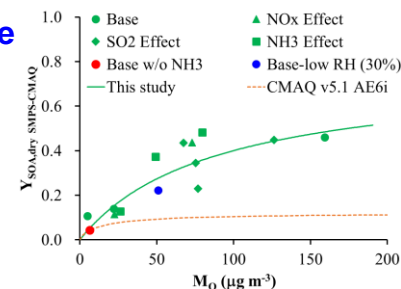
# SOA Formation in ROG/NO<sub>x</sub>/SO<sub>2</sub>/NH<sub>3</sub> Mixture

49

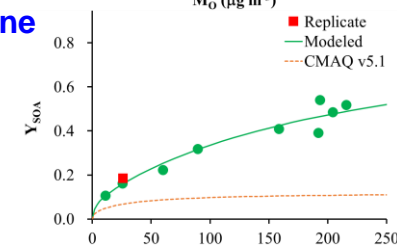
➤ Hypothesis: Increase in SOA yield in ROG/NO<sub>x</sub>/SO<sub>2</sub>/NH<sub>3</sub> mixture



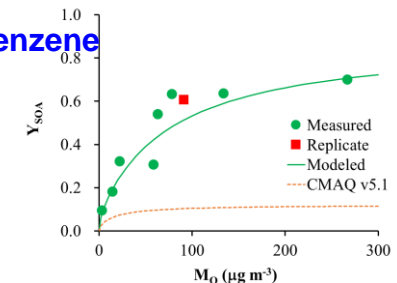
Toluene



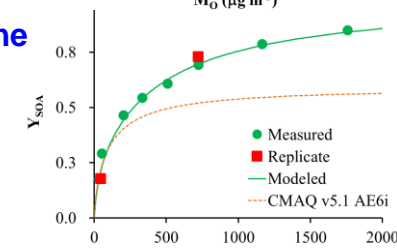
m-Xylene



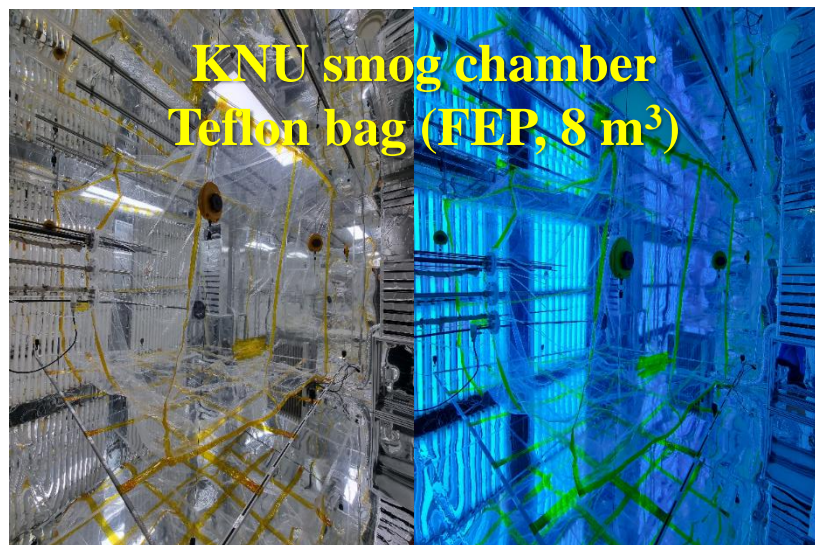
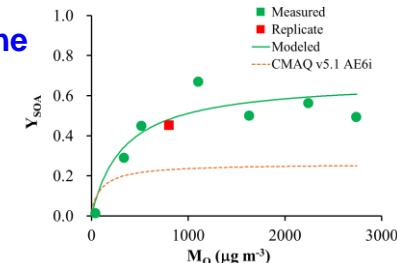
Ethylbenzene



$\alpha$ -Pinene



Isoprene



ROG = 10-1000 ppb  
 NO<sub>x</sub>/ROG = 10  
 NO<sub>2</sub>/NO = 1  
 NH<sub>3</sub>/ROG = 5  
 SO<sub>2</sub>/ROG = 2  
 •OH source = HONO  
 Seed = (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>  
 RH = 60%  
 Temp = 25 °C

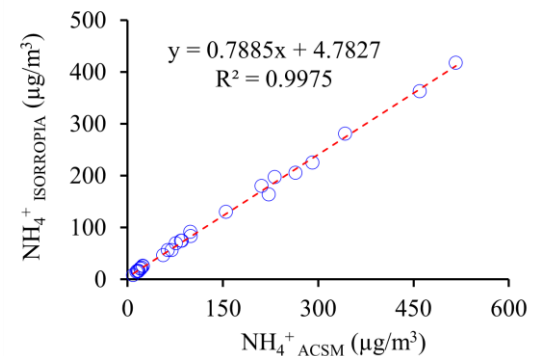
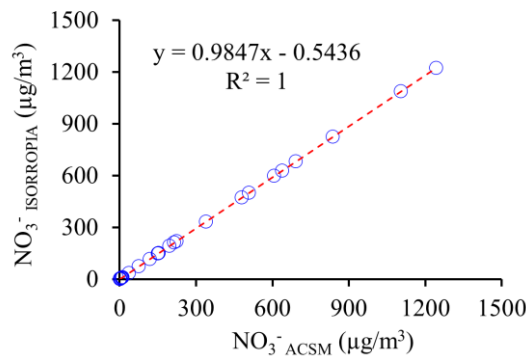
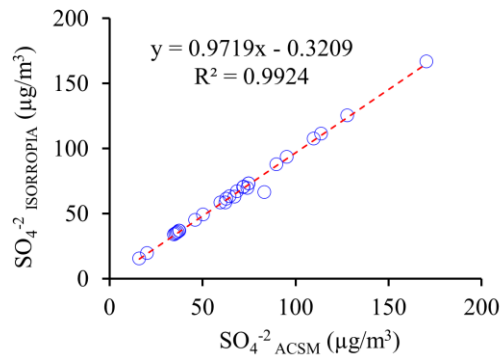
Only particle wall loss was corrected

# 에어로졸상 물 및 산도

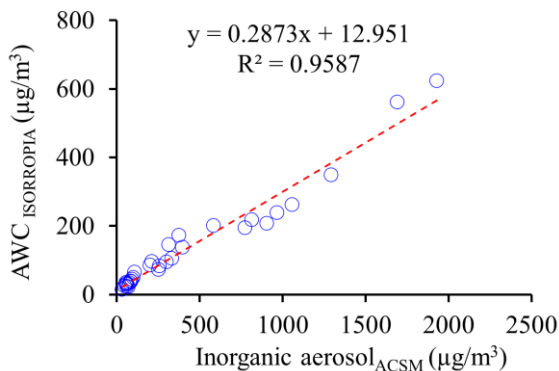
## ➤ 열역학 모델 : ISORROPIA2.1

- Forward 모드
- Metastable phase
- 입력 데이터 :  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_3(\text{g})$ , 온도, RH
- 가정
  - $[\text{NH}_3]_{\text{total}} = [\text{NH}_3]_{\text{g}} + [\text{NH}_3]_{\text{p}} + [\text{NH}_4^+]_{\text{p}}$  ( $[\text{NH}_3]_{\text{total}} =$  초기 농도)
  - $[\text{HNO}_3]_{\text{total}} = [\text{HNO}_3]_{\text{g}} + [\text{HNO}_3]_{\text{p}} + [\text{NO}_3^-]_{\text{p}}$
  - $[\text{H}_2\text{SO}_4]_{\text{total}} = [\text{H}_2\text{SO}_4]_{\text{g}} + [\text{H}_2\text{SO}_4]_{\text{p}} + [\text{HSO}_4^-]_{\text{p}} + [\text{SO}_4^{2-}]_{\text{p}}$

## ➤ 신뢰도 평가



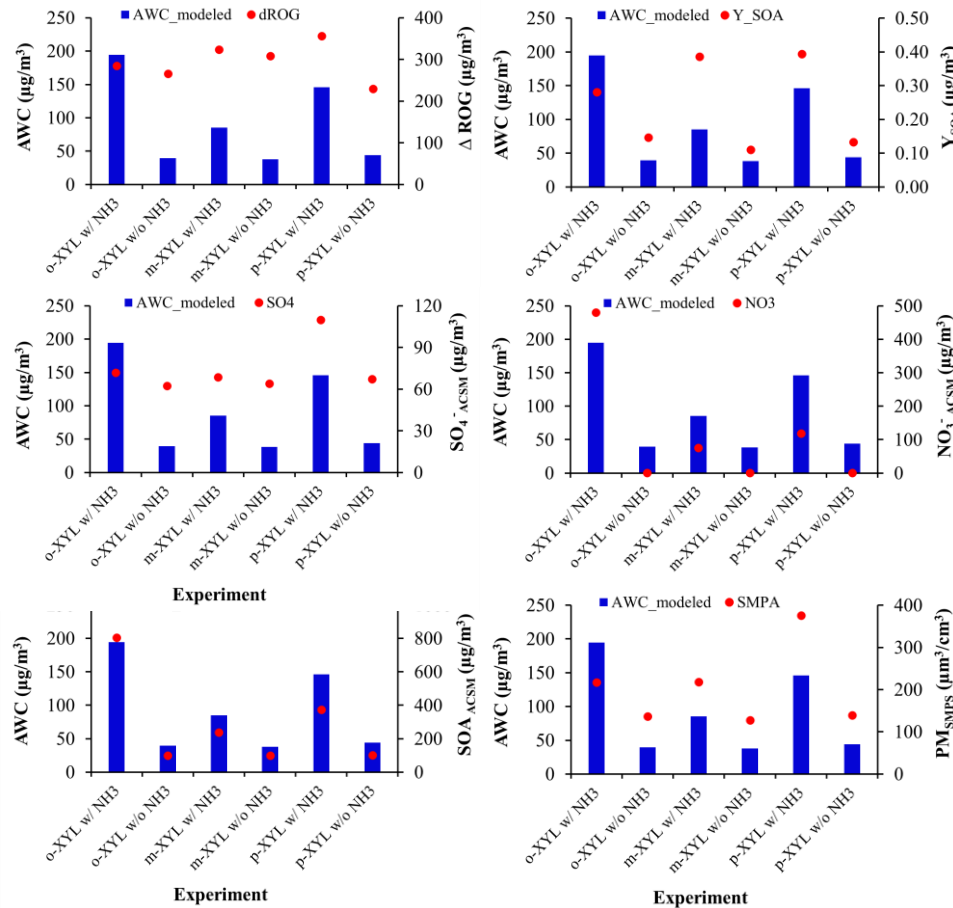
## ➤ AWC vs. SIA 농도



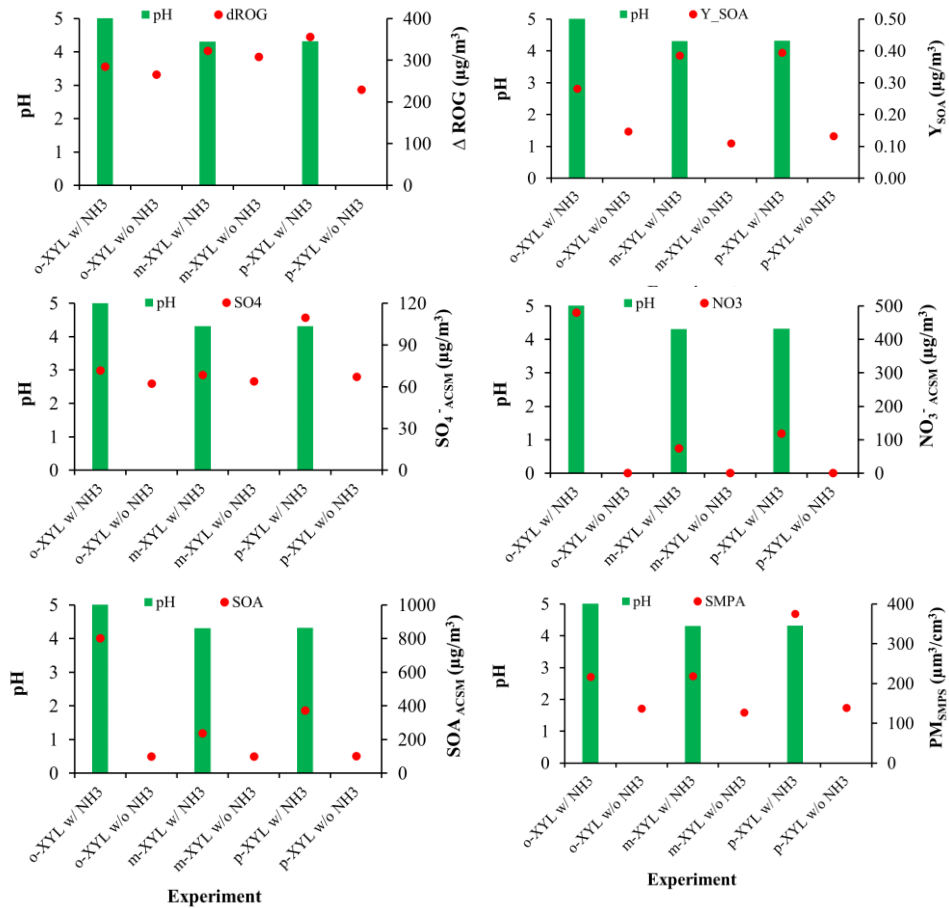
- $\text{NH}_4^+$ 의 경우 모델값이 측정값에 비해 과소 평가  
➔ pH 모델값 과대평가
- AWC가 SIA의 ~30% 수준으로 예측됨
- AWC에 대한 SOA 화학조성 및 흡습성의 영향 파악 필요

# 수용액상 SOA 생성 가능성 : AWC 및 pH 영향

## ➤ AWC



## ➤ pH

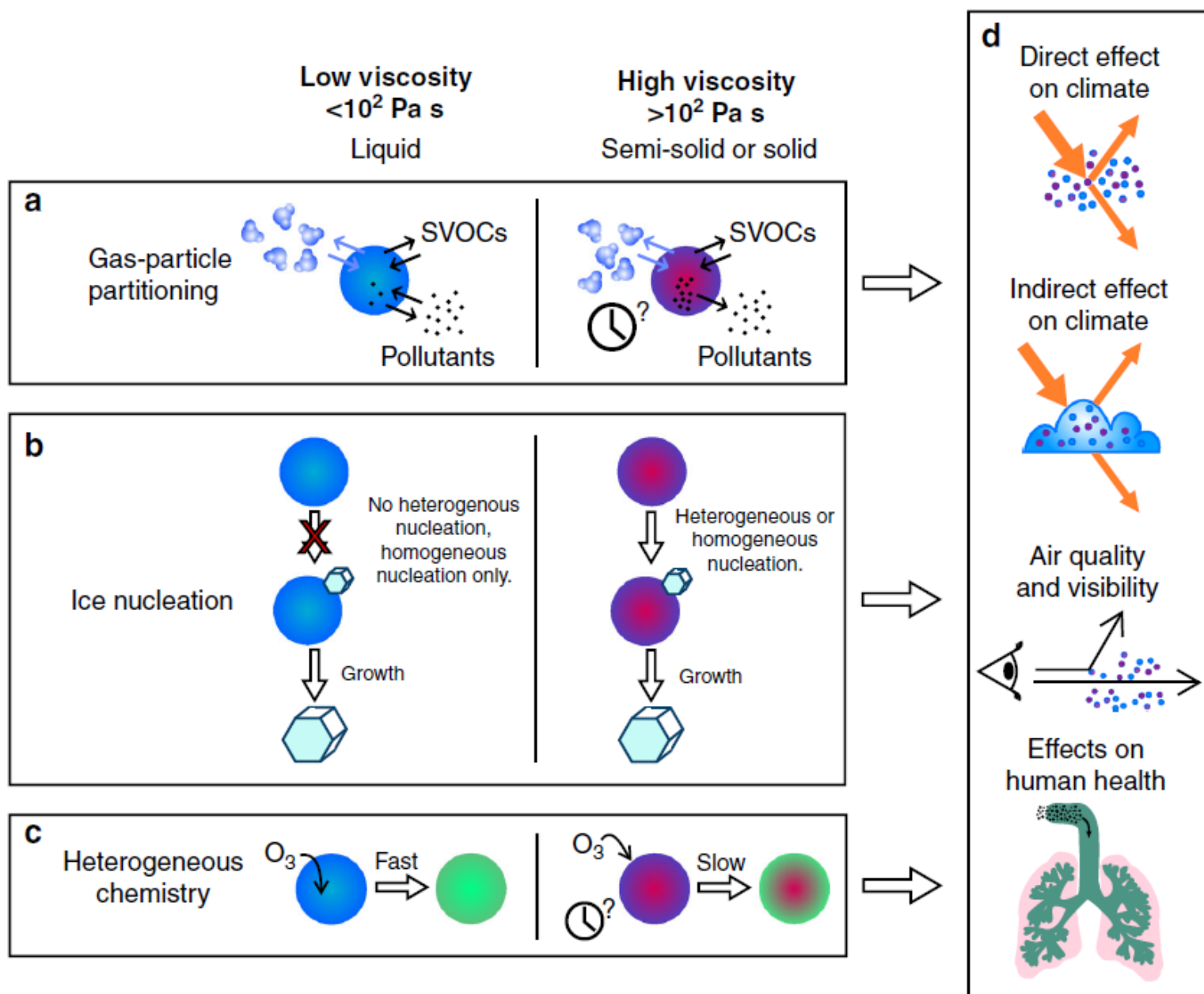


- AWC는  $\text{NH}_3$ 가 있으면 흡습성인  $\text{SIA}(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ 이 생성되어  $\text{NH}_3$ 가 없을 때에 비해 훨씬 더 큼
- $\text{SO}_4^{2-}$ 과 다르게  $\text{NO}_3^-$ 와 SOA 생성은 AWC에 크게 의존
- $\text{NH}_3$ 가 있는 경우 SOA 수율 증가는 AWC 증가에 따른 에어로졸상 반응에 의한 기여 가능

- $\text{NH}_3$ 가 있는 경우 pH는 국내 미세먼지의 pH 3.7 수준이며,  $\text{NH}_3$ 가 없으면 매우 강산(pH < 0)이었음
- o-, m-Xylene 반응 양은 AWC와 pH에 영향을 받지 않았지만, p-Xylene은  $\text{NH}_3$ 가 있을 때 높은 AWC(낮은 pH)에서 더 많이 소모됨
- AWC가 pH보다 이차생성에 더 직접적 영향을 주는 것으로 추정됨

# Effects of Aerosol Viscosity

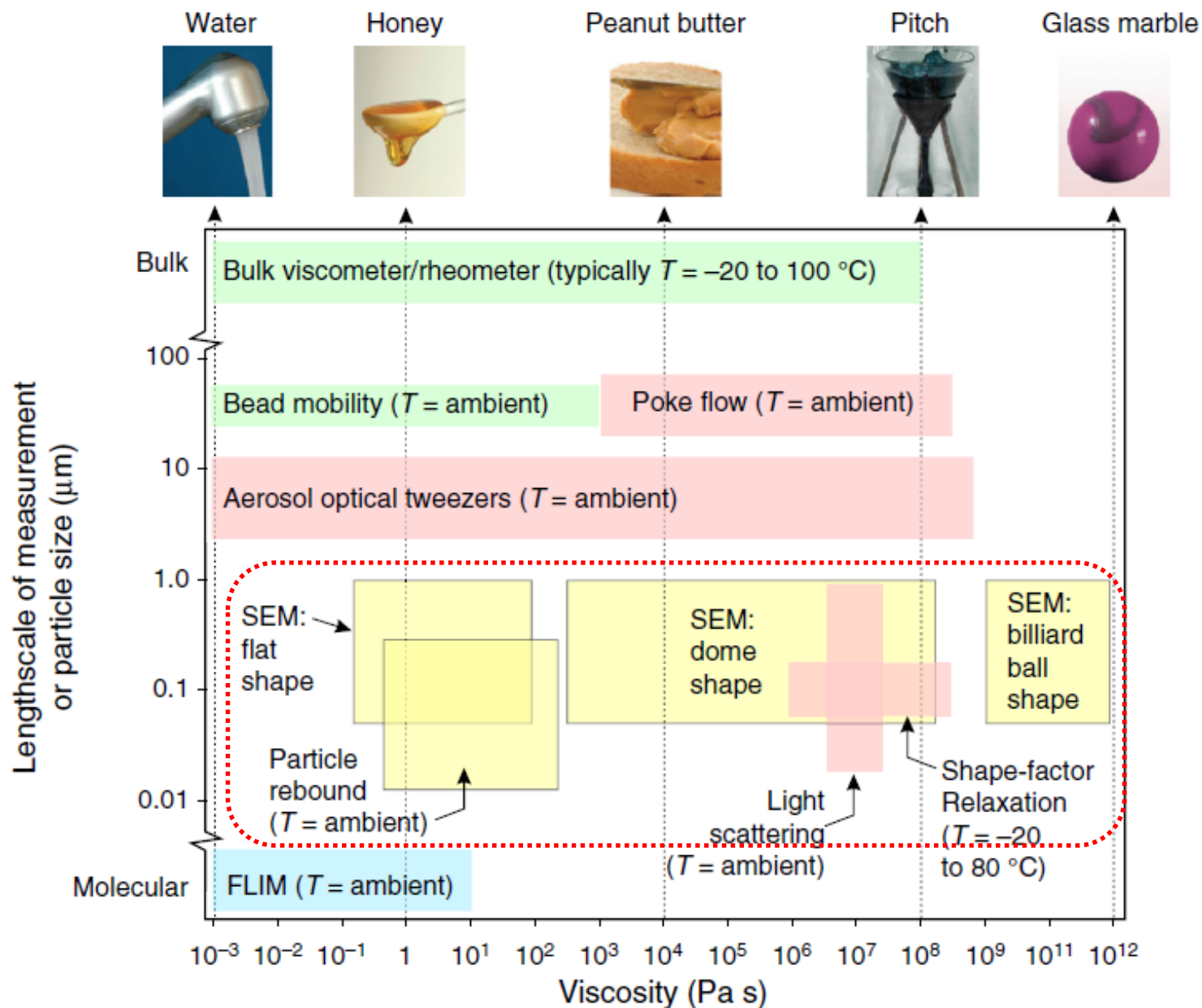
52





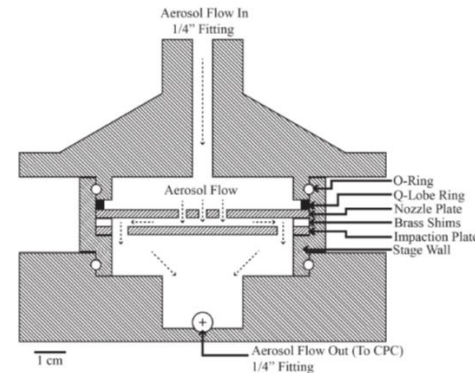
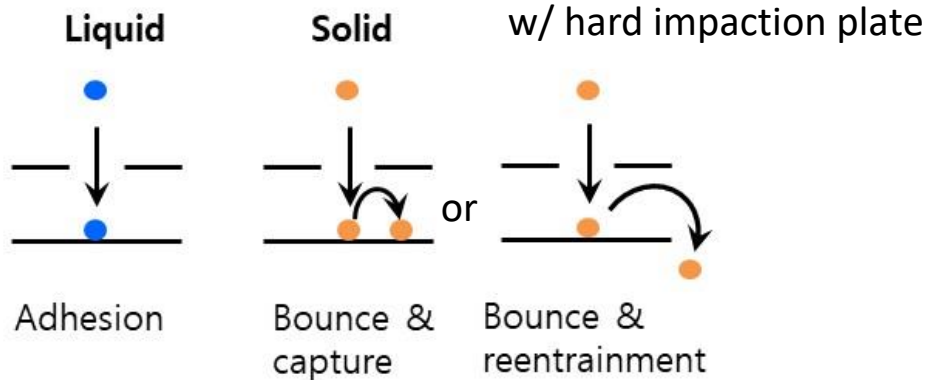
# Methods to Determine Aerosol Viscosity

53

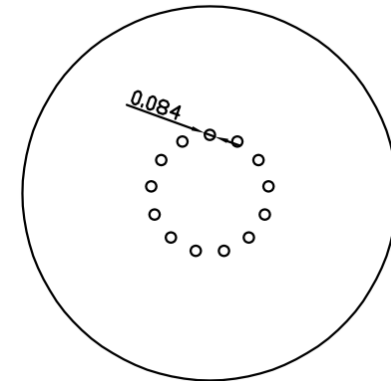


# Particle Rebound Method

## 입자 상에 따른 충돌 측정



Bateman et al. (2014)

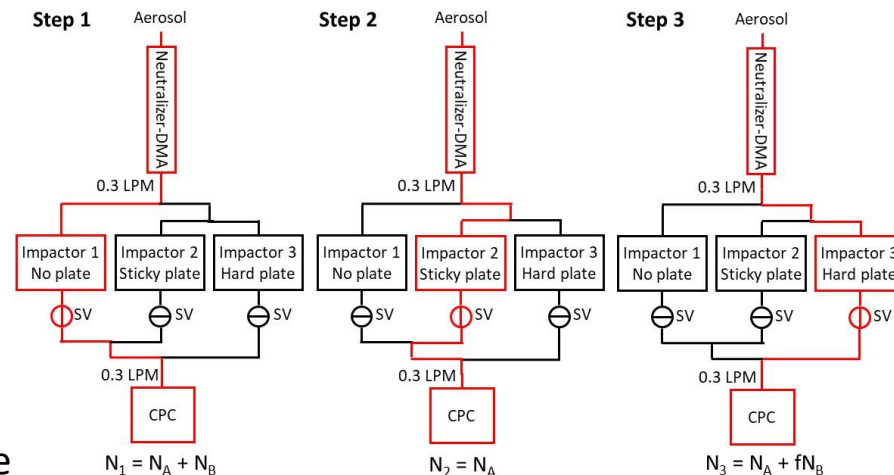


## 미니 임팩터 (0.3 L/min) 제작 : Bateman et al. (2014) 미니 임팩터 (1 L/min) 수정

	Values	Remarks
Cutoff size ( $D_p$ )	~80 nm	
Nozzle dia. ( $D_j$ )	0.084 mm	
Nozzle plate thickness (T)	0.5 mm	$T/D_j = 4.2$
Number of nozzles (N)	13	
Dia. of nozzle cluster ( $D_c$ )	22.4 mm	$D_c = ND_j / (0.03 \times 4)$
Nozzle-plate spacing (L)	0.5 mm	$L/D_j = 5.8$

## 충돌 판 코팅

- n-Hexane solution of 0.015 wt % silicon grease
- 0.2 mL of silicon grease solution on impactor plate
- Shaking the coated plate at 200 rpm for 2 min
- Drying at 150 °C for 80 min



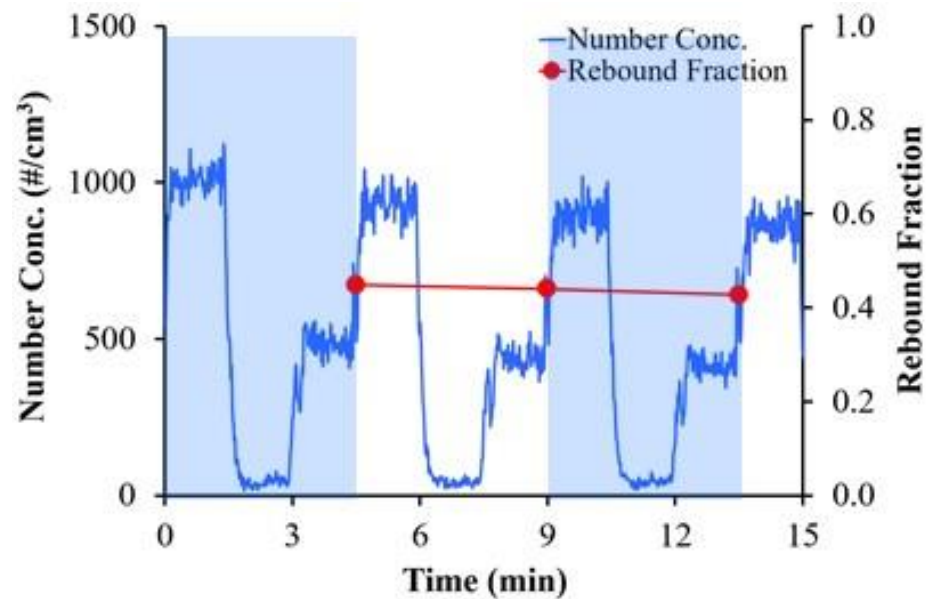
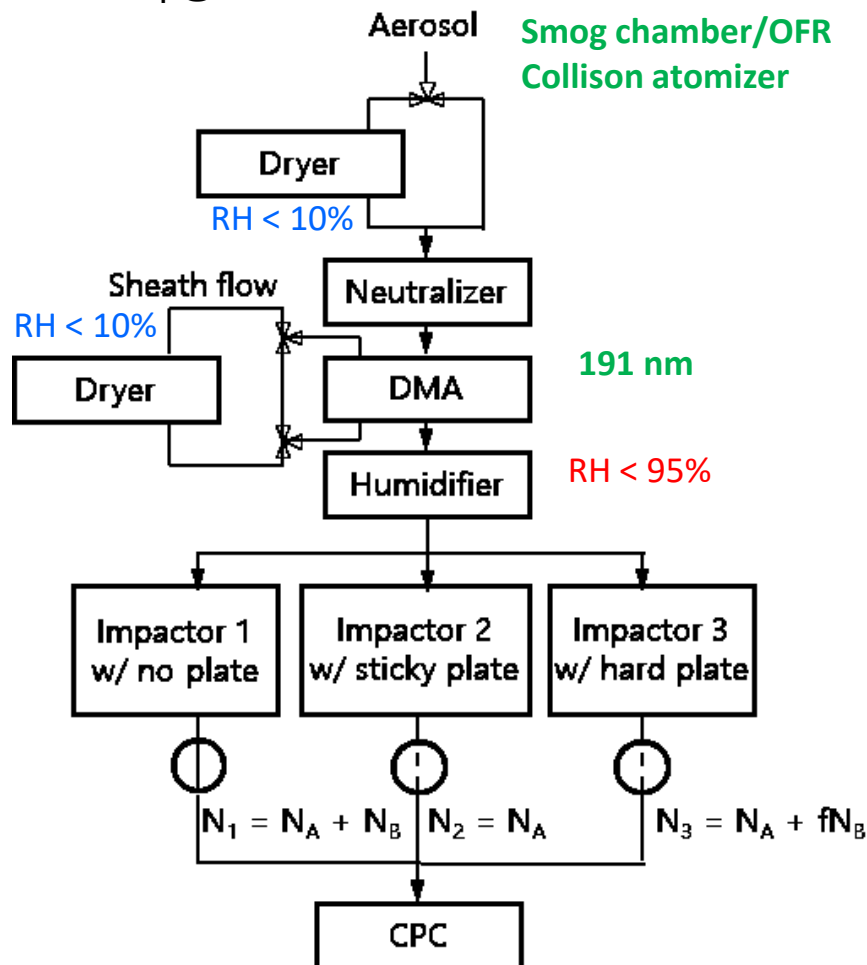
Rebound fraction  

$$f = (N_3 - N_2) / (N_1 - N_2)$$

# Measurement of Humidity-Dependent Particle Rebound

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- 입자의 상과 점도 결정을 위한 리바운드 비율 측정
  - 충돌판이 다른 미니 임팩터 3개 : 무, 점성, 탄성
  - 입자 건조 후 DMA로 입경 선별 (시료 및 DMA sheath 공기 건조)
  - 확산 가습기로 습도 조절
  - 1.5분 간격으로 3개 임팩터를 순차적으로 통과시켜 4.5분 주기 측정



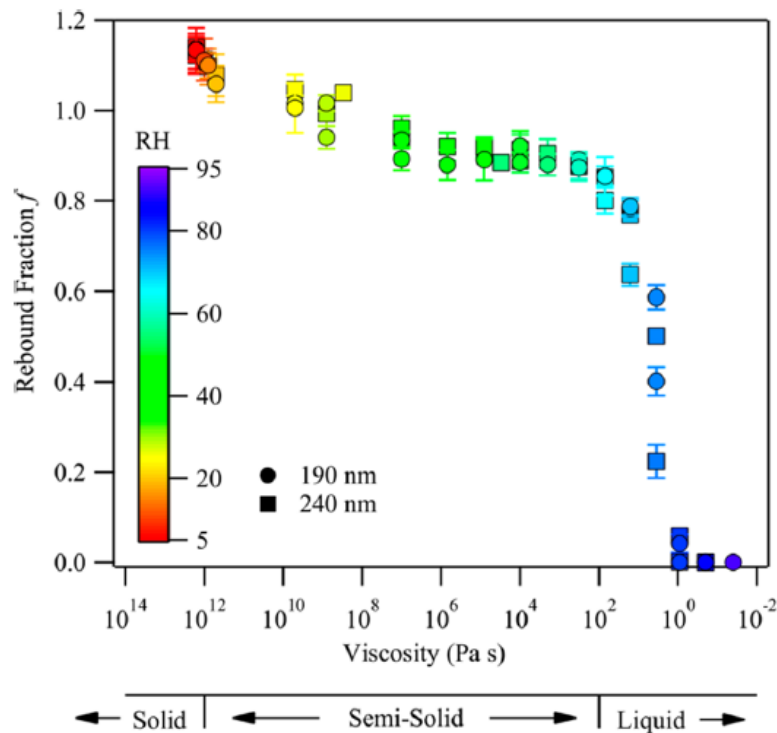
Rebound fraction

$$f = (N_3 - N_2) / (N_1 - N_2)$$

# Characterizing Particle Rebound Impactor System

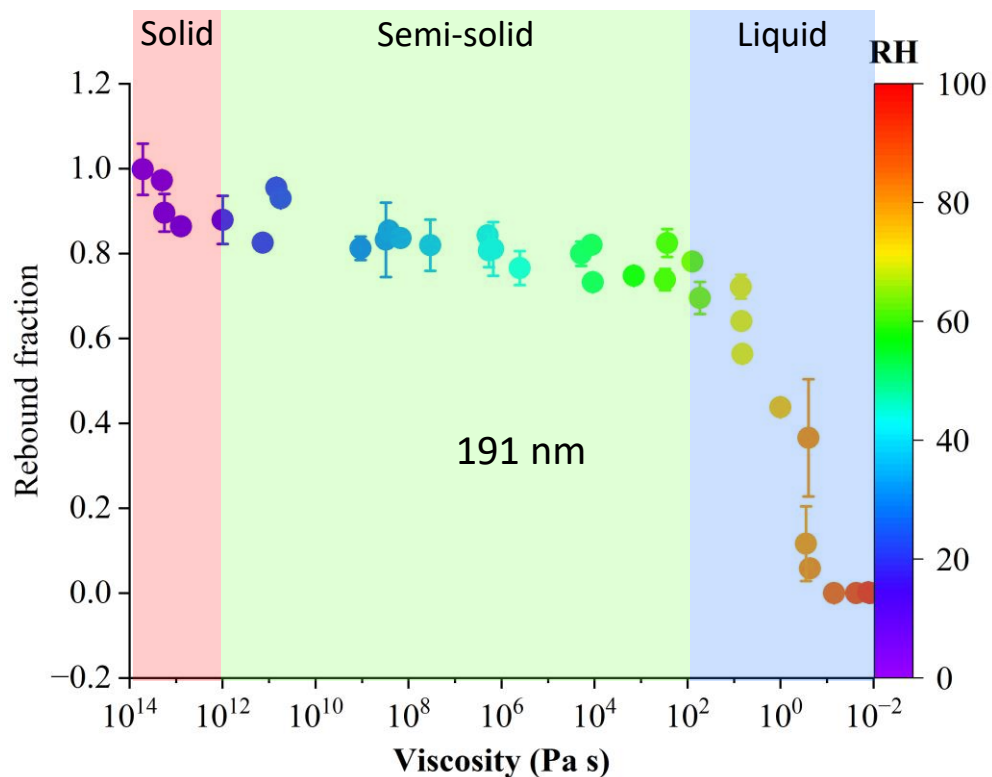
56

## ➤ Viscosity calibration - Sucrose



Bateman et al., EST (2015)

## ➤ Viscosity calibration - Sucrose



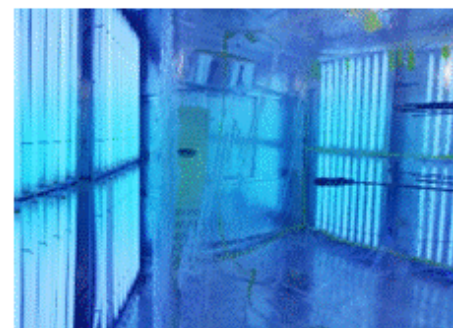
$$\log \eta = 15.92 - 0.276RH\% + 8.68 \times 10^{-4} \times RH\%^2$$

Song et al. (2016)



# SOA Viscosity Measurement by Particle Rebound Method

- 입자 되튀김 임팩터를 이용한 SOA 점도 및 상 측정
  - SOA 생성 : 스모그 챔버, 흐름 반응기
  - ROGs : o-xylene, p-xylene, toluene, cyclododecane

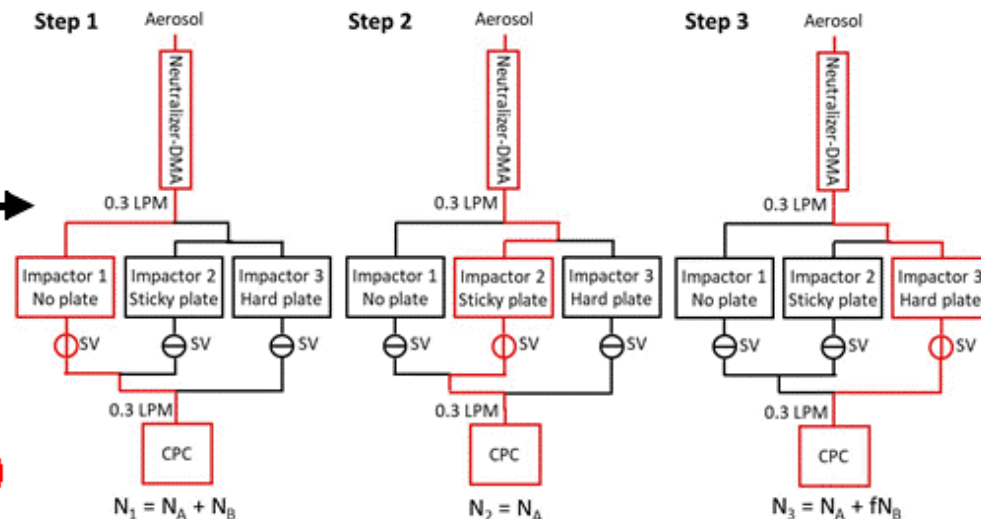


KNU smog chamber  
5 hr Rx



KNU flow reactor  
Controlled aging (1-5 d)

## Particle rebound impactor

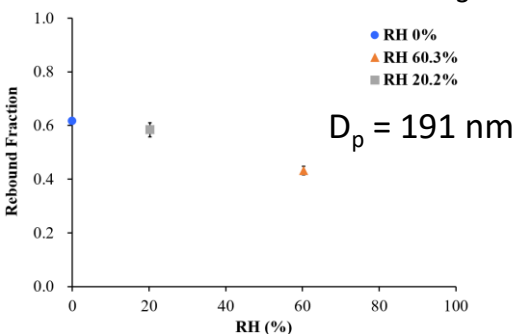


$$\text{Rebound fraction, } f = (N_3 - N_2) / (N_1 - N_2)$$

# Secondary (Organic) Aerosol Phase & Viscosity

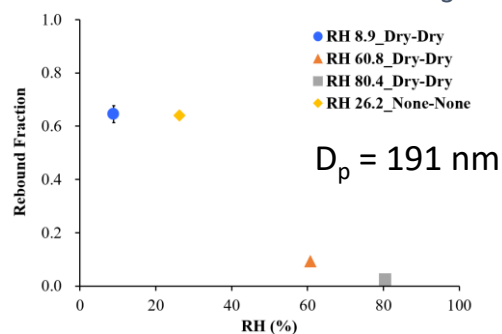
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## ➤ p-Xylene SOA w/o NH<sub>3</sub>



Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	82.6	63.8
NO <sub>3</sub> <sup>-</sup>	1.1	0.9
<b>Org</b>	<b>22.2</b>	<b>17.1</b>
NH <sub>4</sub> <sup>+</sup>	23.6	18.2

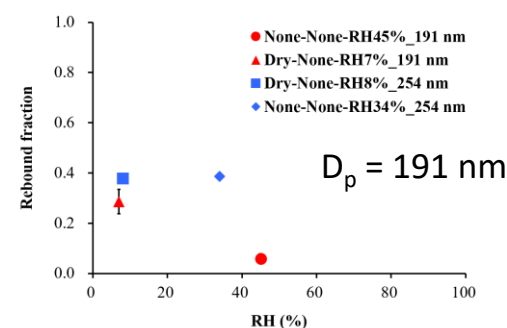
## ➤ p-Xylene SOA w/ NH<sub>3</sub>



Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	93.9	10.8
NO <sub>3</sub> <sup>-</sup>	500.0	57.8
<b>Org</b>	<b>63.2</b>	<b>7.3</b>
NH <sub>4</sub> <sup>+</sup>	208.7	24.1

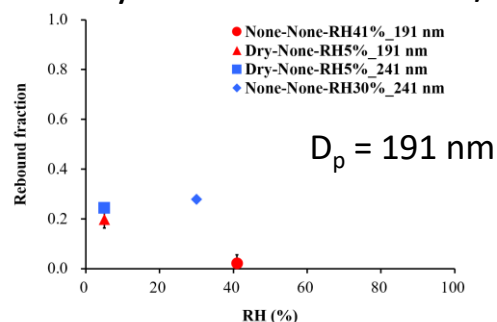
- Xylene SOA의 점도가 cyclododecane SOA보다 큼
- NH<sub>3</sub> 주입 조건의 SOA가 더 낮은 습도에서 액상으로 변환
- 다양한 SOA는 습도 변화에 따른 리바운드 패턴이 매우 상이함 (Bateman et al., 2015)
- SIA 함량이 높을수록 액상 변환 습도가 낮아지는 경향

## ➤ Cyclododecane SOA w/o NH<sub>3</sub>

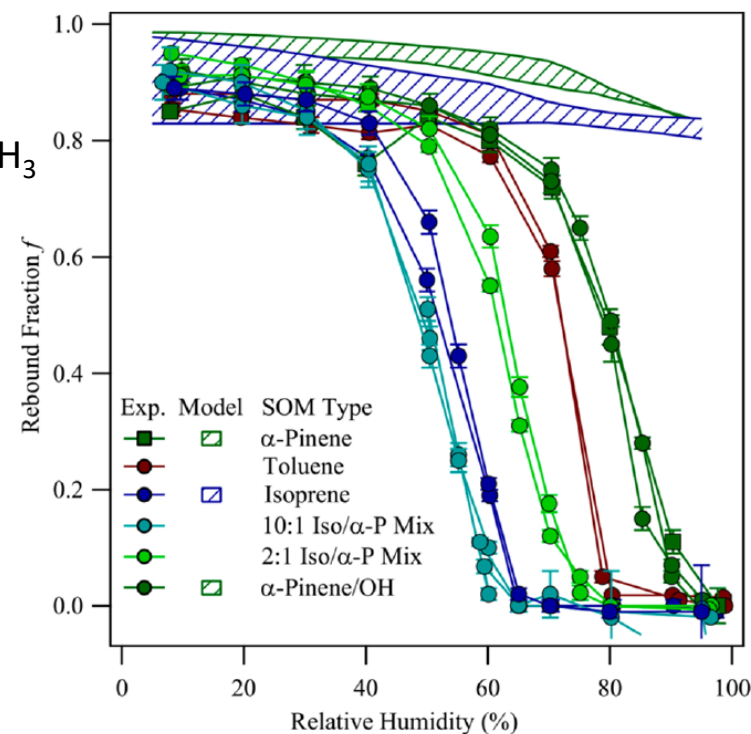


Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	16.3	30.5
NO <sub>3</sub> <sup>-</sup>	3.5	6.6
<b>Org</b>	<b>24.1</b>	<b>45.2</b>
NH <sub>4</sub> <sup>+</sup>	9.4	17.7

## ➤ Cyclododecane SOA w/ NH<sub>3</sub>



Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	18.9	9.0
NO <sub>3</sub> <sup>-</sup>	110.3	52.7
<b>Org</b>	<b>38.6</b>	<b>18.4</b>
NH <sub>4</sub> <sup>+</sup>	41.6	19.9

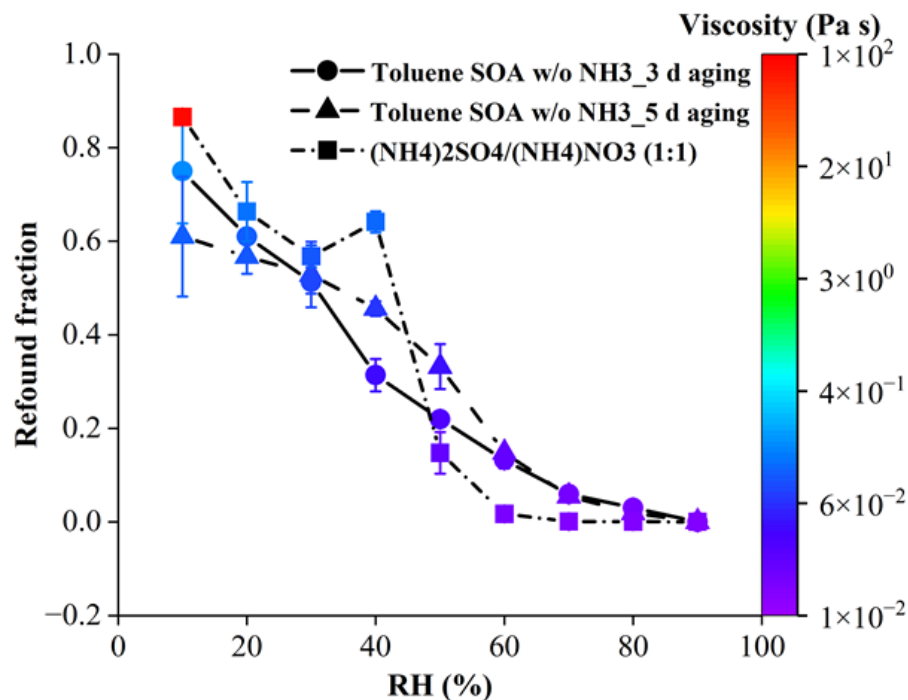


Bateman et al., EST (2015)

# Secondary (Organic) Aerosol Phase & Viscosity

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- Aging effect : Toluene/NO<sub>x</sub> SOA w/o NH<sub>3</sub> (flow reactor)



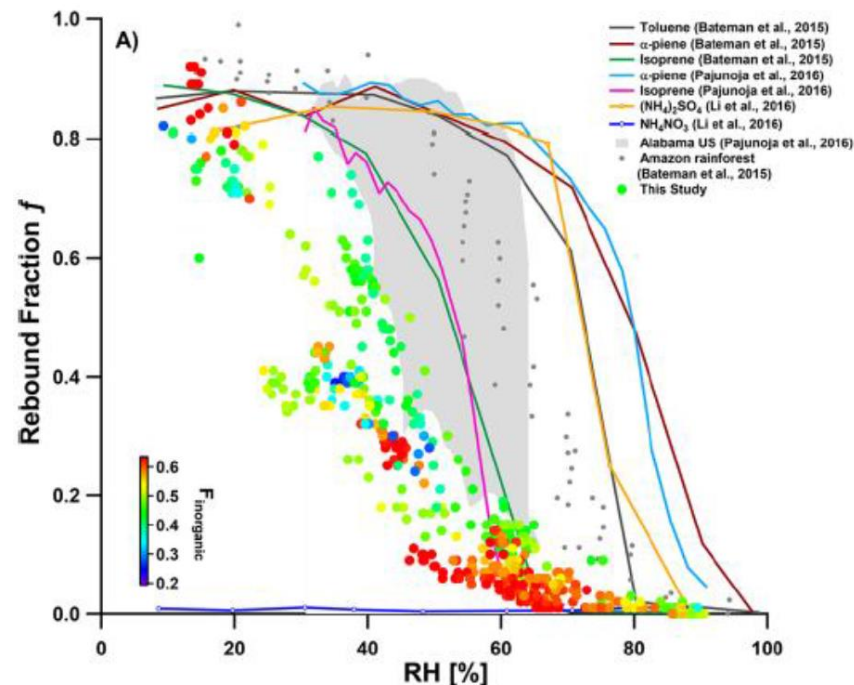
## 3 d aging

Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	-0.7	-0.1
NO <sub>3</sub> <sup>-</sup>	284.4	54.6
Org	145.5	27.9
NH <sub>4</sub> <sup>+</sup>	91.6	17.6

## 5 d aging

Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	-1.1	-0.1
NO <sub>3</sub> <sup>-</sup>	614.5	49.6
Org	417.1	33.7
NH <sub>4</sub> <sup>+</sup>	206.7	16.7

Beijing winter, Jan. 2017



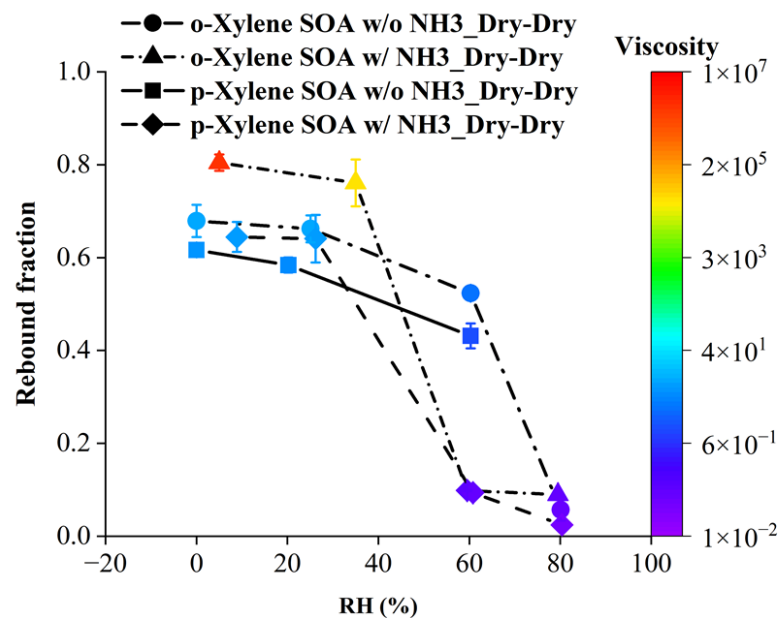
Liu et al., EST (2017)

- SIA (NH<sub>4</sub>NO<sub>3</sub>)와 혼합된 톨루엔 SOA는 Bateman et al. (2015)의 순수한 톨루엔 SOA에 비해 상당히 낮은 리바운드 비 (점도)를 나타냄
- SIA (NH<sub>4</sub>NO<sub>3</sub>)와 혼합된 톨루엔 SOA는 리바운드에 대한 노화 영향이 미미함. RH 50% 전후로 리바운드 비의 양상이 변함
- SIA (NH<sub>4</sub>NO<sub>3</sub>)와 혼합된 톨루엔 SOA의 리바운드 패턴은 중국 북경과 선전의 에어로졸과 유사한 경향을 보임 (Liu et al. 2017; 2019)

# Secondary (Organic) Aerosol Phase & Viscosity

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## ➤ Xylene SOA (smog chamber)



### ■ o-Xylene SOA w/o NH<sub>3</sub>

Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	72.7	59.6
NO <sub>3</sub> <sup>-</sup>	1.5	1.2
Org	24.1	19.8
NH <sub>4</sub> <sup>+</sup>	23.7	19.4

### ■ o-Xylene SOA w/ NH<sub>3</sub>

Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	61.4	6.9
NO <sub>3</sub> <sup>-</sup>	553.1	61.9
Org	67.5	7.6
NH <sub>4</sub> <sup>+</sup>	212.0	23.7

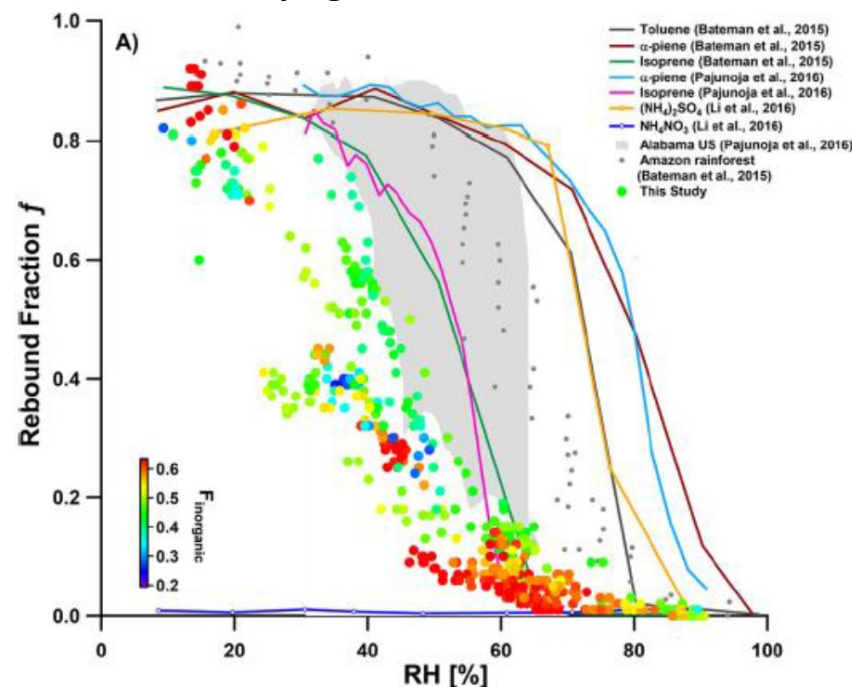
### ■ p-Xylene SOA w/o NH<sub>3</sub>

Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	82.2	64.0
NO <sub>3</sub> <sup>-</sup>	1	0.8
Org	22.2	17.3
NH <sub>4</sub> <sup>+</sup>	23.1	18.0

### ■ p-Xylene SOA w/ NH<sub>3</sub>

Species	Conc. (μg/m <sup>3</sup> )	Fraction (%)
SO <sub>4</sub> <sup>2-</sup>	93.1	10.8
NO <sub>3</sub> <sup>-</sup>	500.5	57.9
Org	63.1	7.3
NH <sub>4</sub> <sup>+</sup>	208.6	24.1

Beijing winter, Jan. 2017



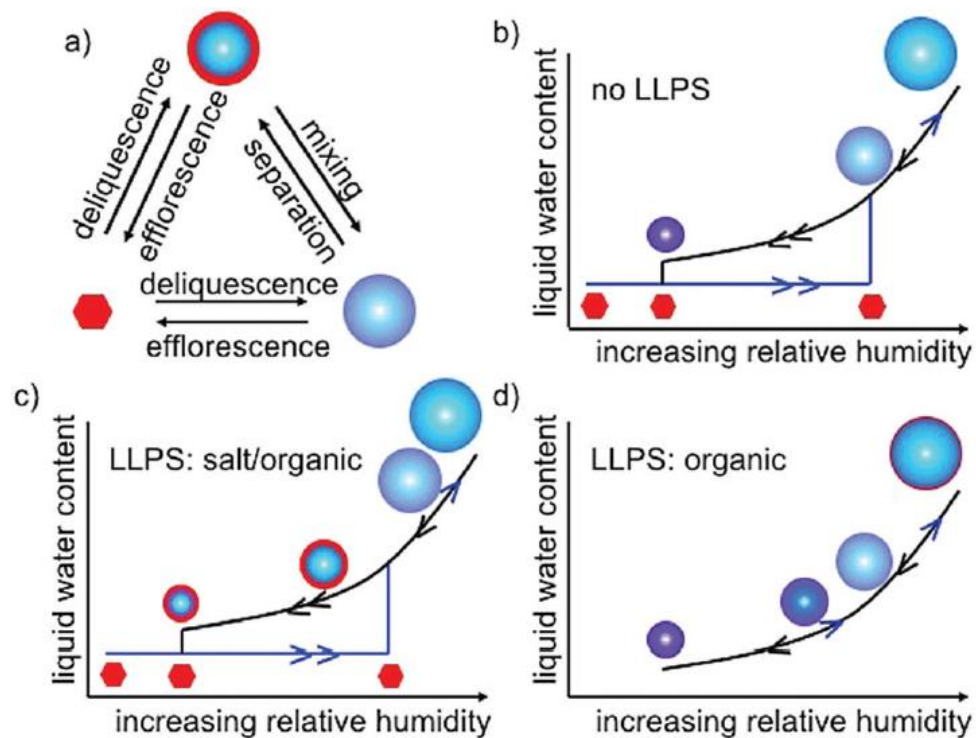
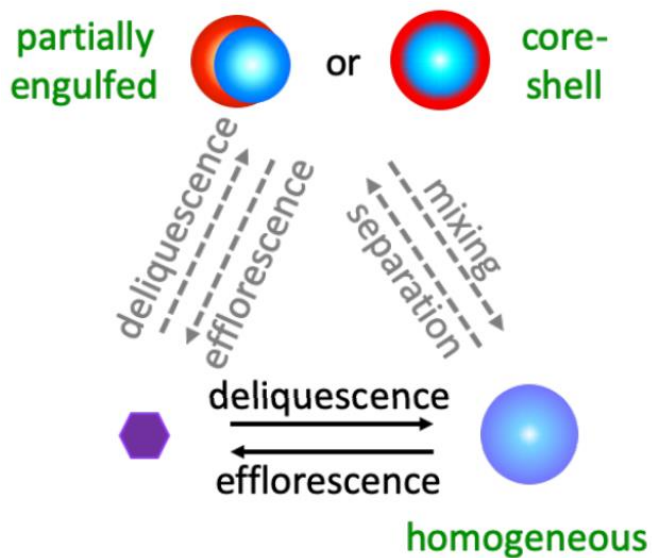
Liu et al., EST (2017)

- SIA (NH<sub>4</sub>NO<sub>3</sub>)와 혼합된 톨루엔 SOA는 Bateman et al. (2015)의 순수한 톨루엔 SOA에 비해 상당히 낮은 리바운드 비 (점도)를 나타냄
- SIA (NH<sub>4</sub>NO<sub>3</sub>)와 혼합된 톨루엔 SOA는 리바운드에 대한 노화 영향이 미미함. RH 50% 전후로 리바운드 비의 양상이 변함
- SIA (NH<sub>4</sub>NO<sub>3</sub>)와 혼합된 톨루엔 SOA의 리바운드 패턴은 중국 북경과 선전의 에어로졸과 유사한 경향을 보임 (Liu et al. 2017; 2019)

# Aerosol Mixing and Phase Separation

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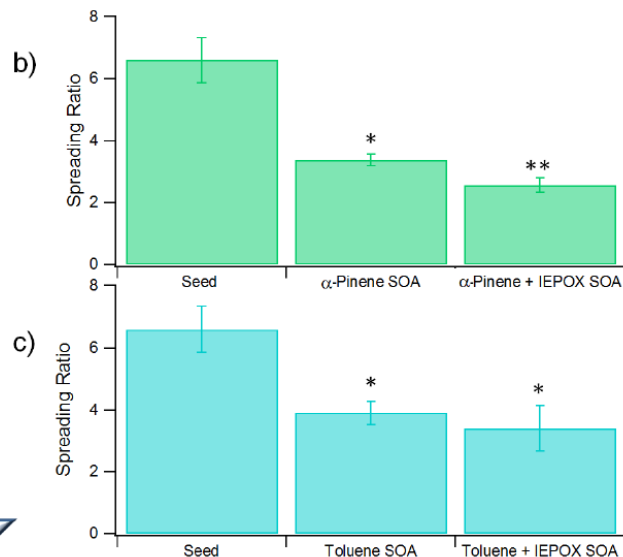
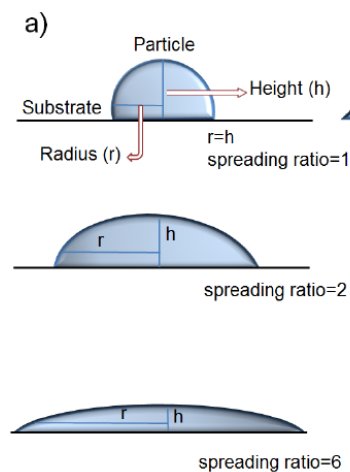
## ➤ 에어로졸 내부 상 혼합 및 분리



Freedman et al., Royal Soc. Chem. (2017)

## 측정 방법

- Atomic Force Microscopy (AFM)
- SEM (tilting)
- Digital microscopy (tilting)



Olson et al. (2021)



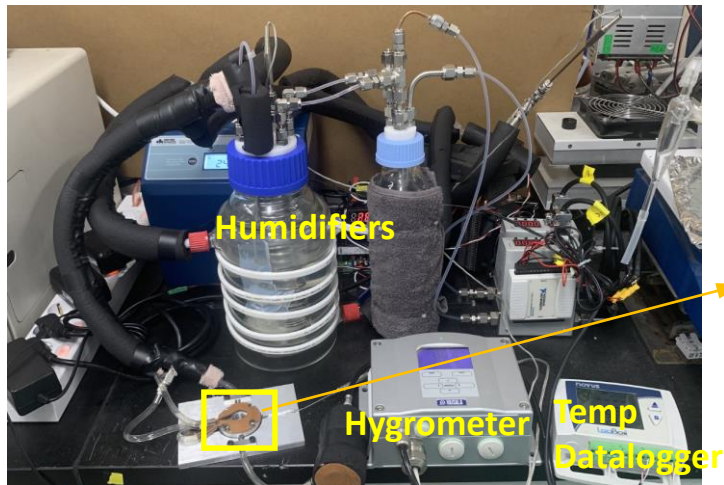
# Optical/Digital Microscopic Imaging System

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## 입자 샘플링

- 에어로졸 발생 : 스모그 챔버, 흐름 반응기, Collision 분무기
- 샘플링 장치 : 멀티 홀 (33,  $\phi$  84 nm) 노즐이 장착된 미니 임팩터, 1 L/min
- 임팩터 판 : 소수성 물질이 코팅된 석영 디스크 ( $\phi$  15 mm x t 1 mm)

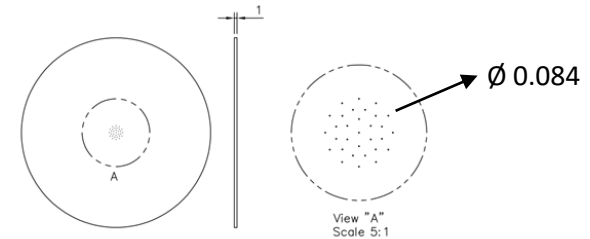
## 습도조절 : flow cell에 석영 디스크를 장착하고, 25 °C 건조/습윤 N<sub>2</sub> 가스를 0.5 L/min으로 흘림



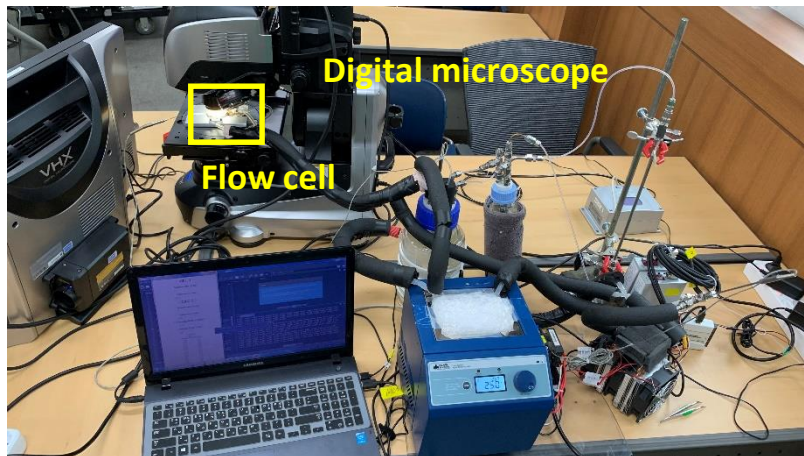
Flow cell



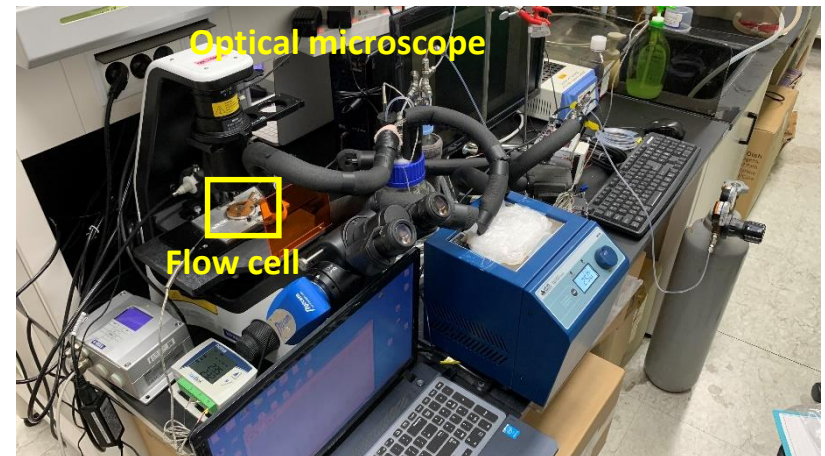
- ID 15 mm x depth 3.8 mm
- RTD Pt100 sensor inside the flow cell
- Thermohygrometer (Vaisala HMT 330) at outlet of the flow cell



## 디지털 현미경 이미징 시스템



## 광학 현미경 이미징 시스템



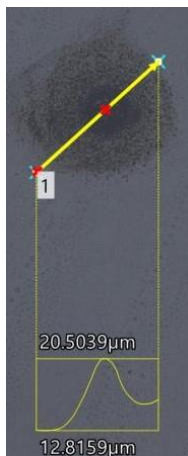
# Secondary Aerosol Shape & Phase: Digital Microscopy

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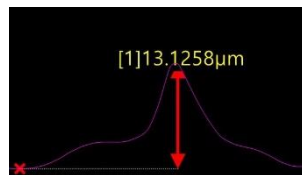
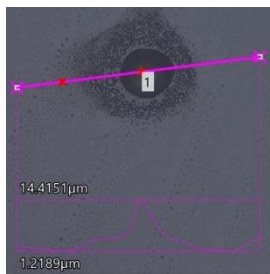
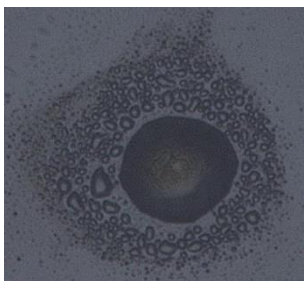
- SOA의 물 흡수에 의한 흡습 성장 확인
- $\text{NH}_3$  주입 실험의 SOA가  $\text{NH}_3$  미주입 실험의 SOA에 비해 더 크게 성장
- 흡수 전후에 입자의 종횡비 변화

- p-Xylene SOA w/o  $\text{NH}_3$

- Dry (RH 0%)

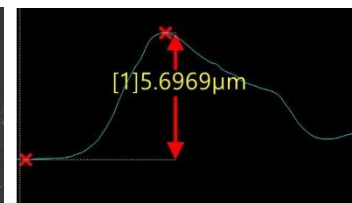
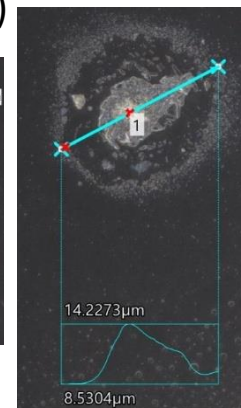
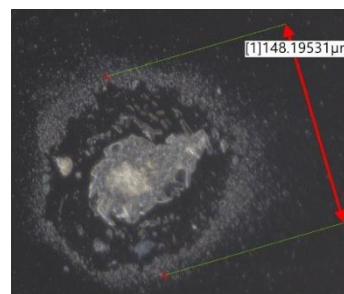


- Humid (RH 85%)

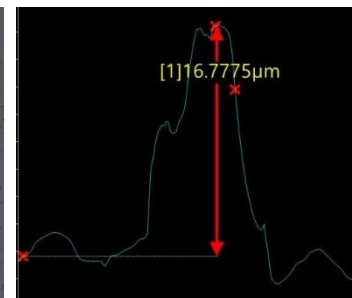
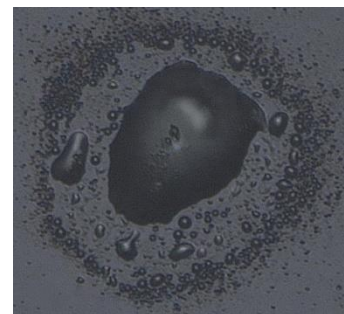


- p-Xylene SOA w/  $\text{NH}_3$

- Dry (RH 0%)



- Humid (RH 86%)

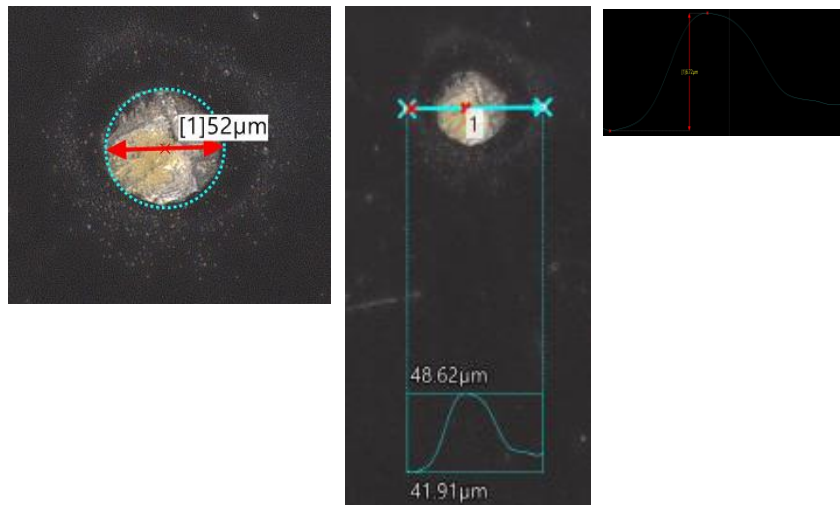


# Secondary Aerosol Shape & Phase: Digital Microscopy

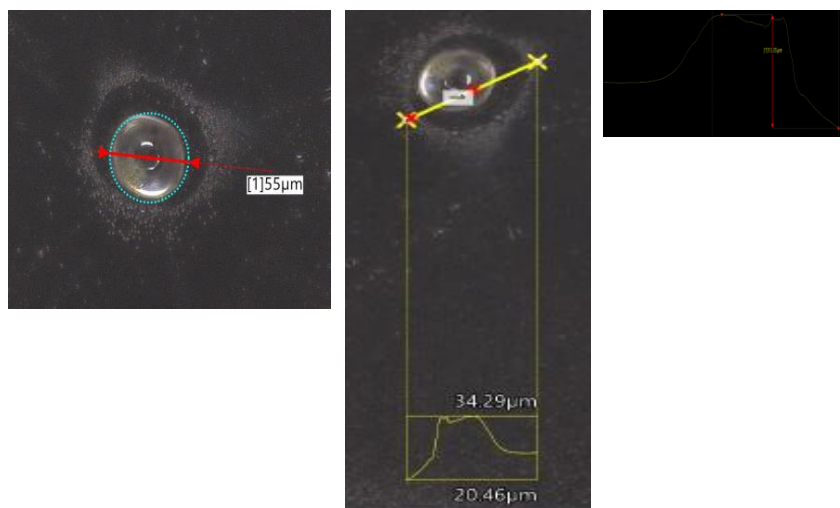
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## ➤ Cyclododecane SOA w/ $\text{NH}_3$

### ■ Dry (RH 0%)

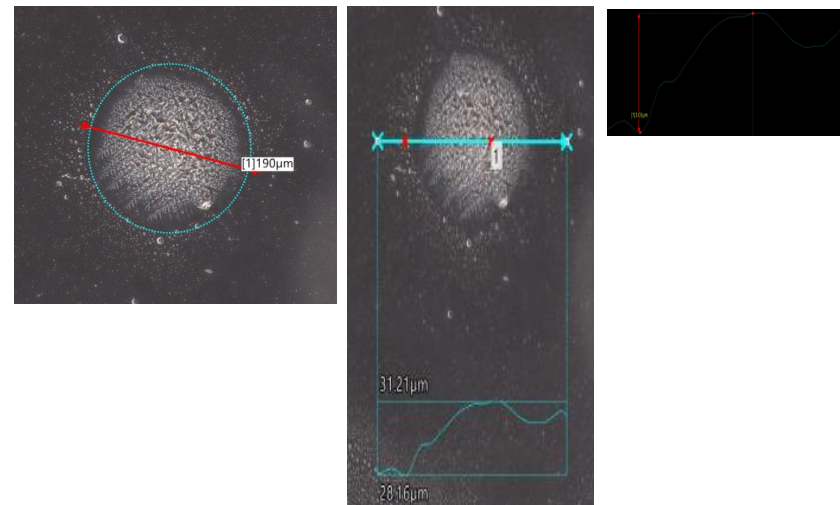


### ■ Humid (RH 97.4%)

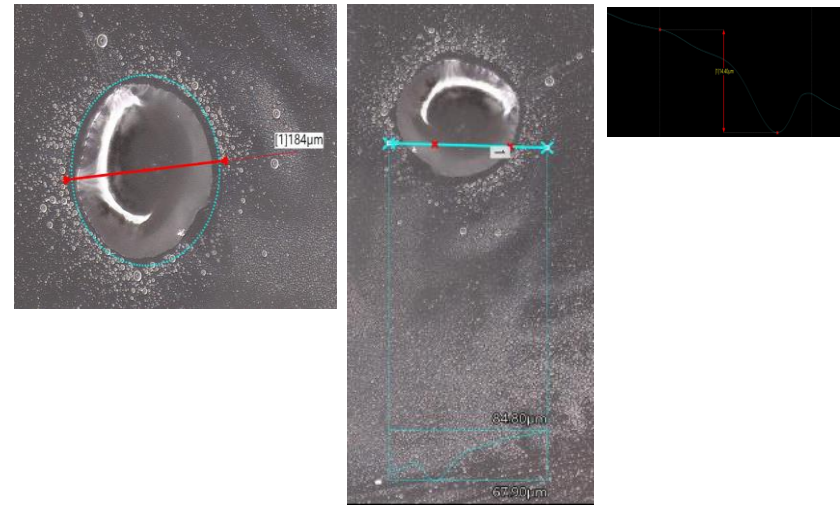


## ➤ o-Xylene SOA w/ $\text{NH}_3$

### ■ Dry (RH 0%)



### ■ Humid (RH 86%)



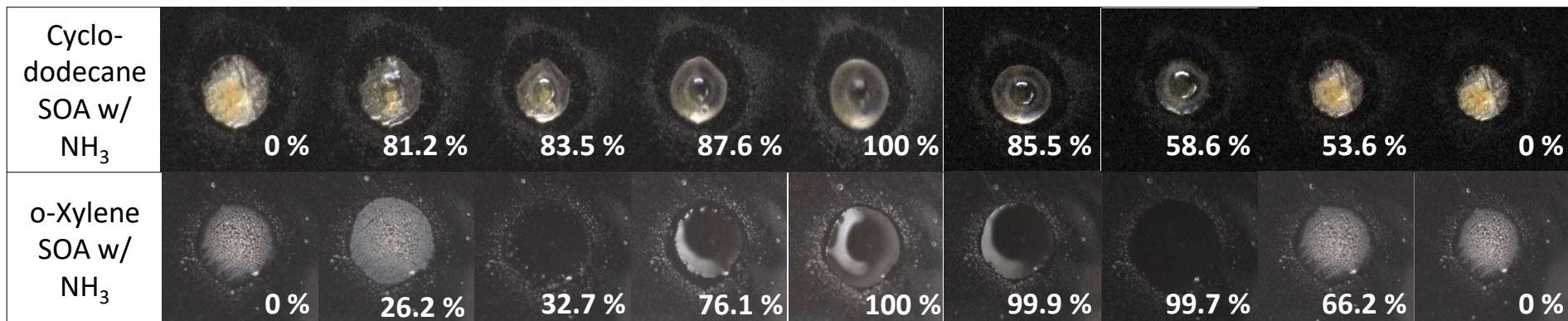


# Aerosol Mixing and Phase Separation: Digital Microscopy

65

RH increase

RH decrease



C-DOD  
w/  $\text{NH}_3$   
(Dry  $\rightarrow$  Wet)

C-DOD  
w/  $\text{NH}_3$   
(Wet  $\rightarrow$  Dry)

o-XYL  
w/  $\text{NH}_3$   
(Dry  $\rightarrow$  Wet)

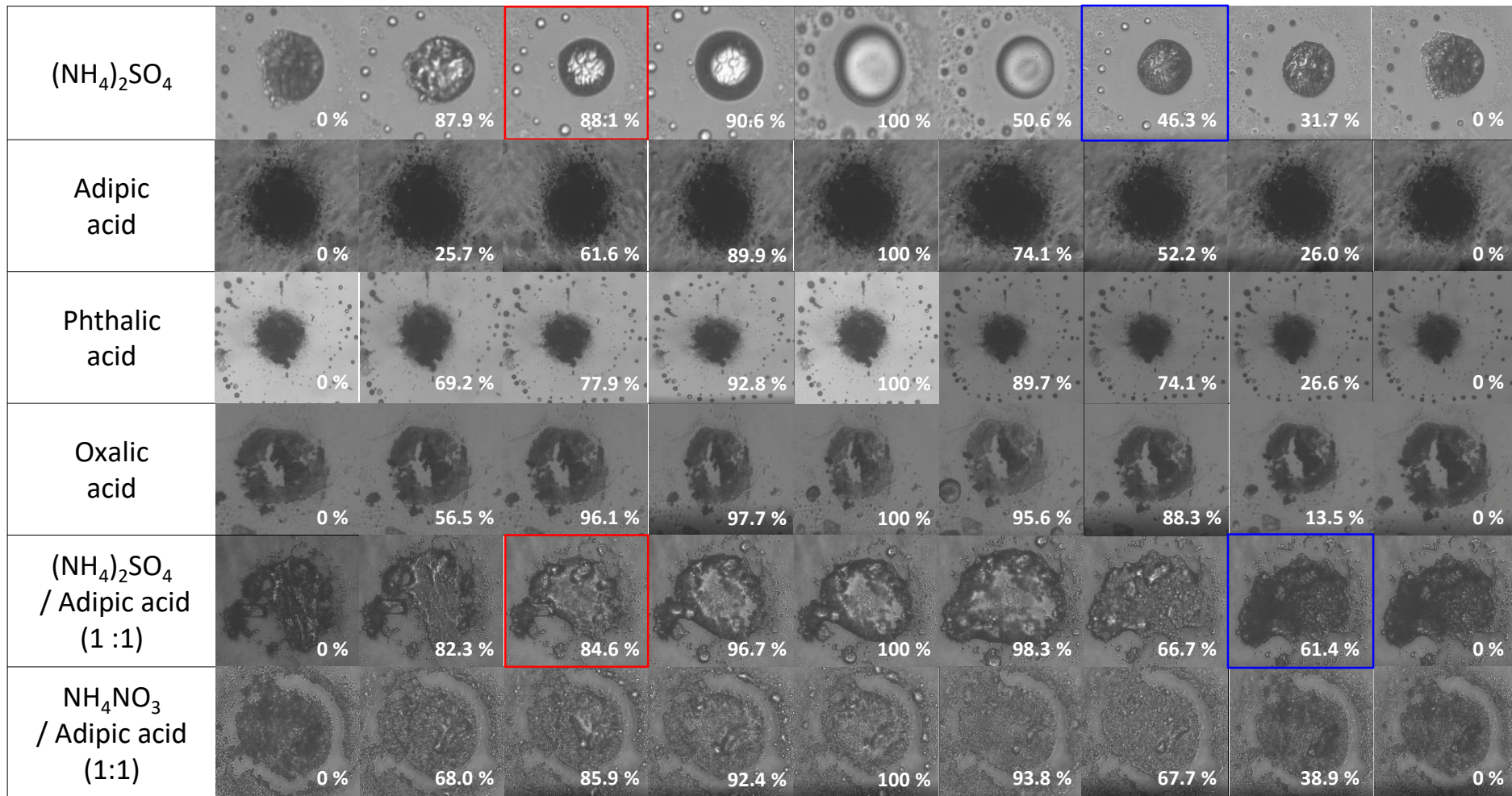
o-XYL  
w/  $\text{NH}_3$   
(Wet  $\rightarrow$  Dry)

# Aerosol Mixing and Phase Separation: Optical Microscopy

66

RH increase

RH decrease

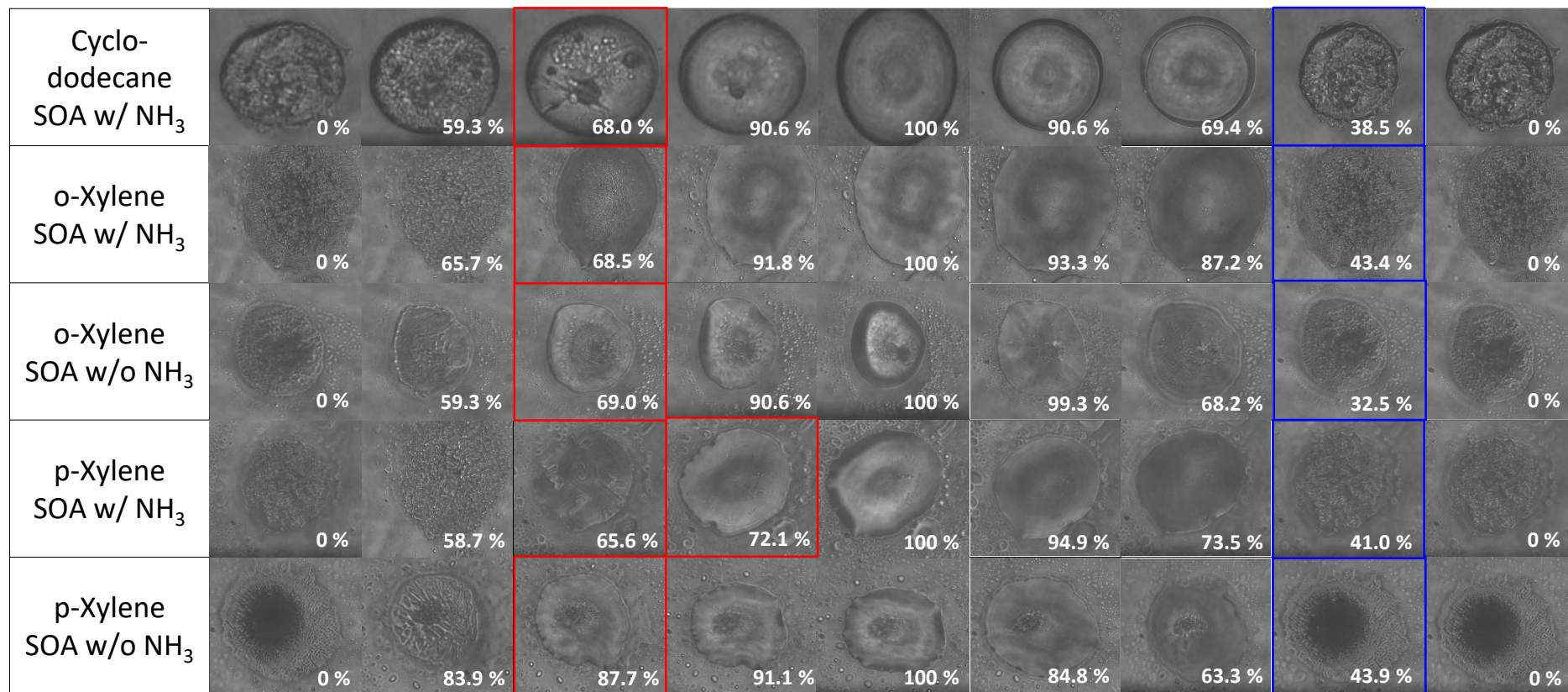




# Aerosol Mixing and Phase Separation: Optical Microscopy <sup>67</sup>

RH increase

RH decrease



(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

Adipic acid

Phthalic acid

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> /  
Adipic acid  
(1:1)

NH<sub>4</sub>NO<sub>3</sub> /  
Adipic acid  
(1:1)

Cyclododecane  
SOA  
w/ NH<sub>3</sub>

o-Xylene  
SOA  
w/ NH<sub>3</sub>

o-Xylene  
SOA  
w/o NH<sub>3</sub>

p-Xylene  
SOA  
w/ NH<sub>3</sub>

p-Xylene  
SOA  
w/o NH<sub>3</sub>

DRH (%) 88.1

-

-

84.6

-

68.0

68.5

69.0

72.1

87.7

ERH (%) 46.3

-

-

61.4

-

38.5

43.4

32.5

41.0

43.9

C-DOD  
w/ NH<sub>3</sub>



C-DOD  
w/ NH<sub>3</sub>



o-XYL  
w/ NH<sub>3</sub>



o-XYL  
w/ NH<sub>3</sub>



o-XYL  
w/o NH<sub>3</sub>



o-XYL  
w/o NH<sub>3</sub>



(Dry → Wet)

(Wet → Dry)

(Dry → Wet)

(Wet → Dry)

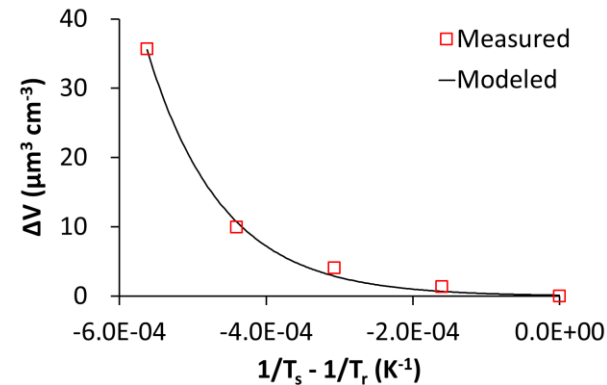
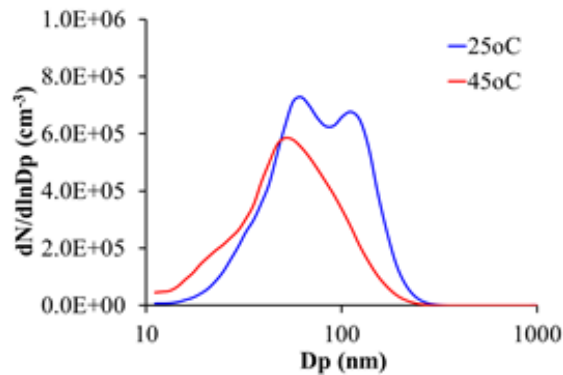
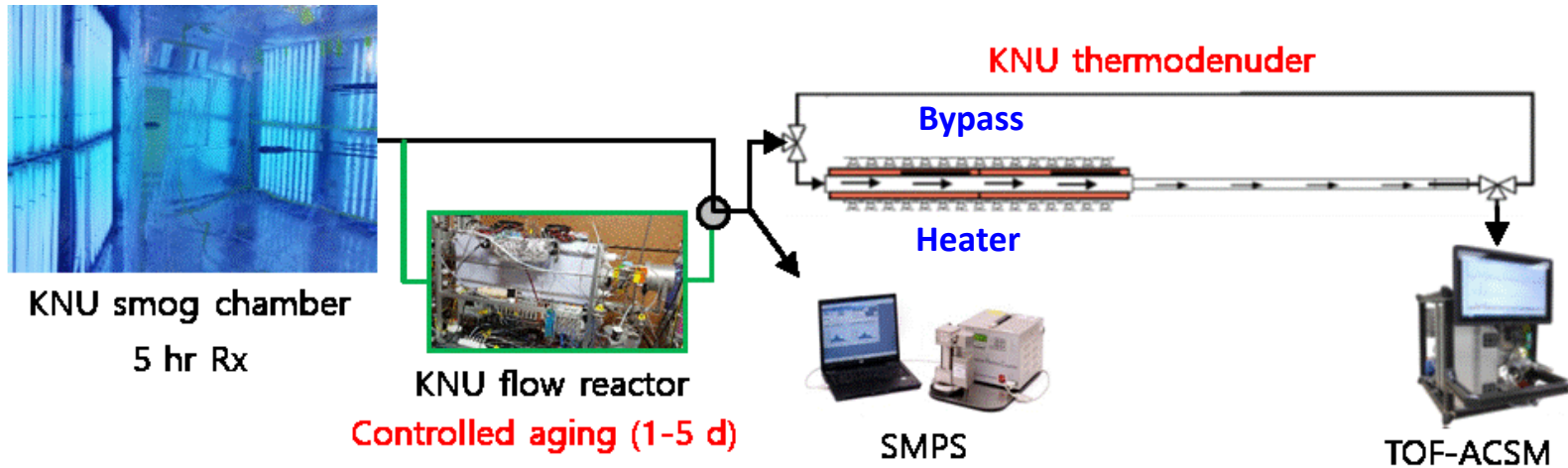
(Dry → Wet)

(Wet → Dry)

# Aerosol Volatility: Thermodenuder System

## 입자 휘발도 측정

- 열디누더를 이용하여 온도 증가에 따른 입자의 휘발 양을 측정 (SMPS, ACSM)
- 휘발 인자(포화 증기압, 휘발 엔탈피)를 이상기체식과 Clausius-Claperyon 식을 이용하여 결정



$$\Delta V = \frac{P^0 M}{\rho_p R T_r} \left[ \exp \left( -\frac{\Delta H_v}{R} \left( \frac{1}{T_s} - \frac{1}{T_r} \right) \right) - 1 \right]$$

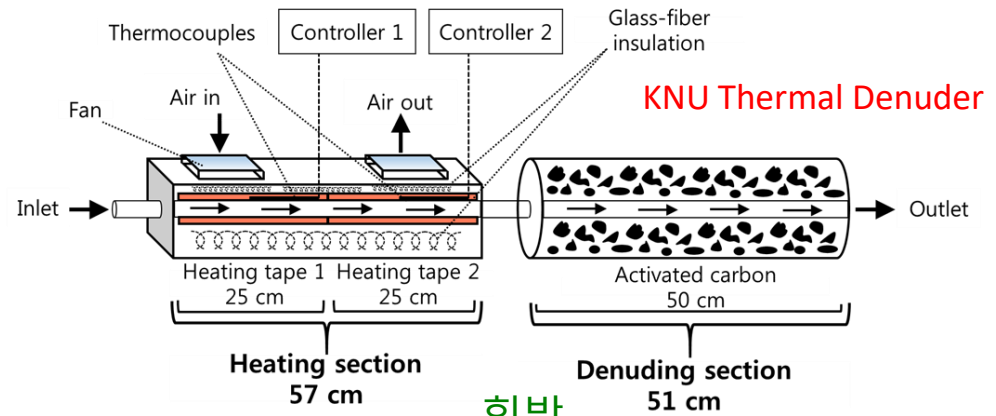
$\Delta V$  (μm<sup>3</sup> cm<sup>-3</sup>),  $P^0$  (Pa),  $M$  (g mol<sup>-1</sup>),  $\rho_p$  (g cm<sup>-3</sup>),  $R$  (8.314 J K<sup>-1</sup> mol<sup>-1</sup>),  $\Delta H_v$  (J mol<sup>-1</sup>),  $T_s$  (K), and  $T_r$  (K)

# 열 디누더를 이용한 휘발도 측정 : IVM - $P_{\text{sat}}$ & $\Delta H_v$

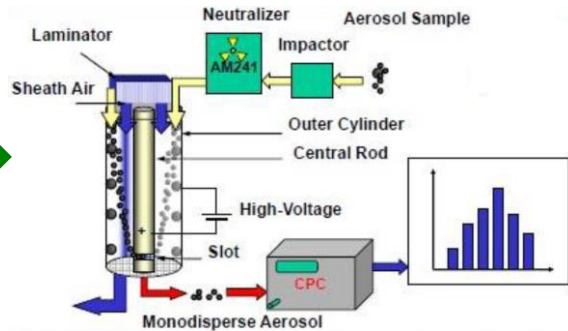
## SOA 생성효율의 $\Delta H_v$ 의존성

$$Y_{\text{SOA}} = \frac{\text{SOA}}{\Delta \text{VOC}} = M_o \left( \frac{\alpha_1 K_1}{1 + K_1 M_o} + \frac{\alpha_2 K_2}{1 + K_2 M_o} \right)$$

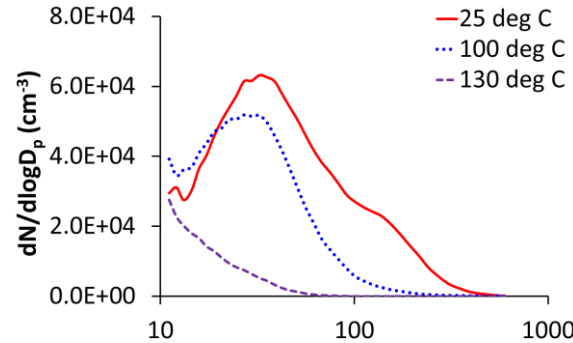
$$K_{T2} = K_{T1} \exp \left( \frac{\Delta H_v}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$



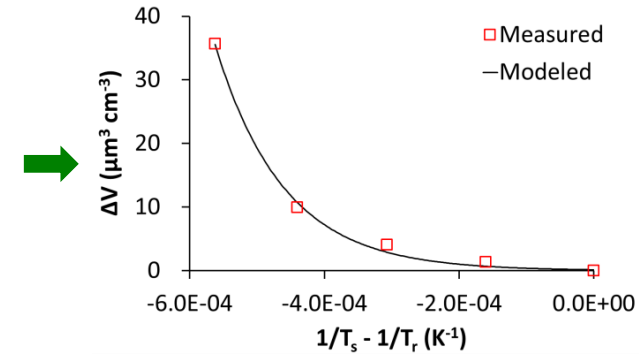
휘발



입도분포 측정



휘발 데이터 수집



휘발도( $P_{\text{sat}}$  &  $\Delta H_v$ ) 추정

Clausius-Claperyon 방정식

$$\ln(P_s^0) - \ln(P^0) = -\frac{\Delta H_v}{R} \left( \frac{1}{T_s} - \frac{1}{T_r} \right)$$

이상기체방정식

$$\Delta V = \frac{M}{\rho_p R T_r} (P_s^0 - P^0)$$

Integrated volume method (IVM)

$$\Delta V = \frac{P^0 M}{\rho_p R T_r} \left[ \exp \left( -\frac{\Delta H_v}{R} \left( \frac{1}{T_s} - \frac{1}{T_r} \right) \right) - 1 \right]$$

$\Delta V$  ( $\mu\text{m}^3 \text{cm}^{-3}$ ),  $P^0$  (Pa),  $M$  ( $\text{g mol}^{-1}$ ),  $\rho_p$  ( $\text{g cm}^{-3}$ ),  $R$  ( $8.314 \text{ J K}^{-1} \text{mol}^{-1}$ ),  $\Delta H_v$  ( $\text{J mol}^{-1}$ ),  $T_s$  (K), and  $T_r$  (K)

## SOA 휘발도 측정

### 단계별 승온

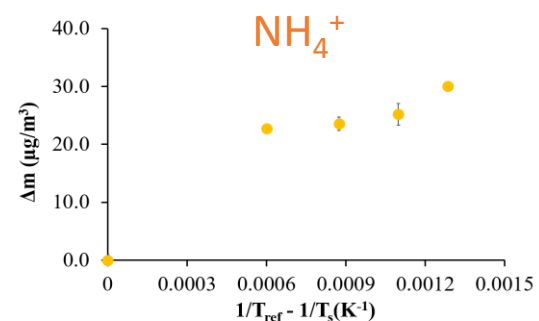
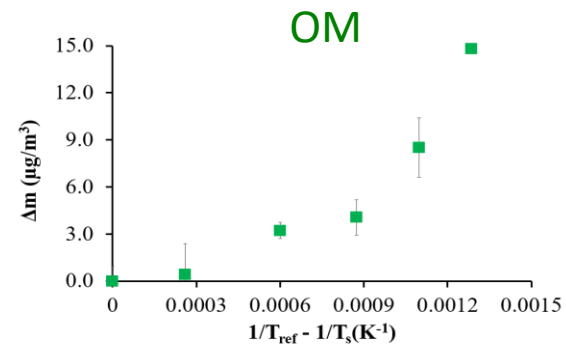
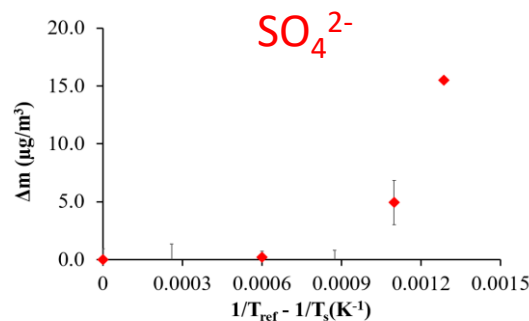
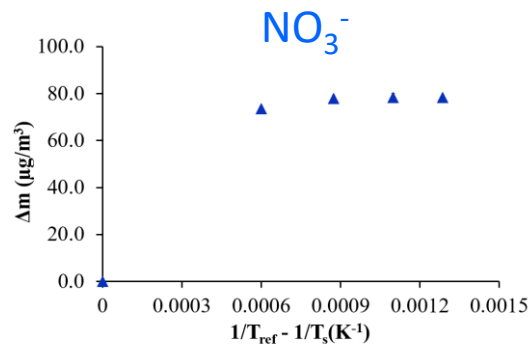
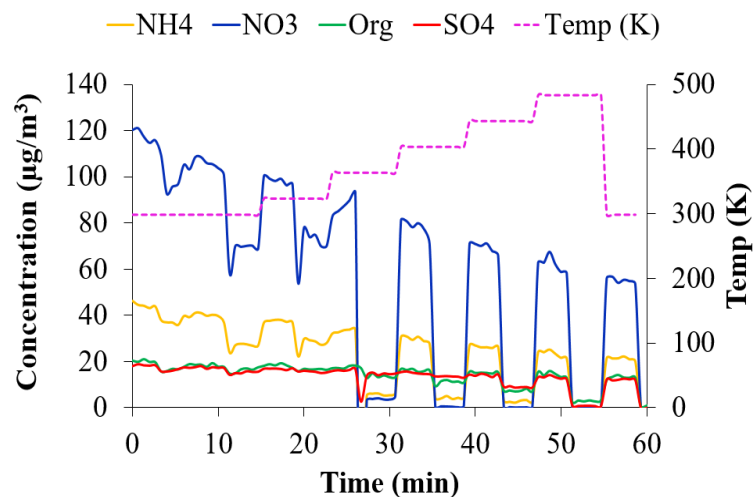
- SOA : 25–210 °C, 4 min/step x 6 steps (denuder 2 min, bypass 2 min)
- 표준 유기물 : 25–70 °C, 4 min/step x 6 steps (denuder 2 min, bypass 2 min)

### 자동 운전 : 프로그래머블 온도조절기 / 릴레이 타이머

### $\Delta H_{\text{vap}}$ 결정 : 총부피 방법 (integrated volume method : IVM)

## o-Xylene 200 ppb w/ $\text{NH}_3$

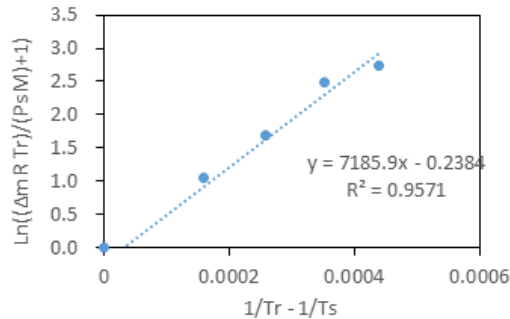
### Volatility: $\text{NO}_3^- \gg \text{SOA} > \text{SO}_4^{2-}$



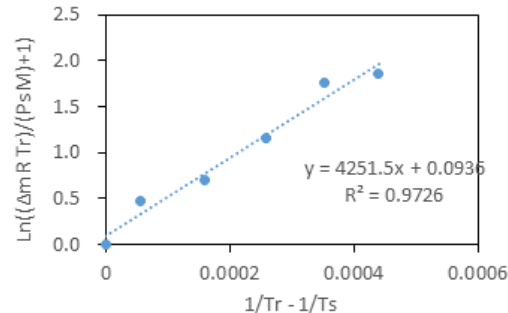
# Volatility of SOA Representative Compounds

## ➤ 휘발도 결정

### ■ Adipic acid



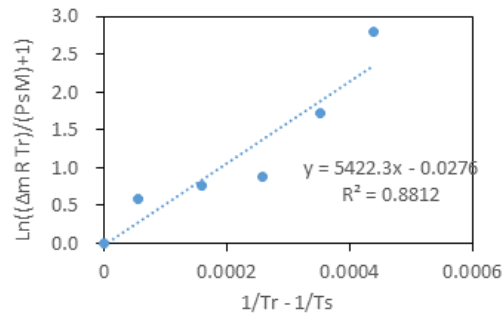
### ■ Adipic acid + NH<sub>4</sub>OH (1:1)



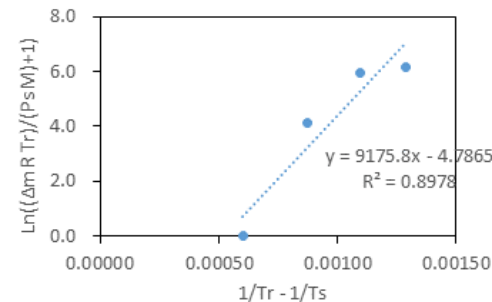
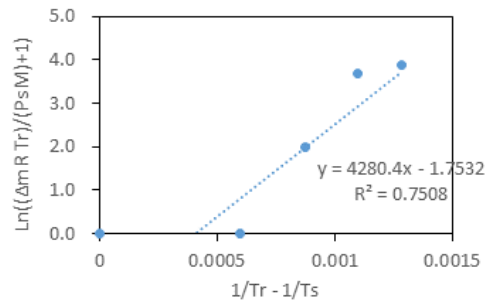
### ■ Adipic acid

C*	Ps	ΔH <sub>v</sub>	R <sup>2</sup>
μg/m <sup>3</sup>	Pa	kJ/mol	
100	1.65E-03	18.37	0.953
10	1.65E-04	59.74	0.957
1	1.65E-05	104.58	0.920
0.1	1.65E-06	152.63	0.861
0.01	1.65E-07	200.73	0.823
0.001	1.65E-08	248.84	0.941

### ■ Phthalic acid



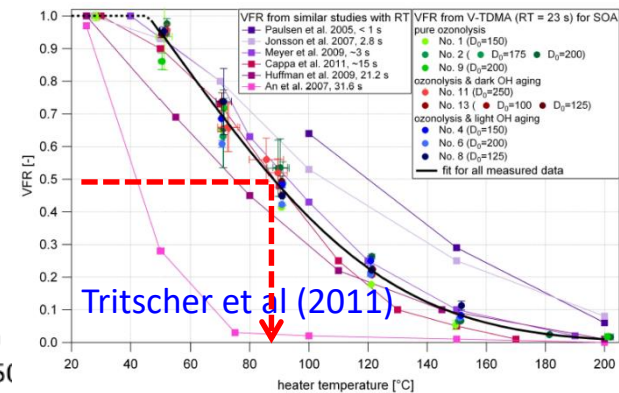
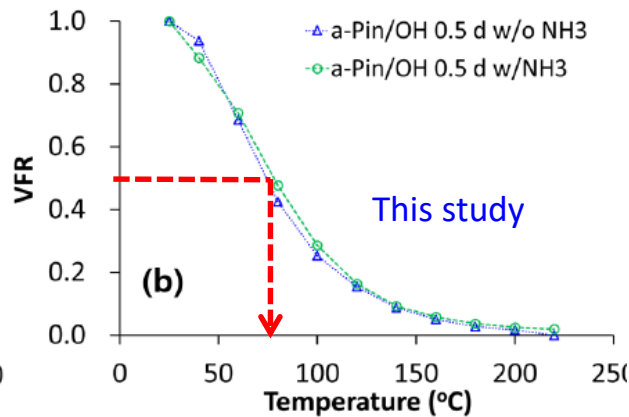
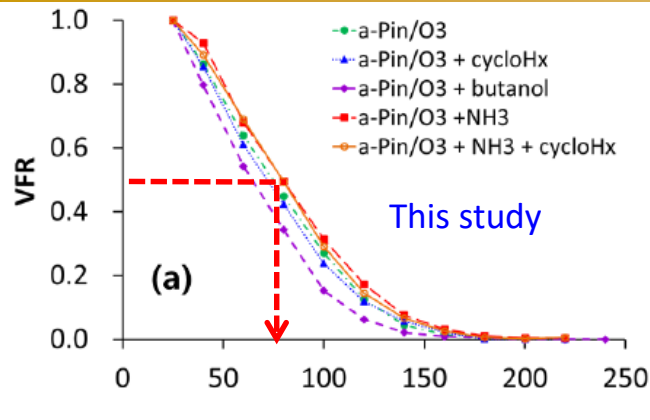
### ■ Phthalic acid + NH<sub>4</sub>OH (1:1)



Species	P <sup>0</sup> <sub>sat</sub> kPa	MW g/mol	ΔH <sub>v</sub> kJ/mol	P <sup>0</sup> <sub>sat</sub> kPa	ΔH <sub>v</sub> kJ/mol
Adipic acid (AA)	1.65E-04	146.14	59.74	2.96E-4	37.38
AA + NH <sub>4</sub> OH (1:1)	1.65E-04	180.20	35.35	3.13E-4	22.26
Phthalic acid (PA)	1.65E-04	166.14	45.08	5.57E-6	109.9
PA + NH <sub>4</sub> OH (1:1)	1.24E-06	200.19	47.01(76.29)	2.93E-5	58.63
AA + PA (1:1)					
AA + PA + NH <sub>4</sub> OH (1:1:2)					



# $\alpha$ -피넨 SOA의 휘발도 측정 : IVM - $P_{sat}$ & $\Delta H_v$



## ➤ SOA 휘발도의 2성분 모델

- 실제 SOA는 수 천종의 혼합물
- 1 성분은 실제 SOA를 반영하지 못할 가능성 큼
- 따라서, 가스/입자 상분배의 2성분 모델처럼 2성분 모델이 휘발도에 적용됨

$$\Delta V = \alpha_1 \frac{P_{sat,1}^0 M_1}{\rho_{p,1} R T_r} \left[ \exp \left( -\frac{\Delta H_{v,1}}{R} \left( \frac{1}{T_s} - \frac{1}{T_r} \right) \right) - 1 \right] + \alpha_2 \frac{P_{sat,2}^0 M_2}{\rho_{p,2} R T_r} \left[ \exp \left( -\frac{\Delta H_{v,2}}{R} \left( \frac{1}{T_s} - \frac{1}{T_r} \right) \right) - 1 \right]$$

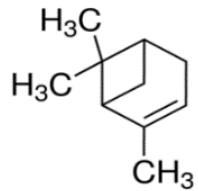
Exp. ID	$\Delta H_{v,1}$ (kJ mol <sup>-1</sup> ) more volatile	$P_{sat,1}^0 \times 10^{-2}$ (Pa) more volatile	$\Delta H_{v,2}$ (kJ mol <sup>-1</sup> ) less volatile	$P_{sat,2}^0 \times 10^{-4}$ (Pa) less volatile	References
$\alpha$ -Pin/ $O_3$	11.31	1.31	27.15	8.15	This study
$\alpha$ -Pin/ $O_3$ +CycloHx	9.28	1.72	21.78	15.7	This study
$\alpha$ -Pin/ $O_3$ +Butanol	7.71	2.55	21.22	20.5	This study
$\alpha$ -Pin/ $O_3$ +NH <sub>3</sub>	14.21	0.97	28.51	8.04	This study
$\alpha$ -Pin/ $O_3$ +NH <sub>3</sub> +CycloHx	11.06	1.35	25.25	8.30	This study
$\alpha$ -Pin/OH 0.5 d w/o NH <sub>3</sub>	15.12	1.24	28.71	8.11	This study
$\alpha$ -Pin/OH 0.5 d w/ NH <sub>3</sub>	16.24	0.94	29.96	7.84	This study
NO <sub>x</sub> photooxidation	-	-	33-43.5	-	Offenberg et al. (2006)
O <sub>3</sub> only	-	-	29.2±9	-	Salo et al. (2010)
CMAQ model <sup>a</sup>	-	-	40	-	Carlton et al. (2010)
Aerosol dynamic model	-	-	45	-	Lee et al. (2011)
Mass transfer model	-	-	30	-	Riipinen et al. (2010)

Chemical Species	$\Delta H_v$ (kJ mol <sup>-1</sup> )	$P^o_{sat}$ (Pa)	Method	References
Succinic acid (C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> )	86.5 ± 2.5 (298-318 K)	4.7 ± 0.7 × 10 <sup>-4</sup>	IVM <sup>a</sup>	This study
	88.0 (298-318 K)	3.7 × 10 <sup>-4</sup>	IVM <sup>a</sup>	Saleh et al. (2008)
	112.0 (303-328 K)	6.40 × 10 <sup>-5</sup>	TDMA <sup>b</sup>	Salo et al. (2010)
	111.9 (298-598 K)	-	VDMA <sup>c</sup>	Offenberg et al. (2006)
Adipic acid (C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> )	146.1 (298-318 K)	1.98 × 10 <sup>-5</sup>	IVM <sup>a</sup>	This study
	135.0 (298-318 K)	3.40 × 10 <sup>-5</sup>	IVM <sup>a</sup>	Saleh et al. (2008)
	97.0 (303-333 K)	5.80 × 10 <sup>-5</sup>	TDMA <sup>b</sup>	Salo et al. (2010)
	140.0	1.7 × 10 <sup>-5</sup>	TD <sup>d</sup>	Chattopadhyay et al. (2001)
	154.0 (296-314 K)	3.40 × 10 <sup>-5</sup>	TDMA <sup>b</sup>	Bilde et al. (2003)
	68.1 (298-598 K)	-	VDMA <sup>c</sup>	Offenberg et al. (2006)
Pimelic acid (C <sub>7</sub> H <sub>12</sub> O <sub>4</sub> )	139.2 (298-318 K)	8.91 × 10 <sup>-5</sup>	IVM <sup>a</sup>	This study
	147.0 (296-314 K)	7.60 × 10 <sup>-5</sup>	TDMA <sup>b</sup>	Bilde et al. (2003)
	149.0 (298-318 K)	7.20 × 10 <sup>-5</sup>	IVM <sup>a</sup>	Saleh et al. (2008)
	127.0 (301-323)	1.7 × 10 <sup>-4</sup>	TDMA <sup>b</sup>	Salo et al. (2010)
	140.4 (298-598 K)	-	VDMA <sup>c</sup>	Offenberg et al. (2006)
Pinic acid (C <sub>9</sub> H <sub>14</sub> O <sub>4</sub> )	93.8 ± 1.8 (298-318 K)	1.6 ± 0.5 × 10 <sup>-4</sup>	IVM <sup>a</sup>	This study
	83 (301-323)	1.0 × 10 <sup>-4</sup>	TDMA <sup>b</sup>	Salo et al. (2010)
3-MBTCA (C <sub>8</sub> H <sub>12</sub> O <sub>6</sub> )	118.8 (298-318 K)	1.54 × 10 <sup>-5</sup>	IVM <sup>a</sup>	This study
Ketopinic acid (C <sub>10</sub> H <sub>14</sub> O <sub>3</sub> )	136.6 (298-318 K)	5.81 × 10 <sup>-5</sup>	IVM <sup>a</sup>	This study
DTAA (C <sub>10</sub> H <sub>16</sub> O <sub>6</sub> )	135.4 ± 3.7 (298-318 K)	3.0 ± 0.3 × 10 <sup>-5</sup>	IVM <sup>a</sup>	This study
Terpenylic acid (C <sub>8</sub> H <sub>12</sub> O <sub>4</sub> )	88.4 (298-318 K)	1.74 × 10 <sup>-4</sup>	IVM <sup>a</sup>	This study
Organosulfate (C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> Na)	35.7 (298-393 K)	5.41 × 10 <sup>-5</sup>	IVM <sup>a</sup>	This study

<sup>a</sup>Integrated volume method (IVM); <sup>b</sup>Tandem differential mobility analyzer (TDMA); <sup>c</sup>Volatility differential mobility analysis (VDMA); <sup>d</sup>Thermal desorption

# $\alpha$ -피넨 SOA에 대한 $\text{NH}_3$ 영향 : 흐름반응기를 이용한 SOA 생성

## SOA 생성



50-400 ppb

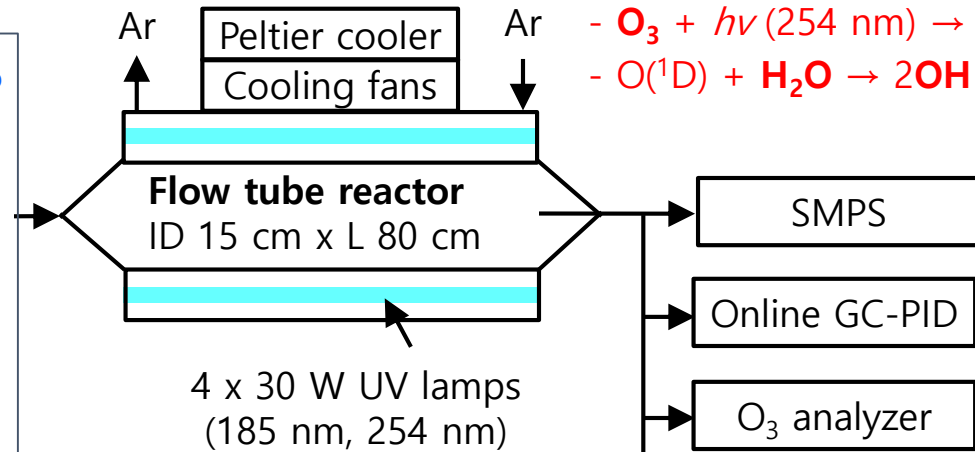
RH 50%

+

1.  $\text{O}_3$ :  $\text{O}_3$ \_w/o  $\text{NH}_3$
2.  $\text{O}_3 + \text{NH}_3$ :  $\text{O}_3$ \_w/  $\text{NH}_3$
3.  $\text{O}_3 + \text{H}_2\text{O} + h\nu$ 
  - OH\_0.5d\_w/o  $\text{NH}_3$
  - OH\_1.0d\_w/o  $\text{NH}_3$
  - OH\_3.0d\_w/o  $\text{NH}_3$
4.  $\text{O}_3 + \text{H}_2\text{O} + \text{NH}_3 + h\nu$ 
  - OH\_0.5d\_w/  $\text{NH}_3$
  - OH\_1.0d\_w/  $\text{NH}_3$
  - OH\_3.0d\_w/  $\text{NH}_3$

## OH radical formation

- $\text{O}_3 + h\nu (254 \text{ nm}) \rightarrow \text{O}(^1\text{D}) + \text{O}_2$
- $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$



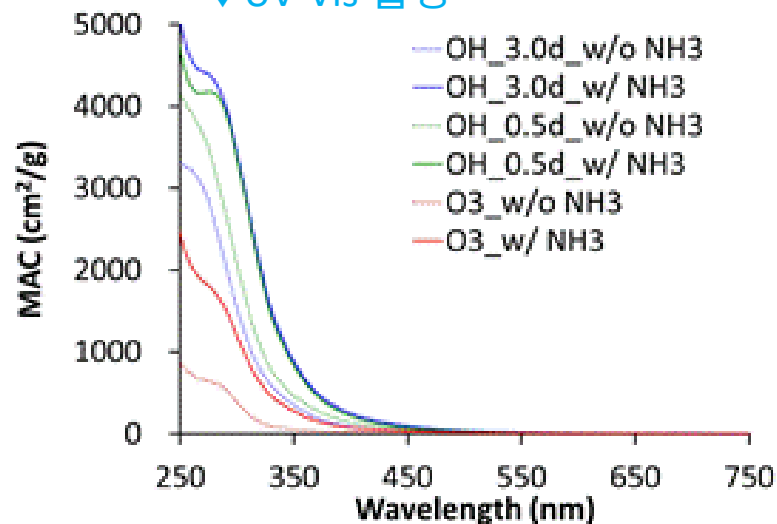
## 광학적 성질 분석

- 용매 추출 (UV-Vis 간섭 없는 용매 선택)
- UV-Vis 흡광 및 형광 분석

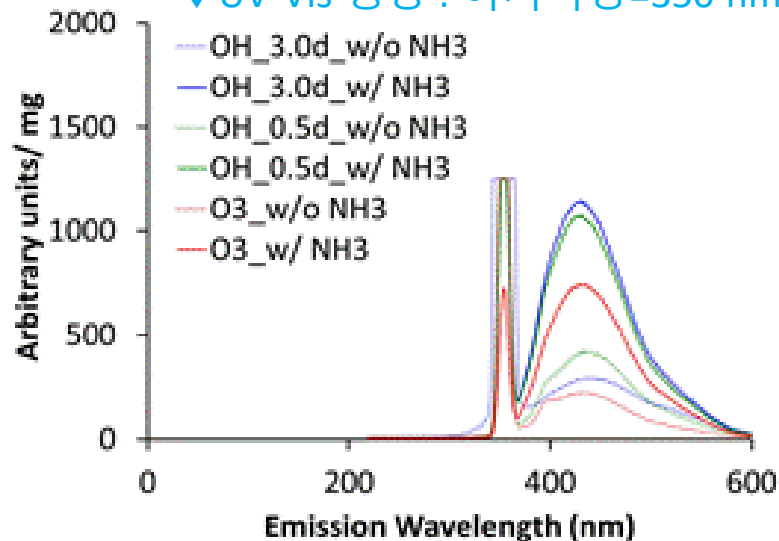
# $\alpha$ -피넨 SOA에 대한 $\text{NH}_3$ 영향 : 광학적 성질

필터 시료의 메탄올 추출액

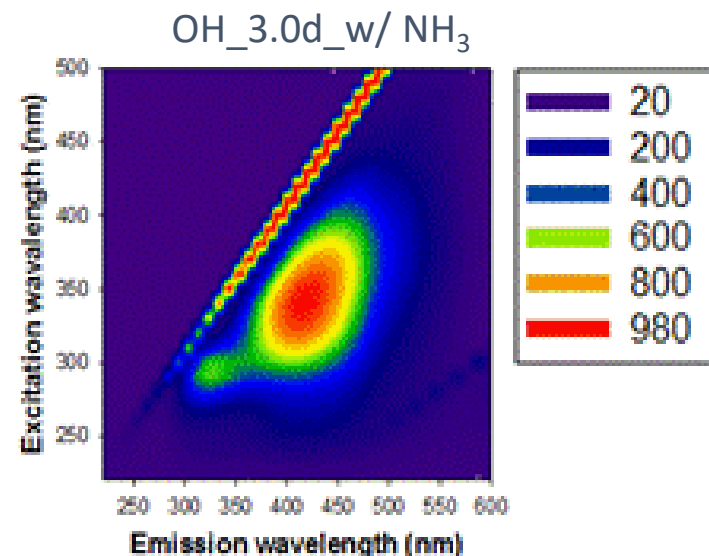
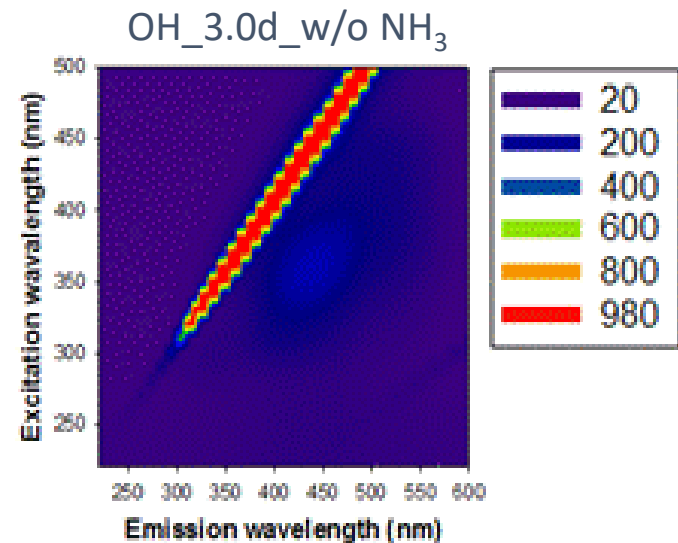
## UV-Vis 흡광



## UV-Vis 형광 : 여기파장=350 nm



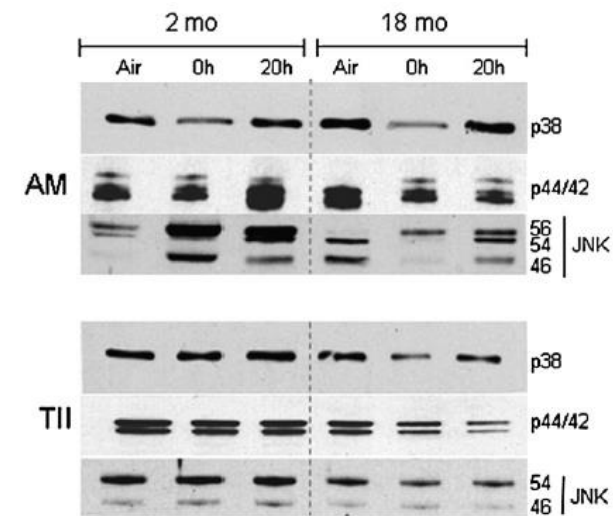
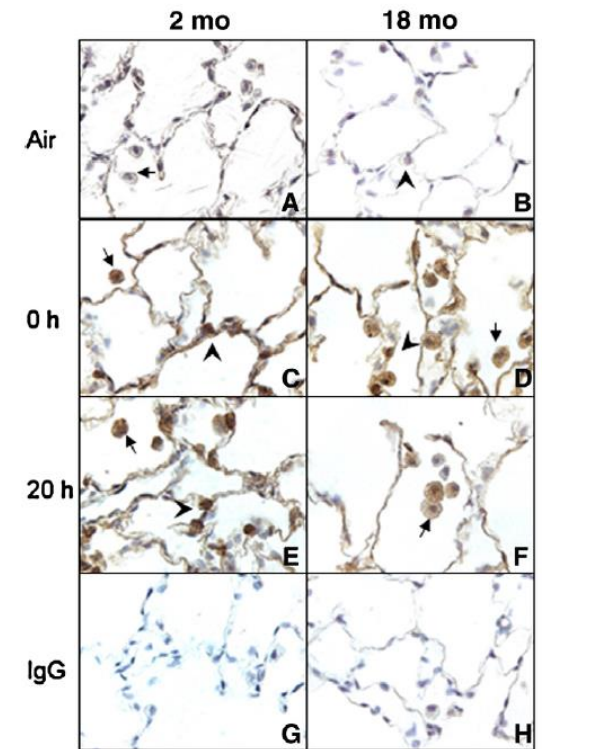
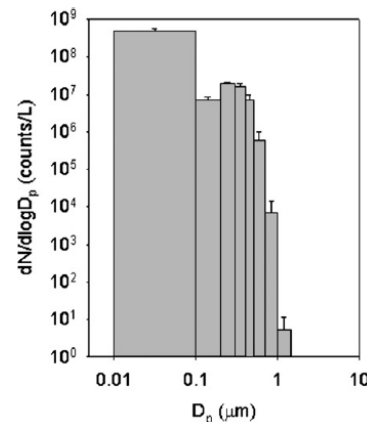
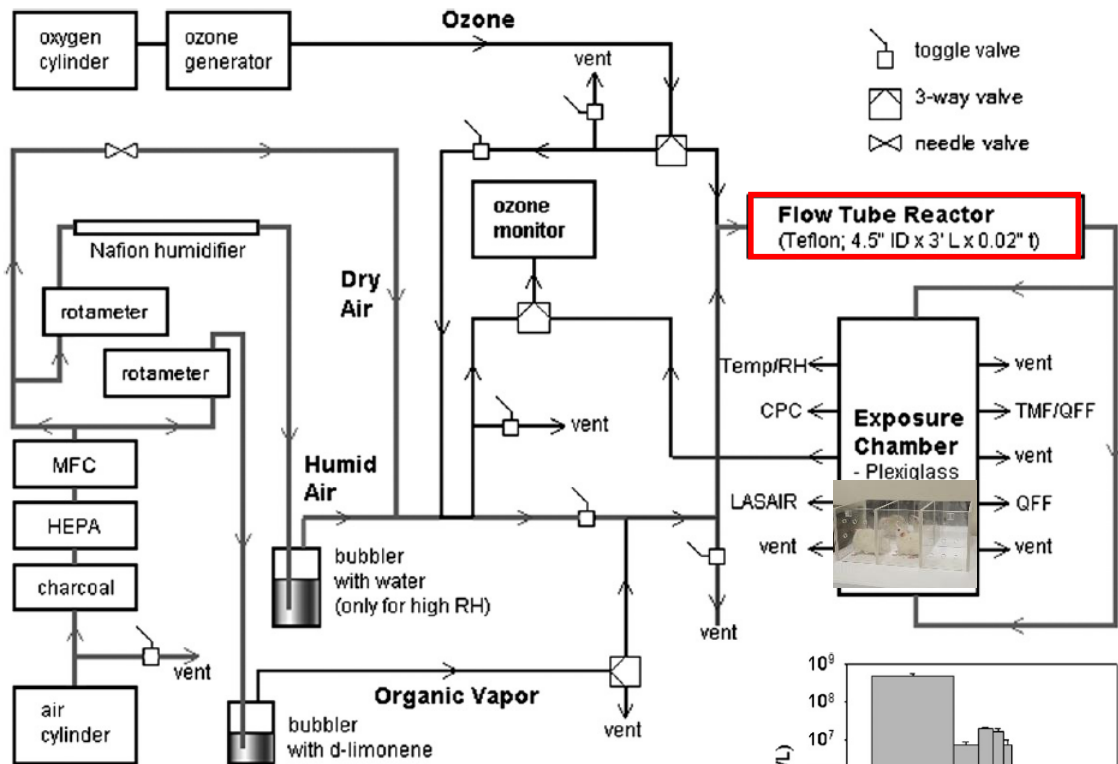
## UV-Vis excitation emission matrix



흡광과 형광 모두  $\text{NH}_3$ 가 있을 때 크게 증가하였고, 노화가 길수록 더 많이 증가

# SOA의 호흡 독성 : Rutgers Univ. 흐름반응기

- 흐름반응기를 이용한 SOA 생성
- 동물 실험
  - 생쥐 / 쥐
  - 전신 노출



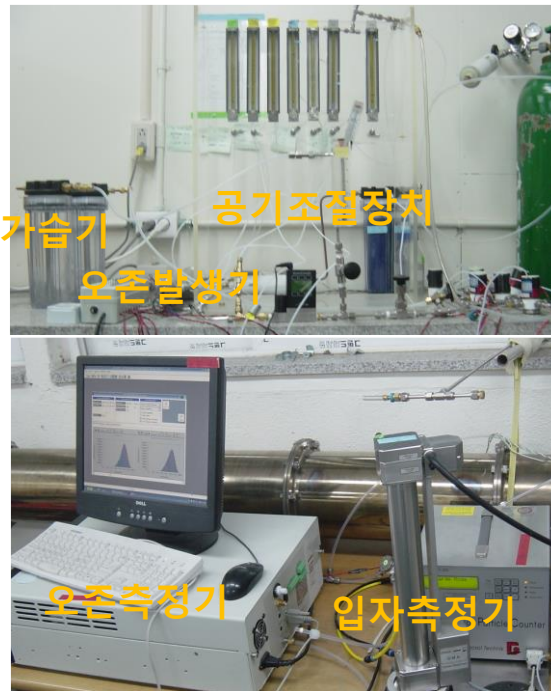
Sunil et al. (2007) Pulmonary effects of inhaled limonene ozone reaction products in elderly rats, Toxicology and Applied Pharmacology



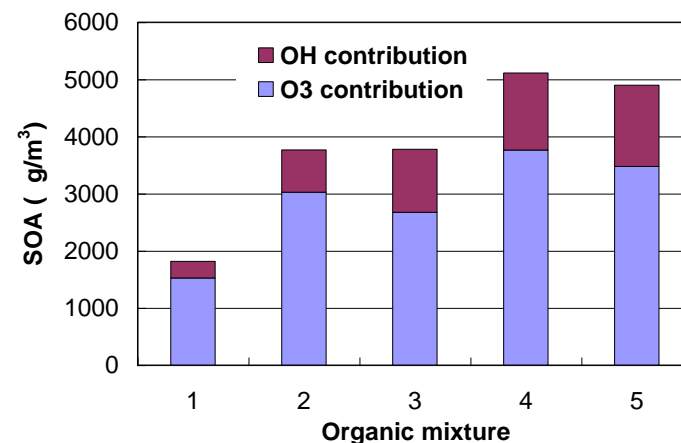
# SOA의 세포/호흡 독성 : KNU 스테인리스강 흐름반응기

77

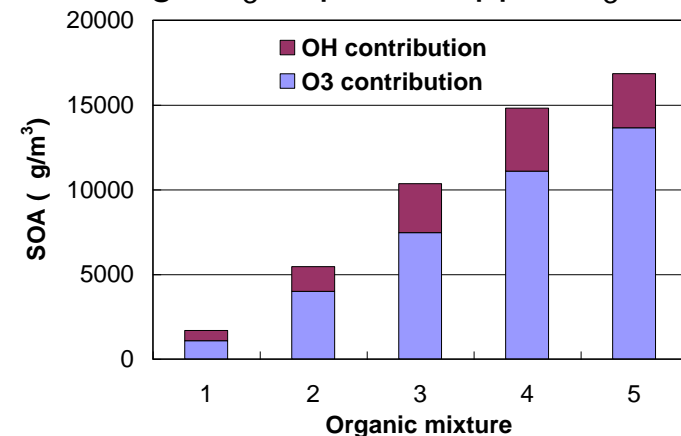
## ➤ 흐름반응기를 이용한 SOA 생성



Low  $O_3$ /terpene: 1 ppm  $O_3$



high  $O_3$ /terpene: 4 ppm  $O_3$



## Sampling

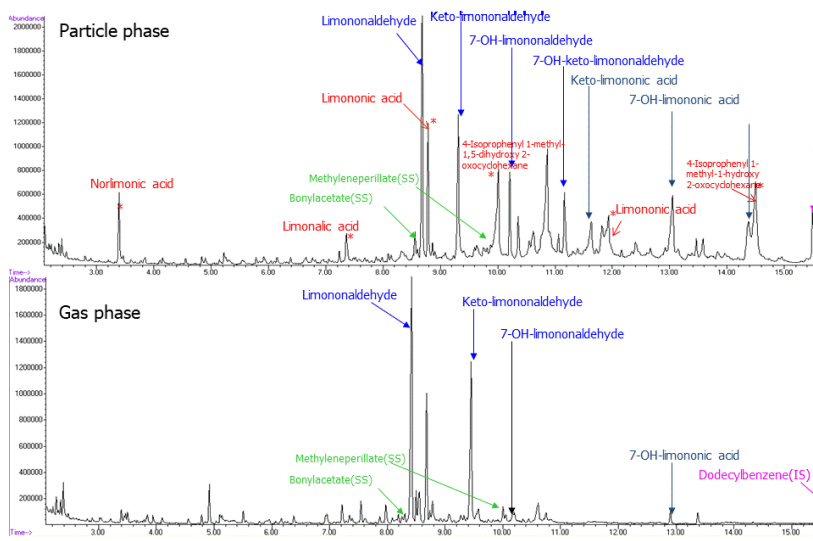
- Particle : QFF

- Gas : PUF

## Analysis

- GC-MS

- Agilent 5ms

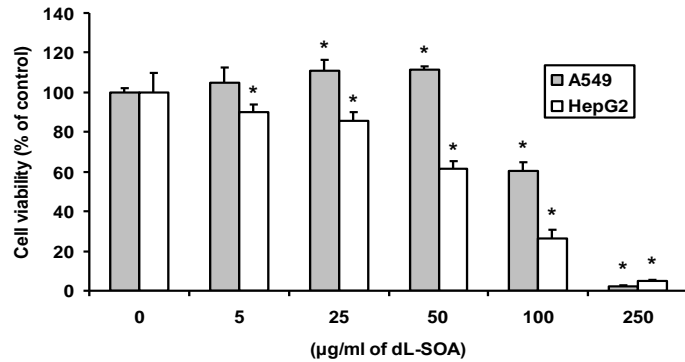


- Mixture 1: 2.0 ppm PIN + 0 ppm LIM
- Mixture 2: 1.5 ppm PIN + 0.5 ppm LIM
- Mixture 3: 1.0 ppm PIN + 1.0 ppm LIM
- Mixture 4: 0.5 ppm PIN + 1.5 ppm LIM
- Mixture 5: 0 ppm PIN + 2.0 ppm LIM

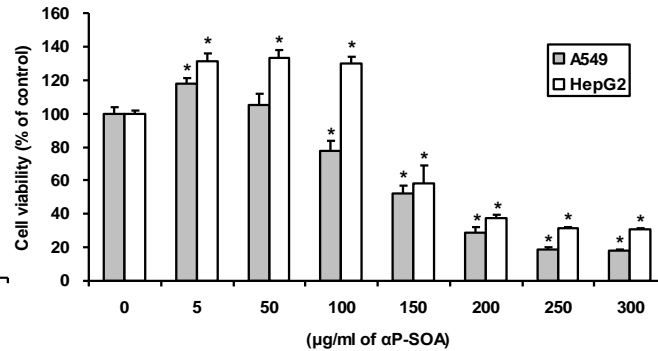
# SOA의 세포 독성 : KNU 스테인리스강 흐름반응기

## ➤ 세포 생존도

### (a) d-Limonene SOA (dL-SOA)

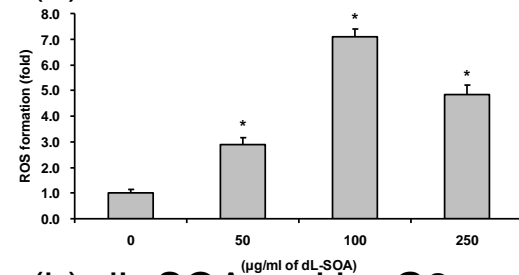


### (b) α-Pinene SOA (αP-SOA)

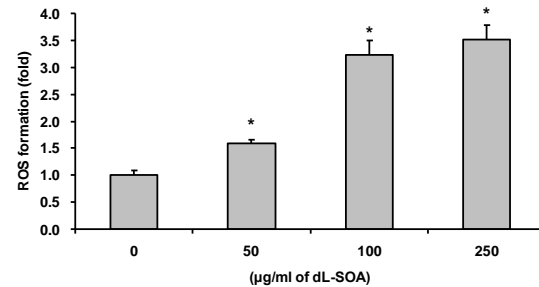


## ➤ 활성 산소 생성

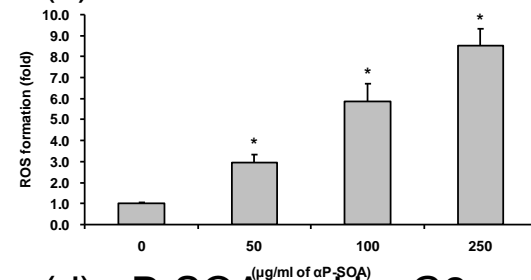
### (a) dL-SOA on A549



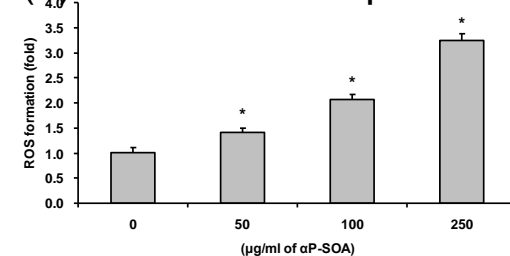
### (b) dL-SOA on HepG2



### (c) αP-SOA on A549

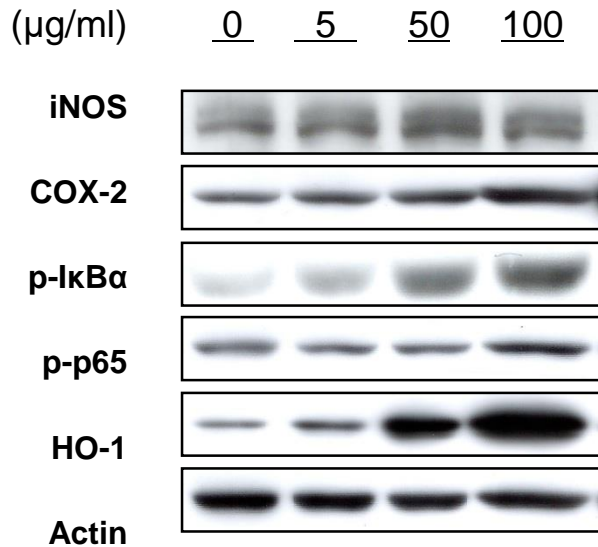


### (d) αP-SOA on HepG2



## ➤ 염증반응

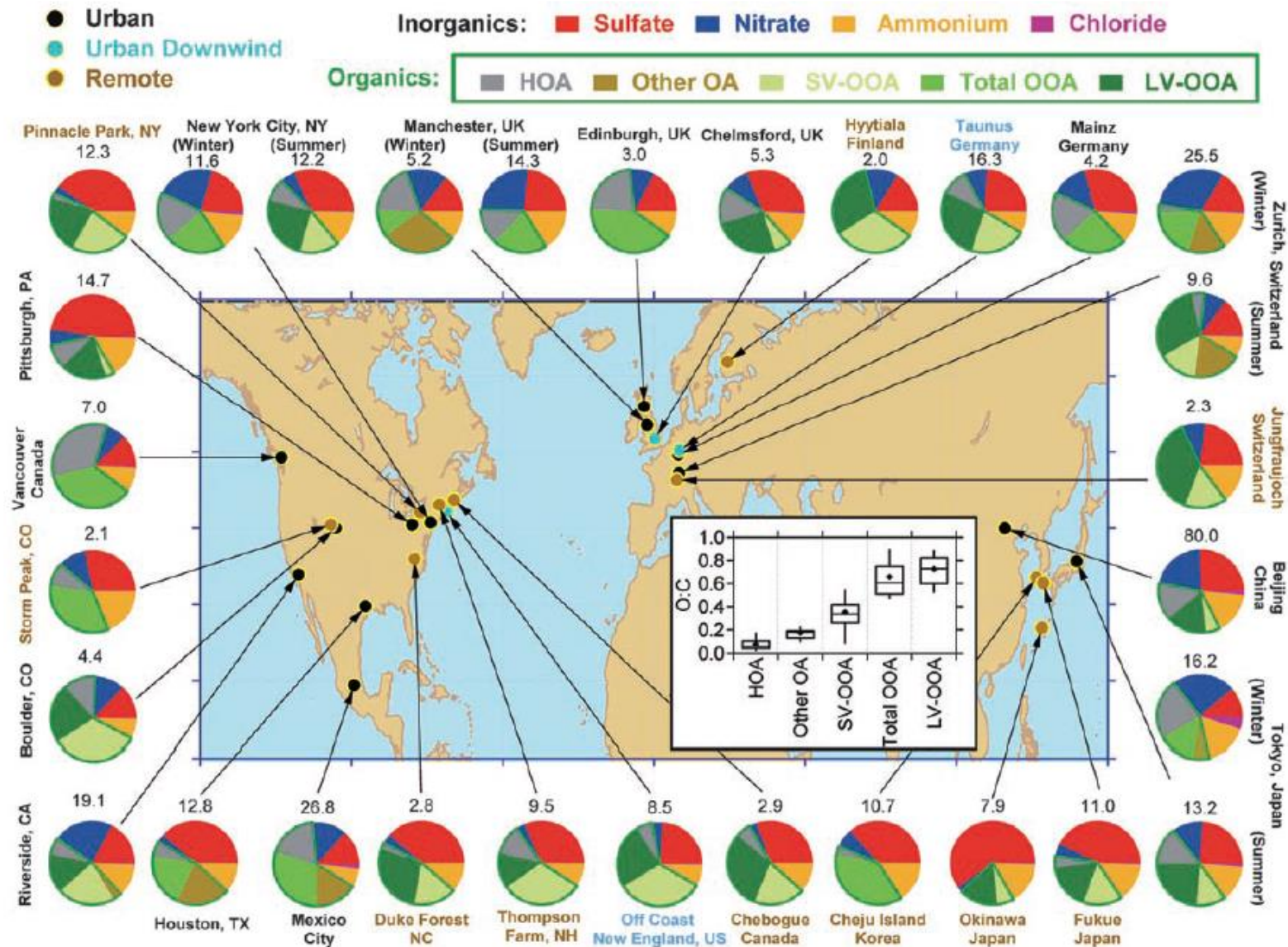
### (a) dL-SOA



### (b) αP-SOA



# Global Distribution of Atmospheric Aerosol Composition Implies the Diversity of Their Physical Properties and Atmospheric Processing





## Household products make surprisingly large contributions to air pollution

Consumer products might be next target for air pollution cleanup

BY [LAUREL HAMERS](#) 2:00PM, FEBRUARY 15, 2018

지속적 개선을 통한 해결



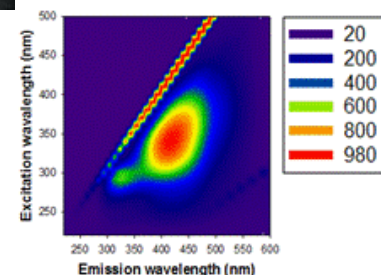
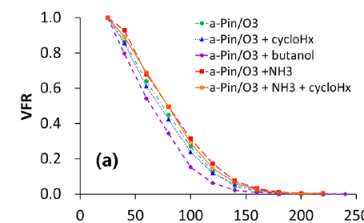
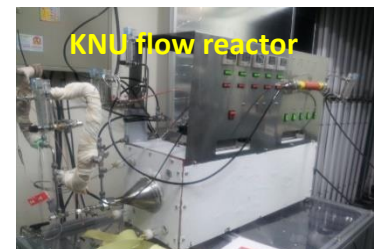
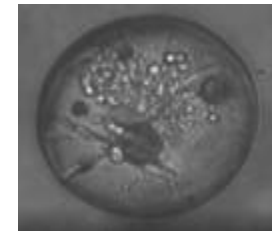
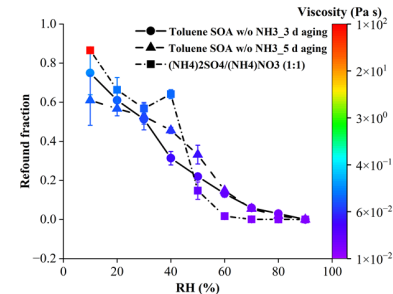
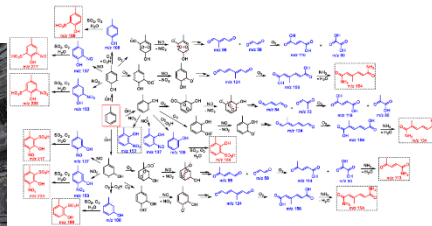
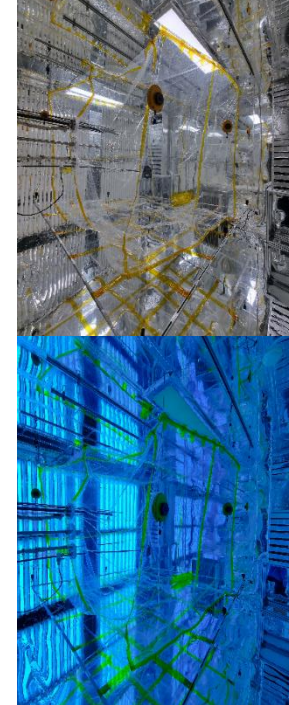
**SMOG CITY** Los Angeles, shown here, is one of the smoggiest cities in the United States. That haze of air pollution comes **not just from cars, but also from an array of consumer products** that emit chemicals into the air.



# 요약 및 제언

- 대기화학의 연구에 중요한 장치인 광화학반응기를 이용한 다양한 연구가 국내에서도 진척 중
  - 스모그 챔버
  - 흐름반응기
- 광화학 반응을 이용하여 다양한 미세먼지의 특성에 대한 규명 가능함
  - 성분 분석 및 반응 메커니즘
  - 상 상태 및 점도
  - 상 혼합 및 분리
  - 휘발도
  - 독성
- 고습도 ROG/NO<sub>x</sub>/SO<sub>2</sub>/NH<sub>3</sub> 반응에서 SOA 생성수율이 저습도 ROG/NO<sub>x</sub> 반응에 비해 상당히 증가함
  - 고습도에서 SIA의 흡수에 의한 에어로졸 수용액상 반응의 기여
  - 에어로졸 수용액의 존재는 열역학 모델, 상 상태, 점도 측정 등을 통해 확인
  - 에어로졸상 반응에서 생성 가능한 유기 성분의 확인 및 메커니즘 제언
- 관련 분야의 세계적 연구 동향을 고려하여, 국내 연구자들의 미세먼지 분야 기초 연구의 발전을 기대함

KNU smog chamber



## 연구비 사사

연구비 지원에 감사드립니다,

- 동북아초미세먼지사업 (NRF-2020M3G1A1114560)
- 국가전략미세먼지사업 (No. 2017M3D8A1090658)
- 기후변화대응사업 (2019M1A2A2103956)
- 국립환경과학원

**감사합니다!**