

# Particle-Phase Diffusion Limitations in Fresh Isoprene Secondary Organic Aerosol

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## Motivation

Previous studies (Shilling et al., 2020, Zaveri et al., 2018, 2020) have shown

- Fresh isoprene SOA (iSOA) is unable to partition into aged (16–18 h at  $[OH] \sim 2 \times 10^6$  molecules  $cm^{-3}$ ) SOA (e.g. derived from  $\alpha$ -pinene and isoprene photooxidation).
- Traditional vapor-pressure dependent equilibrium partitioning model overpredicts observed SOA growth due to the neglect of kinetic or thermodynamic limitations.

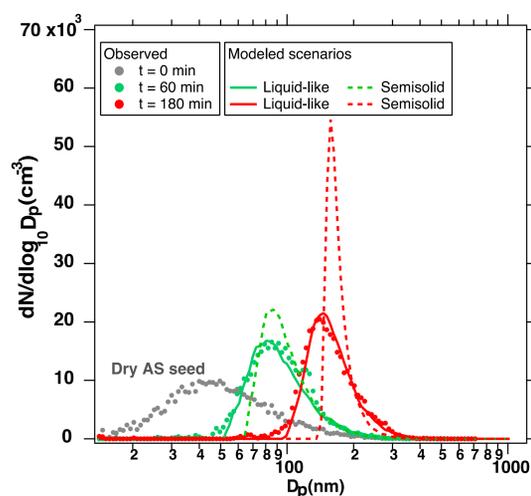
In this work, we continue to explore

- The influence of aging on inducing non-equilibrium partitioning behavior.

## Growth Period 1 (P1) Results

Diffusion limitation is not needed to model growth in P1.

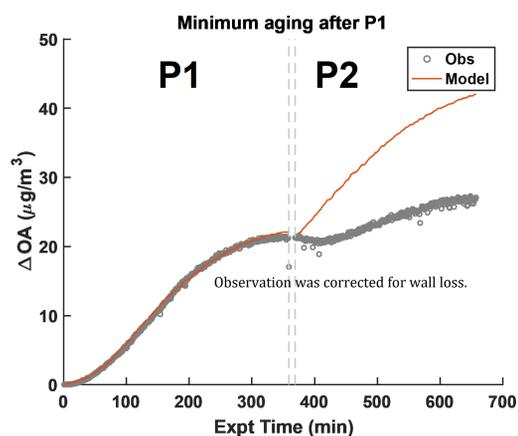
- MOSAIC box model was used to predict size distribution evolution.
- A liquid-like scenario is sufficient to reasonably reproduce the evolution of size distribution in P1.
- A semi-solid scenario predicts taller and slimmer size distributions.



## Growth Period 2 (P2) Results

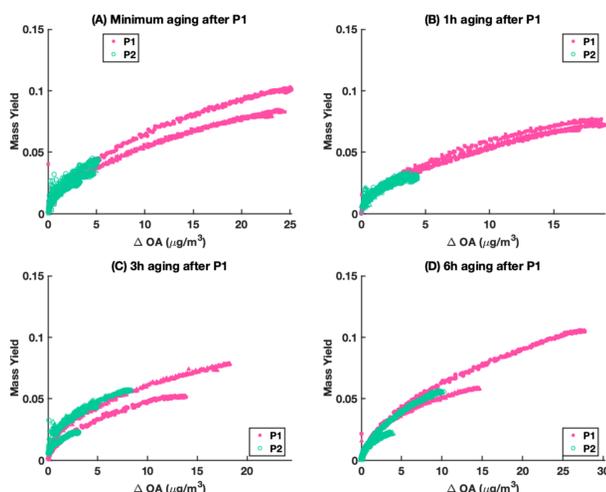
Equilibrium partitioning model significantly overpredicts OA in P2.

- A four-product model ( $C^* = 0.1, 1, 10, 100 \mu g m^{-3}$ ) was used to test for non-equilibrium partitioning behavior.
- Model parameters were derived by fitting the SOA growth in P1 and applied to P2.
- The parameterization significantly overpredicted the observations for P2.



Partitioning limitation for P2 observed even with minimum aging after P1.

- If gas-particle equilibrium is achieved, the presence of OA should enhance SOA growth in P2.
- This was not observed.
- Instead, fresh iSOA did not partition into aged iSOA ( $[OH] \sim 1-2 \times 10^6$  molecules  $cm^{-3}$ ) for all aging cases.
- Similar phenomenon was observed for dark aging experiments within the same time scale (0–6h).



## Experimental

### 1. Preparation

- Chamber was humidified to 50% RH.
- Crystalline 50 nm monodisperse or polydisperse ammonium sulfate (AS) seed particles were injected.

### 2. Growth Period 1 (P1)

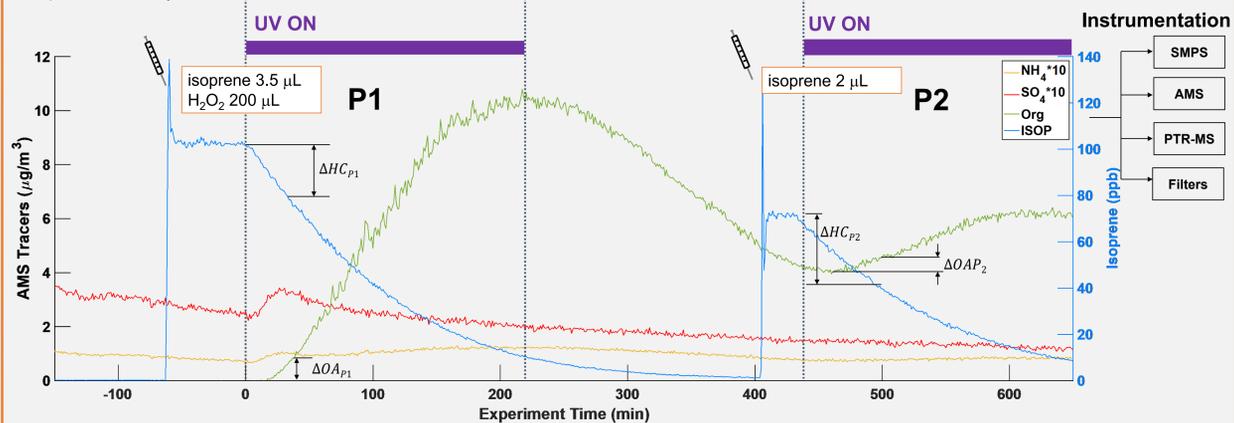
- UV was turned on to initiate the isoprene oxidation.
- SOA grew until plateau reached.

### 3. Aging

- UV was either left on or switched off for photochemical aging or dark aging, respectively.

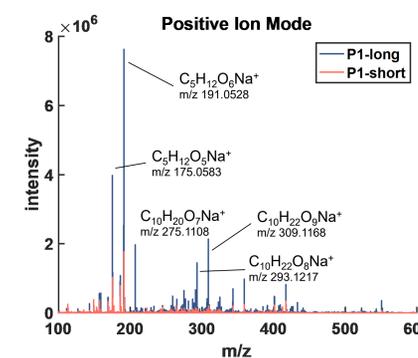
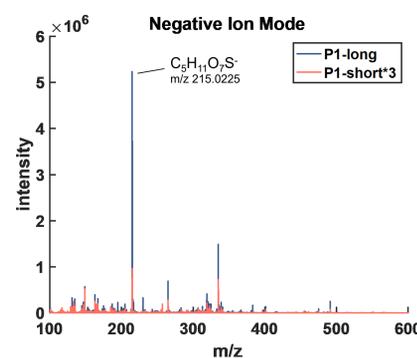
### 4. Growth Period 2 (P2)

- Isoprene was replenished and UV was switched on again.



No. of Expts	P1		Photochemical Age (hr)	P2		RH (%)	Temperature (°C)
	Isoprene (ppb)			Isoprene (ppb)			
4	107 ± 13		0	66 ± 3		52.2 ± 0.1	22.4 ± 0.4
4	94 ± 4		1 (1.01 ± 0.03)	69 ± 9		50.9 ± 2.4	23.9 ± 1.6
4	97 ± 6		3 (2.82 ± 0.31)	66 ± 8		51.4 ± 4.4	23.1 ± 1.6
3	100 ± 3		6 (6.28 ± 0.37)	68 ± 5		51 ± 2	22.7 ± 0.4

Preliminary NanoDESI-MS results reveal formation of oligomers and organosulfates



- Multiple dimers and  $C_5H_{11}O_7S^-$ , presumably methyltetrol sulfate (IEPOX-OS monomer), were identified.
- Previous studies have shown IEPOX-OS inhibits IEPOX reactive uptake (Riva et al., 2019); oligomers may also induce mass transfer limitations (Zaveri et al., 2018).
- Two previously reported major hydroxyhydroperoxides ( $C_5H_{12}O_5$  and  $C_5H_{12}O_6$ ) were also identified (Krechmer et al., 2015; Riva et al, 2016; Liu et al., 2016).
- We will collect MS/MS data on the most intense MS peaks to get structural information.

## Summary

- P1 exhibits equilibrium partitioning behavior.
- P2 exhibits non-equilibrium partitioning behavior regardless of post P1 aging time and conditions (light or dark).
- Together, these results indicate some chemical and/or physical process has occurred shortly (<0.5 h) after P1, which inhibits partitioning between fresh iSOA vapors and aged SOA in P2.
- The exact cause of the non-equilibrium partitioning is currently unknown and needs to be investigated further. A surface process may relocate the detected oligomers and/or IEPOX-OS to the aerosol particle surface, limiting gas-particle partitioning.

## References:

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