

Isoprene Suppression of Biogenic Nucleation in a Mixed Deciduous Forest

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WHERE DISCOVERIES BEGIN

Aerosol Nucleation

- ❑ **Nucleation (or new particle formation, NPF) is the process in which solid or liquid aerosol particles form directly from gas phase species. (Secondary aerosol formation)**
- ❑ **NPF takes place globally:** from tropics to polar regions, from the ground level to the upper troposphere and lower stratosphere, from remote to polluted environments, and from forests to coastal regions.
- ❑ **NPF is an important initial step in the chain reactions that lead to cloud formation; NPF can contribute 15-55% of the global CCN production (Spracklen et al., 2008).**
- ❑ **Nanoparticles can be easily diffused into the lung to cause adverse health effects.**

Nucleation in Biogenic Environments?

❑ Forests cover 30% of the Earth's land surface

- Contribute about two thirds of biogenic volatile organic compounds (BVOC) emissions (Goldstein and Galbally, 2007; Guenther 1995).

- Isoprene emission: 440 - 660 Tg year⁻¹ (account nearly one third of the total global VOC emissions from natural and anthropogenic sources) (Guenther 2006).

❑ NPF takes place in many forests:

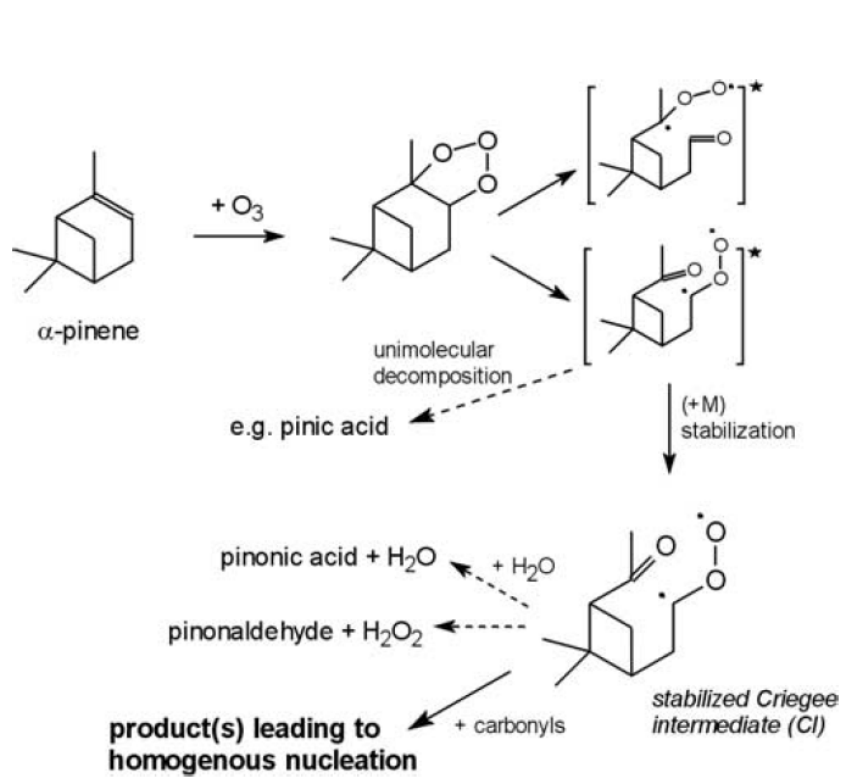
- Finland boreal forests (*Makela 1997; Sihto 2006*)
- European coniferous forests (*Held 2004*)
- African savanna forests (*Laakso 2008*)

❑ No NPF was seen in Amazon rainforests (*Poschl 2010; Ekman 2008; Rizzo 2010*):

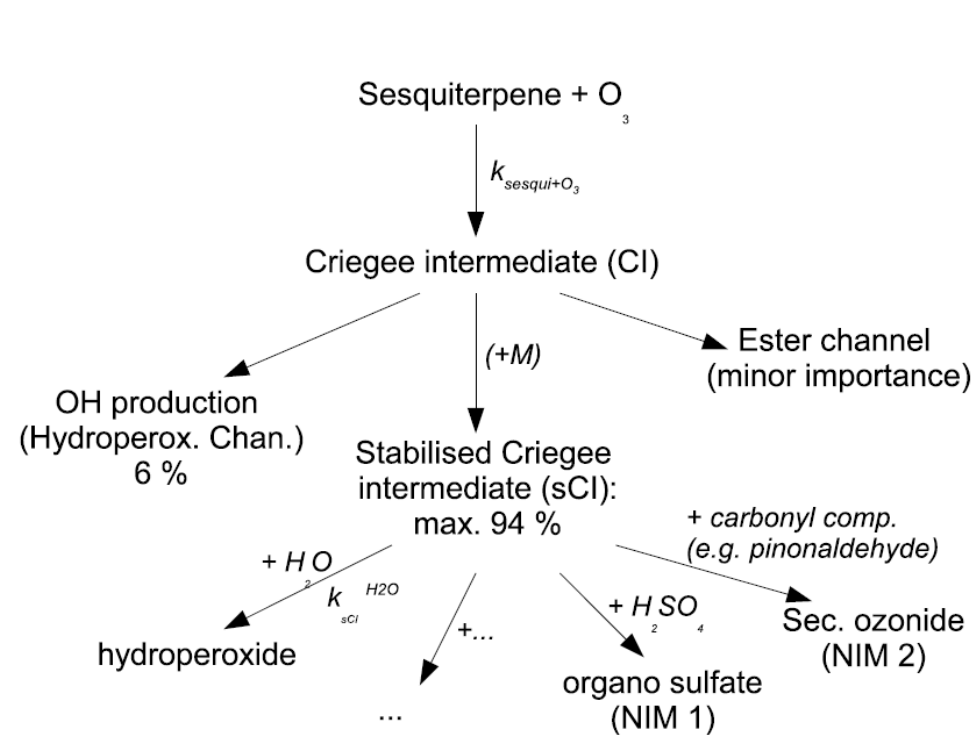
- Due to high aerosol loading and low H₂SO₄

Monoterpene and sesquiterpene ozonolysis products can form new particles.

Bonn et al., JGR 2003

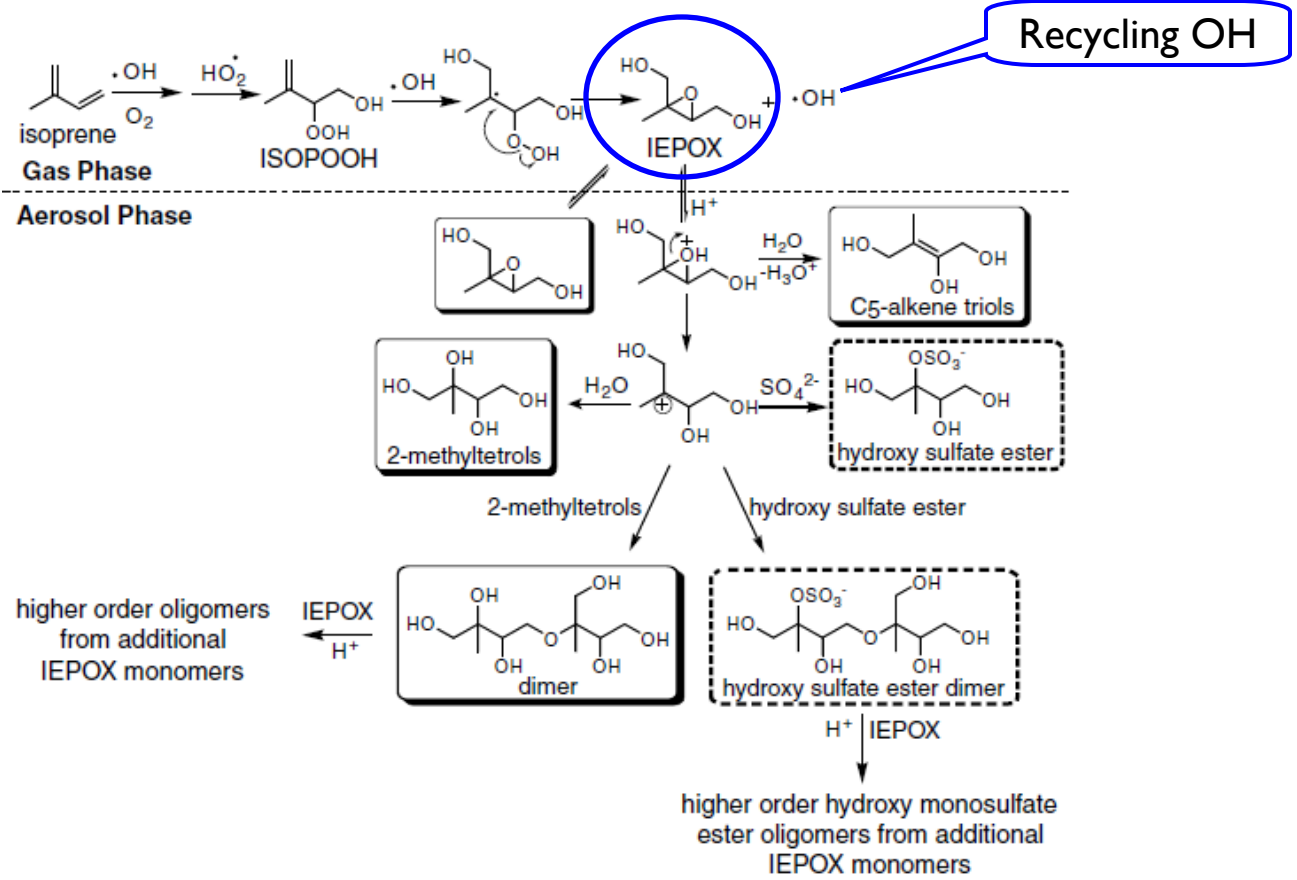


Bonn et al., JGR 2008



SOA formation under low-NO_x (Surratt et al., PNAS, 2010)

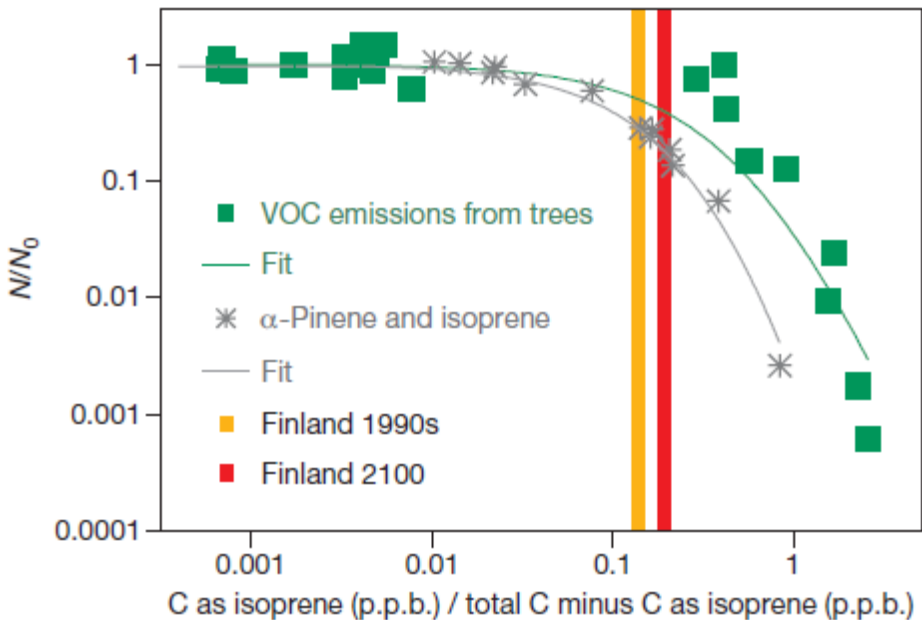
- via formation of epoxydiols of isoprene (IEPOX = β-IEPOX + δ-IEPOX)



SOA formation from isoprene under lower-NO_x conditions due to increased aerosol acidity.

Plant chamber experiment (Kiendler-Scharr et al., Nature, 2009)

- Excessive isoprene suppresses biogenic nucleation → reducing aerosol climate cooling effects over forests.
- Suppression effects: Dependent on the ratio (R) of emitted isoprene carbon to monoterpene carbon. (Isoprene suppresses OH).



Inhibition of particle number concentration as a function of R .

PROPHET 2009 CABINEX Experiment

□ Michigan forest → a typical mid-western mixed deciduous forest

(70% aspen trees and rest consisting paper birch with white pine, red maple, and red oak)

□ Isoprene >> monoterpenes emissions

• Isoprene comprises >95%; monoterpene 4%; sesquiterpene 0.3% (Ortega et al., 2007)



□ Aerosol size number distribution (3-110 nm): in-canopy at 5 m above ground

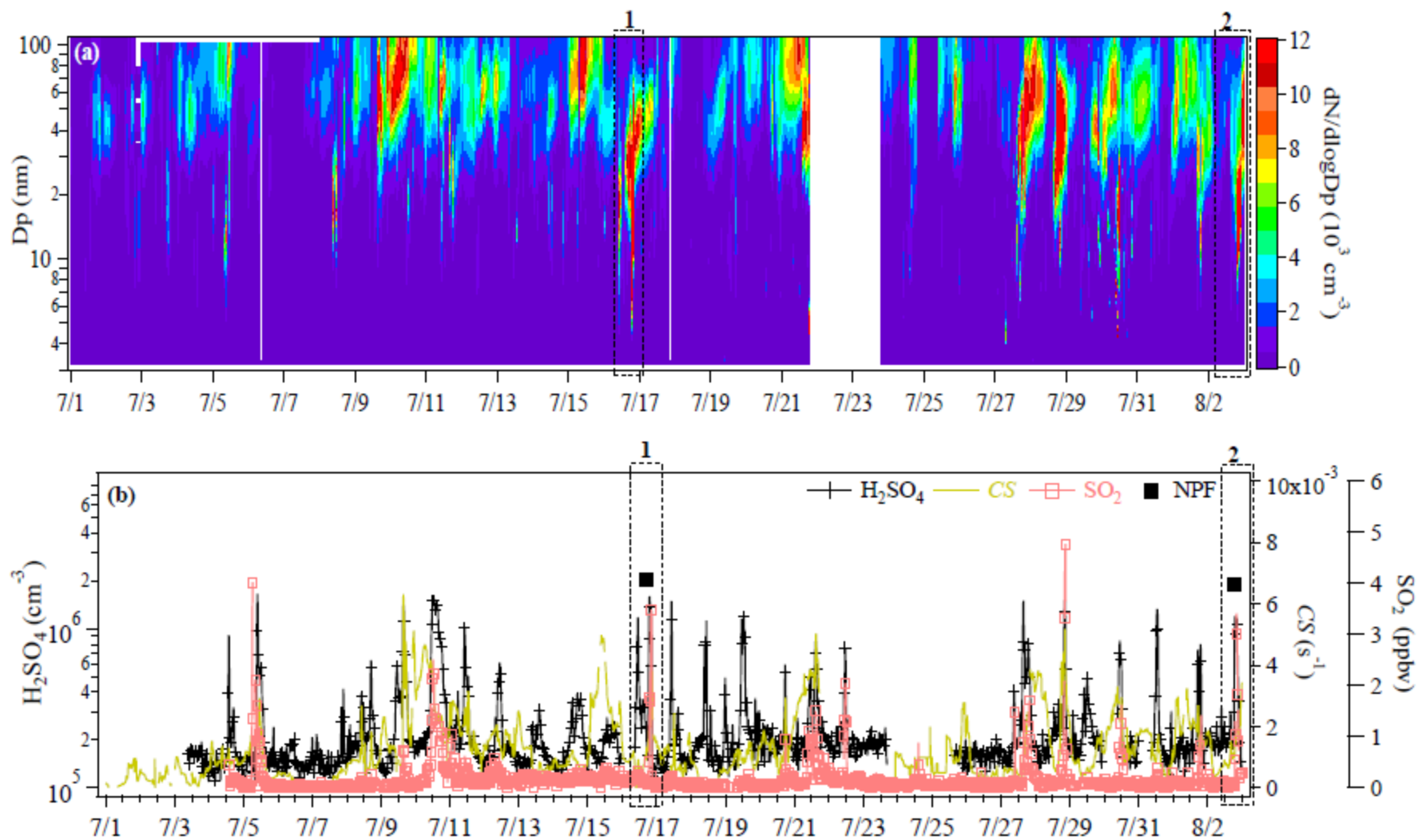
□ In-situ measurements: H_2SO_4 , NH_3 , VOCs, OH, SO_2 , and NO_x

Isoprene suppression of NPF in a mixed forest

- **No NPF events during 6 weeks in summer.**
- **Only two evening ultrafine particle events (July 16 and August 2).**

Kanawade et al., ACP, 2011

All data:



No NPF – why ?

□ Isoprene suppression on biogenic nucleation depends on → ratio (R) of the emitted isoprene carbon to monoterpene carbon [Kiendler-Scharr et al., 2009]

	No NPF		NPF
Locations	Michigan forest ^a	Amazon forest ^b	Finland forest
Parameters			
R	26.4±4.5	15.2 (Greenberg et al., 2004)	0.18 (Spirig et al., 2004)
OH (cm ⁻³) ^c	1.2-1.5×10 ⁶	5.5×10 ⁶ (Martinez et al., 2010)	7.7×10 ⁵ (Petaja et al., 2009)
H ₂ SO ₄ (cm ⁻³) ^c	2.6×10 ⁶	1-5×10 ^{5d}	1.4×10 ⁶ (Petaja et al., 2009)
CS (s ⁻¹) ^c	1.5×10 ⁻³	0.9±0.3 (Zhou et al., 2002) ^e	4.2×10 ⁻³ (Kulmala et al., 2001)

^a this study.

^b data from wet season only.

^c noontime peak values.

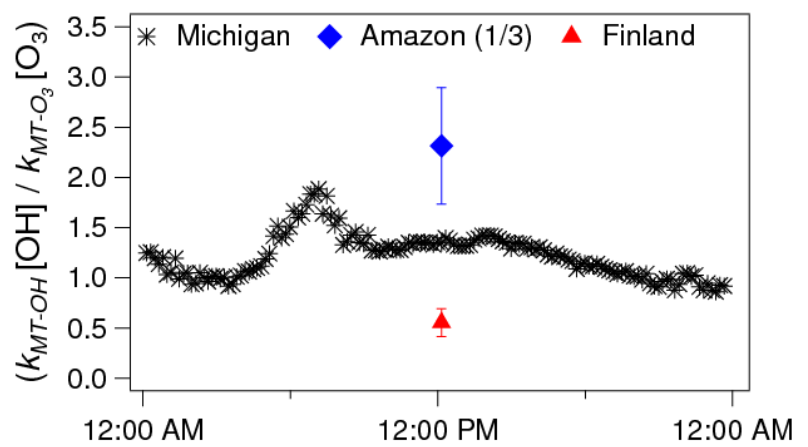
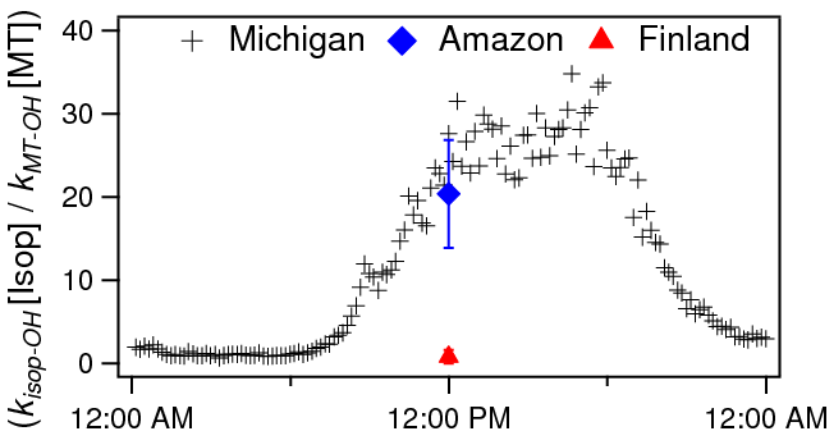
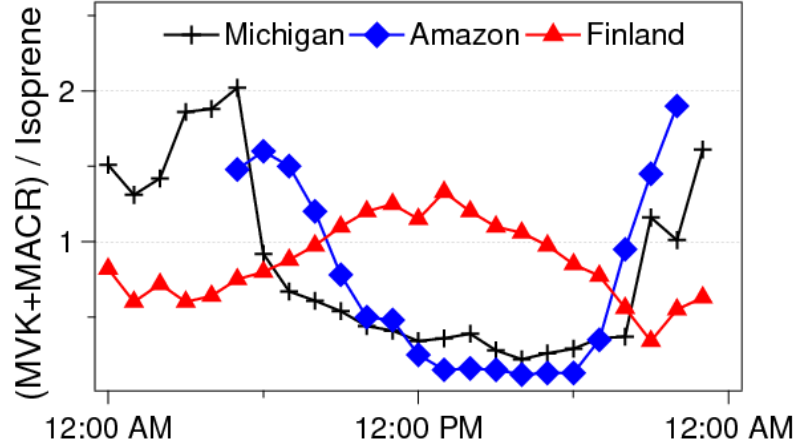
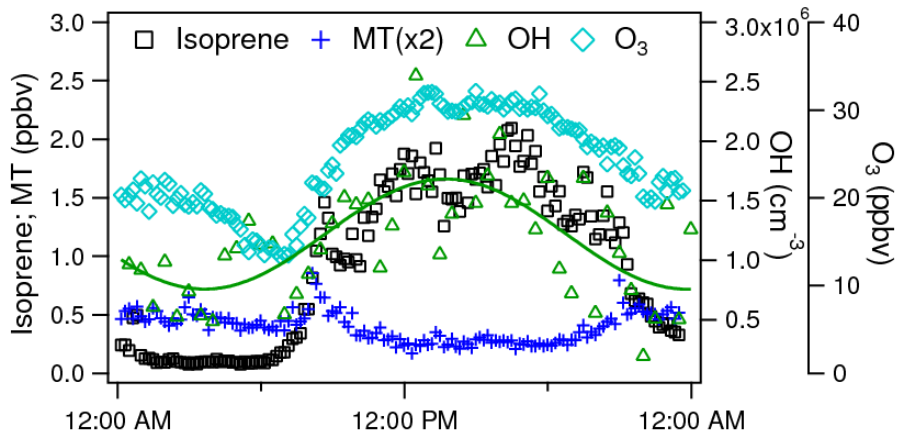
^d calculated H₂SO₄ from the measured SO₂ of the order of 0.02-0.03 ppbv (Andreae and Andreae, 1988) and OH of 5.5×10⁶ cm⁻³ (Martinez et al., 2010) over Amazon basin.

^e calculated total CS from statistical data (number concentration, geometric mean diameter and geometric standard deviation) for particle size distributions measured during March-April 1998 (Zhou et al., 2002).

□ Ratio of $(k_{\text{iso-OH}}[\text{Isoprene}]) / (k_{\text{MT-OH}}[\text{MT}])$

□ Ratio of $(\text{MVK} + \text{MACR}) / \text{isoprene}$: isoprene oxidation extent

□ Ratio of $k_{\text{MT-OH}}[\text{OH}] / k_{\text{MT-O}_3}[\text{O}_3]$



MVK: methyl vinyl ketone

MACR: methacrolein

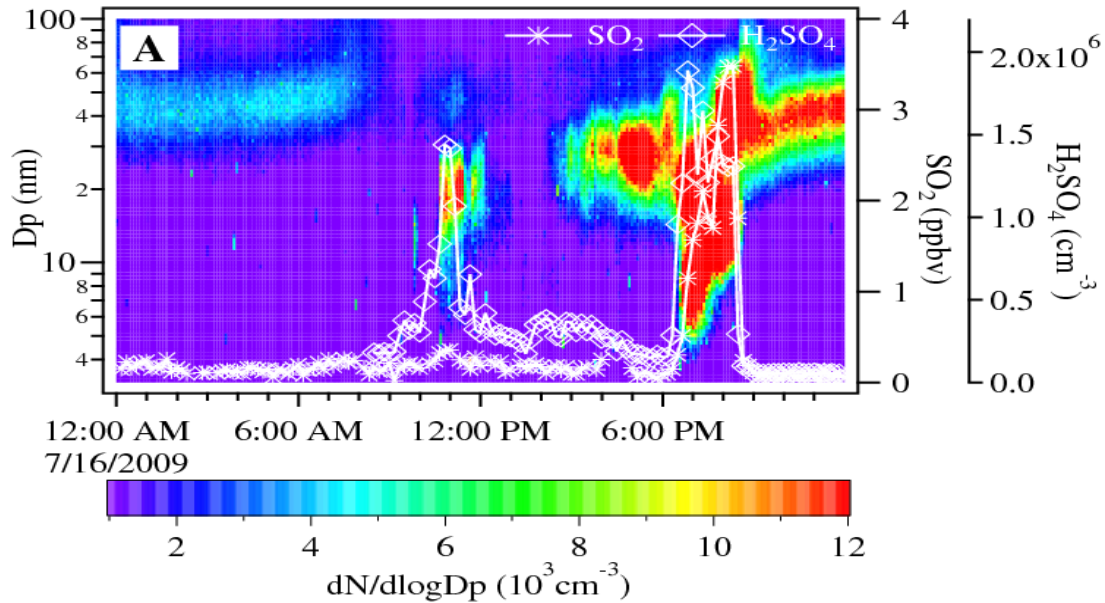
What we learned from non-NPF events:

- Non-NPF was related to high R. But OH was not suppressed in real forests (rather was higher than model-predicted values).
- (MVK + MACR) and (MVK + MACR)/isoprene were both low, indicating oxidation of isoprene was not complete (thus, IEPOX formation was unlikely).
- MT reaction with ozone was not as active as in Finland.
- These factors are common in Michigan and Amazon forests. But different in Boreal forests.
- In Amazon forests, also H_2SO_4 may be too low, and CS is also too high.

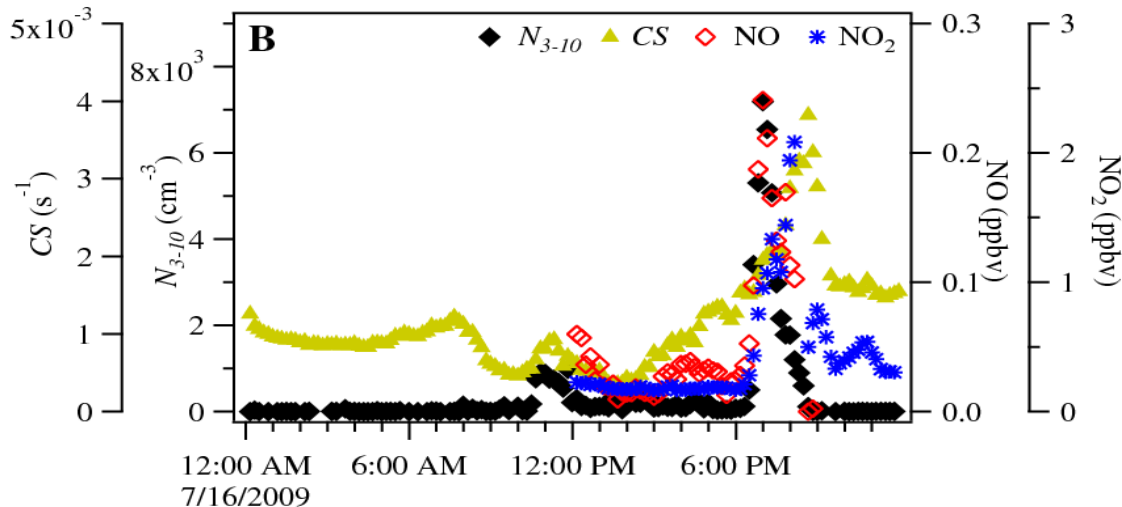
Evening Ultrafine Particle Events: Long Range Transport

- **Only two NPF events (July 16 and August 2) in 6 weeks.**

NPF events (Rare in summer): July 16

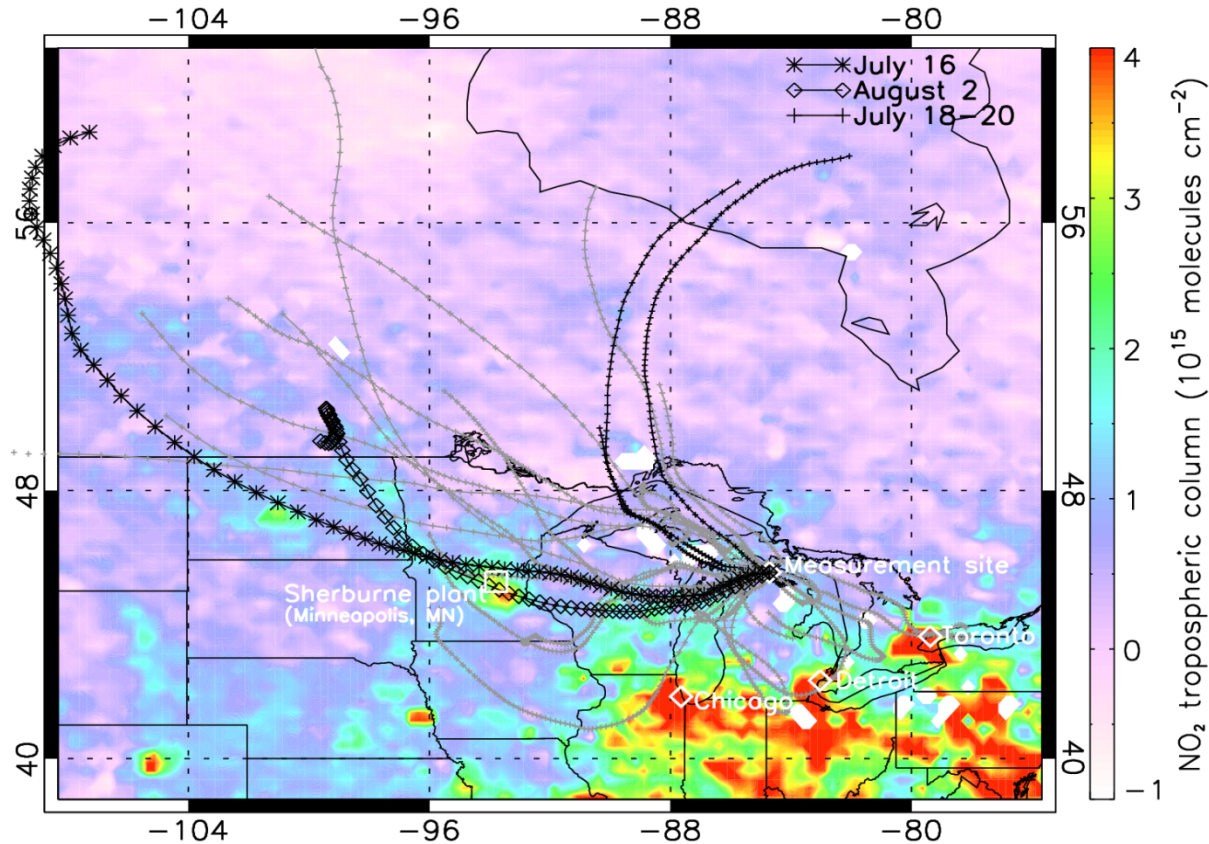


Ultrafine particles were observed between 18:30 - 21:30 local time, as opposed to typical noon-time NPF events.



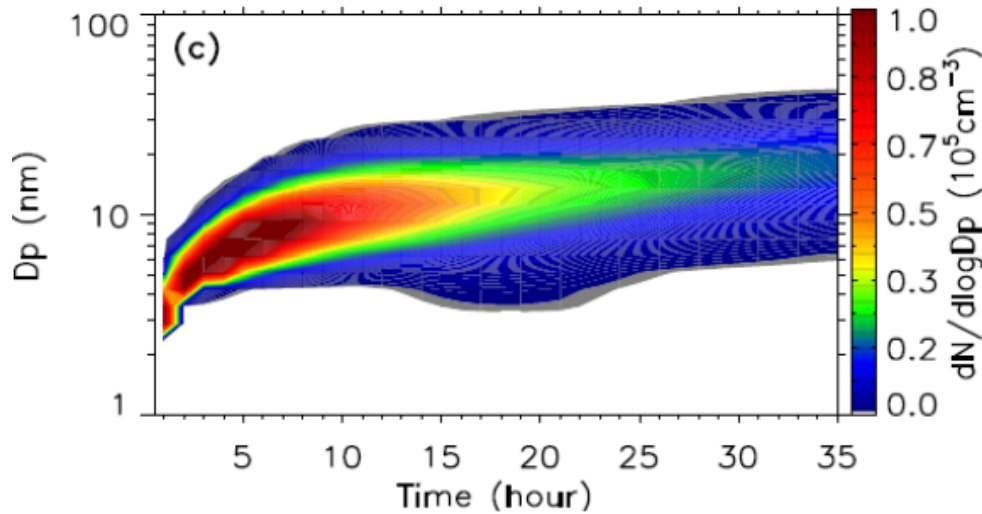
SO_2 , H_2SO_4 and NO_2 increased rapidly nearly at the same time as N_{3-10} .

Satellite NO₂ & Trajectories: Source of Plumes



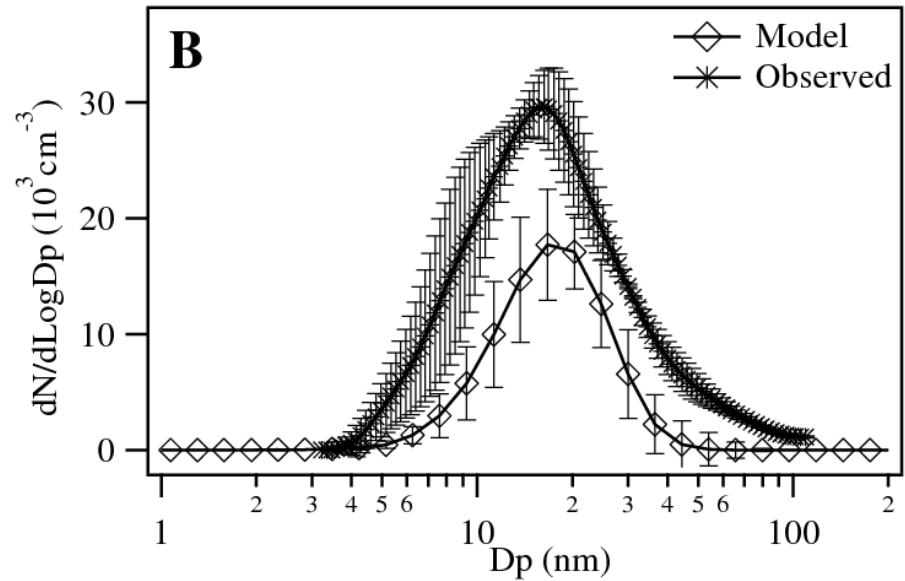
□ Only on the two ultrafine particle event days, the air masses curled to the Sherburne power plant (Minneapolis, MN), implying the anthropogenic source of SO₂ and NO_x plumes.

Box model results – 16 July



The particle size distributions simulated from the ion-induced nucleation (IIN) box model along the backward air trajectory on July 16.

The size distributions predicted from the model at the end of 35 hours simulation compared with those measured at the forest site



→ IIN involving high concentrations of SO_2 and H_2SO_4 can explain the observed evening ultrafine particles in the Michigan forest.

Atmospheric implications

- ❑ No NPF during the summer in the Michigan forest where isoprene is abundant: only two evening ultrafine particle events out of 6 weeks of measurements, under the sulfur plume influence.
- ❑ Our results are in-line with Kiendler-Scharr et al. (2009) plant chamber study showing that isoprene suppresses biogenic nucleation, but OH is unlikely suppressed in the real biogenic atmosphere.
- ❑ Our results thus provide the first atmospheric evidence that the specific pattern of the emitted BVOCs can affect secondary aerosol formation in biogenic environments.
- ❑ 70% of aspen trees in the northern Michigan forest are ~50 years. When switching from bigtooth aspen (isoprene emitter) to white pine tree species (monoterpene emitter), $R < 1$. Expect a substantial increase in NPF events in the coming decade, thus increasing the aerosol cooling effect over forests.
- ❑ Increase in isoprene (22%) and monoterpene (18%) by 2100, as a result of the increased temperature (1.8°C), but this temperature increase will not change the R values on a global scale.