

Secondary Organic Aerosol Formation from Ozonolysis of β -pinene

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Outline

Why?

Volatile Organic Compounds

Monoterpenes

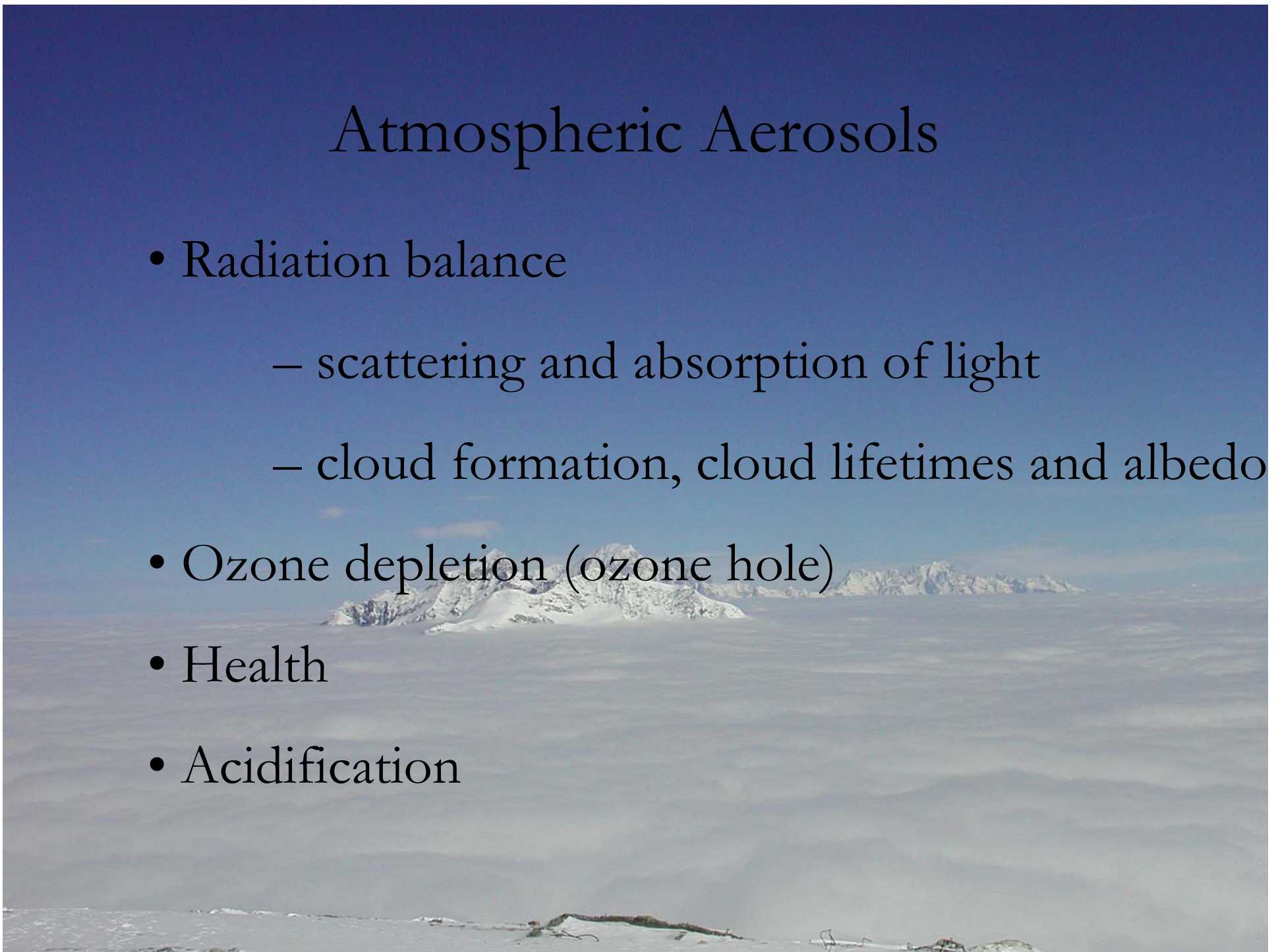
G-FROST

Results

3 Things to remember

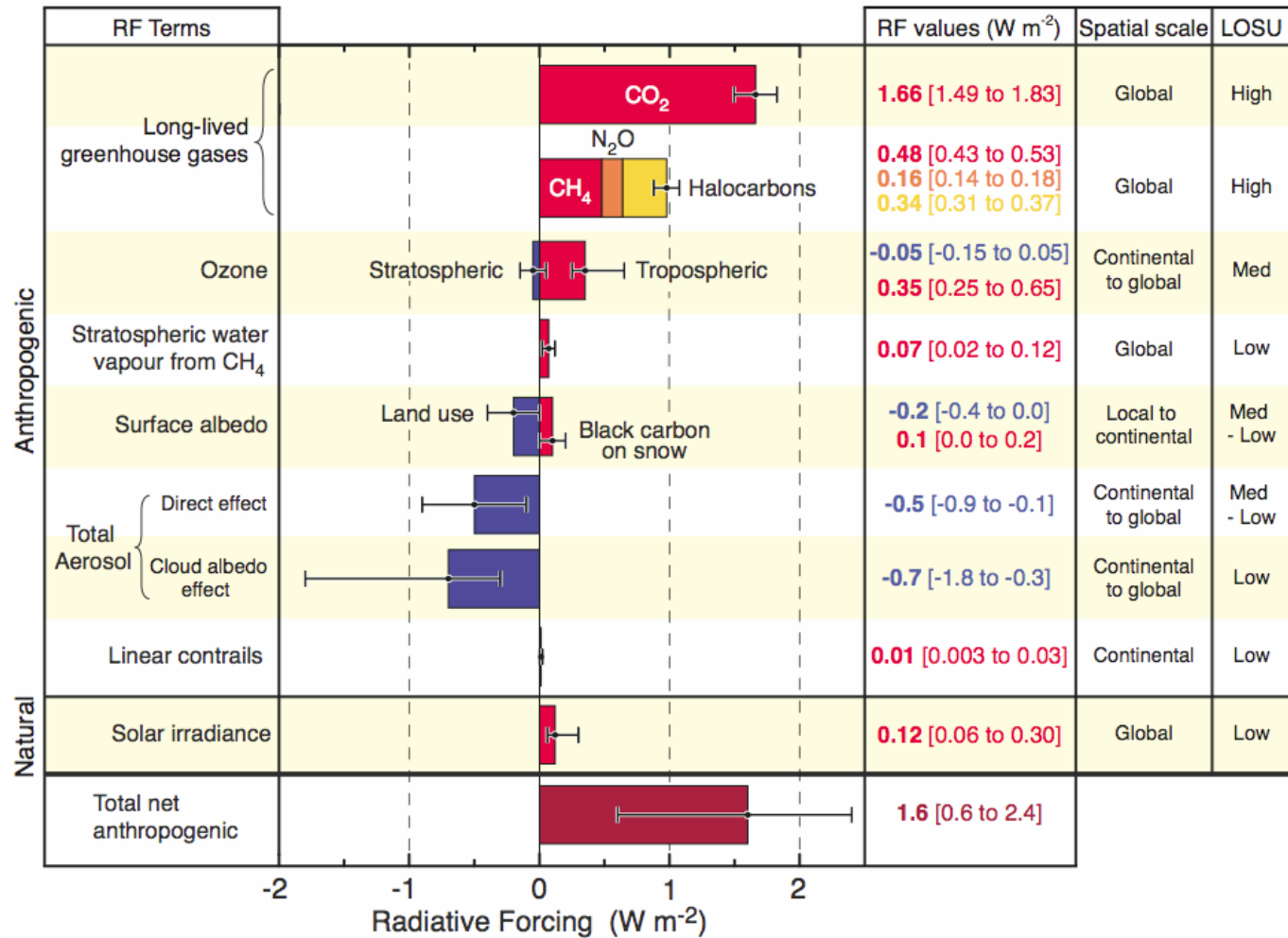
Atmospheric Aerosols

- Radiation balance
 - scattering and absorption of light
 - cloud formation, cloud lifetimes and albedo
- Ozone depletion (ozone hole)
- Health
- Acidification



IPCC 2007

Radiative Forcing Components



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Volatile Organic Compounds

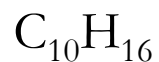
Volatile Organic Compounds (VOC) are emitted both from anthropogenic and biogenic sources

Globally total anthropogenic emissions are estimated to $\sim 186 \text{ TgC/year}$ (Koppmann 2007)

Biogenic emissions are globally estimated to $\sim 1300 \text{ Tg C/year}$ (Guenther 2002)

Of them are $\sim 127\text{-}480 \text{ Tg C/year}$ monoterpenes + isoprene (Kesselmeir and Staudt 1999)

Monoterpenes

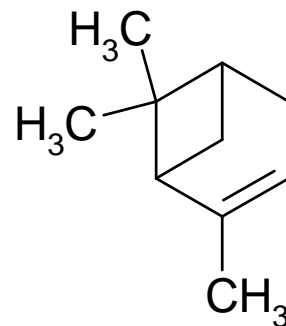


Emitted from vegetation

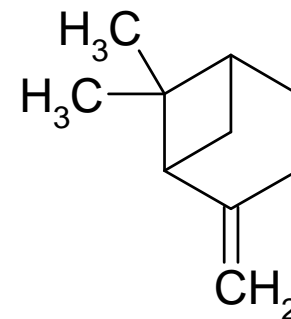
Appropriate molecular mass, (i.e. light enough to be volatilised and still sufficiently heavy to give condensable products)

Endocyclic e.g. α -pinene

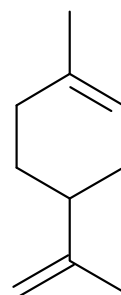
Exocyclic e.g. β -pinene



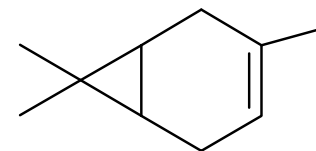
α -pinene



β -pinene



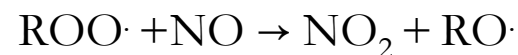
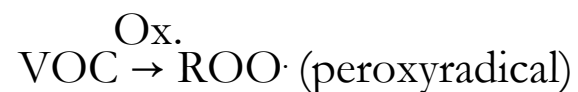
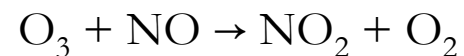
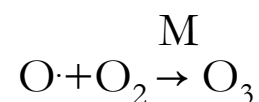
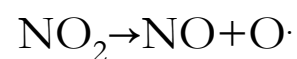
Limonene



Δ^3 Carene

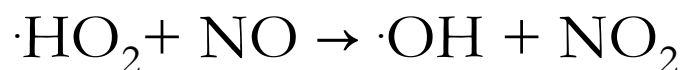
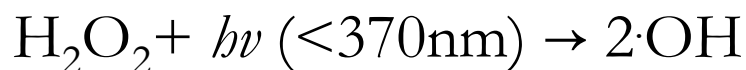
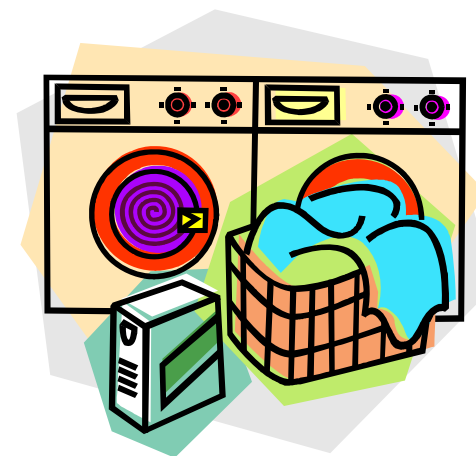
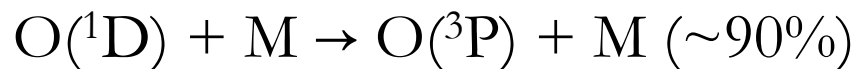
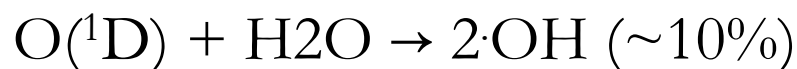
Ozone

Volatile Organic Compounds are important in the tropospheric ozone formation.



Netto \rightarrow increase of O_3

OH· The Washing powder of the atmosphere



How does number ($N_{10-300 \text{ nm}}$) and mass ($M_{10-300 \text{ nm}}$) of the Secondary Organic Aerosol from the ozonolysis of the exocyclic β -pinene change with changing humidity and the use of two different OH-scavengers?

G-FROST

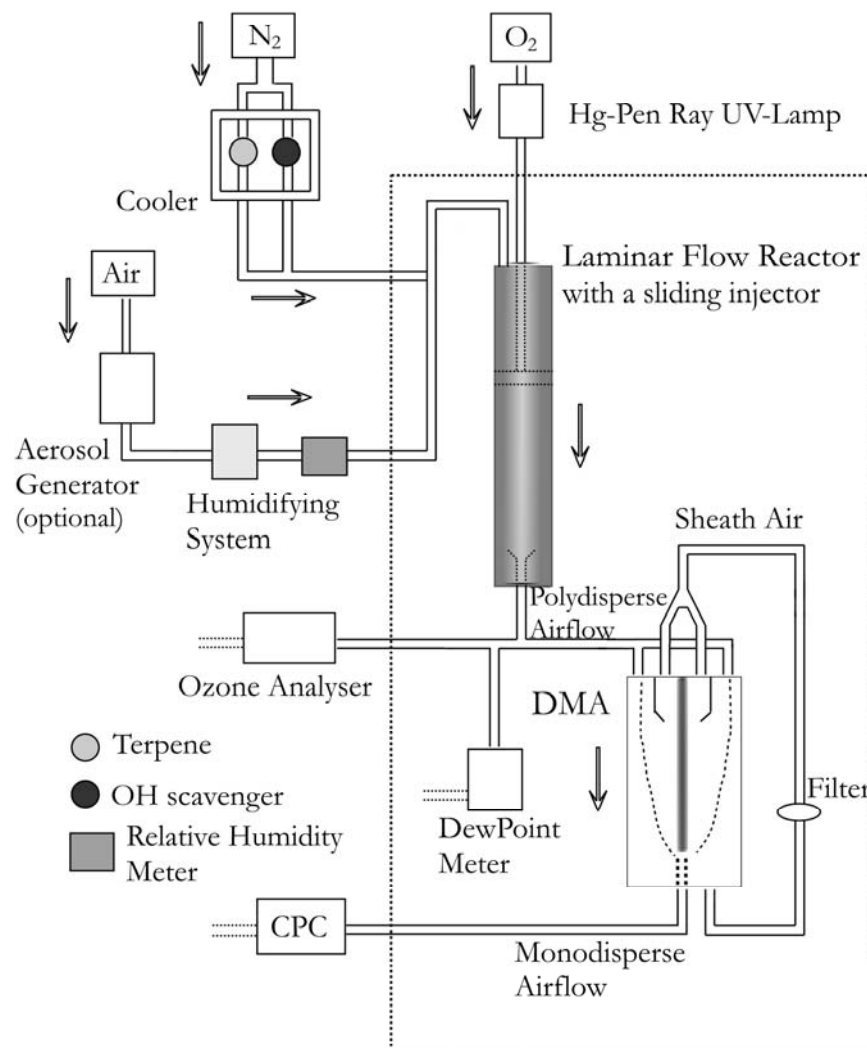
G-FROST Göteborg- Flow
Reactor for Oxidation Studies
at low Temperatures

Temperature range: 243-325K

RH: GORE-TEX®

Terpene: Diffusion vial

OH-scavenger: wash bottle

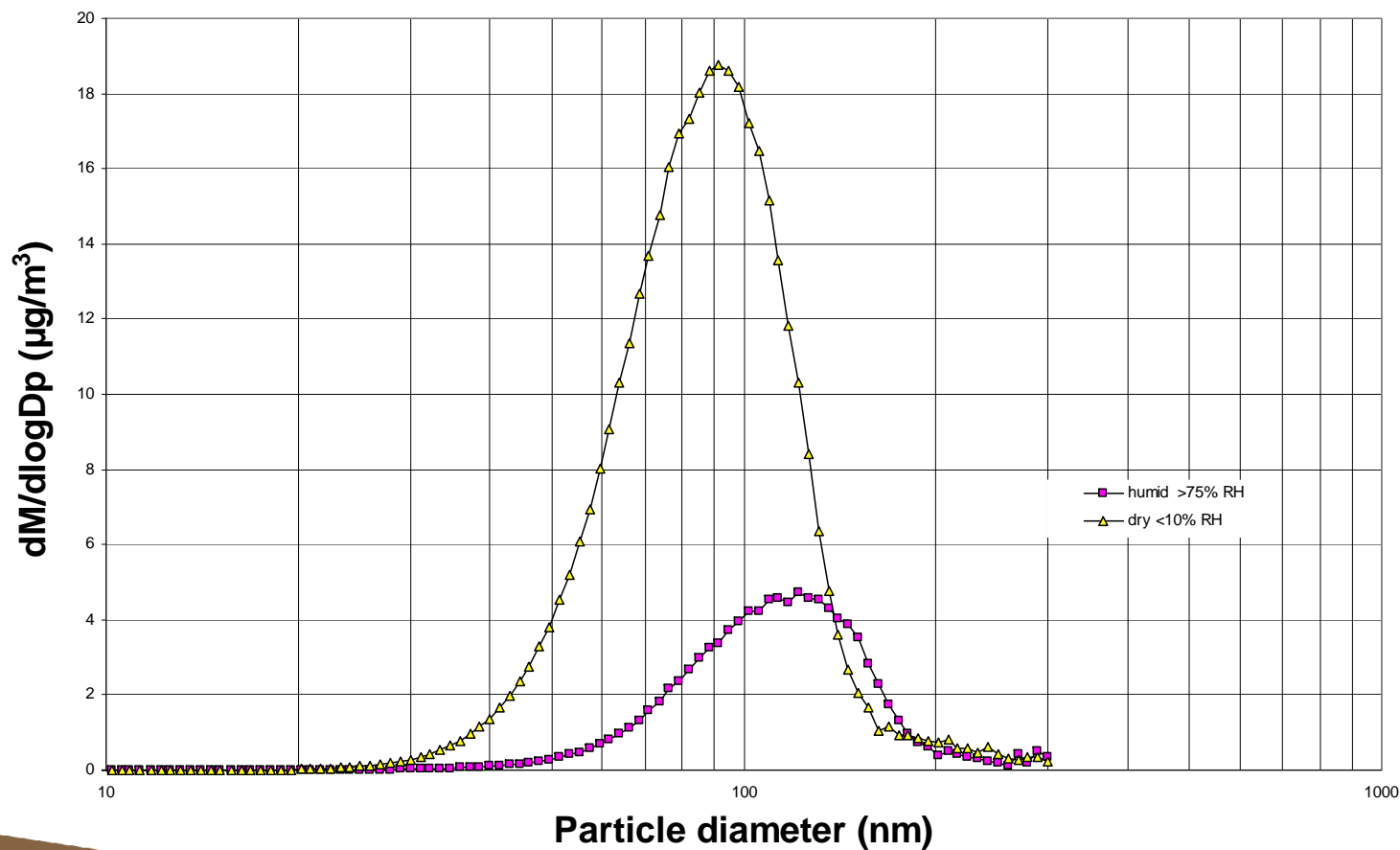


Experimental conditions

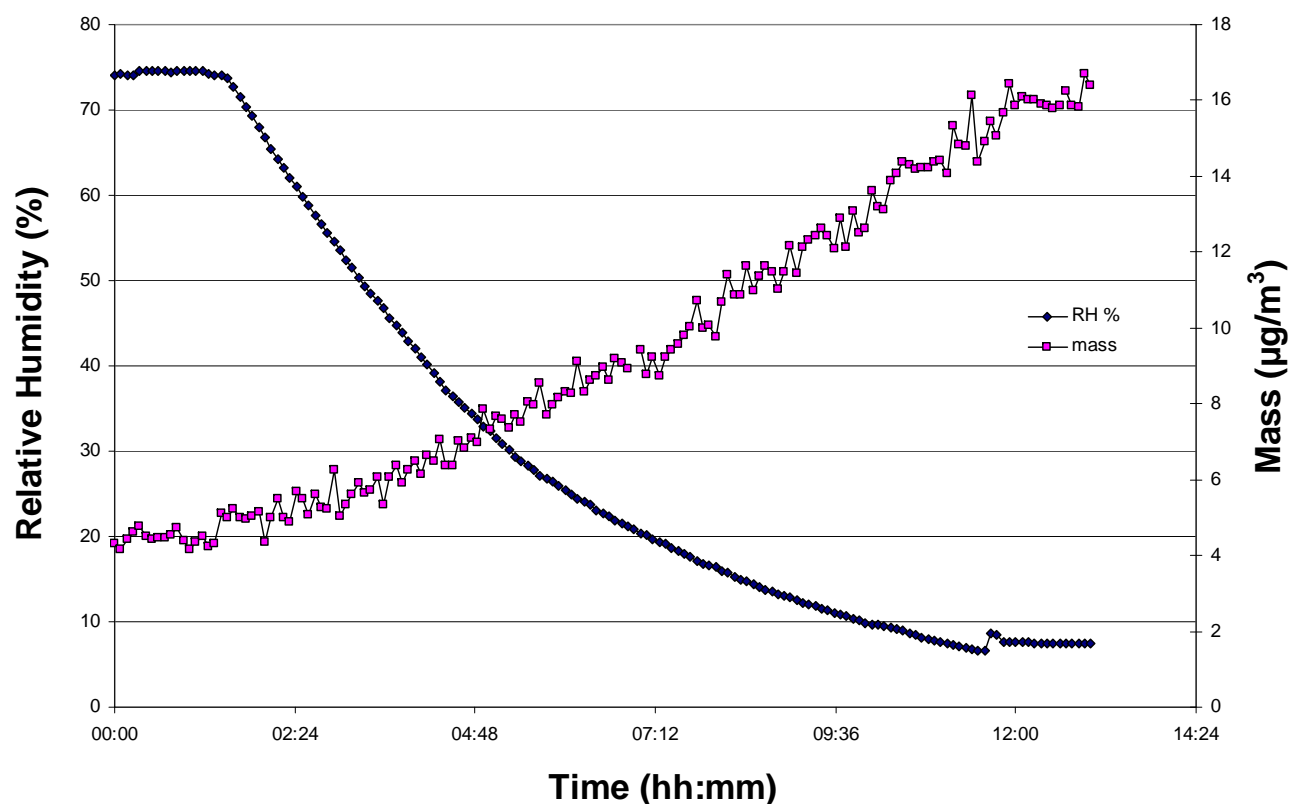
- G-FROST setup at 298K
- scanning the relative humidity from $>75\%$ to $<10\%$ during 10 hours
- OH Scavengers; 2-butanol and cyclohexane.
- initial concentration of β -pinene $4.32 \cdot 10^{11}$ molecules/cm³ (18 ppb) and ozone $1.08 \cdot 10^{14}$ molecules/cm³ (4400 ppb).
- reaction time of 236 seconds in the flow reactor, 46 % of the β -pinene had reacted
- the final SOA produced (number ($N_{10-300\text{ nm}}$) and mass ($M_{10-300\text{ nm}}$)) was measured by a SMPS



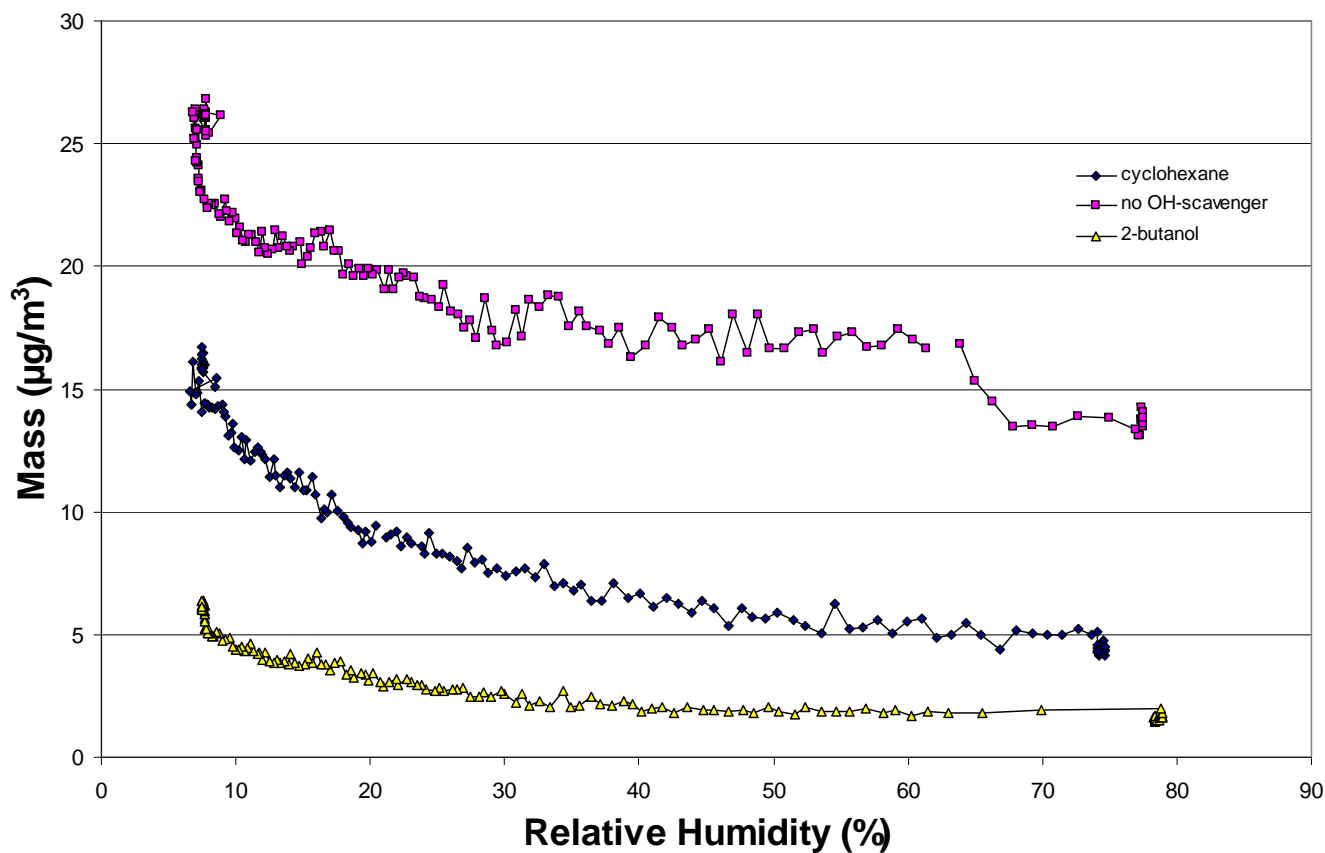
The size distribution on SOA mass of dry and humid conditions at 298 K for β -pinene using 2-butanol as OH-scavenger.



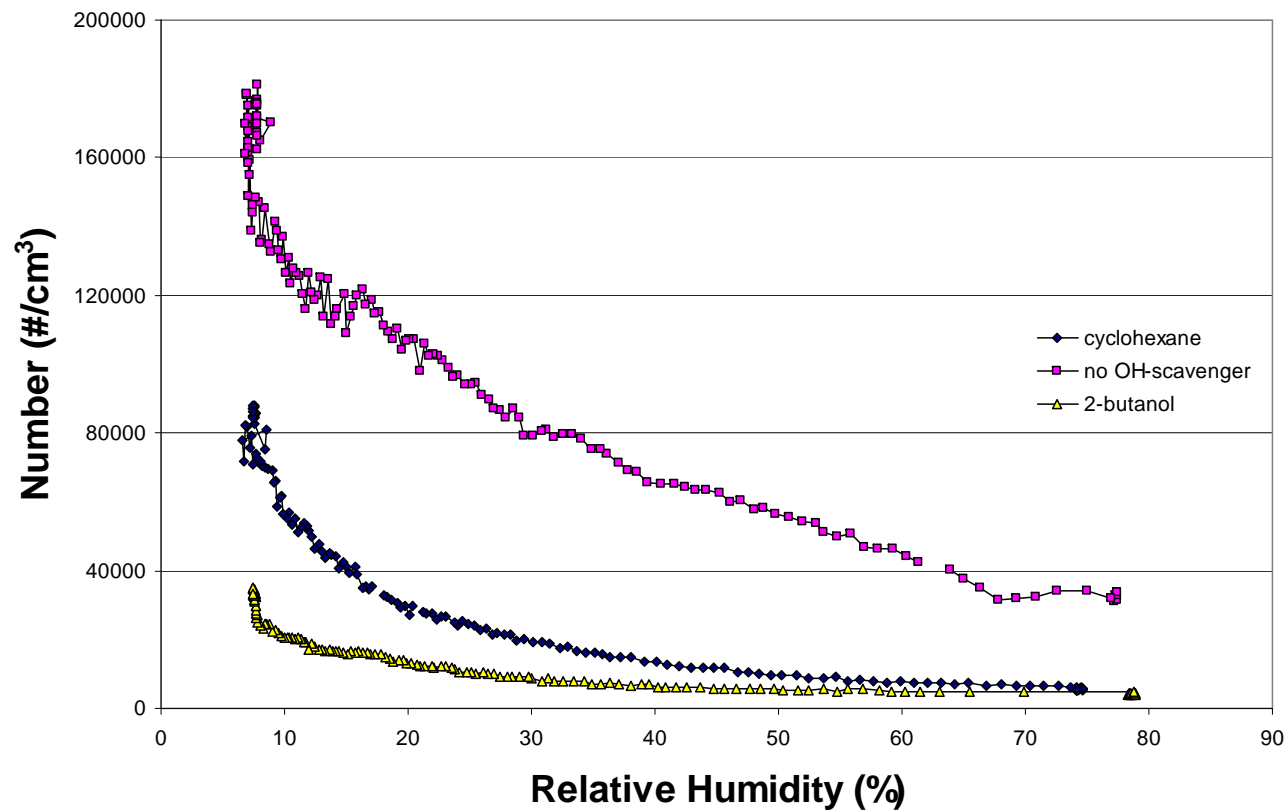
The effect on mass of β -pinene SOA at 298 K when scanning relative humidity. Cyclohexane was used as OH-scavenger



The water-effect on SOA mass from β -pinene at 298 K, using different OH-scavengers



The water-effect on SOA number from β -pinene at 298 K, using different OH-scavengers.



A comparison with literature data on the effect of OH-scavenger on SOA production

Reference	Org. Precursor	Scavenger	SOA Effect
This study	β -pinene	cyclohexane, 2-butanol, without	$SOA_{WO} > SOA_{CH} > SOA_{2-B}$
Jonsson et al. 2007	limonene α -pinene Δ^3 -carene	cyclohexane, 2-butanol, without	$SOA_{WO} > SOA_{2-B} > SOA_{CH}$ $SOA_{WO} > SOA_{2-B} > SOA_{CH}$ $SOA_{WO} > SOA_{2-B} > SOA_{CH}$
Iinuma et al. 2005	α -pinene	cyclohexane, 2-butanol	$SOA_{2-B} > SOA_{CH}$
Docherty and Ziemann, 2003	β -pinene	cyclohexane 1-propanol	$SOA_{CH} > SOA_{1-P}$
Docherty et al. 2005	α -pinene β -pinene Δ^3 -carene sabinene	cyclohexane, 1-propanol, formaldehyde	$SOA_{1-P} \geq SOA_{CH} \geq SOA_{HCHO}$ $SOA_{CH} > SOA_{1-P} > SOA_{HCHO}$ $SOA_{1-P} \geq SOA_{CH}$ $SOA_{CH} \geq SOA_{1-P}$

Conclusions

1. The water effect can be *both* positive and negative for different monoterpenes even between compounds with minor changes in chemical structure.
2. β -pinene shows a clear *negative* response both in mass and number of SOA when increasing the humidity at 298K.
3. The use of OH-scavengers reduces produced SOA from ozonolysis of β -pinene. 2-butanol is more effective than cyclohexane.

3 things to remember

1. **A laminar flow reactor with continuous supply of the reactants and removal of the products is a useful setup to study secondary organic aerosols produced under specific conditions "frozen in time".** These investigations complement the smog chamber experiments where the secondary organic aerosol formation is studied over time. Typically the laminar flow reactor can be used for processes studies where the result of specific changes in experimental conditions (e.g. concentration and/or relative humidity) can be followed with selected analytical instruments.
2. **Water influences mass and number of produced secondary organic aerosols from monoterpenes,** not only as an effect of physical uptake of water but also as reactant taking part in the chemical reactions and pathways. The water effect can be either positive or negative for different monoterpenes, even between compounds with minor change in chemical structure. The ozonolysis of β -pinene shows a clear negative response both in mass and number of produced secondary organic aerosols when increasing the relative humidity at 298K.
3. **The use of OH scavengers is aimed to reduce the influence of atmospheric OH chemistry when investigating the ozonolysis of alkenes.** The addition of OH scavengers when investigating the produced secondary organic aerosols from ozonolysis of β -pinene reduces both mass and number. Primarily this effect is caused by less amount of the precursor is oxidized. Secondary, it could be due to changes in product distribution from OH or ozone initiated oxidation of β -pinene. When using 2-butanol as OH scavenger in the ozonolysis of β -pinene, the reduction in both mass and number of secondary organic aerosol is more pronounced than when using cyclohexane. This suggests that the addition of the extra organic compound to trap OH radicals also has an influence on the chemical reactions and pathways producing secondary organic aerosol.

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Thank you for your attention!

Questions?