# SECONDARY ORGANIC AEROSOL REDUCED BY MIXTURE OF ATMOSPHERIC VAPOURS

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Motivation: Secondary Organic Aerosol (SOA) and HOM
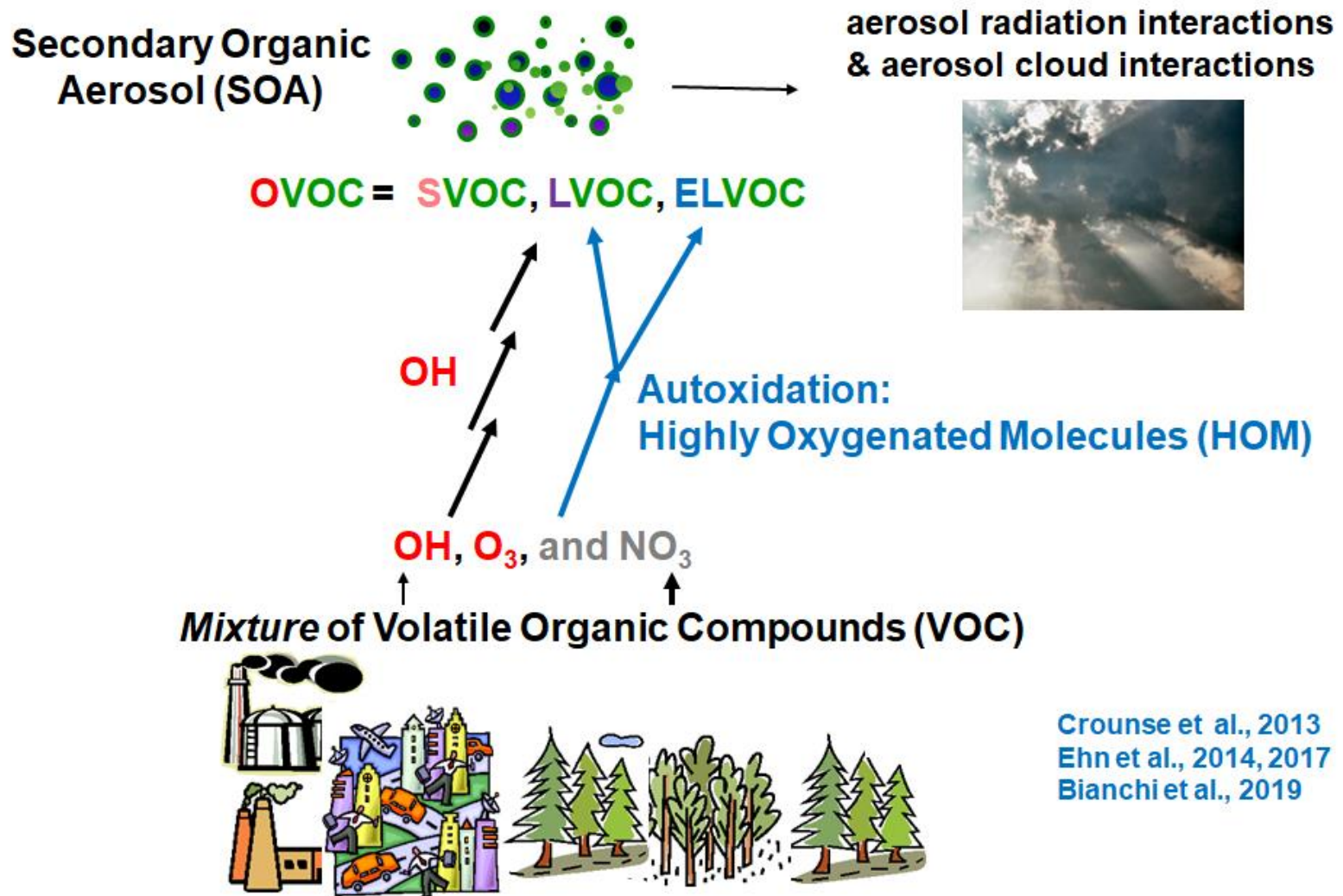
Crounse et al., 2013
Ehn et al., 2014, 2017
Bianchi et al., 2019

The prerequisites for investigating mixtures

VOC are emitted as mixtures into the atmosphere, e.g. isoprene, monoterpenes, sesquiterpenes

Conceptually, *SOA yield in mixtures* predicted by *linear combination* of *individual SOA yields* of the components (more or less).

Mixtures of SOA precursors with *lower yield* (isoprene) and *higher yield* (α-pinene)?
- SOA mass is dependent on oxidant (OH) concentration (turnover)
  => SOA mass is reduced if „good" and „bad" SOA precursor
  compete for oxidants („OH-scavenging")
- SOA yields can be dependent on OH concentration (ageing)

(Differing experimental conditions / differing OH concentrations in SOA formation:
- introduces an operational component into SOA studies
  => different studies -> differing results)

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Experiments: Jülich Plant Atmosphere Chamber (JPAC)
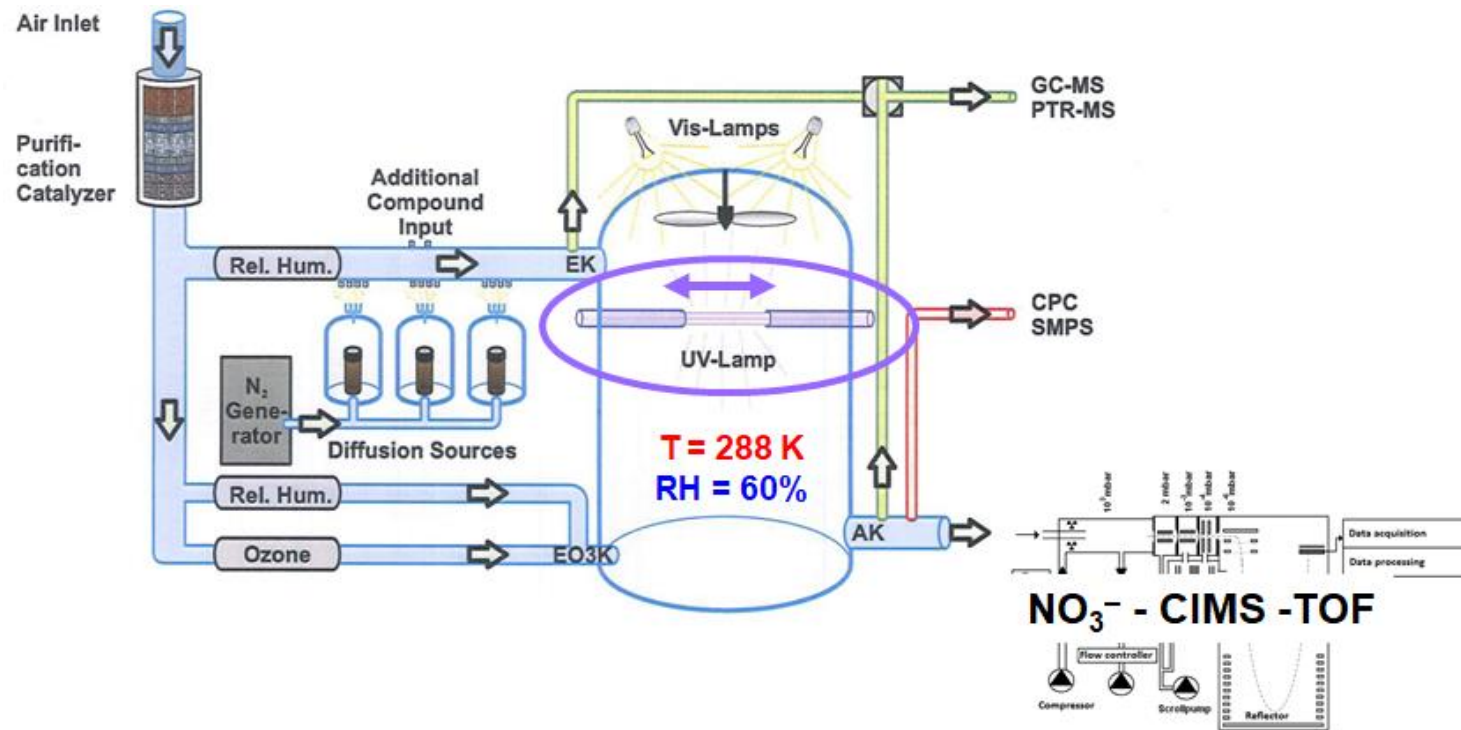
Experimental procedure

- continously stirred tank reactor (1450l), residence time : ≈ 50-60 min.

- mix O_3, H_2O and α-pinene and add **seed aerosol** in the dark

- *UV on*: photolyse O_3 and *produce and vary OH, range 0.1 - 8·10^7 cm^{-3}*

- *add isoprene, re-adjust OH*

Outline: SOA reduced by mixture

Observation: „**Product scavenging**", control of the oxidant (OH)

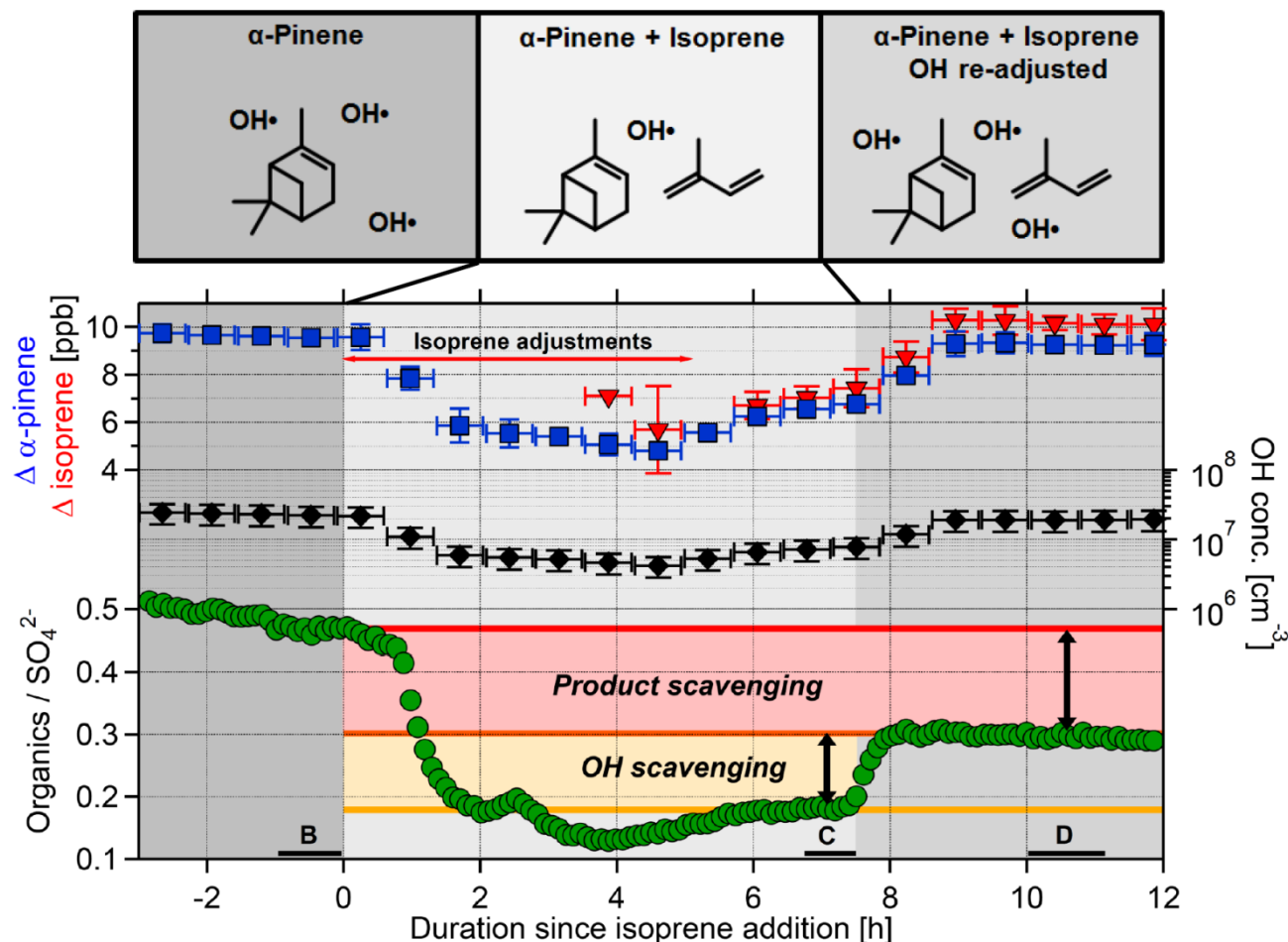**Interpretation:** highly oxygenated molecules (HOM) and their peroxy radicals HOM-RO$_2$

Implications: for lab studies and models

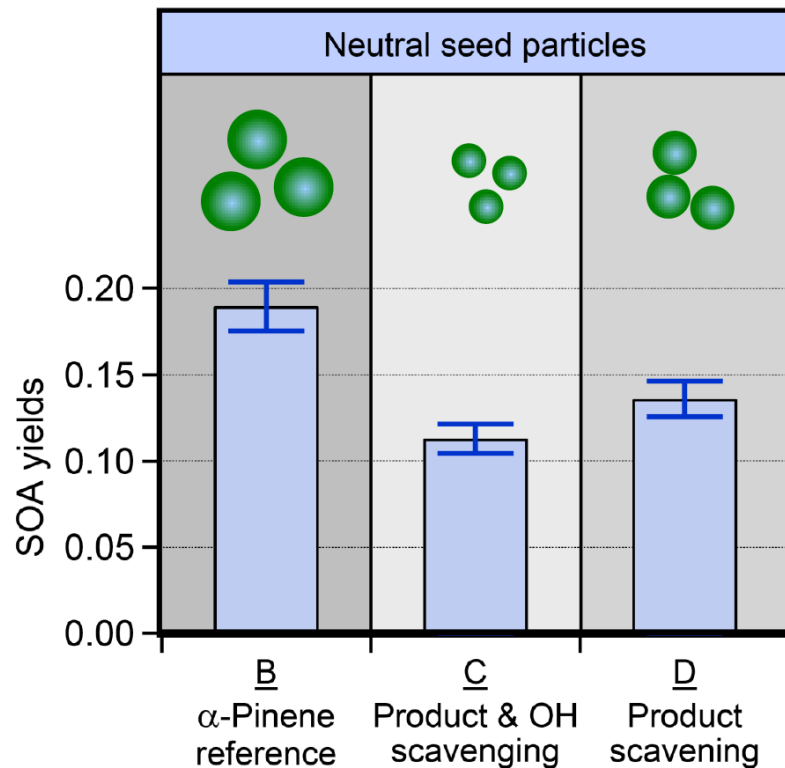**Supplementary information and detailed slide captions at the end**

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Observation

Reduced SOA mass: α-pinene in presence of isoprene

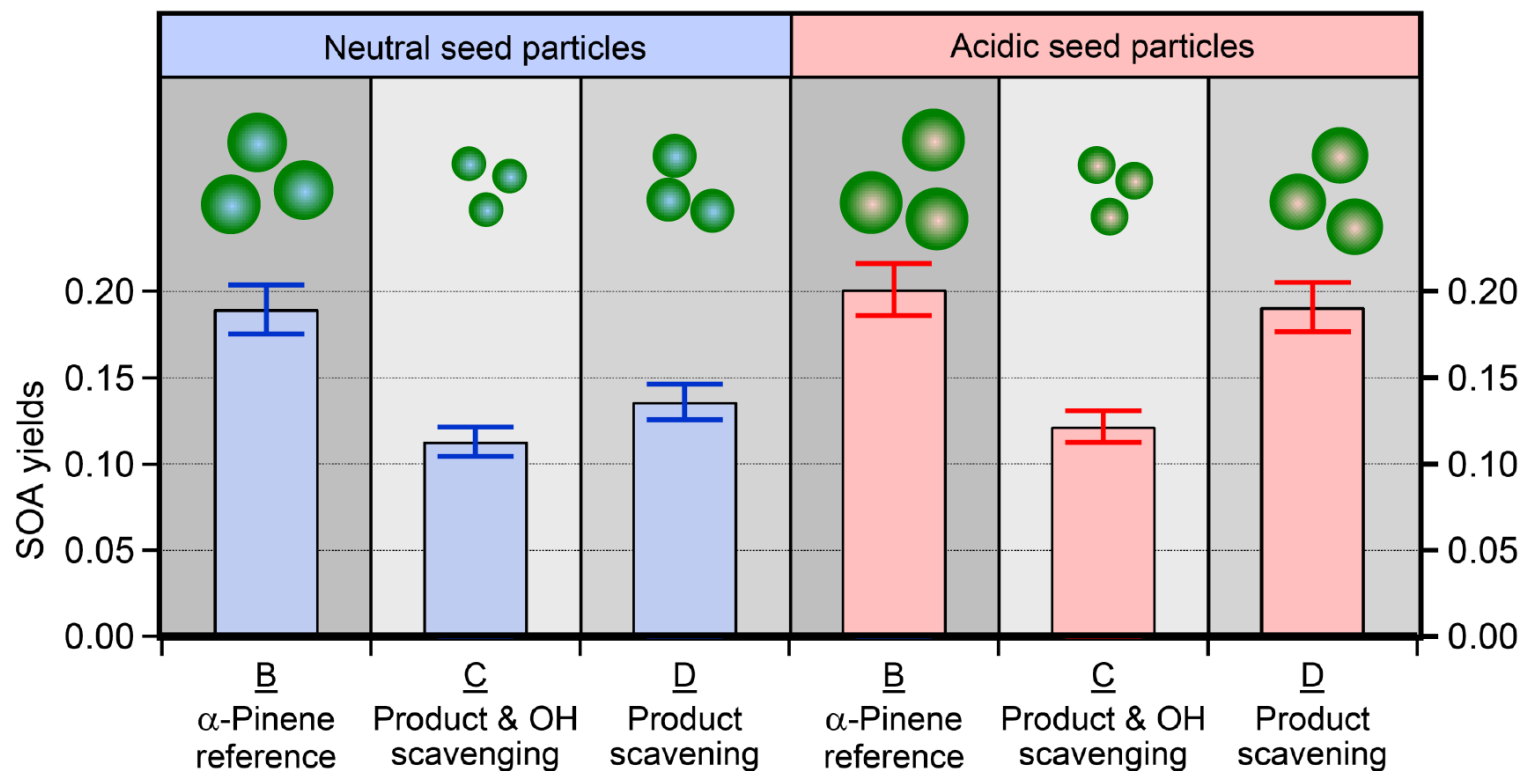## SOA mass on ammonium sulfate: *product scavening*

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SOA yields: OH and product scavenging on $(NH_4)_2SO4$

on neutral seeds:
OH- and product scavenging
reduce SOA yields

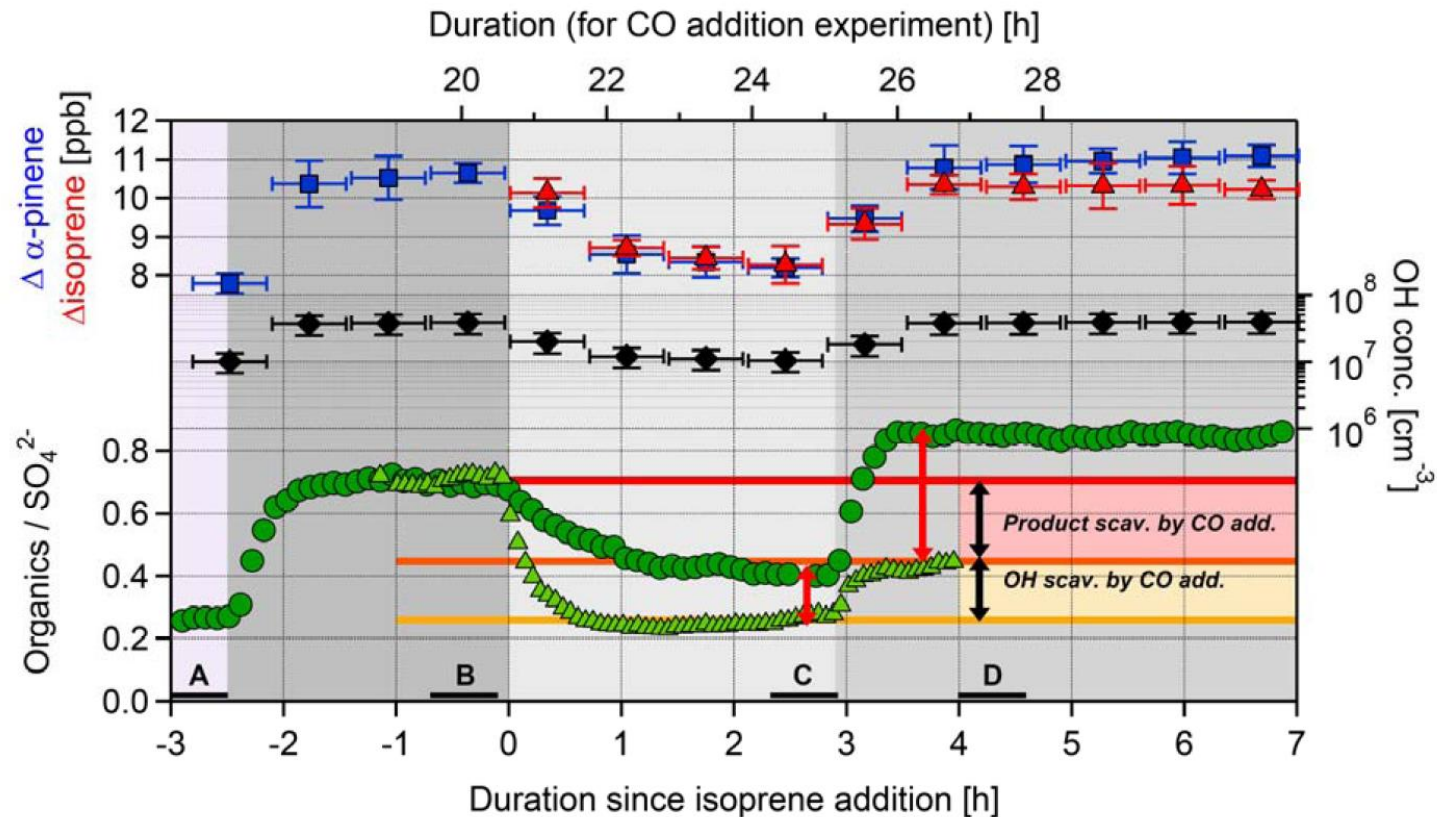JÜLICH
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SOA yields: OH and product scavenging

on neutral seeds:
OH- and product scavenging reduce SOA yields

on acidic seeds:
OH- and product scavenging compensated by reactive uptake

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SOA mass: α-pinene in presence of isoprene (and CO)

SOA mass on ammonium bisulfate

add CO and inspect org ( )△
red arrows isoprene SOA by liquid phase reactions

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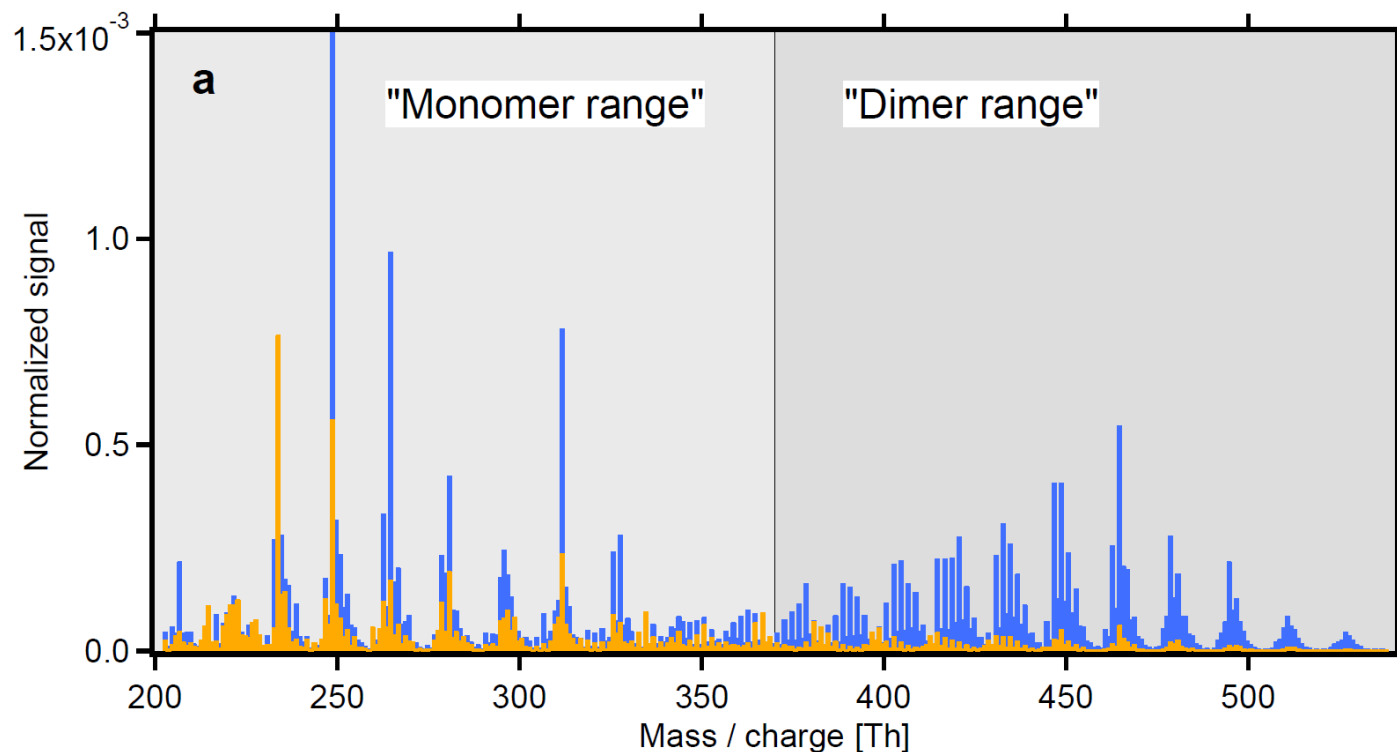# Product scavening parametrized as f(Δisoprene/Δα-pinene)
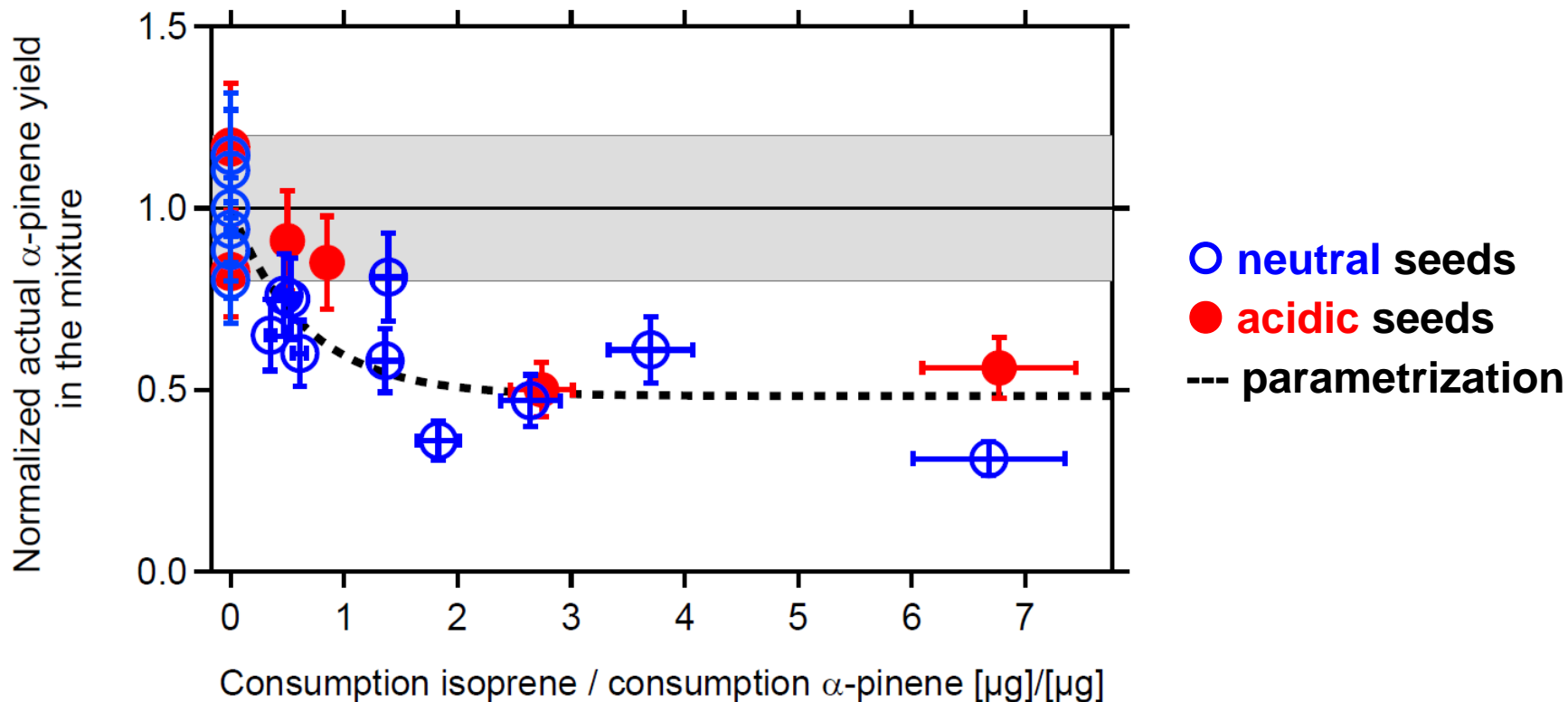
In our system: significant *reduction of α-pinene yield*
(includes OH dependence of the SOA yield)

Interpretation

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Interpretation: mechanism of product scavening and HOM

in presence of isoprene:

- suppression of (mixed) HOM dimers
- shift to lower m/z

Mechanism of product scavening:
isoprene-RO_2 suppress α-pinene HOM-dimers
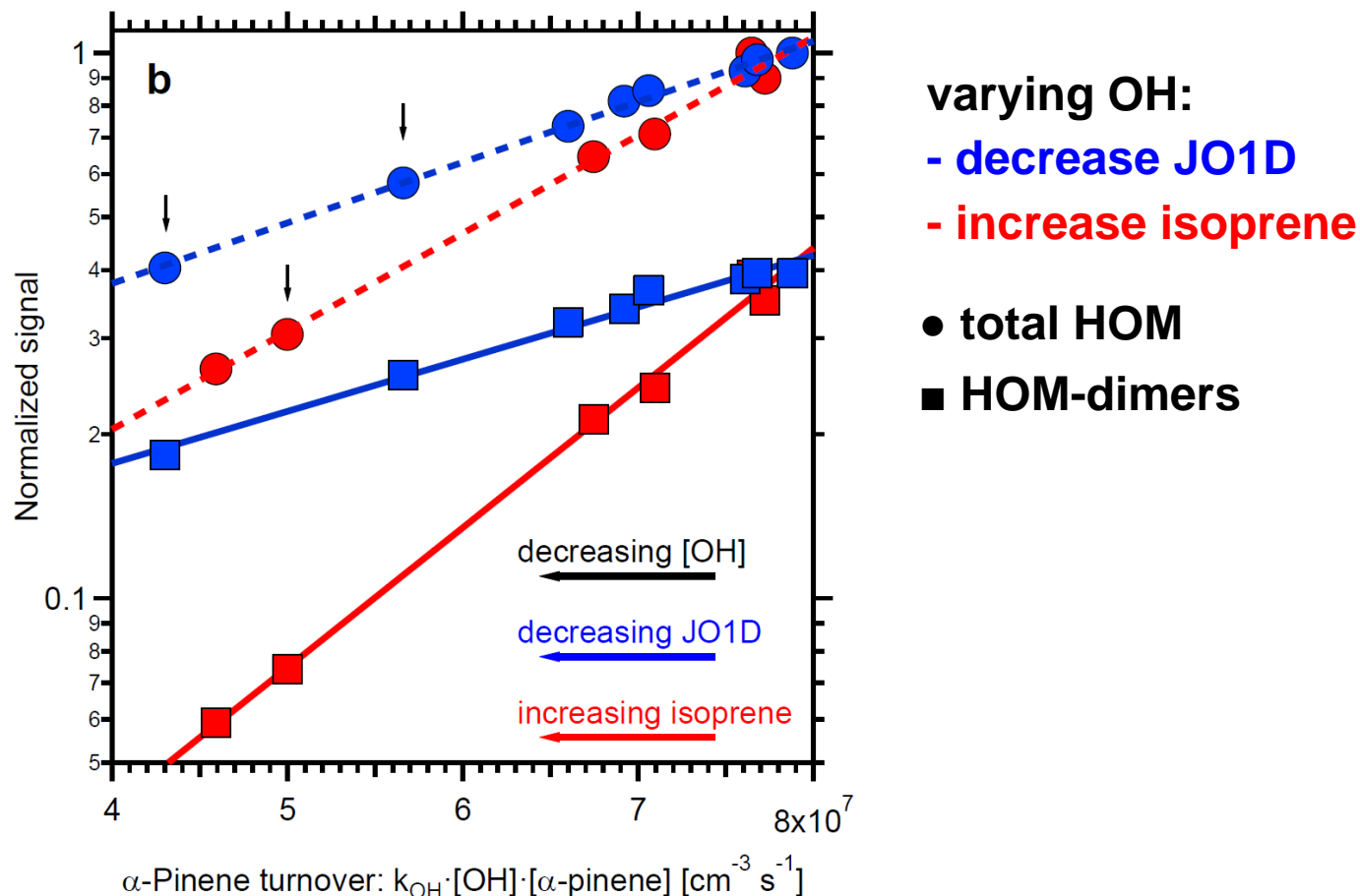
Berndt et al. EST 2018: isoprene product scavenging a factor of 3-4 smaller in the atmosphere (derived from dimer formation rates)

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Product scavenging is ubiquitous

CO

HO$_2$ and CH$_3$O$_2$
suppress SOA yields

CH$_4$
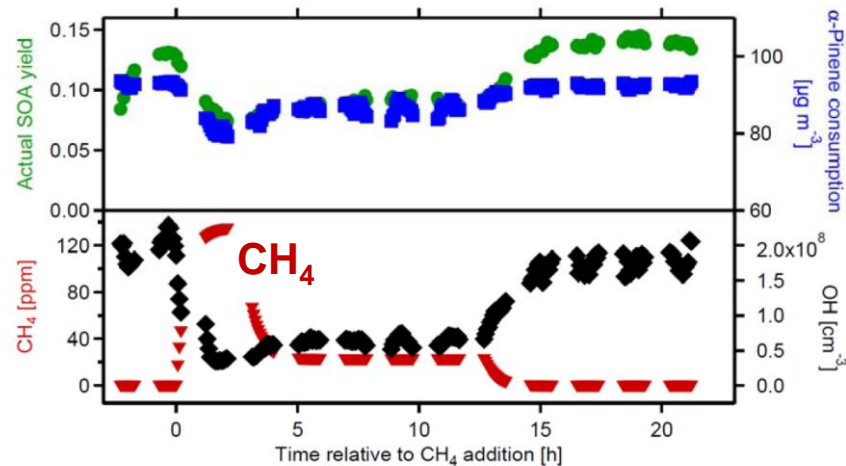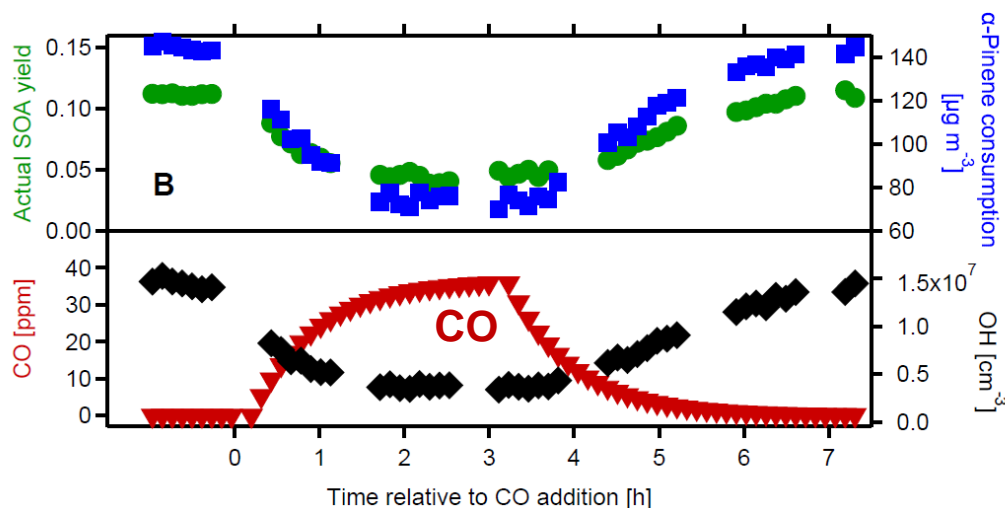
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Implications

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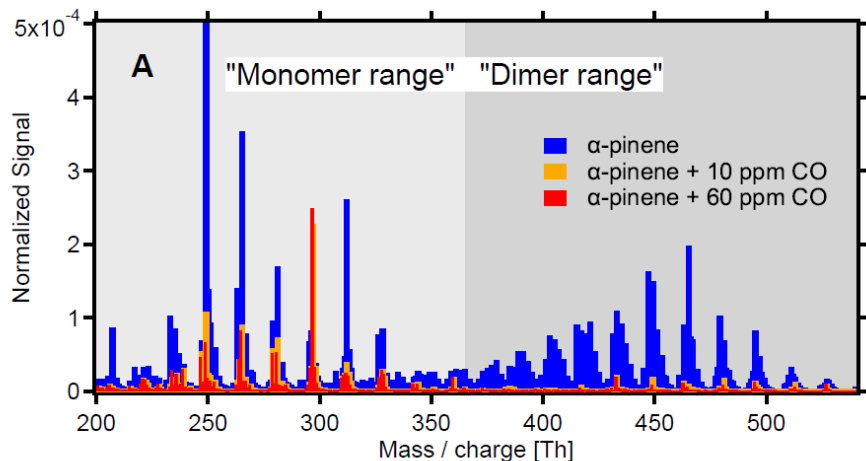# OH- and parameterized Product Scavenging under conditions of atmospheric emissions, transport and oxidation fields

noIso:
no isoprene emissions

OHS:
OH scavenging, only

PS:
+ product scavenging
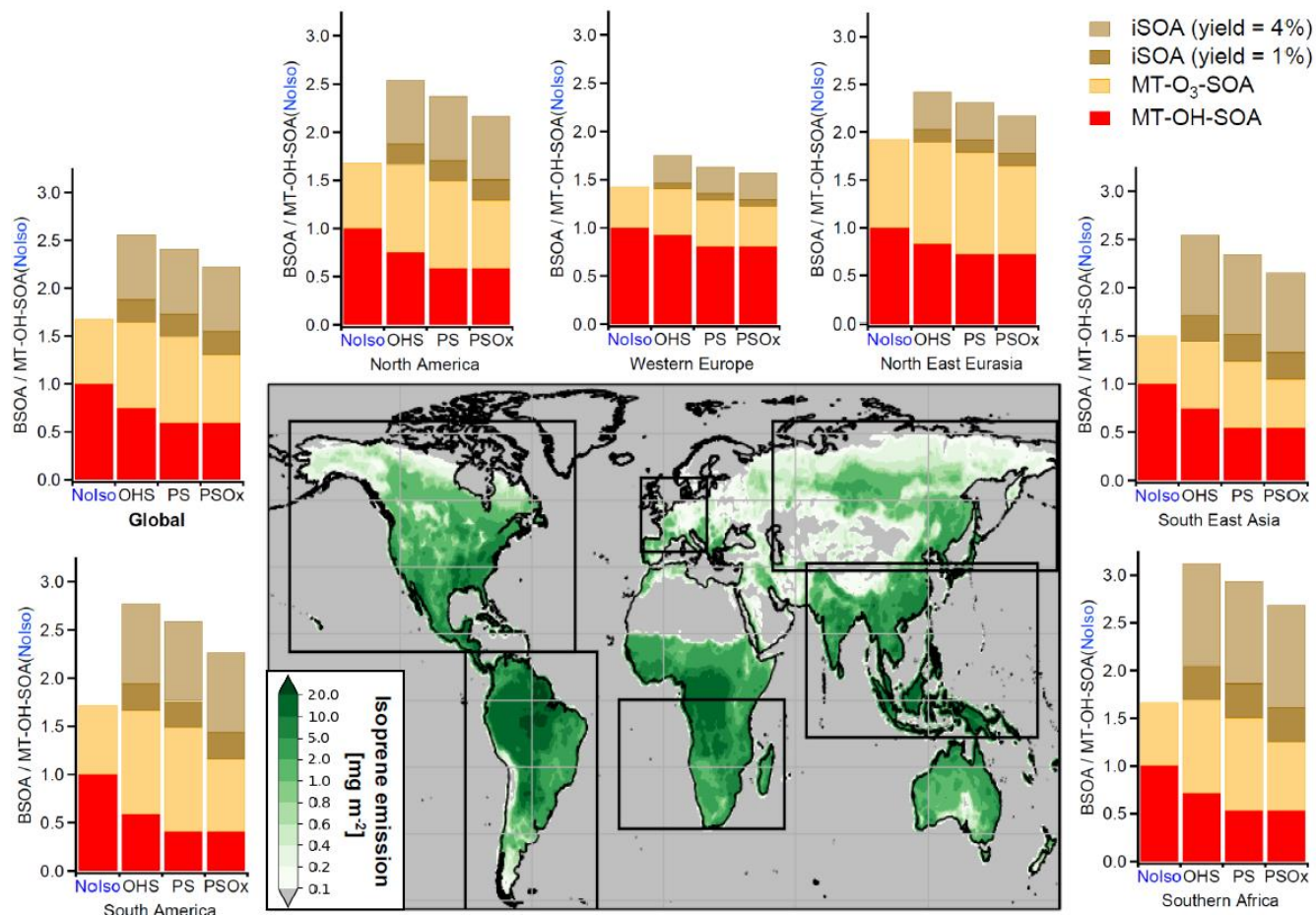
PSOx:
+ product scavening for ozonloysis products

- **Global Model EMEP (MSC-W model)**
- **no explicite HOM-RO$_2$ chemistry (!)**

OH- and parameterized Product Scavenging under conditions of atmospheric emissions, transport and oxidation fields

iSOA (yield = 4%)
iSOA (yield = 1%)
MT-O₃-SOA
MT-OH-SOA

noIso:
no isoprene emissions

OHS:
OH scavenging, only

PS:
+ product scavenging

PSOx:
+ product scavening for ozonloysis products

- Global Model EMEP (MSC-W model)
- no explicite HOM-RO₂ chemistry (!)

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Implications

- **By keeping control of the OH scavenging: Product scavenging in mixtures**

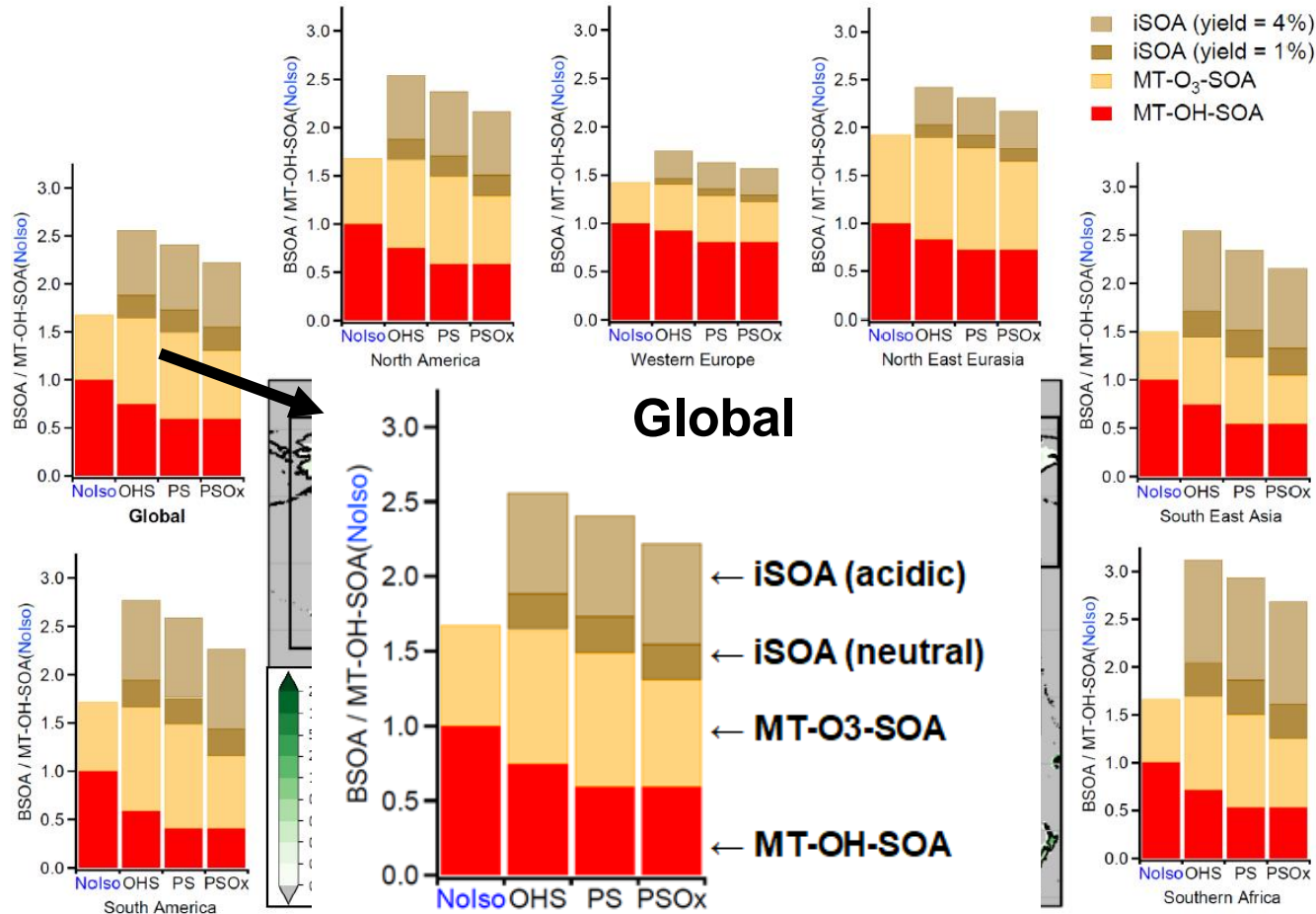- **Product scavening:** peroxy radicals with *modest or no* SOA forming potential can *suppress* SOA forming products of higher SOA yield precursors.

- **HOM, HOM-RO_2 and RO_2 from SOA precursors as well as from major volatile compounds should be considered when predicting the mixture's SOA yield.**

- **Simple linear combination of SOA mass from the individual yields of components:** *substantial overestimation of SOA production*.

- **Need for more realistic (explicit) consideration of SOA formation in the atmosphere: consider interactions between the mechanistic pathways via peroxy radicals in lab studies as well as in models**

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Acknowledgements

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Table S5: Detailed fractions of biogenic SOA on global scale

SOA fractions (FY)	Global Burden	Global Surface Concentration
MT-OH-SOA	21%	20%
MT-O_3-SOA	19%	24%
iSOA (yield 4%)	37%	24%
MT-NO_3-SOA	11%	16%
i-NO_3-SOA	3%	2%
SQT-SOA	9%	15%

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Detailed captions for slide 7 -10

Slide 7-10: Reduced *SOA mass* and *yield* of α-pinene by *product scavenging* and *OH scavenging* by isoprene.

Slide 7: The top panel depicts symbolically the transition of the reaction system. Neutral seed particles: isoprene (red triangles) lowered [OH] (black diamonds) and the corresponding consumption of α-pinene (blue squares), reducing the organic mass dramatically. The organic mass was normalized to sulfate mass (organics/SO_4^{2-}, green circles). The newly discovered product scavenging (red) in the presence of isoprene is separated from OH scavenging (orange) by re-adjustment of [OH]. Because of product scavenging only 60% of the organic mass is formed despite the same α-pinene consumption. (The acidic case is depicted in Slide 10) Vertical error bars for Δα-pinene and Δisoprene are s.d. for averaging 14-15 samples, horizontal bars show the averaging intervals. For OH we estimate an overall error of ±33%.

Slide 8: The SOA yields in presence of neutral ammonium sulfate (blue) and **Slide 9** acidic ammonium bisulfate (red) seed particles were calculated at times <u>B</u>, <u>C</u>, and, <u>D</u> as *organic mass/α-pinene consumption*. Not only the SOA mass (indicated by the green spheres in the middle) but also its yield decreased strongly (bar plots). <u>B</u> shows the SOA yield for α-pinene alone, while <u>C</u> shows the summed effect of the new product scavenging and OH scavenging in the α-pinene & isoprene reaction system. For the neutral seeds <u>D</u> demonstrates the magnitude of the product scavenging effect on the SOA yield, as [OH] and α-pinene consumption were re-adjusted to the same levels as before isoprene addition. On acidic seed aerosol (red) isoprene makes a substantial contribution to SOA, which compensates for some of the OH scavenging effect and most of the product scavenging effect. The errors reflect the estimated overall 15% uncertainty for an individual experiment.

Slide 10: *Product scavenging* and *OH scavenging* effect in the presence of acidic ammonium bisulfate seed aerosols, by isoprene (dark green circles, lower time axis) and by CO (light green triangles, upper time axis).
The dark grey area shows the reaction system α-pinene & OH as a reference. In the beginning of the light grey area isoprene was introduced into the chamber, in the beginning of the medium grey area OH was re-adjusted to the same value as in the dark grey period. The letters indicate periods of steady state for ozonolysis (<u>A</u>), α-pinene & OH (<u>B</u>), α-pinene & isoprene & OH (<u>C</u>); α-pinene & isoprene & [OH] adjusted (<u>D</u>). Values in Figure 1B are taken from these periods. The organic mass was normalized to sulfate mass in order to compensate for fluctuations of the seed aerosol generation and is shown as organic to sulfate ratio (organics/SO_4^{2-}, dark green circles and light green triangles).
Addition of isoprene (red triangles) lowered [OH] (black diamonds) and α-pinene consumption (Δ α-pinene, blue squares), leading to reduced formation SOA mass. Re-adjusting [OH] and α-pinene consumption induced enhanced SOA mass formation. This is different for the acidic seed aerosol compared to the neutral seed aerosol (Figure 1A). Later in the experiment (top axis) isoprene was removed and CO was added to the α-pinene & OH system under otherwise same chamber settings. The observed organics/SO_4^{2-} is shown in light green small triangles. ([OH], Δα-pinene and ΔCO are not shown.) Product scavenging and OH scavenging (black arrows) are taking place in the presence of acidic seed aerosols as expected, since the acidity of the seed particles should not affect the gas-phase chemistry.
The red arrows are an estimate of the gain in SOA mass by isoprene that is due to condensation/acreation reactions of isoprene oxidation products on the acidic seed particles.

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Detailed captions for slide 13 - 18

Slide 13-14: HOM monomer/dimer distribution in the presence and absence of isoprene illustrating the product scavenging effect.
Slide 13: comparison of two mass spectra taken in experiments with (orange) and without isoprene (blue). In the presence of isoprene the dimer/monomer drops to about 1/3, indicating that the formation of these extremely low vapour pressure compounds is efficiently suppressed in the presence of isoprene.
Slide 14: Both the total HOM (monomers+dimers, circles) and HOM dimers (squares, molecular mass > 370 Da) decrease with decreasing α-pinene turnover. Here [OH] was varied in two different ways: i) by decreasing the OH production rate, i.e. by decreasing the photolysis of ozone ($J(O^1D)$, blue) and ii) by adding increasing amounts of isoprene (red). In the presence of isoprene HOM decrease more strongly, mainly because the product scavenging is suppressing the α-pinene HOM dimers. The total HOM from the two different experiments were normalized to 1 for better comparison.

Slide 15: Suppression of α-pinene SOA in presence of CO and CH_4 illustrating the generality of the product scavenging effect.
left hand side upper panel: comparison of three mass spectra taken in experiments with (orange [CO]=10 ppm, red [CO]=57 ppm) and without CO (blue). In the presence of [CO] > 10 ppm the dimer/monomer drops by more than 1/2, indicating that the formation of the dimers is efficiently suppressed in the presence of CO. Because of the high [CO] overall HOM are suppressed by factor of 4 and 5 respectively. **left hand side lower panel:** The product scavenging effect reduces the α-pinene yield in the reaction system α-pinene & CO & OH in the presence of ammonium sulfate seeds. The actual SOA yield, calculated as actual organic mass/actual α-pinene consumption, decreases by more than 50%, when 40 ppm CO was added to the reaction system. CO concentrations were calculated from known inlet concentration, the flow rate through the RC and the reaction rate of CO with OH. Light colored data points show steady state averages, whereby horizontal error bars show the averaging interval; s.d. of the averages are of the same size or smaller than the symbols.
Note, the data in the panels were not taken from the same experiment: experiments to show HOM in the gas-phase and to show SOA suppression cannot be performed in optimal fashion under the same conditions.
Right hand side: Product scavenging effect in reaction system α -pinene & CH_4 & OH. The actual SOA yield, calculated as actual organic mass / actual α -pinene consumption, drops, when CH_4 is added to the reaction system. CH_4 concentrations were calculated from known inlet concentration, the flow rate through the RC and the reaction rate of CH_4 with OH.

Slide 17-18: Atmospheric implications of product scavenging and OH scavenging.
Global model calculations showing that OH scavenging (OHS) and product scavenging (PS) in presence of isoprene reduce the photochemically derived MT-OH-SOA mass (red) significantly compared to the reference cases NoIso. For the calculation a 4% iSOA yield for acidic aerosols was applied (sum of the brownish bars). OHS is inherently considered in models as long as biogenic SOA (BSOA) formation is directly linked to the oxidant fields, but the new PS effect reduces the MT-OH-SOA even further. To illustrate the maximum potential PS effect it was also applied to ozone derived MT-O_3-SOA (orange, PSOx). In this case the iSOA gain for 1% iSOA yield on neutral aerosols (dark brown) would not be able to compensate for the loss of MT-SOA. We show the global average and results for regions with high and low isoprene emissions and high and low population density. The map shows isoprene emissions, green shaded in [mg m^{-2}] and the areas of the selected regions. All contributions are normalised to MT-OH-SOA of the respective NoIso case, when biogenic isoprene emissions were omitted in the model.