EFFECT OF NO_x IN THE PHOTOCHEMICAL SYSTEM OF A-PINENE

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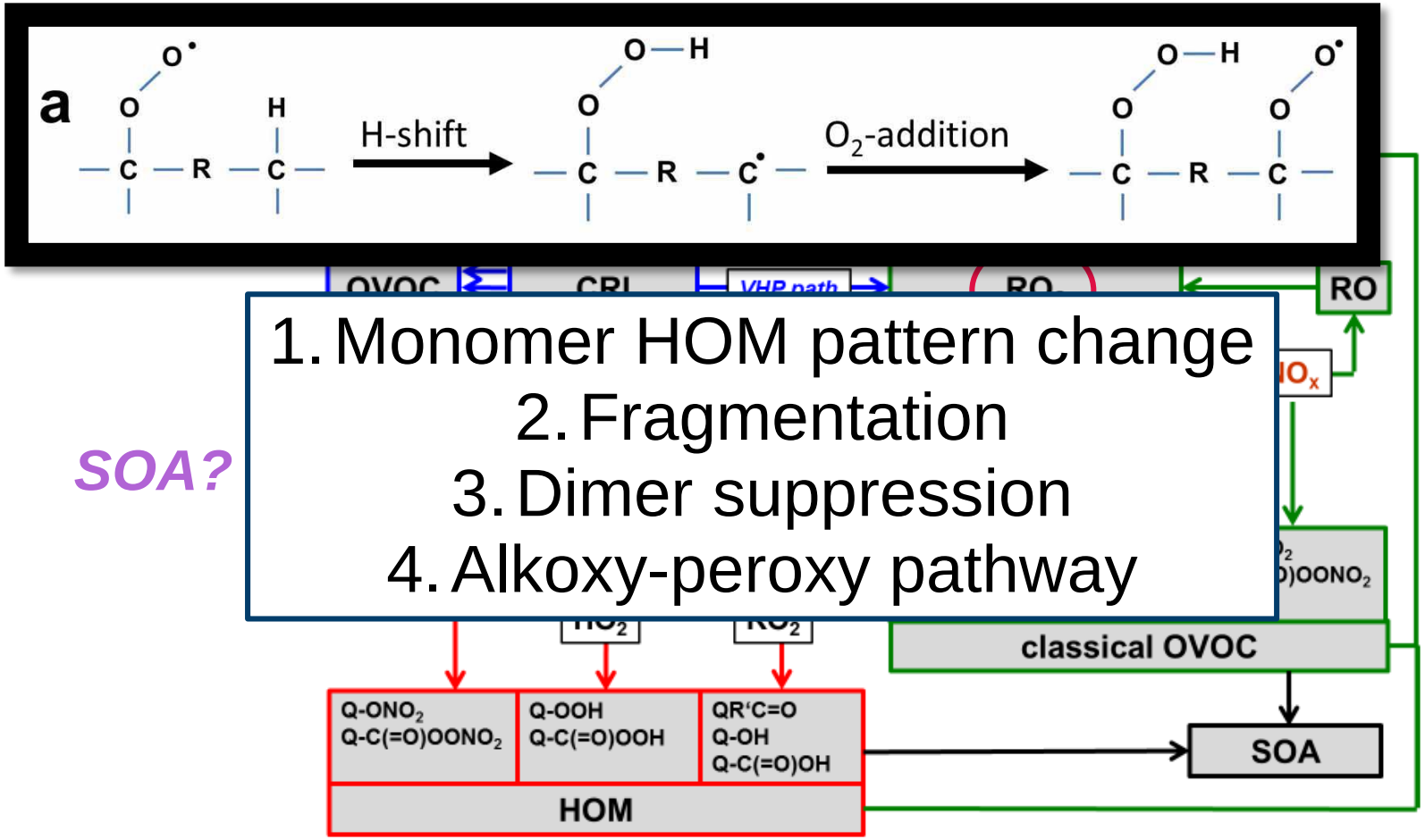
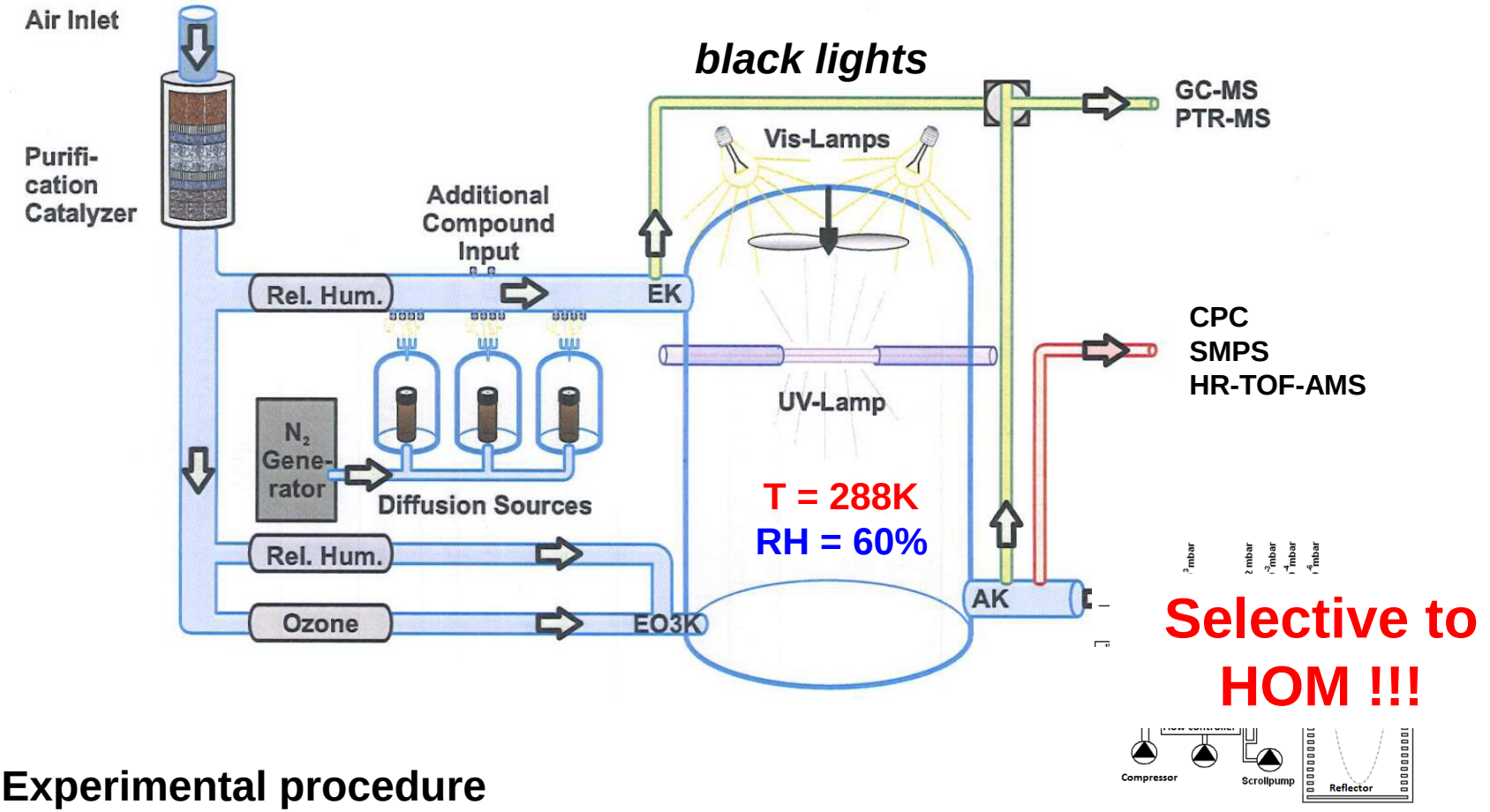
1. MOTIVATION

Peroxy Radical and Highly Oxidized Molecule(HOM)



Iida Pullinen thesis
Ehn et al 2014

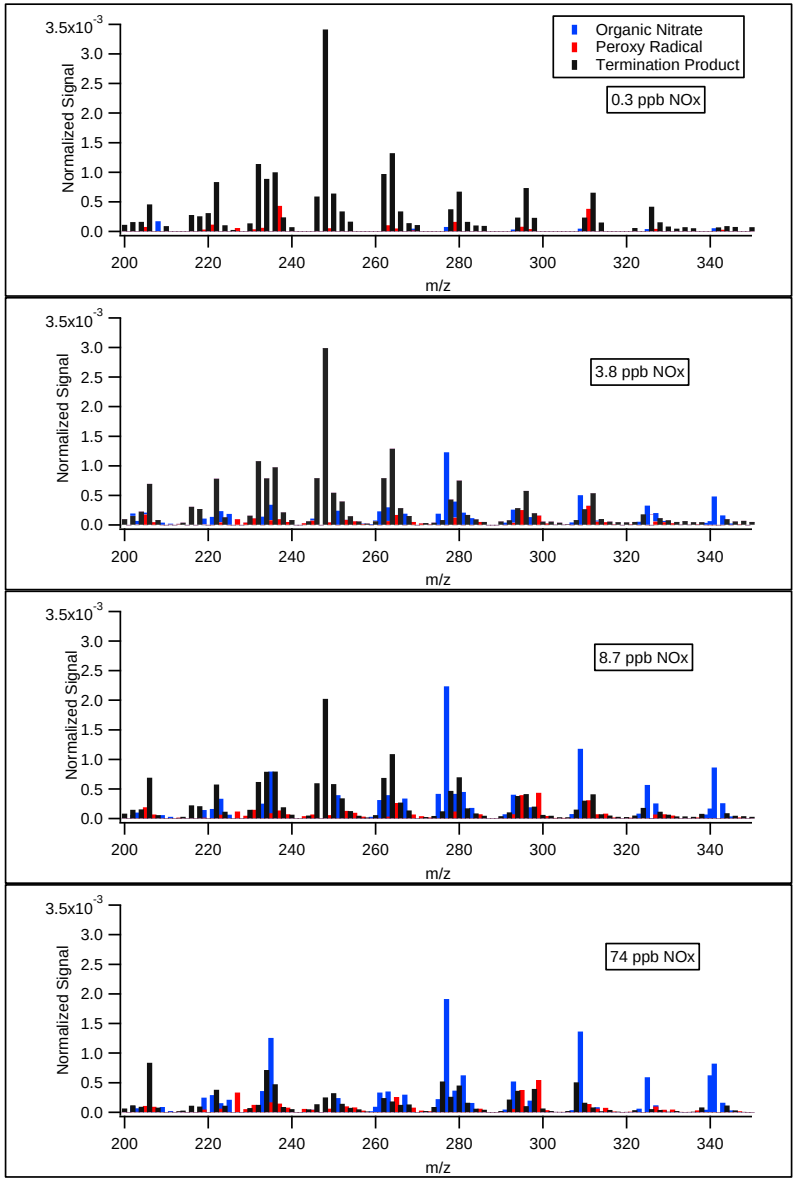
2. EXPERIMENTS: JÜLICH PLANT ATMOSPHERE CHAMBER

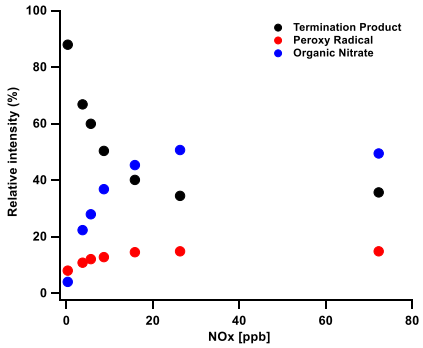


Experimental procedure

- continously stirred tank reactor (1450l), residence time : ≈ 50-60 min.
- bring system into steady state
- UV on: photolyze O_3 and produce OH, range 0.1 - $8 \cdot 10^7$ cm^{-3}
- black lights on: photolyze NO_2 -> NO (0.3-100 ppb)

3.1 RESULT: MONOMER HOM PATTERN CHANGE



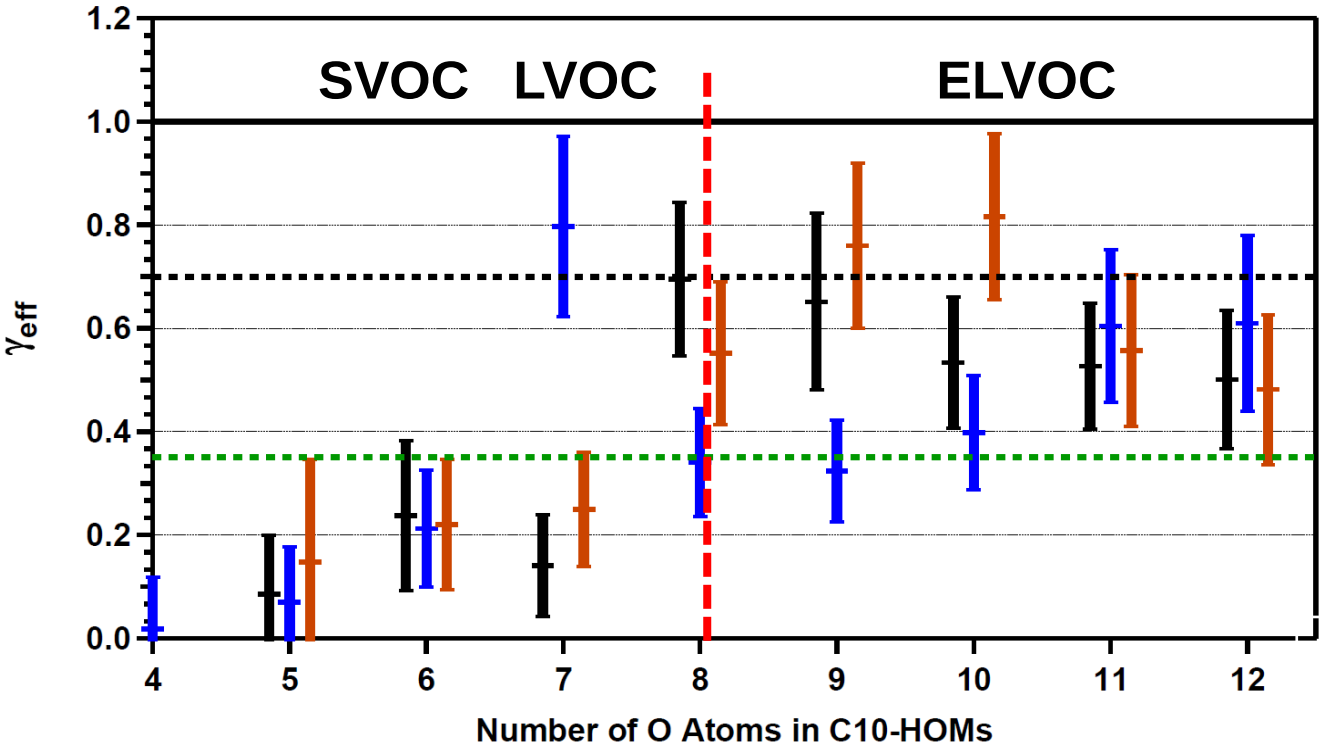


Reaction: RO_2+HO_2 , RO_2+RO_2

↓

RO_2+NO, RO_2+NO_2

3.1 RESULT: MONOMER HOM PATTERN CHANGE



Hydroperoxide+Alcohol
Ketone
Organic Nitrate

Fuchs-Sutugin!

$$c(HOM) = \frac{P(HOM)}{L(HOM)}$$

$$\frac{c(HOM)^0}{c(HOM)} = \frac{L_W(HOM) + L_P(HOM)}{L_W(HOM)}$$

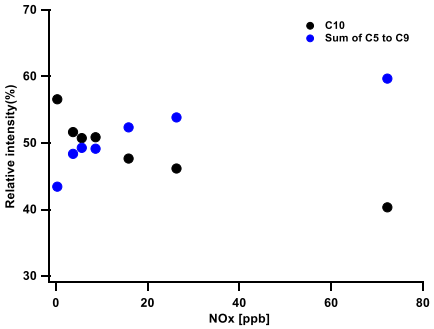
$$L_P(HOM) = \gamma_{eff} \cdot \frac{\bar{\upsilon}}{4} \cdot S_P$$

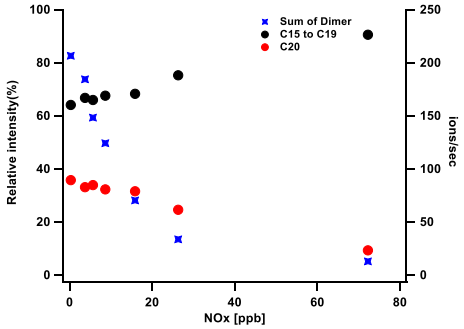
No dependency on **termination functional group**
: Similar functionality (multiple hydroperoxyl groups)

Pullinen et al in preparation

3.2 RESULT: FRAGMENTATION

Fragmentation of Monomer and Dimer formation

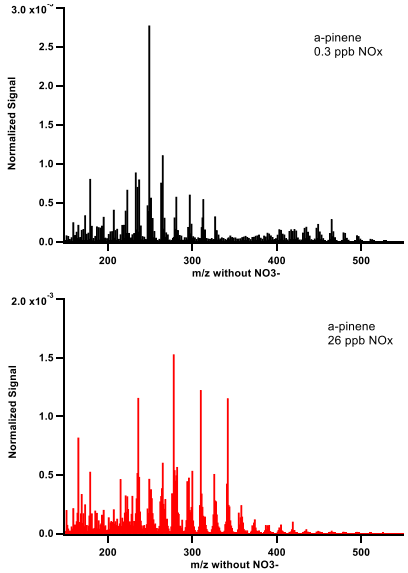




Alkoxy radical: ROO ▪ + NO → RO ▪ + NO_2

Increase of smaller compounds in monomer and dimer range
→ **More volatile compounds**

3.3 RESULT: DIMER SUPPRESSION



Dimer intensity decreased (16times)

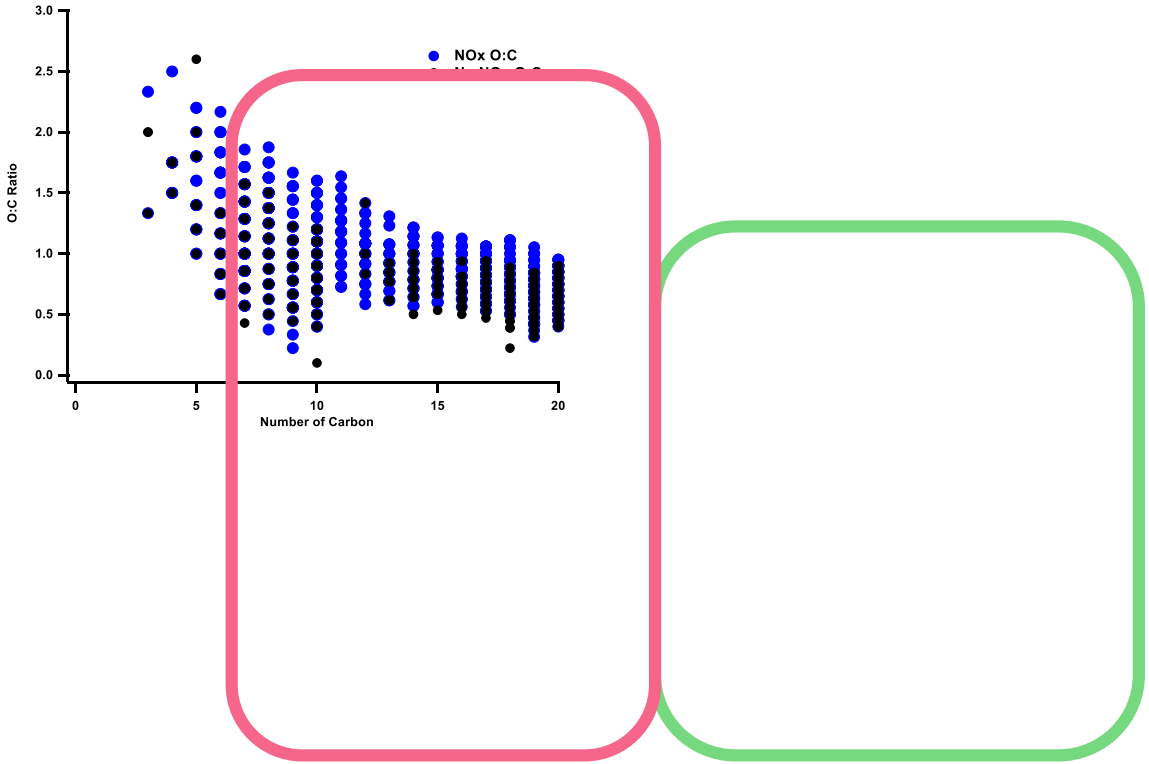
1. RO_2 + NO/NO_2
   → Organic Nitrate

2. Smaller dimer(C<20)
   $C_{15\text{-}19}/C_{20}$ (2→9.5)

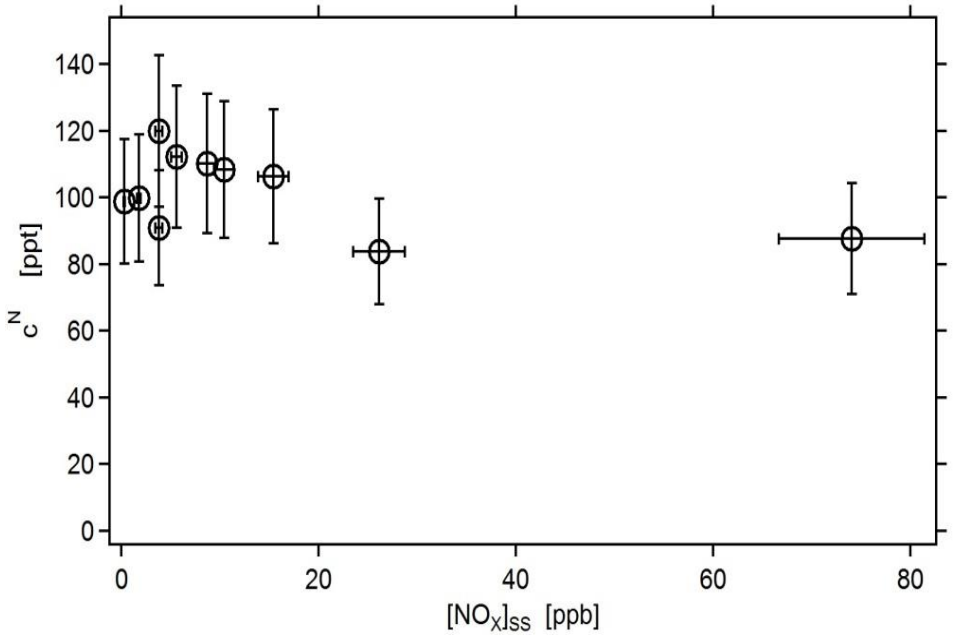
3.3 RESULT: DIMER SUPPRESSION

Effect on SOA?

Dimer → involving one relative volatile compound = lose mass of dimer
(Dimer formation involves less functionalized peroxy radical, SVOC)



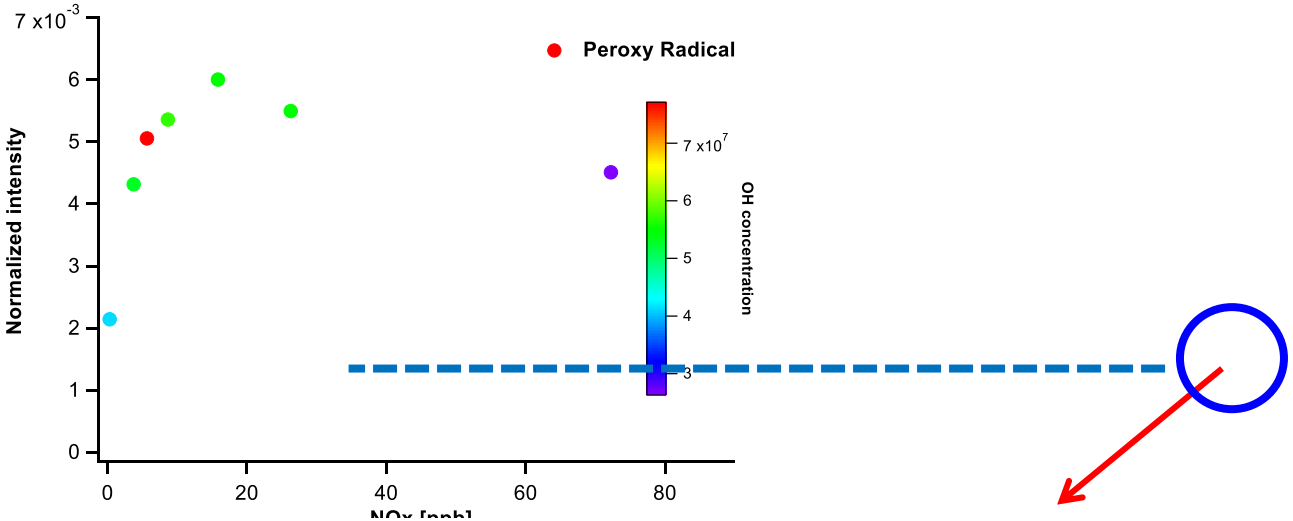
3.4 RESULT: ALKOXY-PEROXY PATHWAY

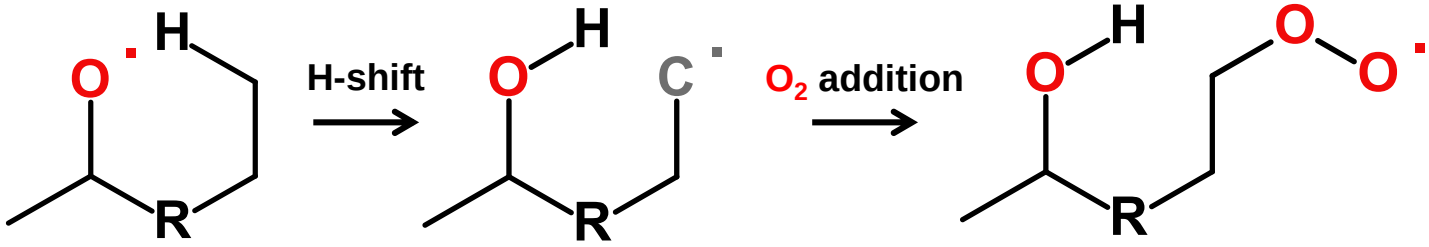


Correction for NPF, factors 1 -1.17, correction for turnover, factors of 0.8 - 1.2
Reference for normalization: ($9.1 \cdot 10^7 \pm 5.8 \cdot 10^6$ cm^{-3} s^{-1} at ~0.3 ppb NO_X)

a) If HOM-alkoxy radical decompose to small fragments
   → ΣHOM number concentration decrease
b) If HOM-alkoxy rearrange, keeping the C-number (observable with NO_3^- CIMS)
   → ΣHOM number concentration ≈constant

3.4 RESULT: ALKOXY-PEROXY PATHWAY

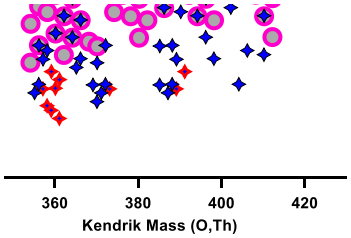




Alkoxy-peroxy pathway keeps RO_2 up

3.4 RESULT: ALKOXY-PEROXY PATHWAY

Mass Defect plot



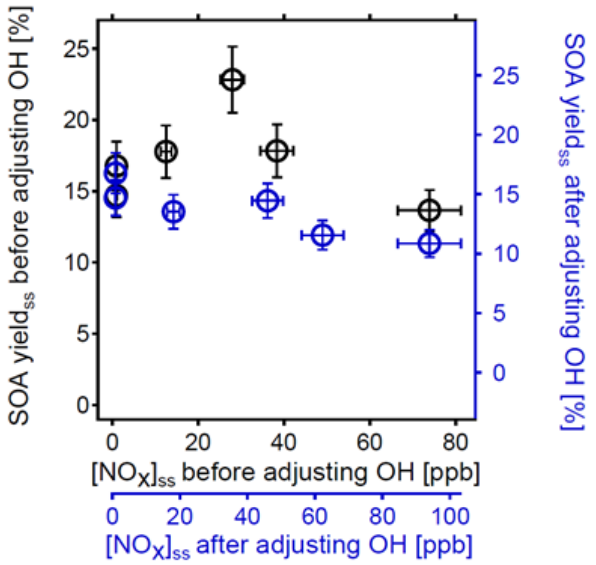
$$\text{Kendrick-mass} = \text{IUPAC-mass} \times \frac{16.00000}{15.99492}$$

C: 12.00000 Da
H: 1.00783 Da
O: 15.99492 Da
N: 14.00307 Da

1. No NOx has only dimer in this middle mass range

2. Monomer only appear when there is NOx
   → oxidation degree increased

4.SUMMARY



Sarrafzadeh et al, 2016

Effect of NOx in photochemical system of α-pinene

a. Monomer HOM pattern change
   Ketone, Hydroperoxide, Alcohol → Organic Nitrate
   → Not much effect on SOA mass (γ_{eff})

b. Fragmentation increased
   Major C10 compounds → Increase of C_5 to C_9 compound
   → SOA mass suppression (Less condensable compound)

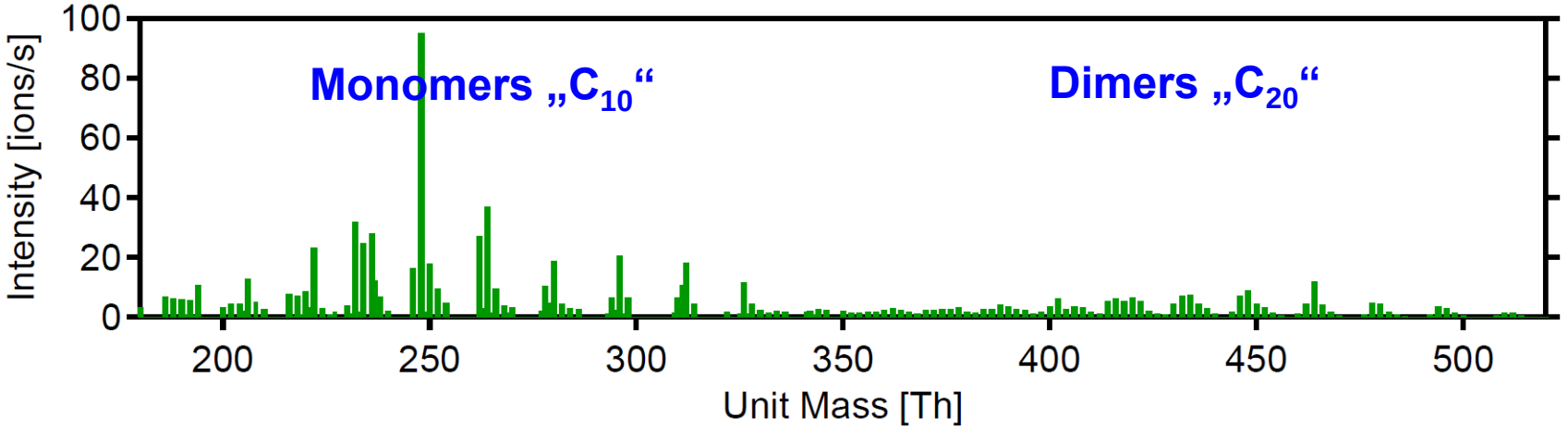
c. Dimer suppression of HOM-SVOC dimers
   Lose chance for SVOC to condense on SOA (Dimer-O_2 lose)
   Smaller dimers because of fragmentation → higher vapor pressure
   → SOA mass suppression (main reason)

However:

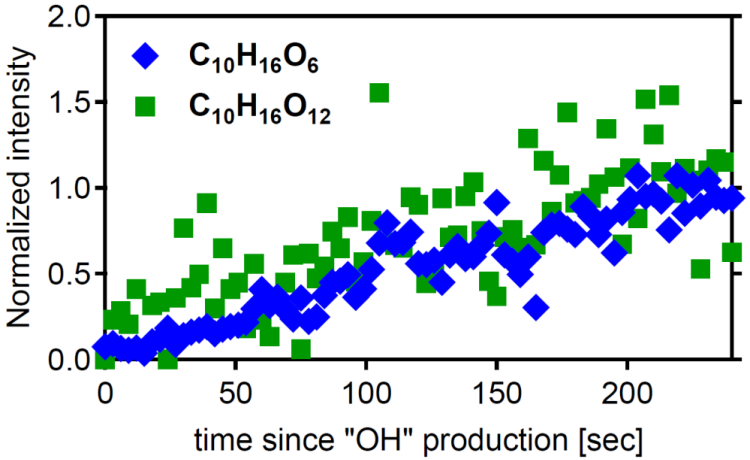
d. Alkoxy-Peroxy Pathway
   Produce more peroxy radical (even with lower [OH])
   → SOA mass gain (Compensate suppression)

Back up slides

HOM in photochemical systems

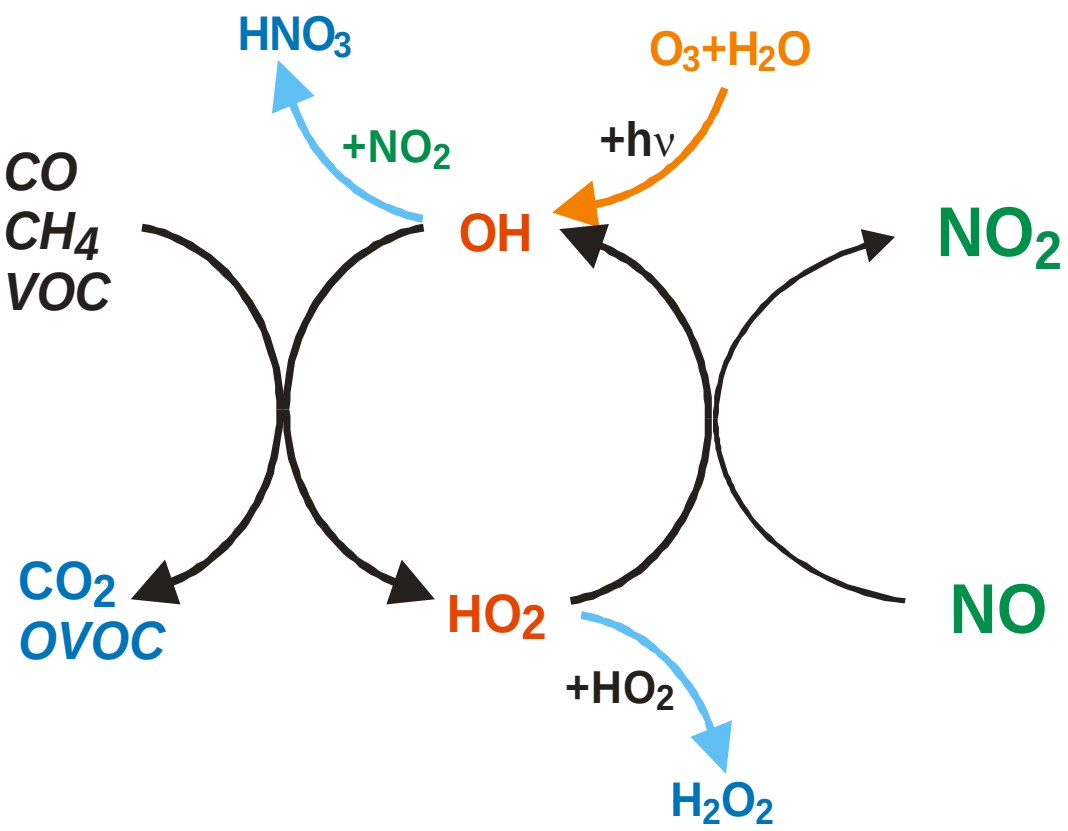


HOM are *efficiently* formed with OH by *α-pinene* (and *β-pinene*)



Berndt et al., 2016
Pullinen, PhD thesis, 2016

NO_X „controls“ photochemical OH / HO_2 system



low NO_X

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

radical sink

medium NO_X

$HO_2 + NO \rightarrow OH + NO_2$

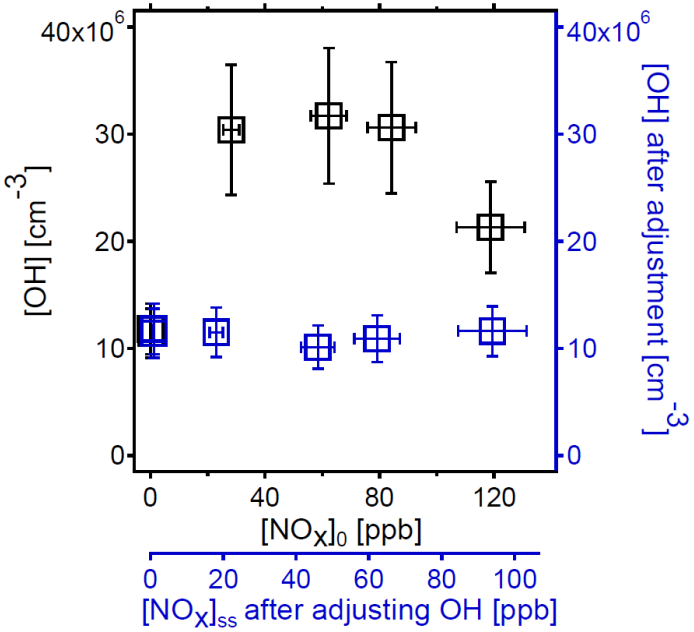
radical recycling

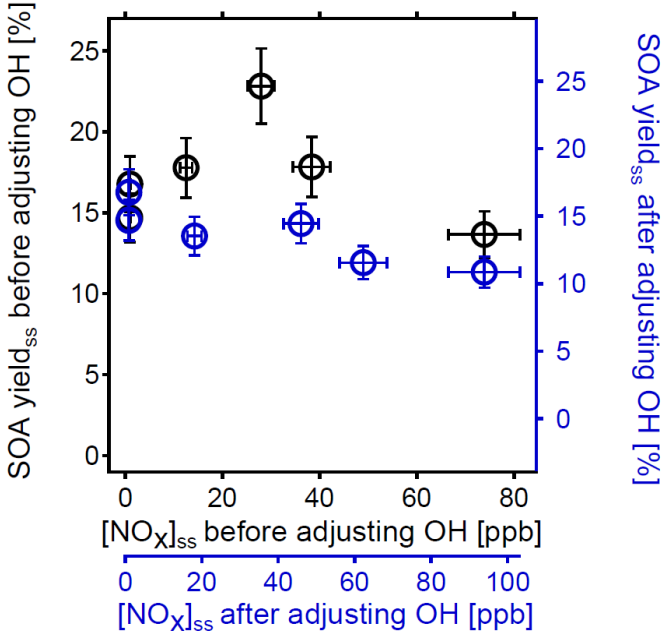
high NO_X

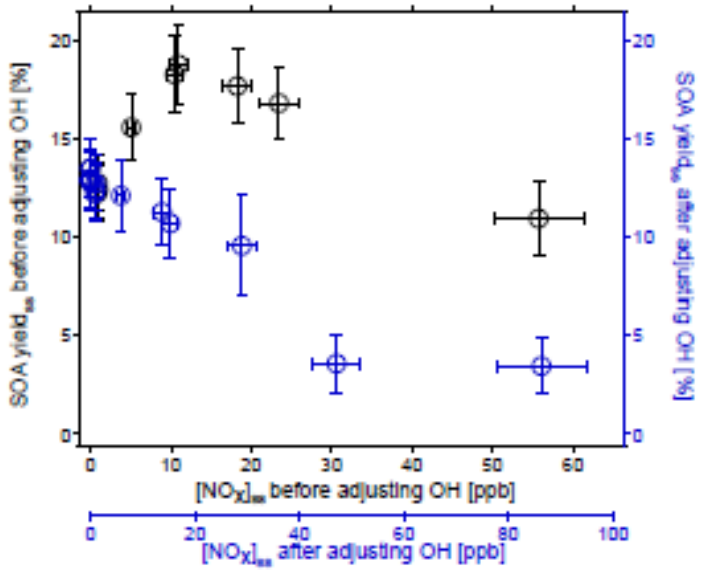
$NO_2 + OH + M \rightarrow HNO_3$

radical sink

Starting point: β-pinene SOA yield as f[NO_X]

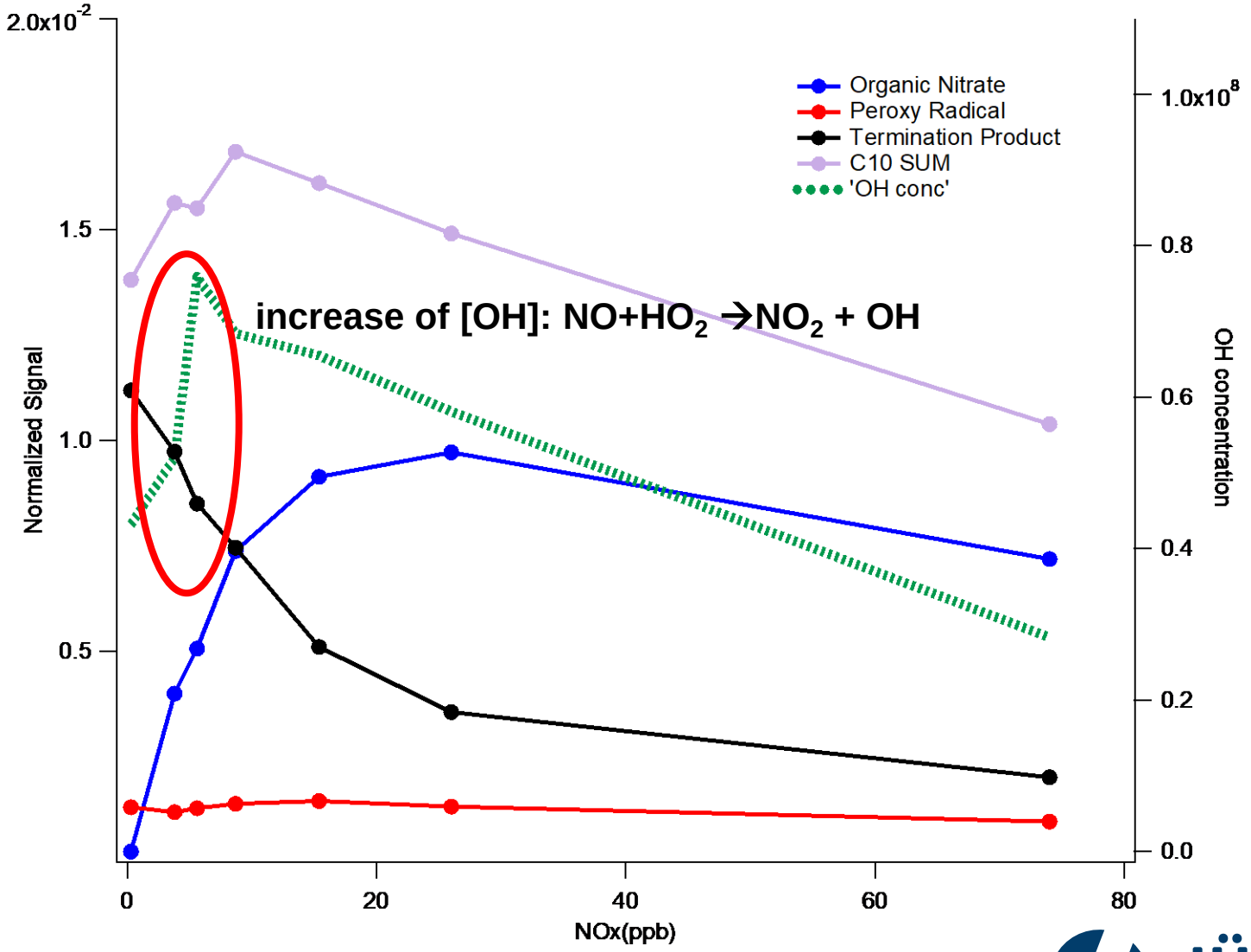






JÜLICH Forschungszentrum

Sarrafzadeh et al., 2016



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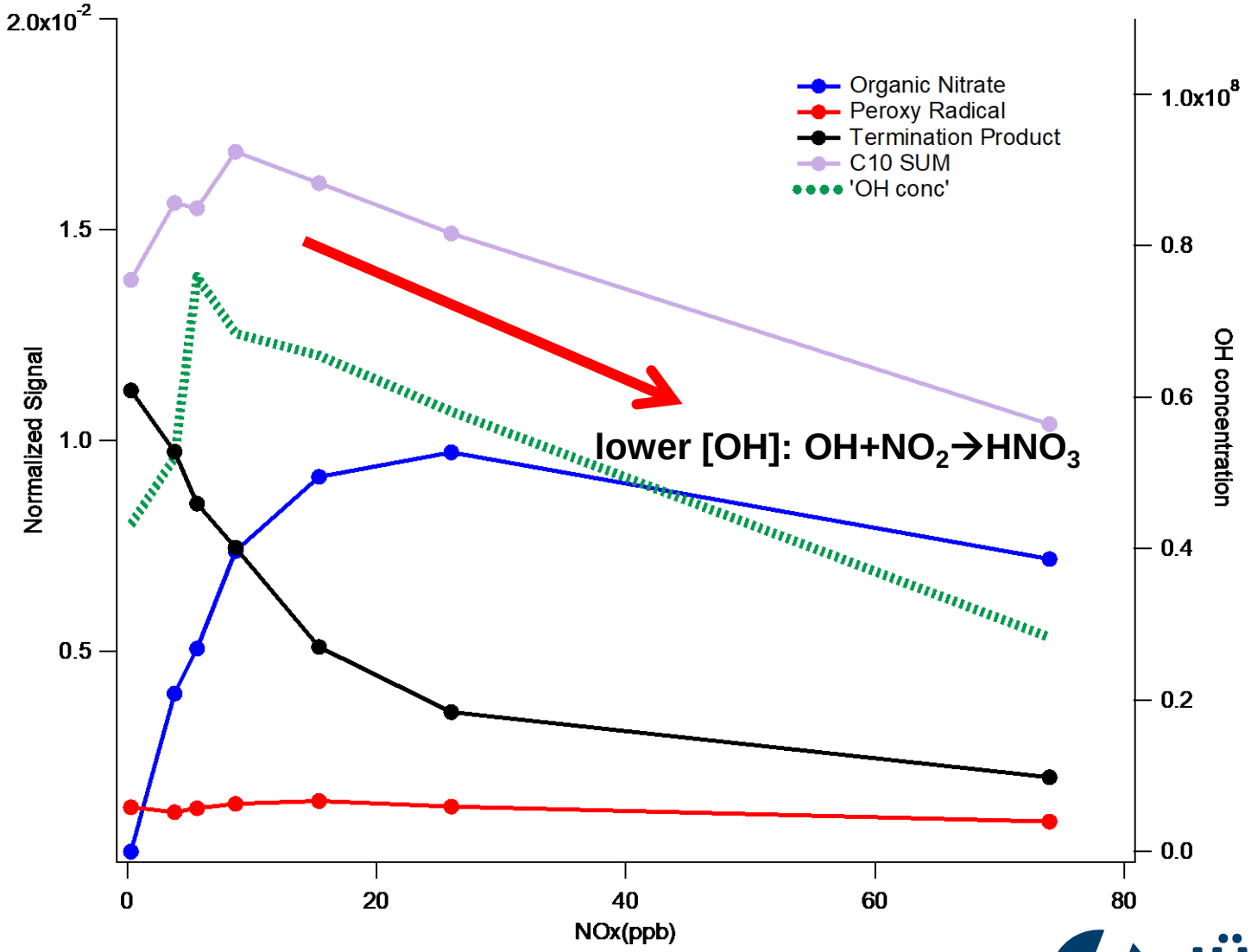
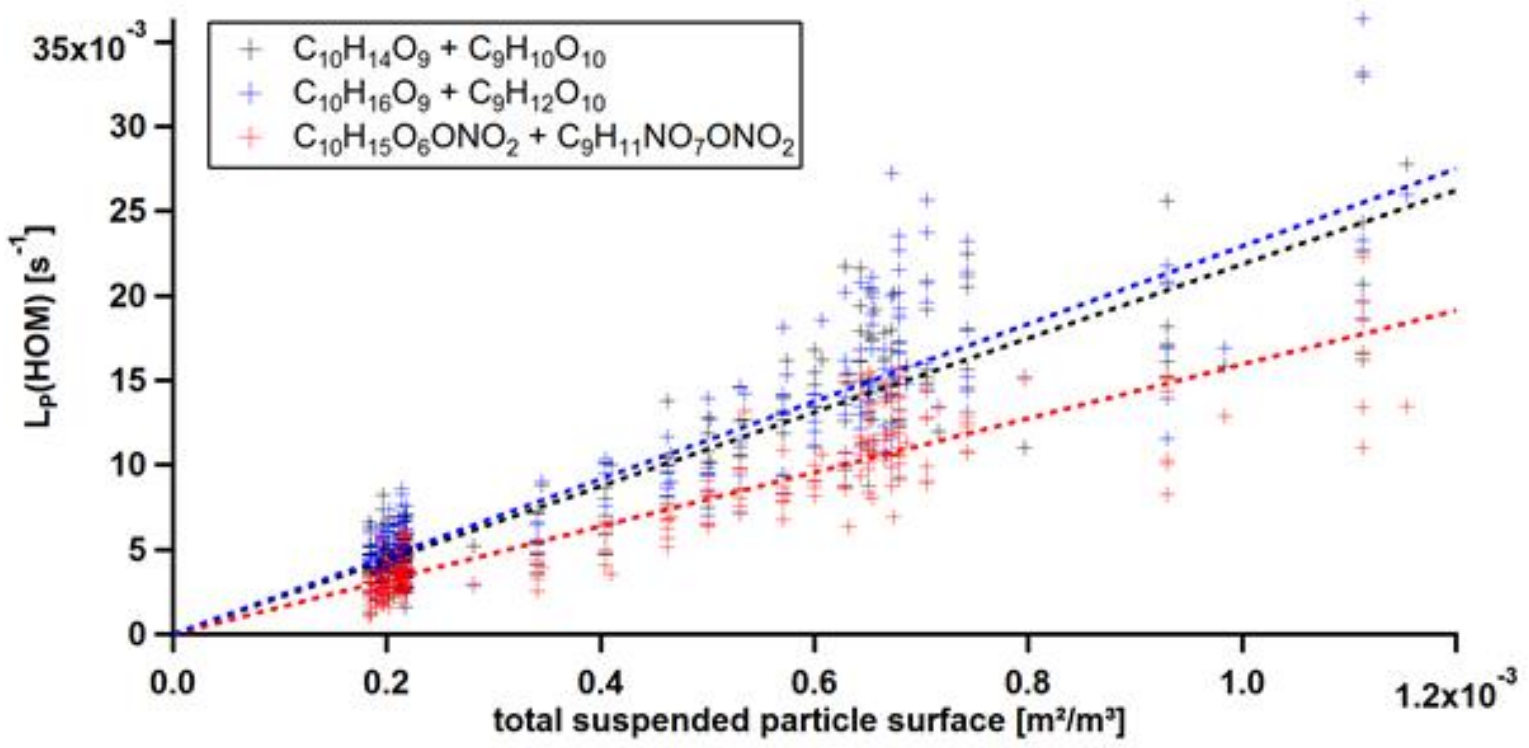

2.0x10-2
1.5
1.0
0.5
Normalized Signal
1.0x108
0.8
0.6
0.4
0.2
0.0
OH concentration
Organic Nitrate
Peroxy Radical
Termination Product
C10 SUM
'OH conc'
lower [OH]: OH+NO2→HNO3
0
20
40
60
80
NOx(ppb)

HOM-ON, HOM-PP -> SOA: condensation

- Photochemistry in JPAC into ss
- Add seed aerosol increase surface sink, decrease HOM lifetime
- Apply gas-phase kinetics



$$L_P(HOM) = \gamma_{eff} \cdot \frac{\bar{\upsilon}}{4} \cdot S_P$$

Apply:
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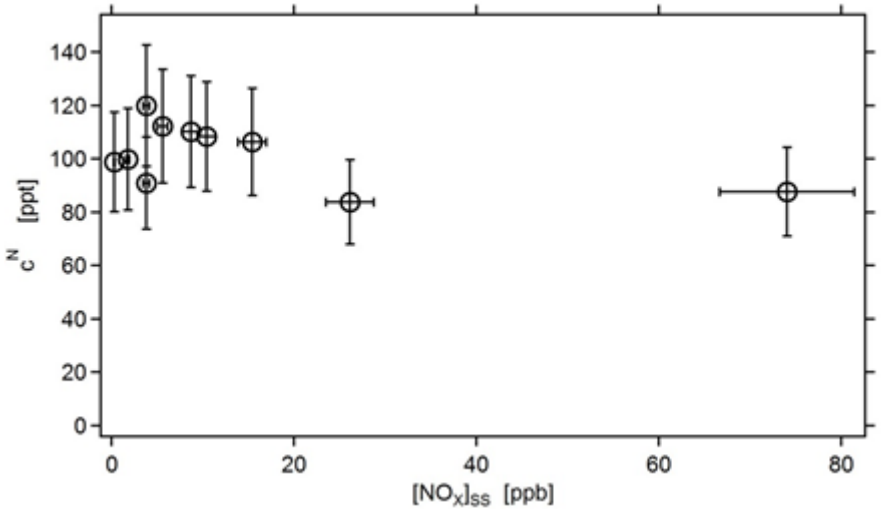

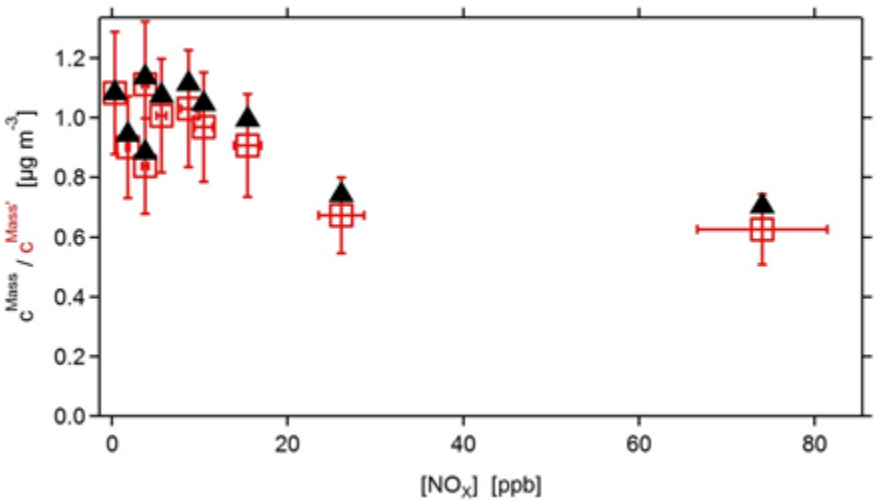

Black:
HOM concentration fairly constant
Mass decreases: HOM lower with lower molecular weight

Red:
Hydrolysis of type HOM-RONO2 –> HOM-ROH will affect the HOM mass