Investigation of the α-pinene & β-pinene photooxidation by OH in the atmospheric simulation chamber SAPHIR

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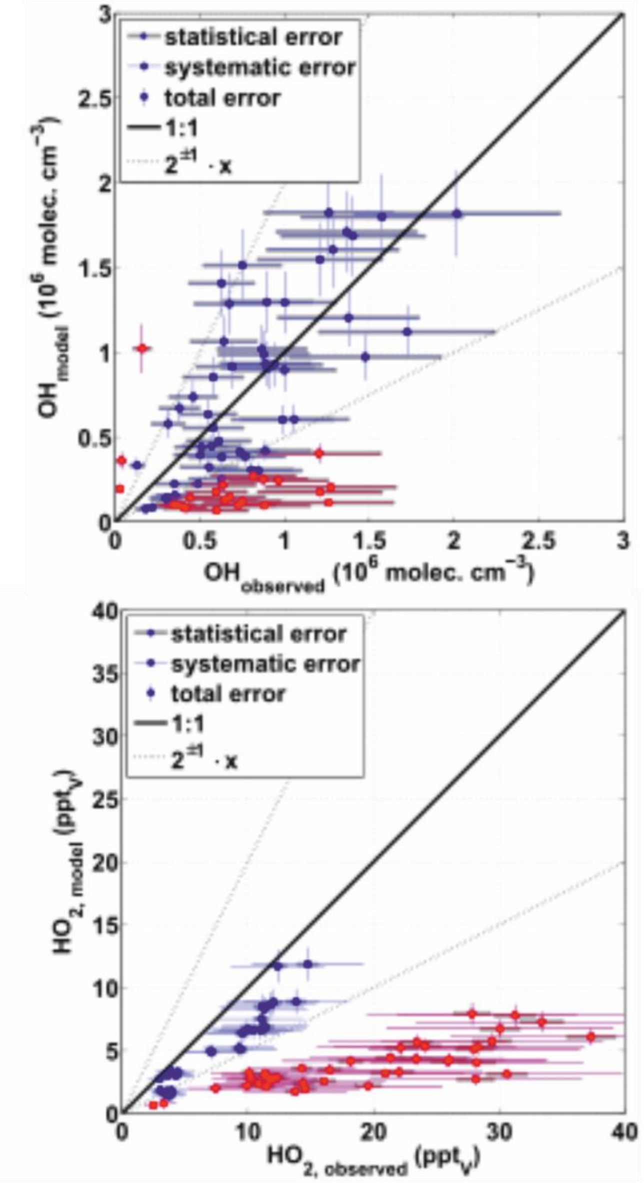
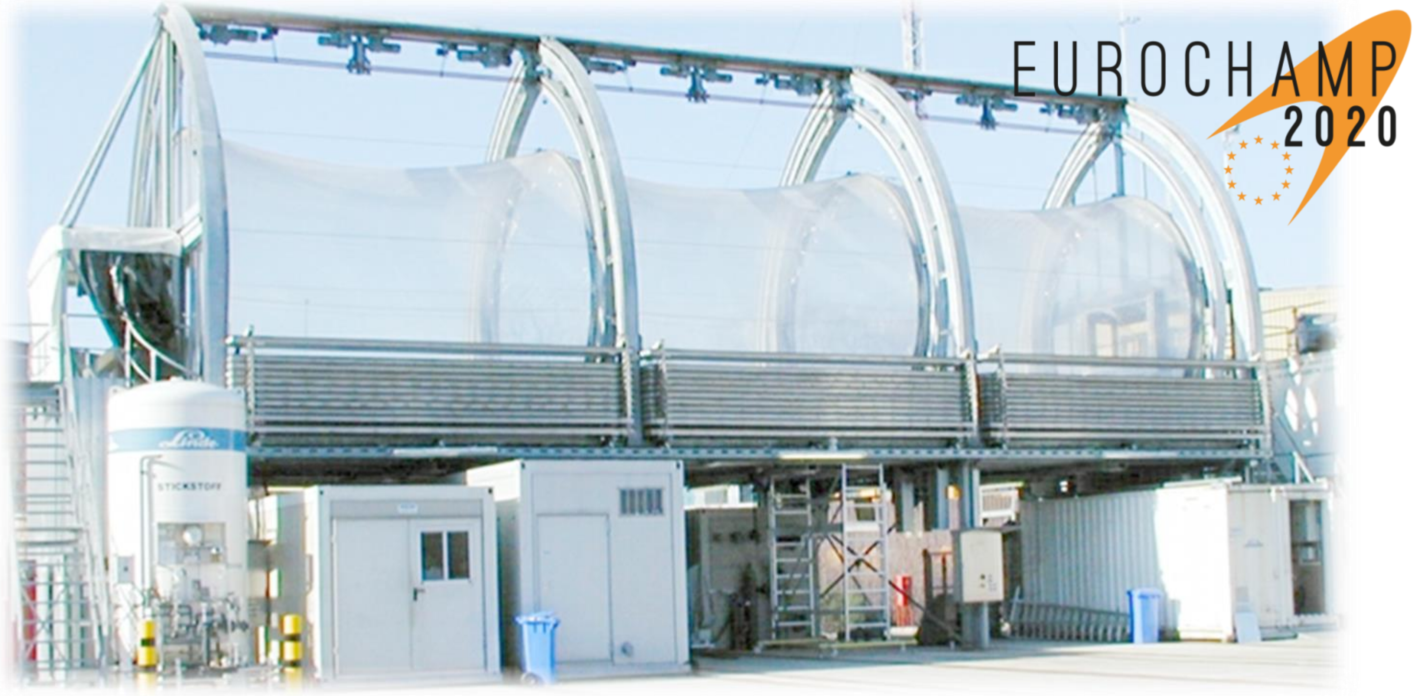
Motivation

- High emission rates and OH reactivity of monoterpenes in forested areas
- Large discrepancies between measured and modeled OH concentrations in monoterpene dominated environments (e.g. Kim et al., ACP 2013; Hens et al., ACP 2014)



Hens et al. 2014

Atmospheric simulation chamber SAPHIR



- Volume 270 m^3
- Walls made of Teflon film (high UV transmission)
- Light source: solar radiation
- Photolysis frequencies calculated based on actinic flux measurements

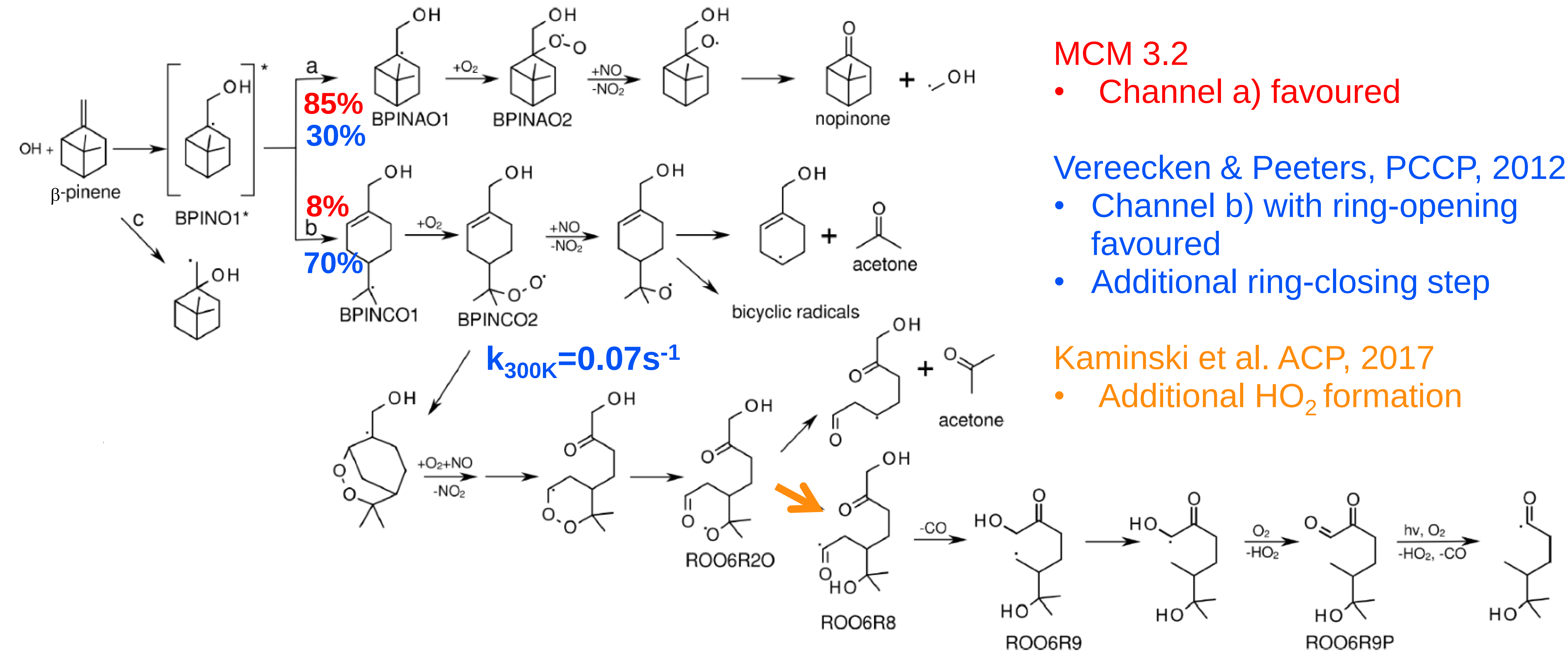
Radical source

Wall + $h\nu$ → HONO(g)
HONO(g) + $h\nu$ → OH + NO

Instrumentation:

- OH, HO_2, k(OH): Laser-induced fluorescence (LIF)
- OH: Differential Optical Absorption (DOAS, absolute technique)
- α- & β-pinene, pinonaldehyde, nopinone, acetone: GC-FID and PTR-TOF-MS,
- HCHO: (Hantzsch, DOAS)
- HONO: Long Path Absorption Photometer (LOPAP)
- NO, NO_2: Chemiluminescence detectors
- O_3: UV Absorption

β-pinene degradation – MCM and modifications

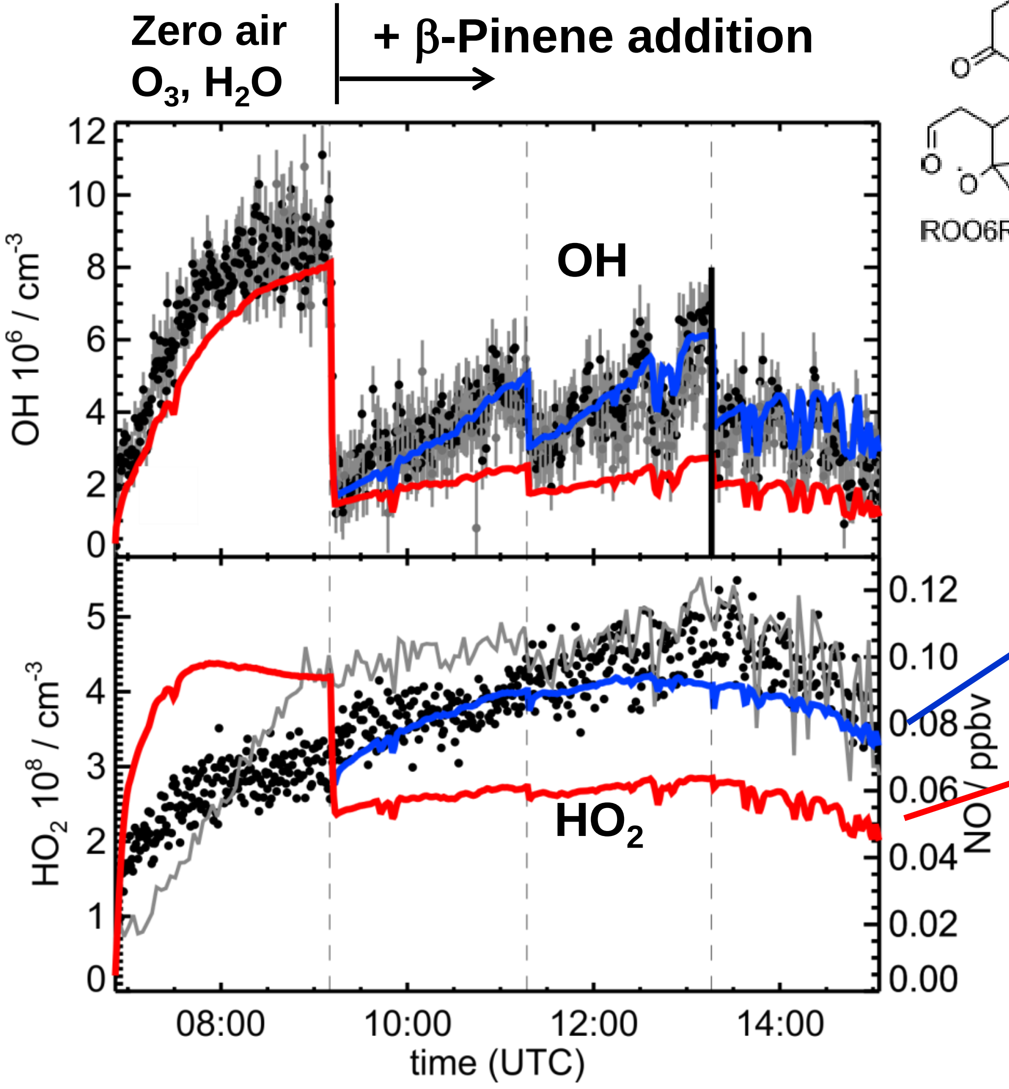


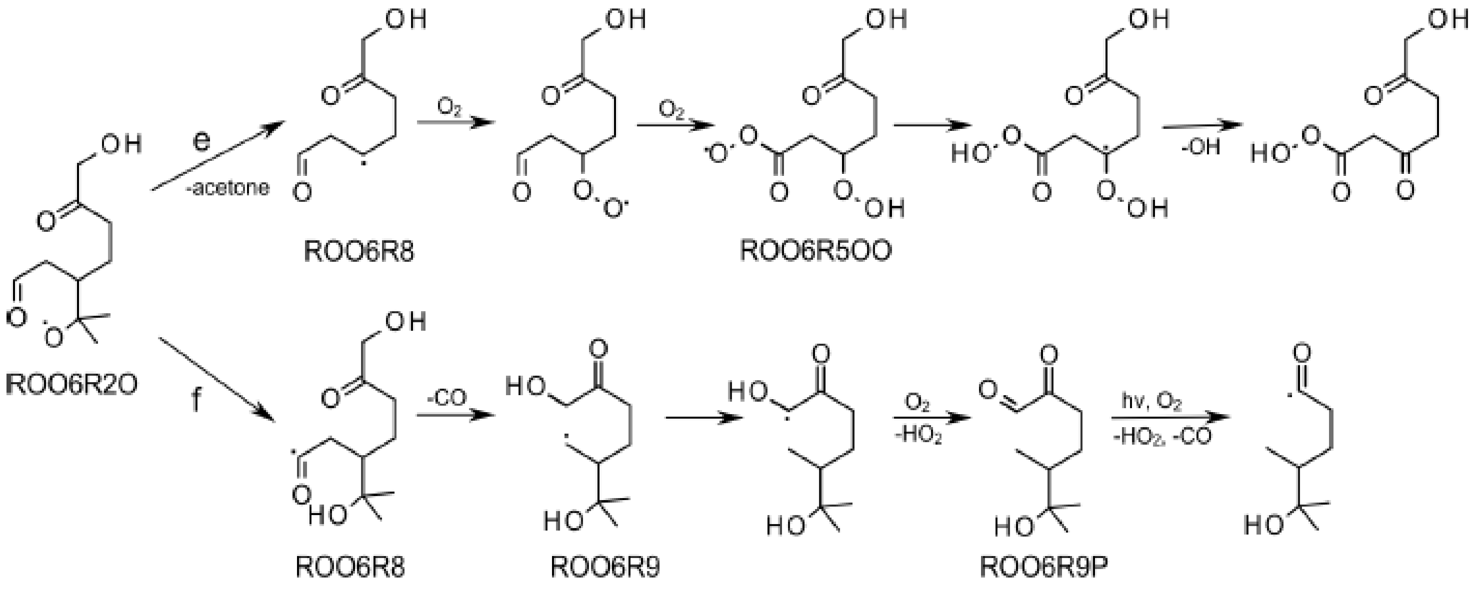
MCM 3.2
- Channel a) favoured

Vereecken & Peeters, PCCP, 2012
- Channel b) with ring-opening favoured
- Additional ring-closing step

Kaminski et al. ACP, 2017
- Additional HO_2 formation

β-pinene degradation



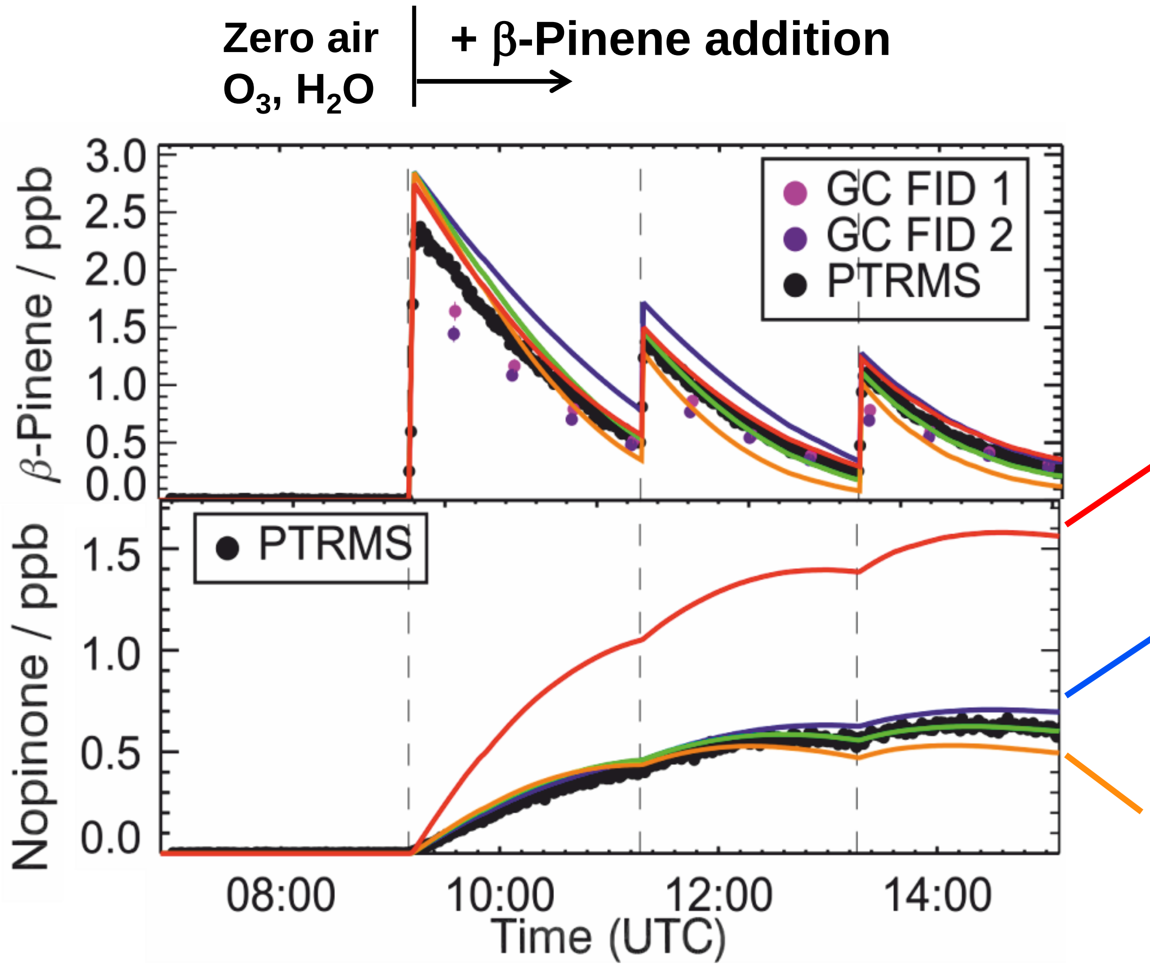


MCM + Vereecken & Peeters 2012
+ Kaminski et al. 2017

MCM v3.2

- HO_2 and OH underpredicted (up to a factor of 2)
- CO underpredicted (factor 2)

β-pinene degradation



MCM v3.2

- Nopinone overpredicted (factor 3)

MCM + Vereecken & Peeters 2012

- Nopinone well described

MCM + Vereecken & Peeters 2012 + Kaminski et al. 2017

- Best agreement for nopinone <u>and</u> radicals

β-pinene results

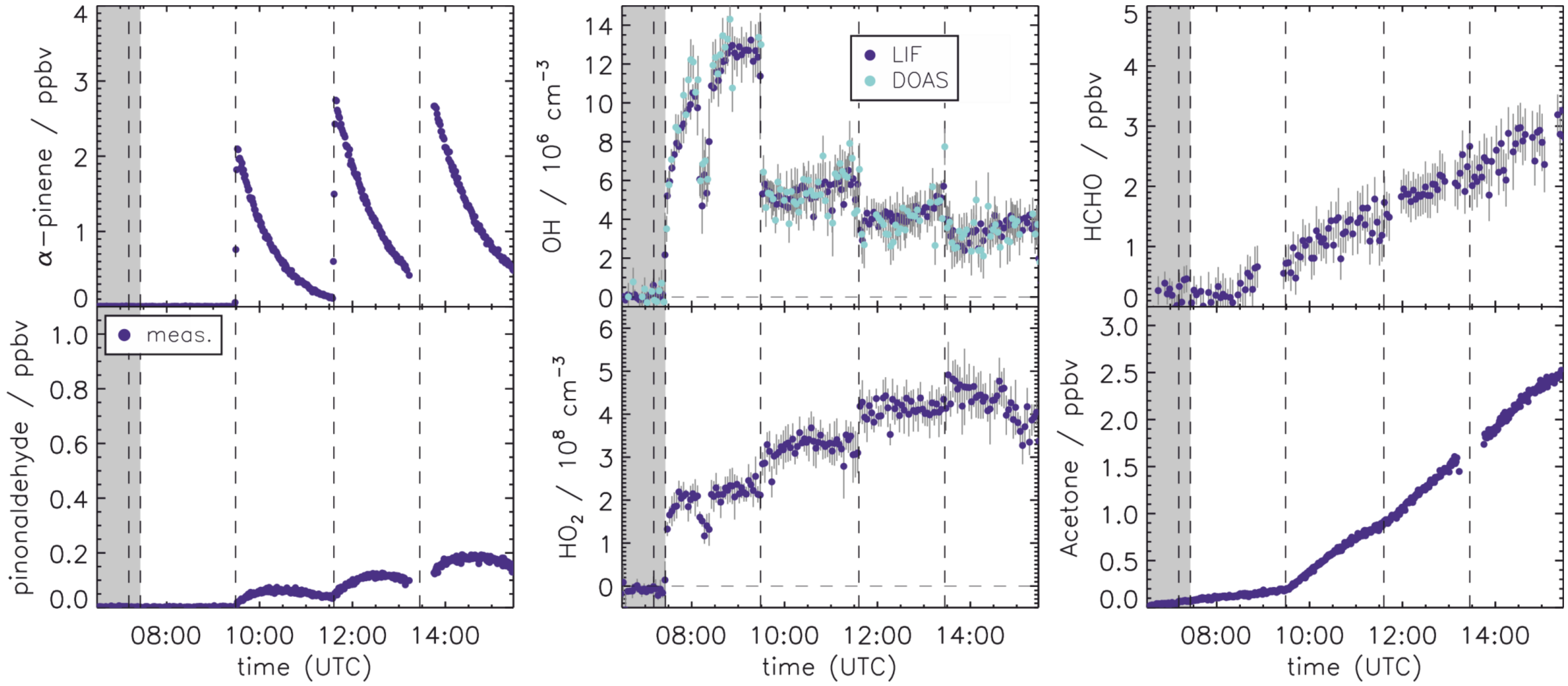
- OH and HO_2 concentrations are underestimated by MCM
- Additional HO_2 increases OH by radical recycling („closed OH budget")

  → Similar findings in field campaigns
- Measured nopinone yields is smaller than the MCM predicts

→ Additional RO_2 chemistry suggested by Vereecken et al. improves model-measurement agreement (radicals and organic products)

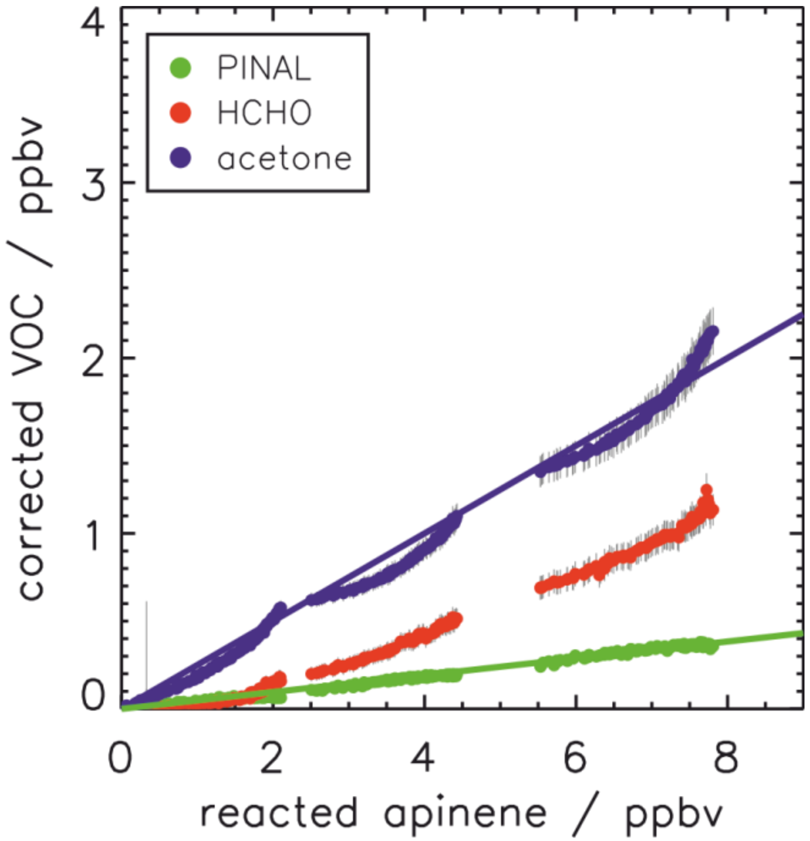
→ Adjustment of branching ratios and assumption additional HO_2 production would explain observations

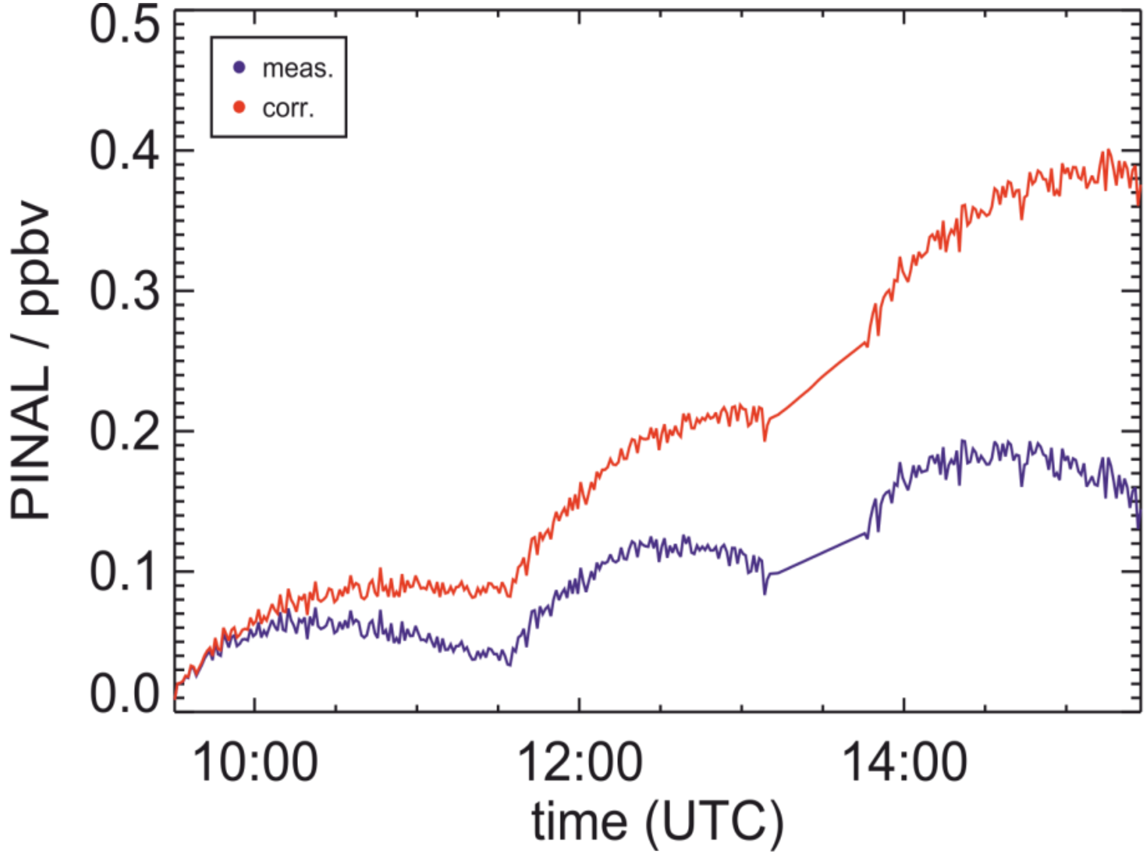
α-pinene degradation



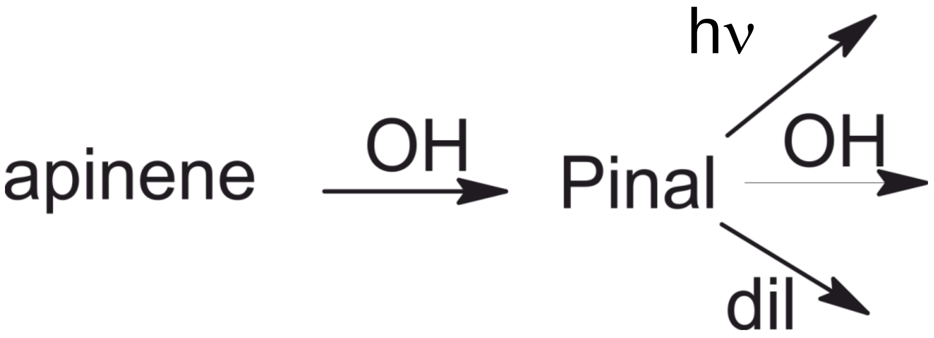
- 3 α-pinene injections
- NO < 100 ppt
- Atmospheric O_3 level
- RH= 30-60 %

Product yields





$$Yield = \frac{P(Pinal)}{D(\alpha pinene)}$$



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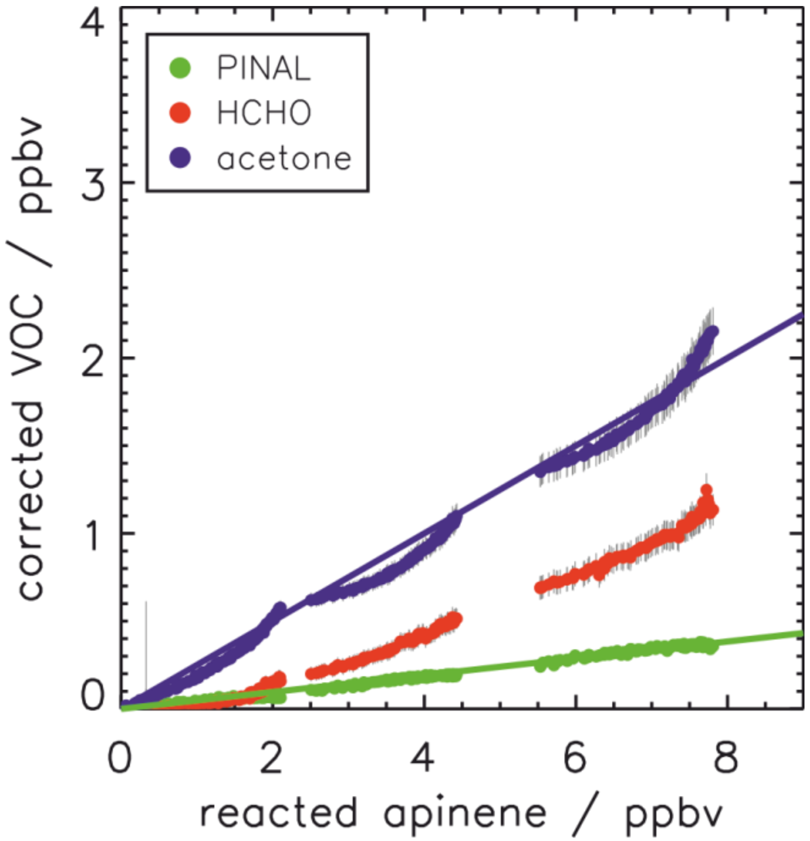
Product yields



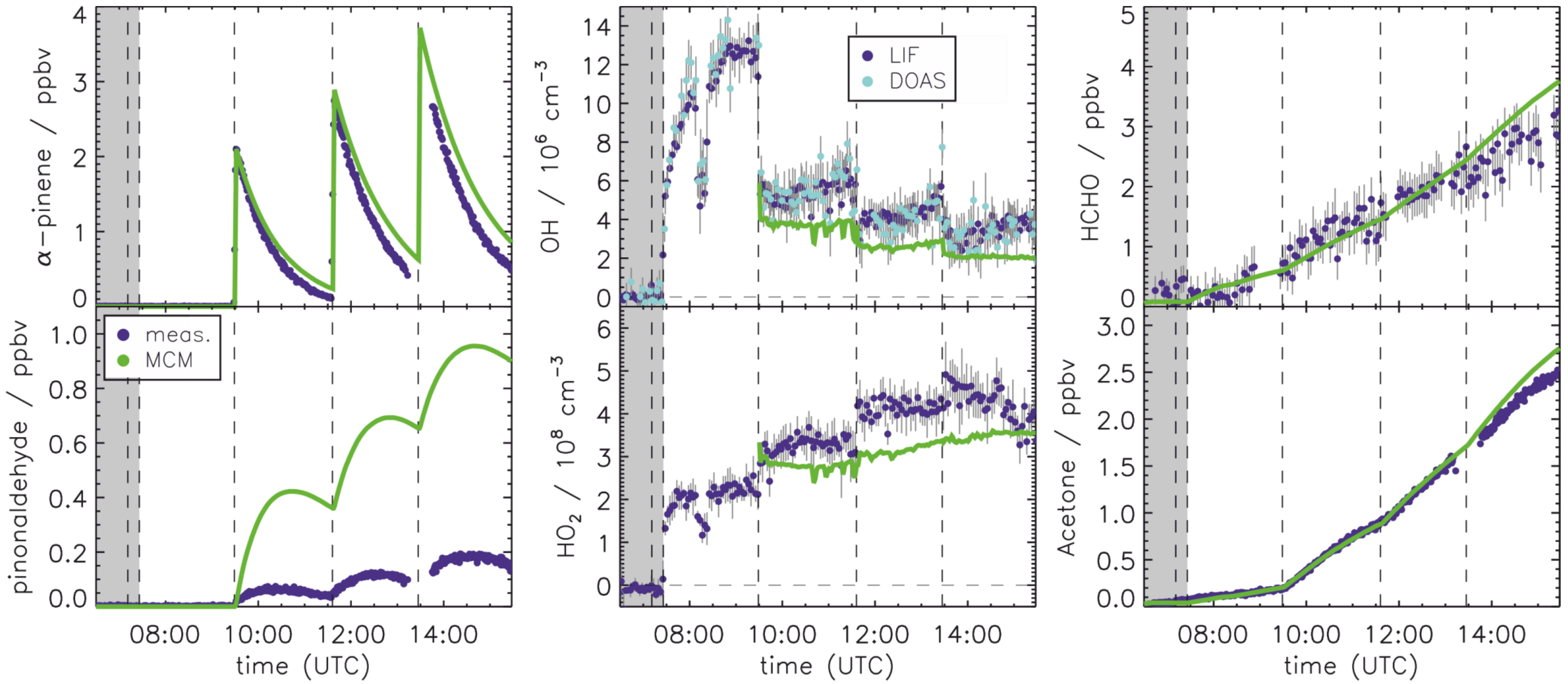
$$Yield = \frac{P(Pinal)}{D(apinene)}$$

- PINAL yield: 8 ± 3 %
- HCHO yield: 5 ± 1 %
- Acetone yield: 24 ± 2 %

Reference	Yield / %			Exp. conditions		
	Pinonaldehyde	Acetone	CH2O	α-pinene / ppb	NO / ppb	Water / rH %
Arey et al. (1990)	29	-	-	400-900	10000	0
Hakola et al. (1994)	28 ± 5	-	-	350-1000	10000	0
Noziere et al. (1999)	87 ± 20	9 ± 6	23 ± 9	200-2700	4000	0
Larsen et al. (2001)	6 ± 2	11± 3	8± 1	1400-1600	1000	2-5
Aschmann et al. (2002)	28 ± 5	-	-	400-900	7000-9000	0
Lee et al. (2006)	30 ± 0.3	6	16	109	9	0
Eddingsaas et al. (2012)	27-35	<10	-	20-50	high NO	<10
Noziere et al. (1999)	37 ± 7	7 ± 2	8 ± 1	200-2700	NO free	0
Wisthaler et al. (2001)	34 ± 9	11 ± 2	8 ± 1	1000-1300	NO free	0
Eddingsaas et al. (2012)	20	-	-	20-50	low NO	<10
this work	8 ± 3	24± 2	5± 1	3.8	<0.1	30-60

→ Lack of studies under realistic atmospheric conditions

α-pinene degradation – MCM 3.3.1



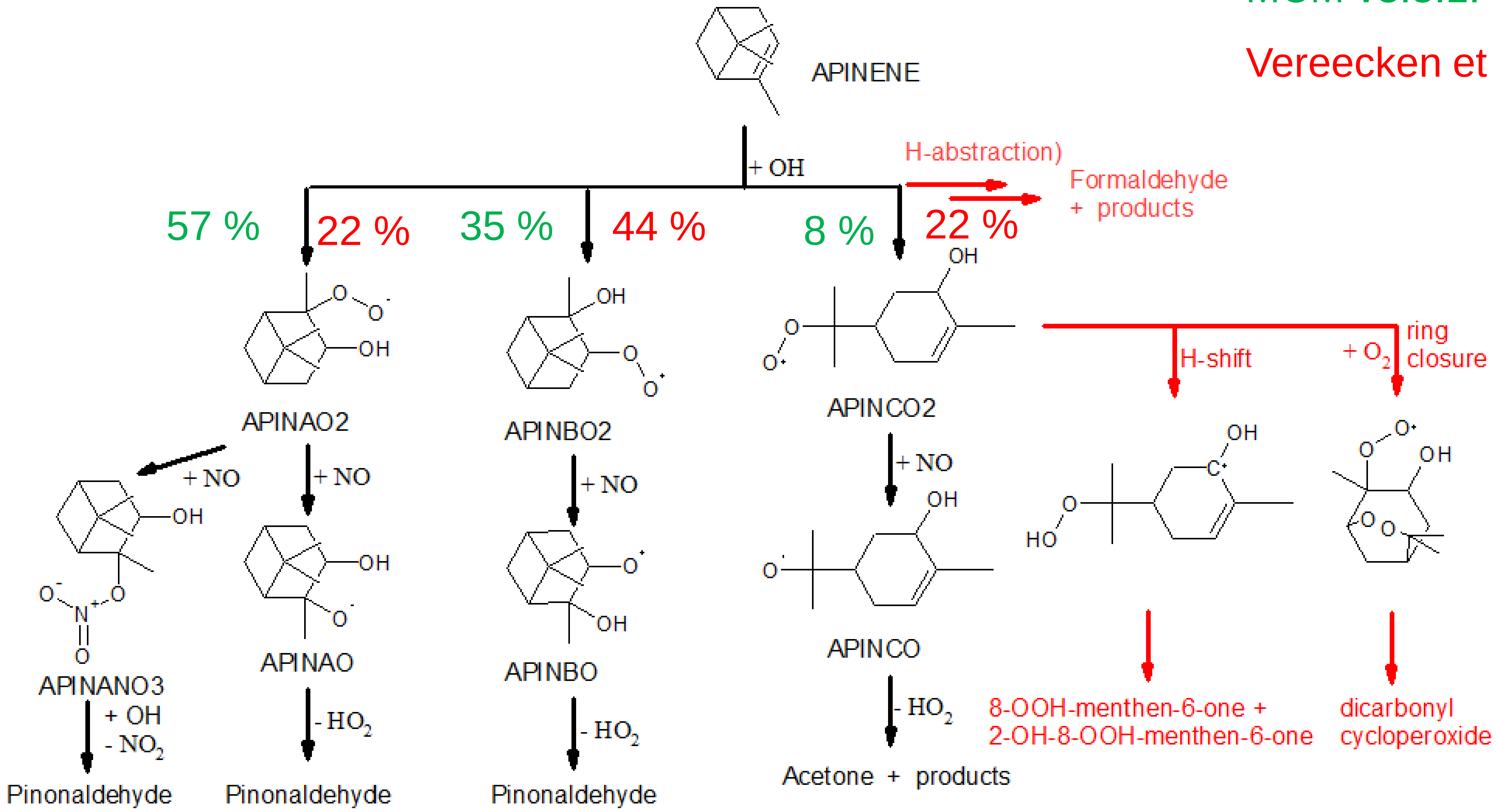
MCM 3.3.1 results:

- Pinonaldehyde production is overestimated by a factor of 4
- OH and HO_2 are underestimated by 25 %

α-pinene mechanism

MCM v3.3.1.

Vereecken et al. 2007

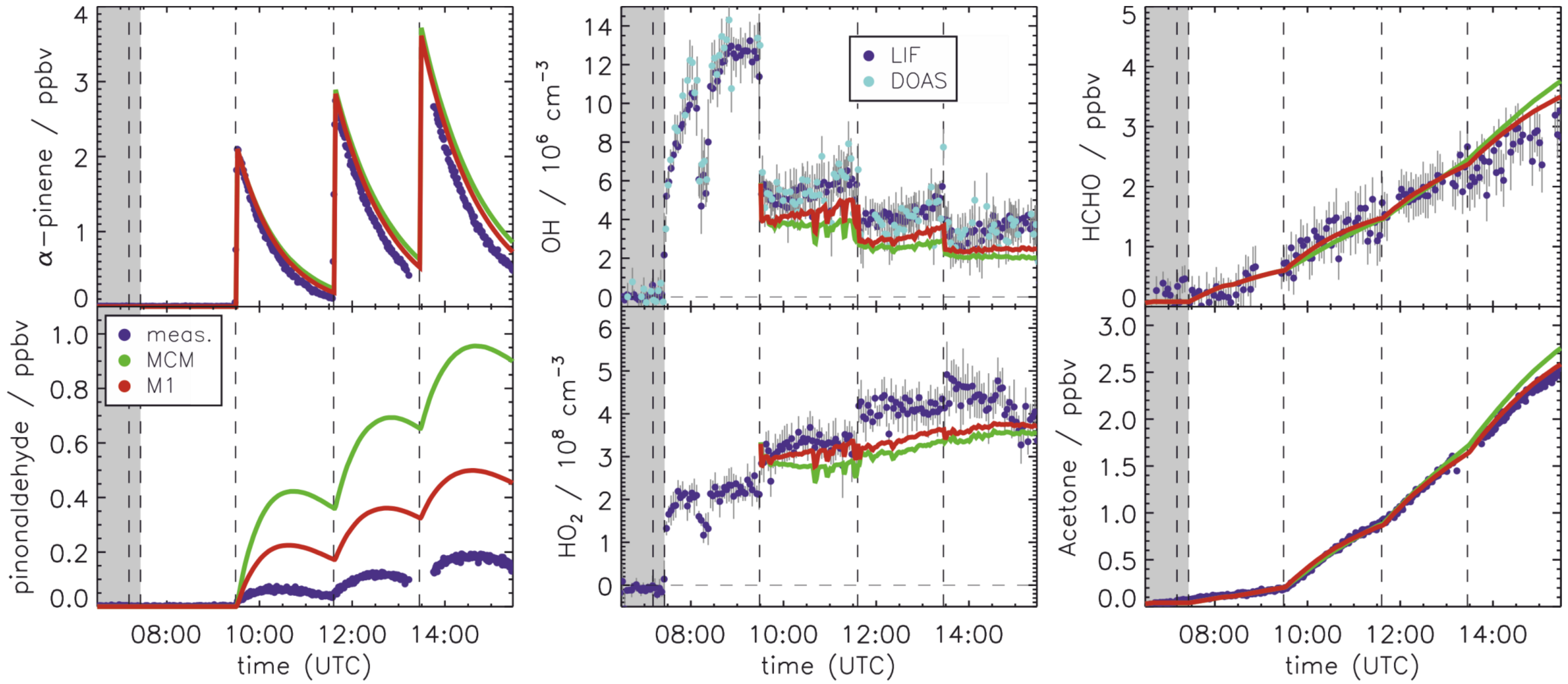


~ 30 % RO_2 react with HO_2

∑(PINAL) = 84 %

∑(PINAL) = 60 %

α-pinene degradation – Vereecken et al.



Vereecken mechanism results:

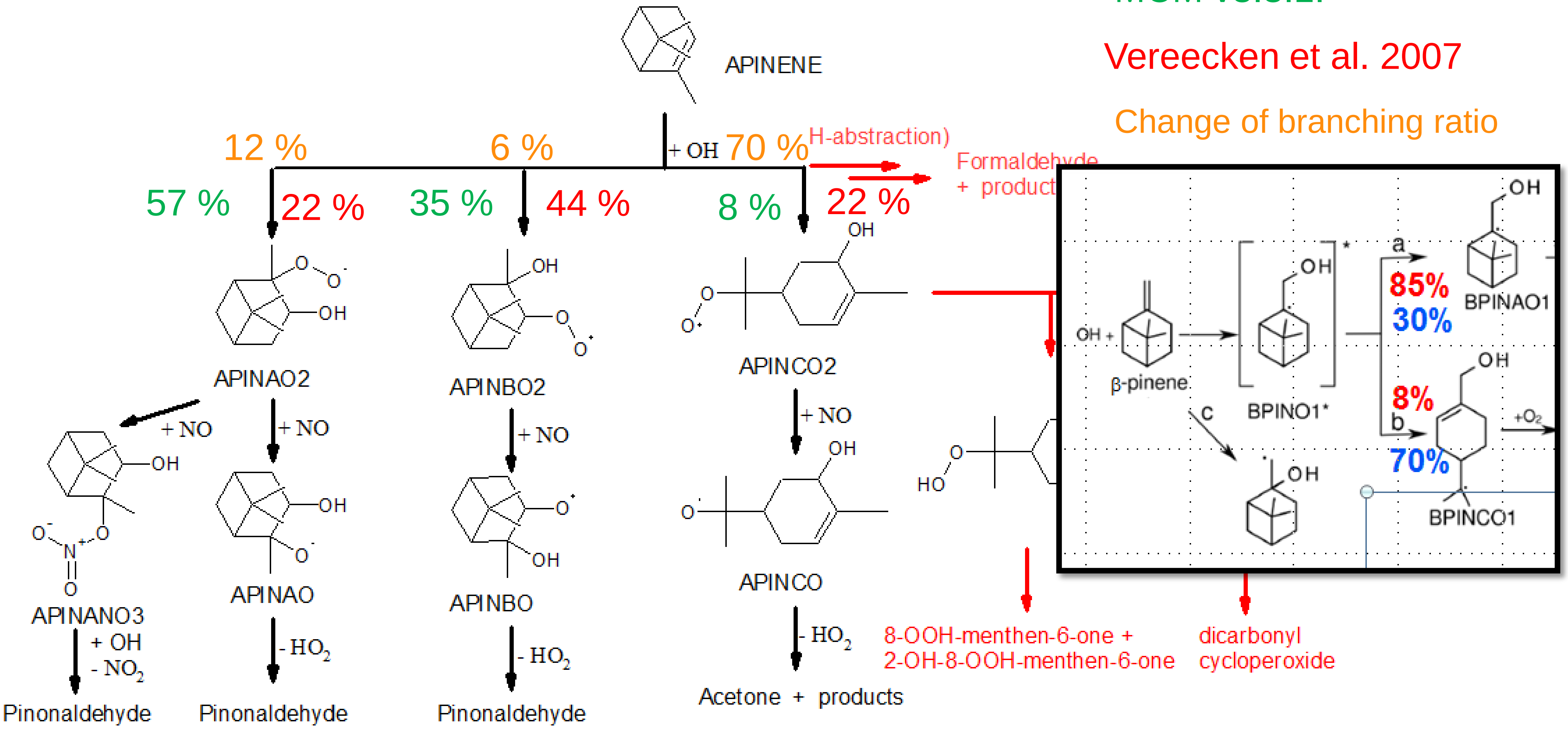
- Pinonaldehyde production is still overestimated by a factor of 2
- OH and HO_2 are still underestimated by 25 %

α-pinene mechanism

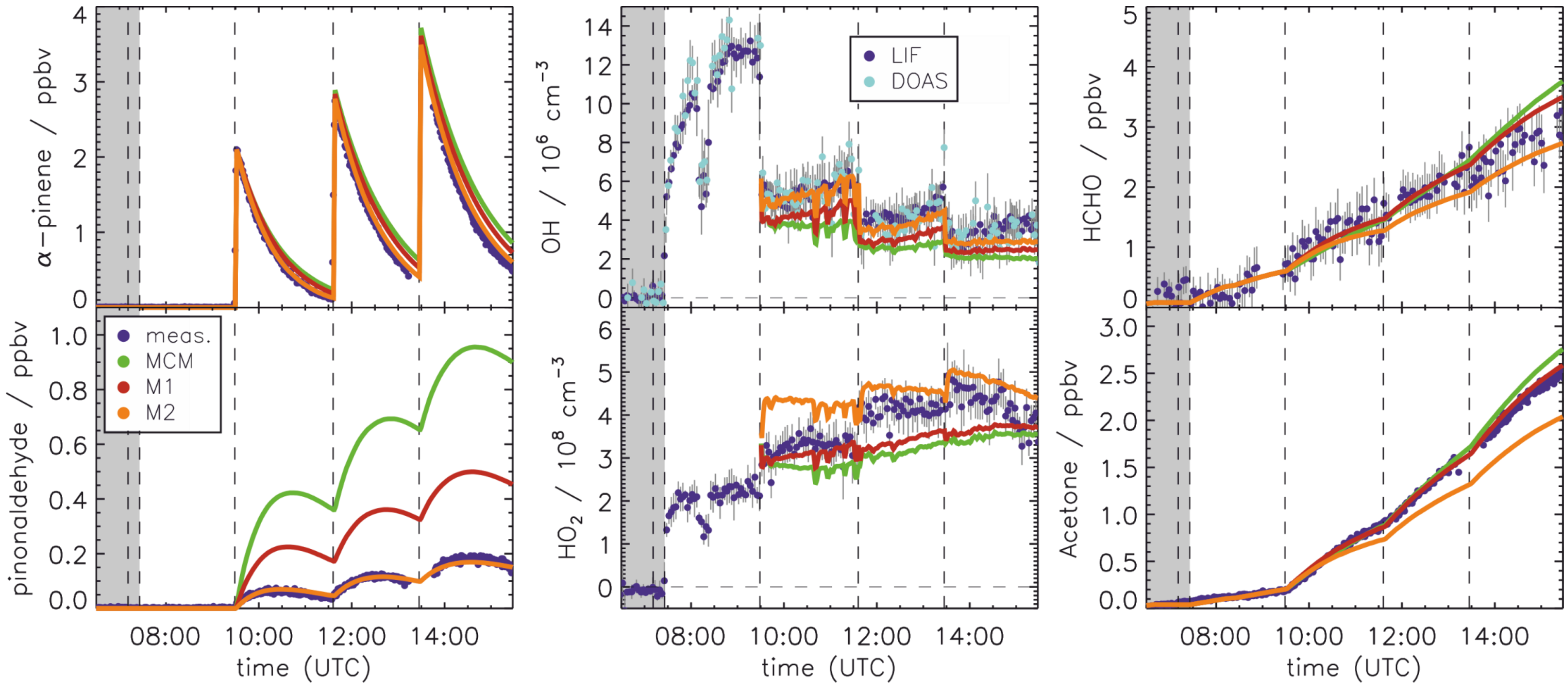
MCM v3.3.1.

Vereecken et al. 2007

Change of branching ratio



α-pinene degradation – modified Vereecken et al.



Change in branching ratio improves OH agreement between measurement and model

Conclusions

- OH and HO_2 concentrations are underestimated by models
- Measured yields of major aldehyde products (pinonaldehyde and nopinone) are smaller than the MCM predicts

→ Additional RO_2 chemistry suggested by Vereecken et al. improves model-measurement agreement (radicals and organic products)

→ Adjustment of branching ratios for RO_2 isomers from OH + α-pinene can bring model prediction into agreement for α-pinene

Further studies (theo. & exp.) are necessary to resolve the detailed α-pinene chemistry under atmospheric conditions

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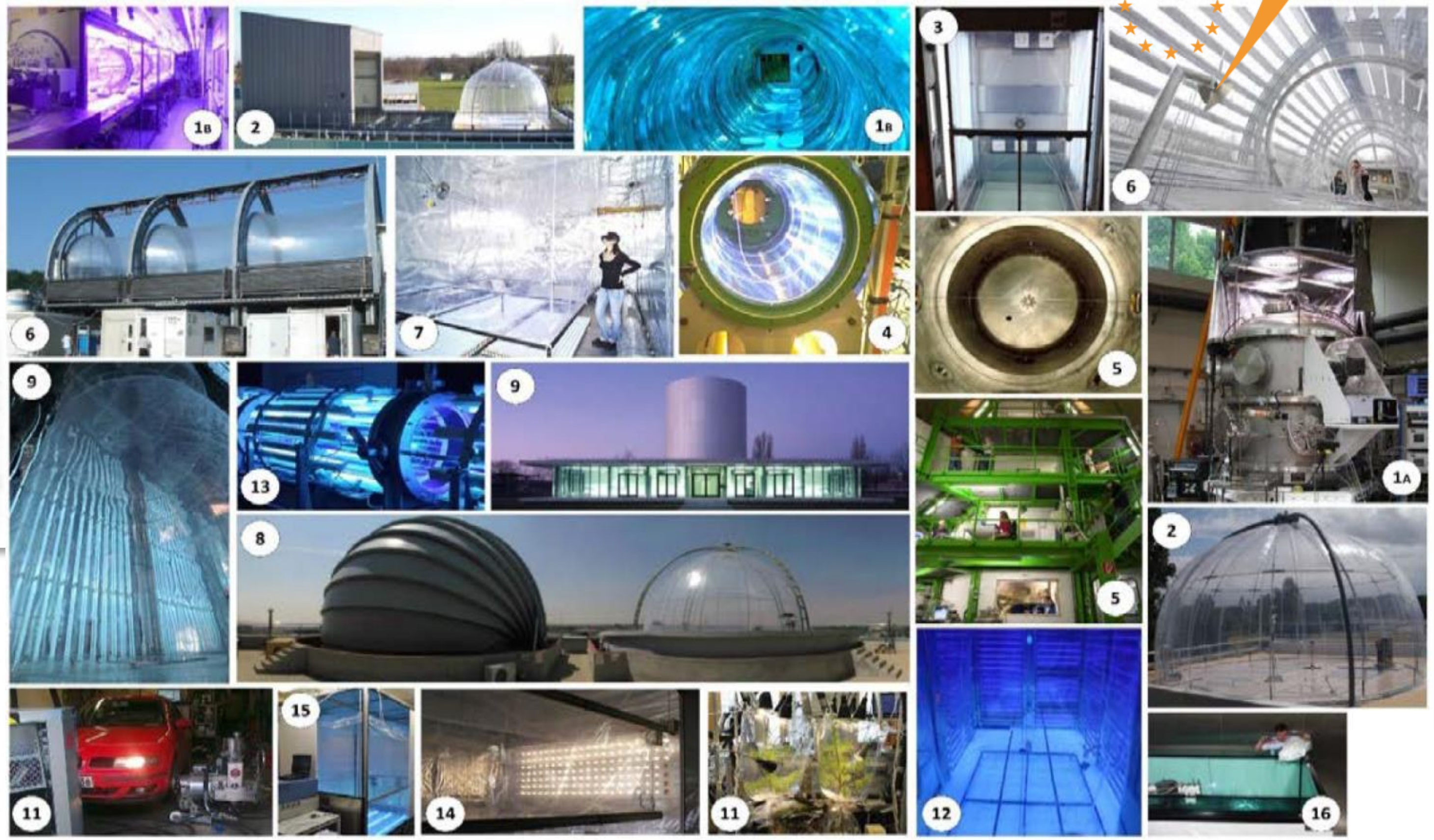

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BACKUP

β-pinene degradation

Kaminski et al., ACP 2017

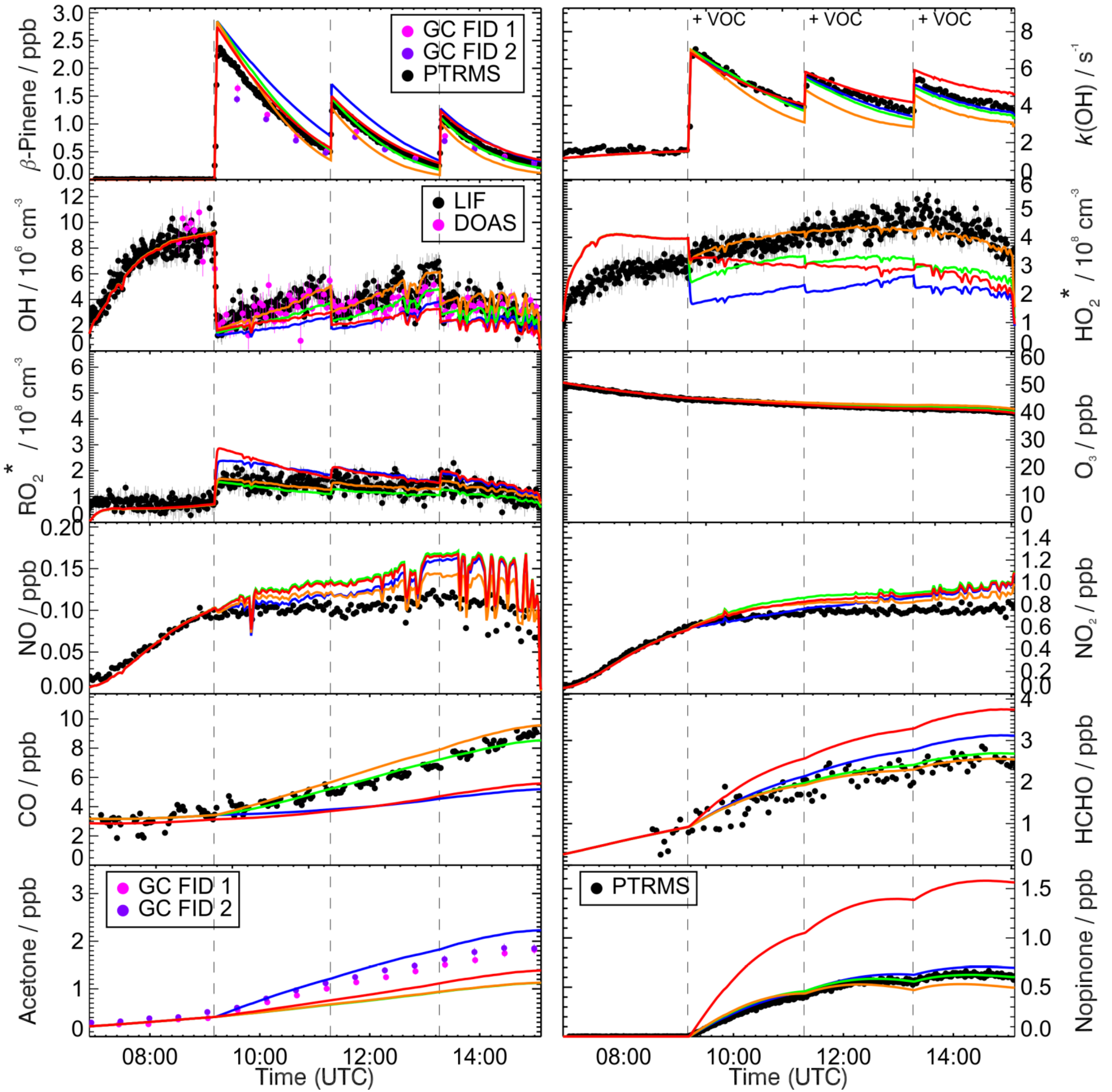
<u>MCM:</u>

- OH and HO_2 underpredicted
- Nopinone over-predicted

<u>Vereecken and Peeters, 2012:</u>

- Nopinone yield fixed
- Radical production still too low

→ OH and HO_2 ratio consistent



MCM
Vereecken & Peeters 2012
VP modified
VP modified + HO_2

β-pinene – OH budget

$$P(OH) = j_{O(^1D)}[O_3] * 2f_{OH} + j_{HONO}[HONO] + \propto k_1[VOC][O_3] + k_2[HO_2][NO] + k_3[HO_2][O_3]$$

$$D(OH) = k(OH) * [OH]$$