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SOA formation in the ozonolysis of biogenic volatile organic compounds performed in a laminar flow reactor

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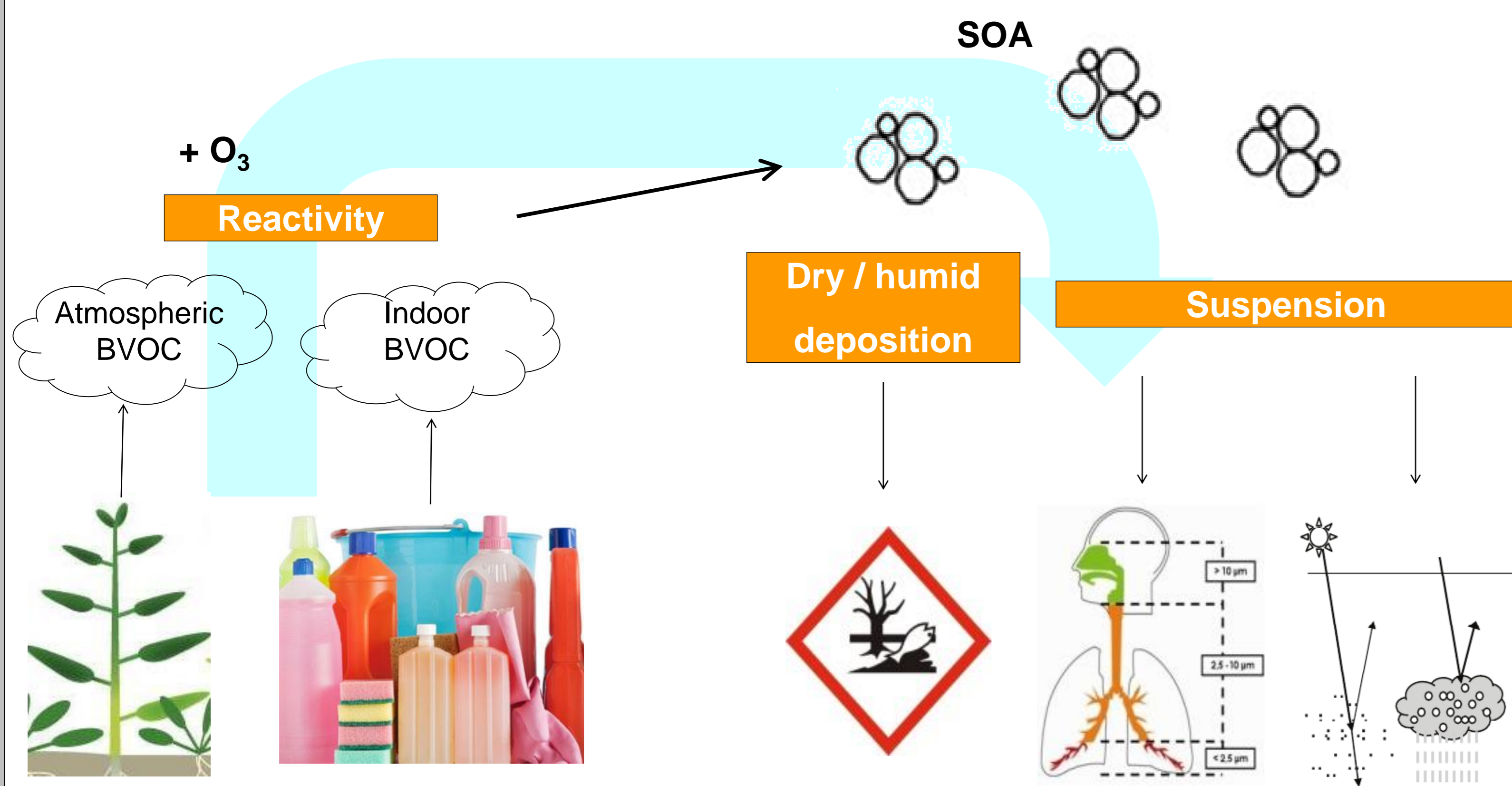
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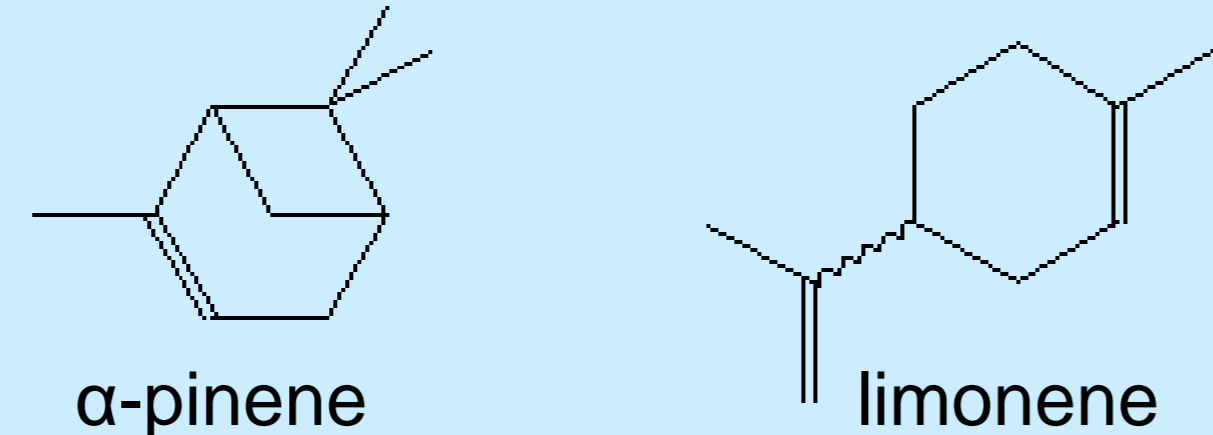
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Atmospheric background



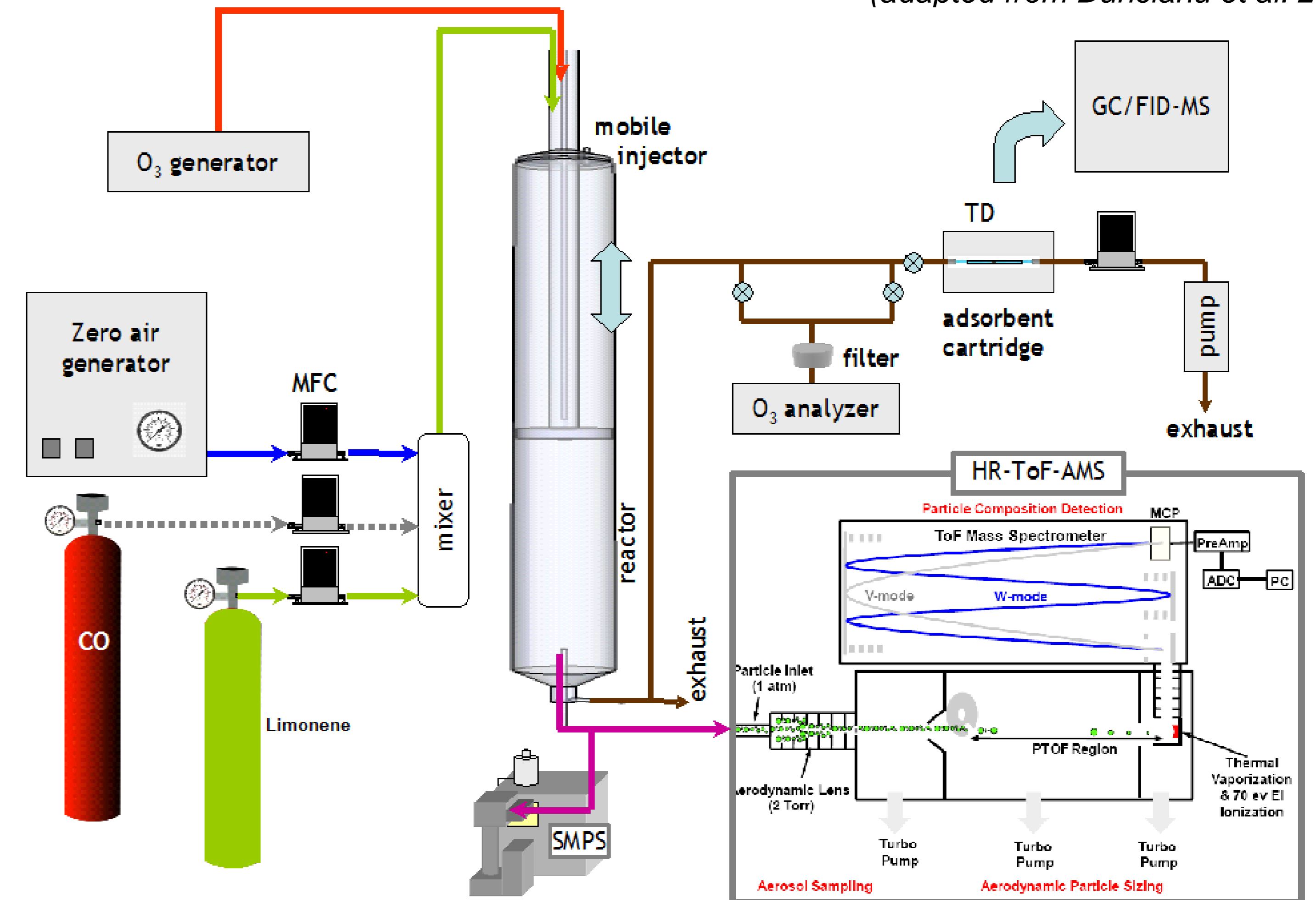
Aim of the study: to characterize the reactions of 2 BVOCs with ozone leading to the formation of SOA by the determination of:

- Rate coefficients
- Gas and particulate products
- Aerosol particle distributions and yields



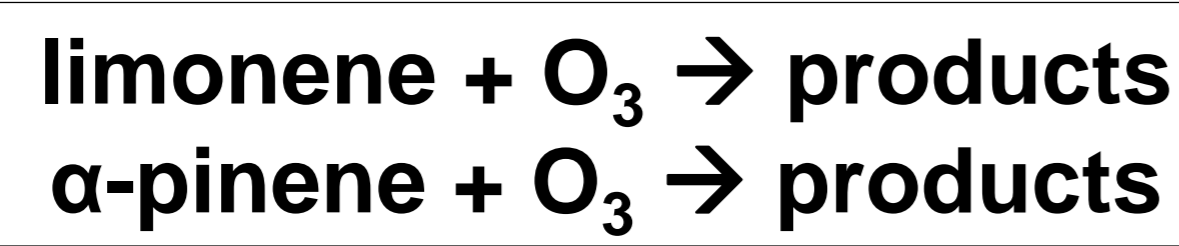
Experimental setup: Laminar flow reactor

(adapted from Duncianu et al. 2012)

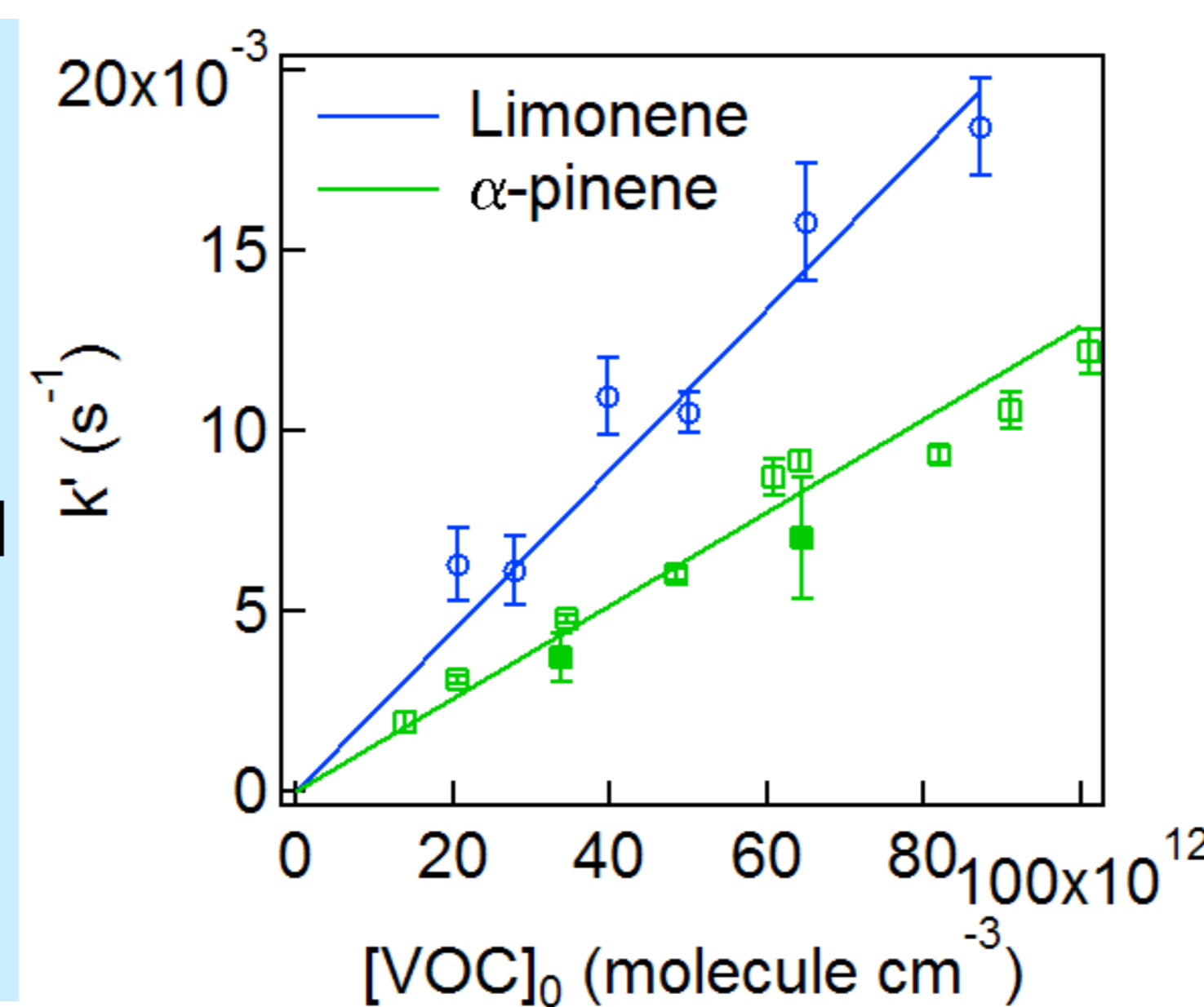


- On-line measurement of [VOC] by thermodesorption and GC-FID-MS analysis
- Measurement of [O₃] = f (reaction time) by ozone analyser (UV absorption at 254 nm)
- ➔ Work in a controlled environment:
 - temperature, concentrations of reactants (O₃, VOC), flow conditions
 - ➔ 1st reaction steps: **short reaction times** from 38 s up to 4 min

Results: kinetics



- Pseudo first order conditions: [VOC]₀ ≥ 10 × [O₃]₀
- Kinetic law: $\frac{d\ln[O_3]}{dt} = k'_{VOC} \times [O_3]_t$
with $k'_{VOC} = k_{VOC} \times [VOC]_0$
- Measurement of [O₃]_t = f (reaction time) for ≠ [VOC]
- Calculation of the pseudo-first order coefficient k' :
 $\ln([O_3]_0/[O_3]_t) = k'_{VOC} \times t$ for ≠ [VOC]
- Determination of the rate coefficient for the ozonolysis reaction k : $k'_{VOC} = k_{VOC} \times [VOC]_0$



Alkene	T (K)	k _{VOC} × 10 ¹⁶ (cm ³ molecule ⁻¹ s ⁻¹)	Setup	Reference
Limonene	296	2.23 ± 0.08	FR	This work
	297	3.8 ± 0.3	FR	Bernard et al. 2012
	304	2.0 ± 0.4	SC	Bernard et al. 2012
	295	2.5 ± 0.3	FR	Witter et al. 2002
	298	2.13 ± 0.15	SC	Khamaganov et Hites 2001
	298	2.0 ± 0.5	Review	Calvert et al. 2000
α -pinene	297	1.29 ± 0.16	FR	This work (Duncianu et al. 2012)
	295	1.1 ± 0.2	FR	Witter et al. 2002
	298	0.84 ± 0.07	SC	Khamaganov et Hites 2001
	298	0.90	Review	IUPAC data

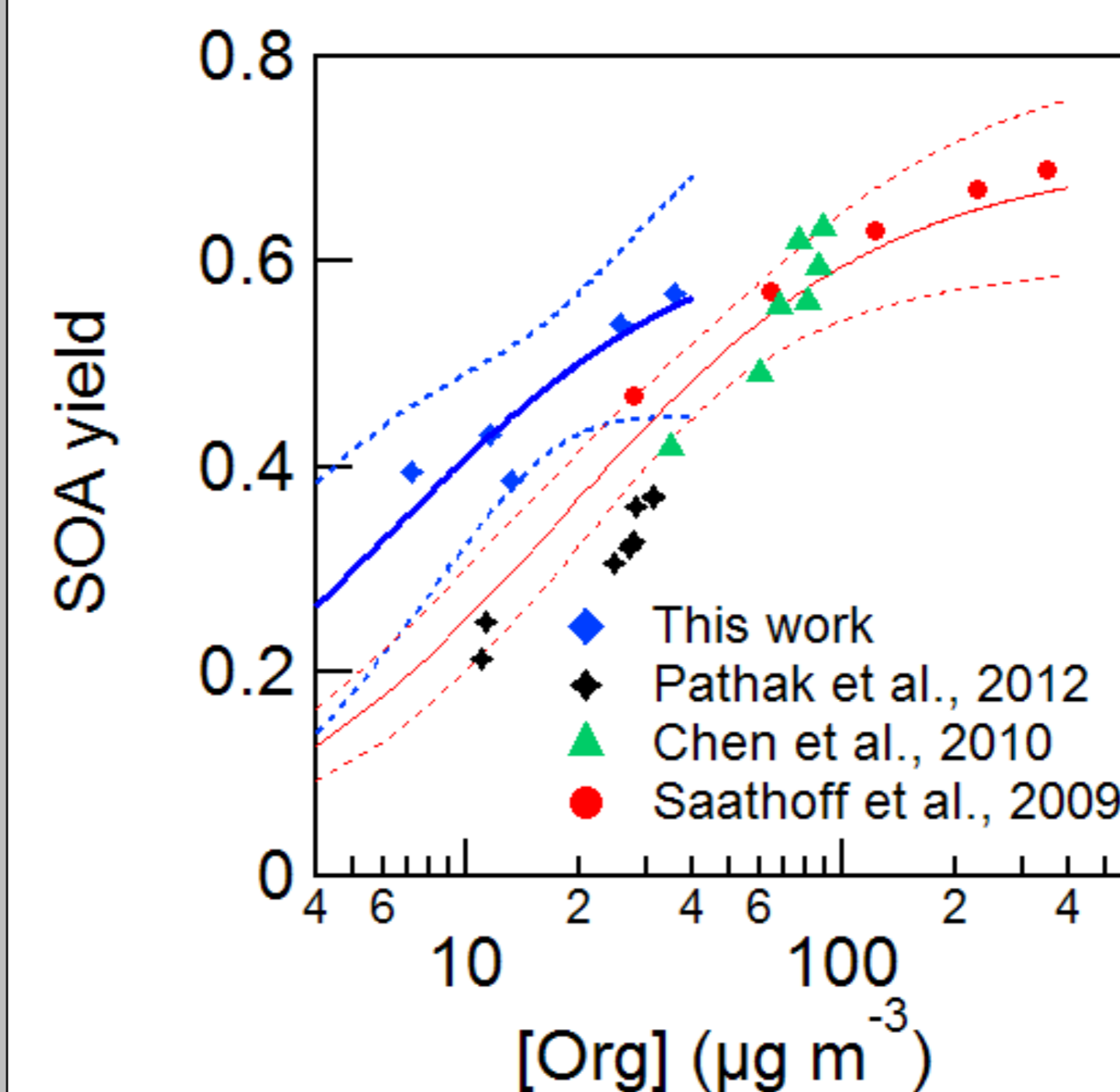
FR: flow reactor; SC: smog chamber

Results: aerosol particle distribution and yield

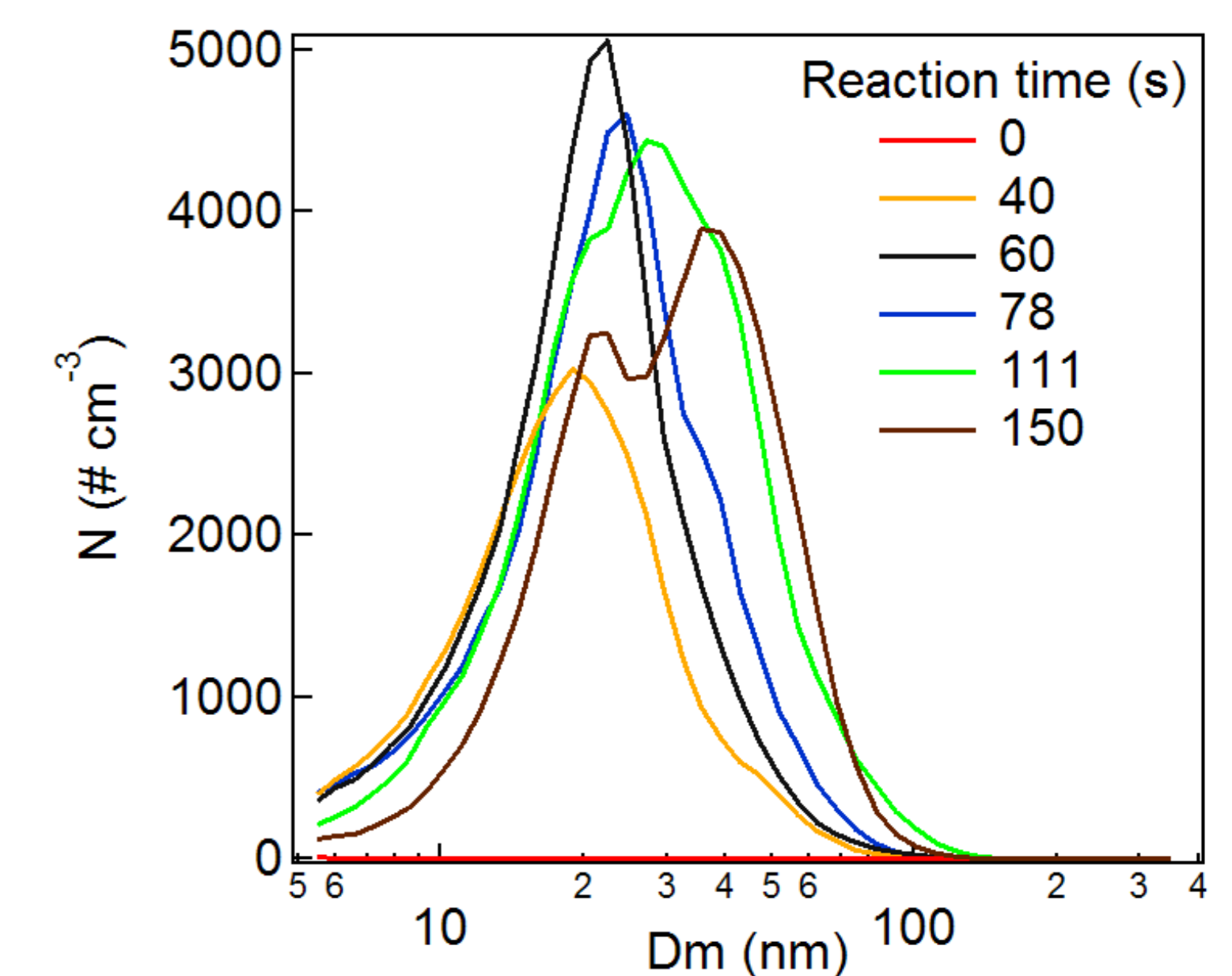
Example of the reaction limonene + O₃ → products

- Particle size distribution given by SMPS data :
- first mode centered on 20 nm
 - enlargement of the particles with reaction time and appearance of a double mode at 20 and 40 nm

➔ Ozonolysis of unsaturated gas products?



Comparison with literature results obtained whether in simulation chambers (Chen et al., 2010; Saathoff et al., 2009) or in a flow reactor (Pathak et al., 2012)



$$Y = \frac{M_0}{\Delta[LIM]} \quad \text{with } M_0 = [Org] (\mu\text{g m}^{-3}) \quad \text{(from AMS data)}$$

$$Y_i = M_0 \left(\frac{\alpha_i k_{om,i}}{1 + k_{om,i} M_0} \right) \quad \text{Odum et al. 1996}$$

Conclusions and perspectives

➤ Conclusions

- Determination of $k_{LIM+O_3} = (2.23 \pm 0.08) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\alpha-PIN+O_3} = (1.29 \pm 0.16) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in agreement with literature
- Determination of SOA yield for the reaction limonene + O₃ → products
 - Relative agreement with Chen et al., 2010 and Saathoff et al., 2009
 - Two times higher than Pathak et al., 2012

➤ Perspectives

- Analysis of gas products for both reactions
- Further characterization of particulate products and additional experiments at lower reaction extent

References

Atkinson et al. (2006), *Atm. Chem. Phys.*, 6, 3625 // Bernard et al. (2012), *J. Aer. SC.*, 43, 14 // Calvert et al. (2000), Oxford Univ. Press // Chen et al. (2010), *Indoor air*, 20, 320 // Duncianu et al. (2012), *J. Phys. Chem A*, 116, 6169 // Khamaganov and Hites. (2001), *J. Phys. Chem. A*, 105, 815 // Odum et al. (1996), *Env. Sc. Tech.*, 30, 2580 // Pathak et al. (2012), *Env. Sc. Tech.*, 46, 11660 // Saathoff et al. (2009), *Atm. Chem. Phys.*, 9, 1551 // Witter et al. (2002), *Int. J. Chem. Kin.*, 34, 394

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