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

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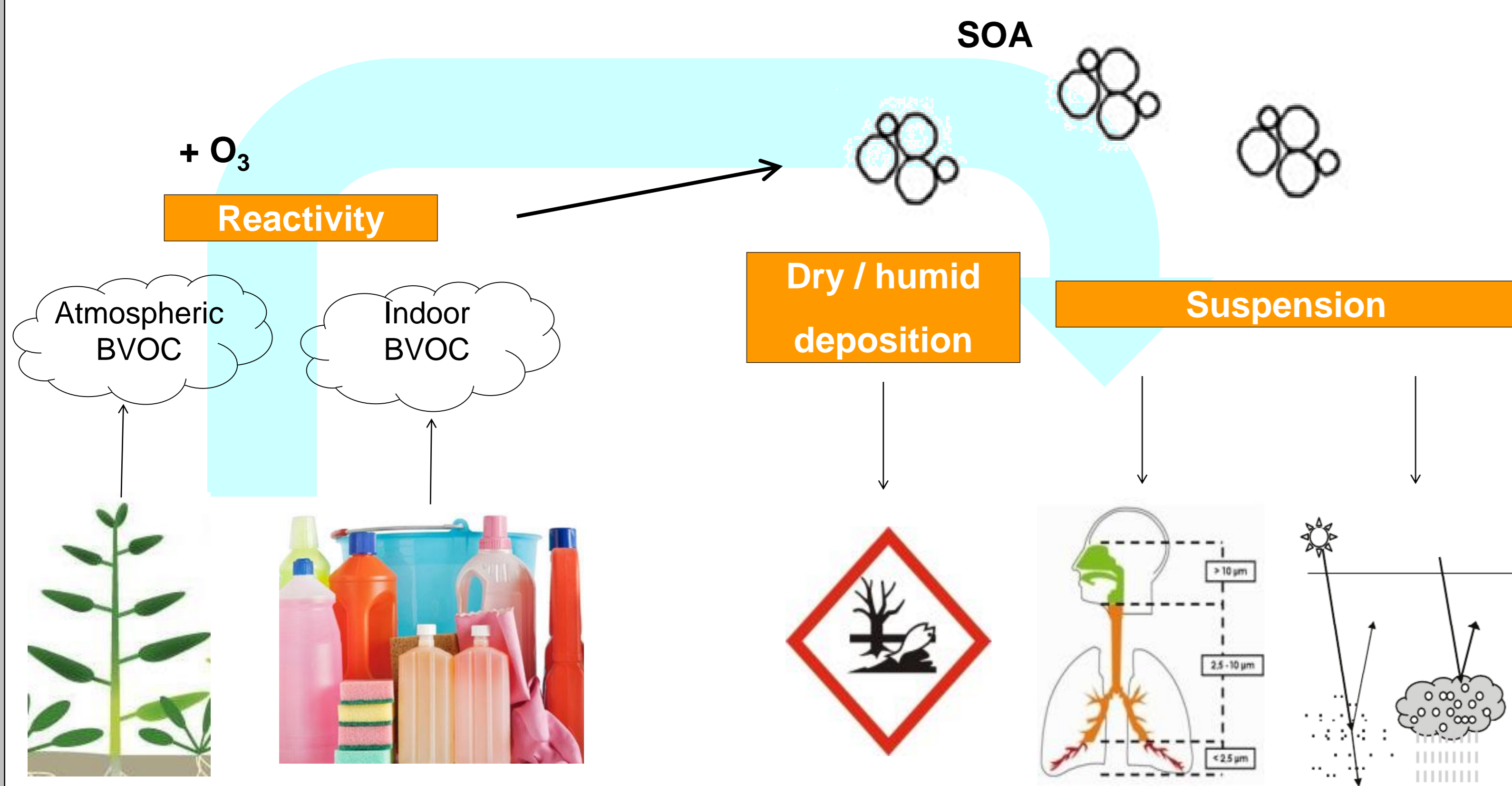
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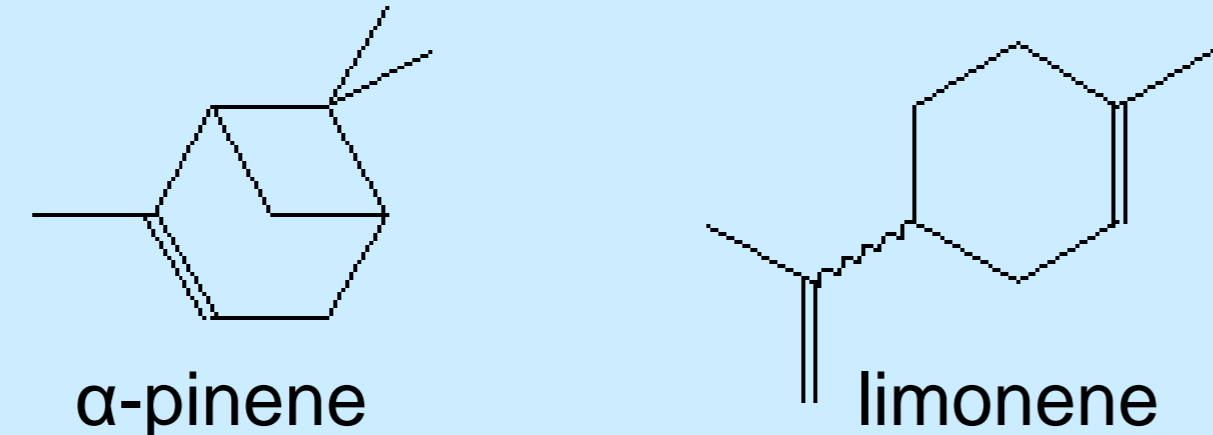
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## Atmospheric background

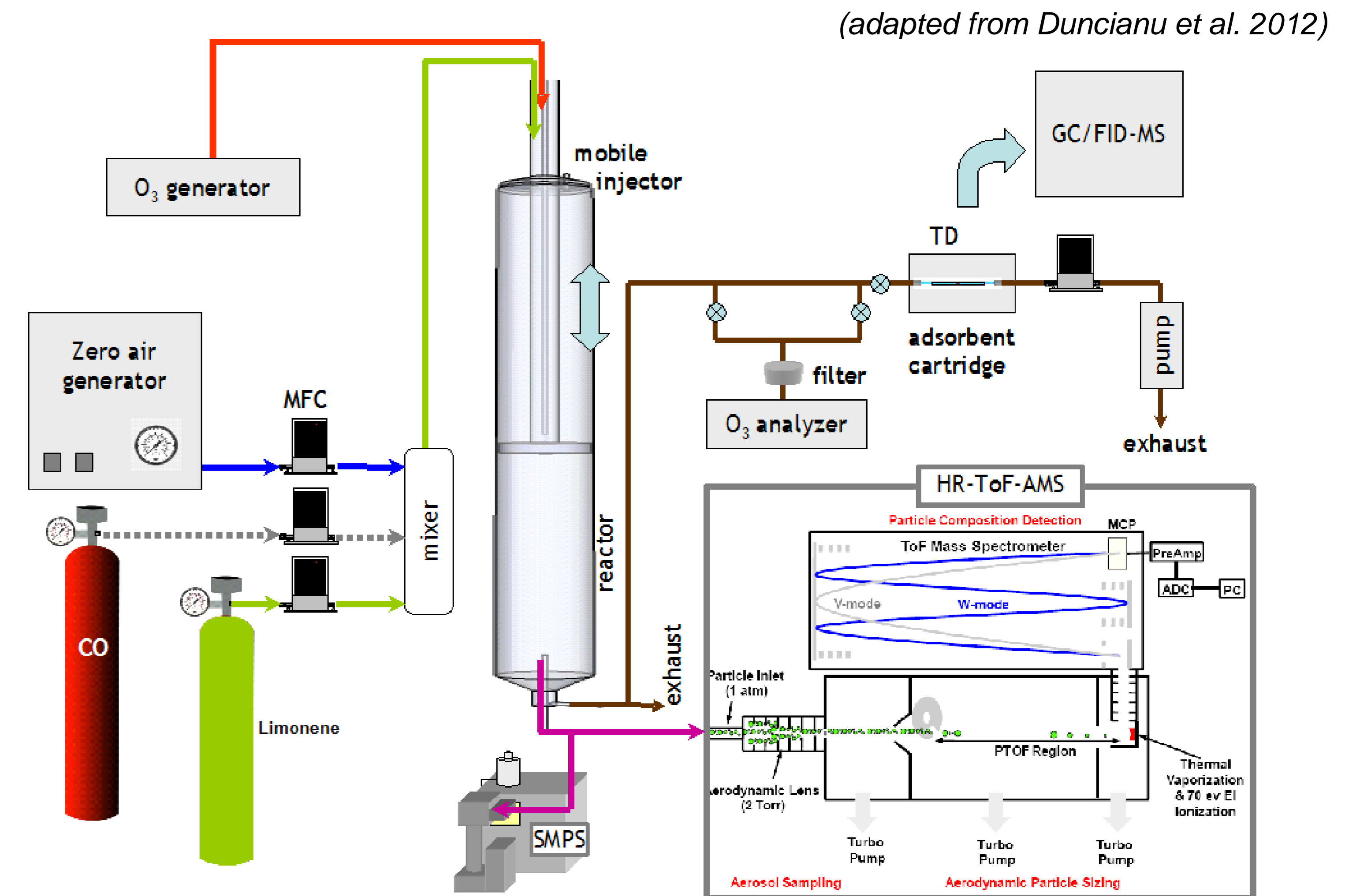


Aim of the study: to characterize the reactions of 2 BVOCs with ozone leading to the formation of SOA by the determination of:

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

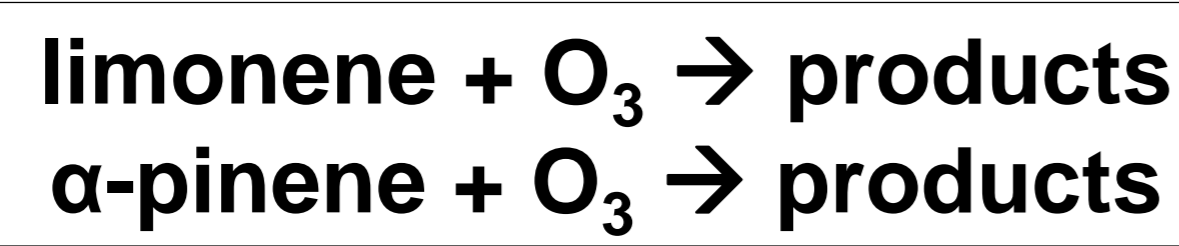


## Experimental setup: Laminar flow reactor

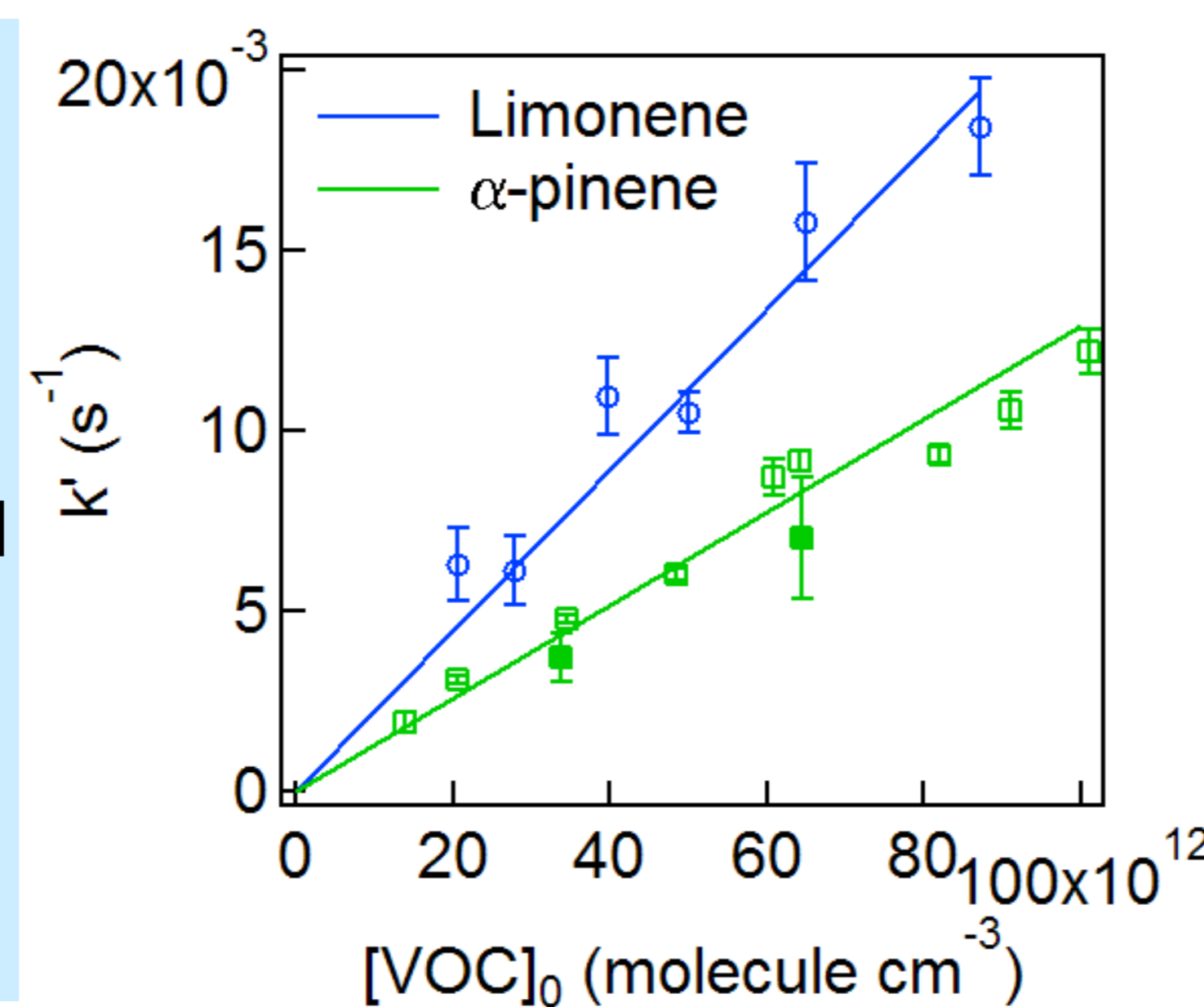


- On-line measurement of [VOC] by thermodesorption and GC-FID-MS analysis
- Measurement of  $[O_3] = f(\text{reaction time})$  by ozone analyser (UV absorption at 254 nm)
- ➔ Work in a controlled environment: temperature, concentrations of reactants ( $O_3$ , VOC), flow conditions
- ➔ 1<sup>st</sup> reaction steps: **short reaction times** from 38 s up to 4 min

## Results: kinetics



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



Alkene	T (K)	$k_{VOC} \times 10^{16}$ ( $cm^3 \text{ molecule}^{-1} s^{-1}$ )	Setup	Reference
Limonene	296	$2.23 \pm 0.08$	FR	This work
	297	$3.8 \pm 0.3$	FR	Bernard et al. 2012
	304	$2.0 \pm 0.4$	SC	Bernard et al. 2012
	295	$2.5 \pm 0.3$	FR	Witter et al. 2002
	298	$2.13 \pm 0.15$	SC	Khamaganov et Hites 2001
	298	$2.0 \pm 0.5$	Review	Calvert et al. 2000
$\alpha$ -pinene	297	$1.29 \pm 0.16$	FR	This work (Duncanu et al. 2012)
	295	$1.1 \pm 0.2$	FR	Witter et al. 2002
	298	$0.84 \pm 0.07$	SC	Khamaganov et Hites 2001
	298	0.90	Review	IUPAC data

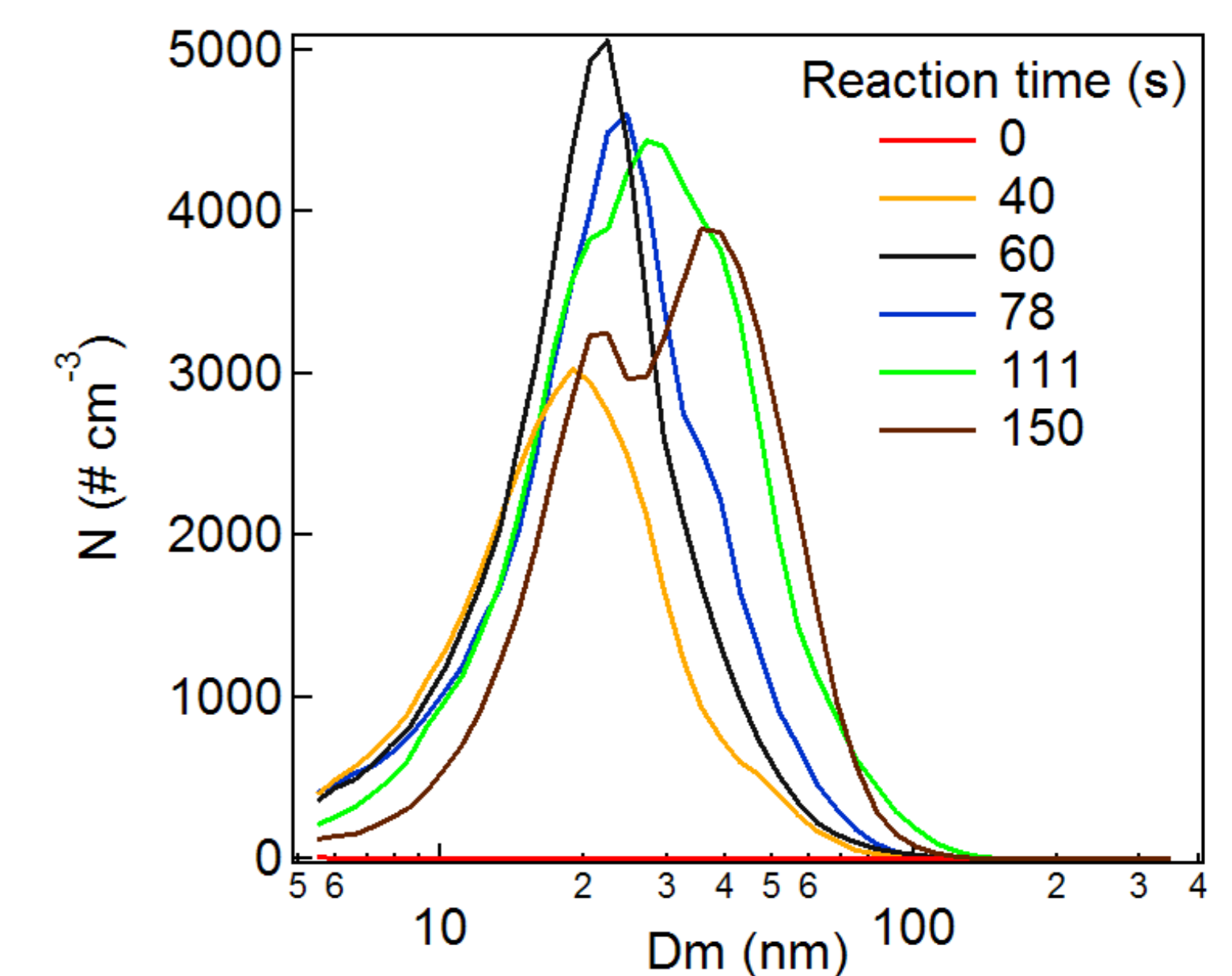
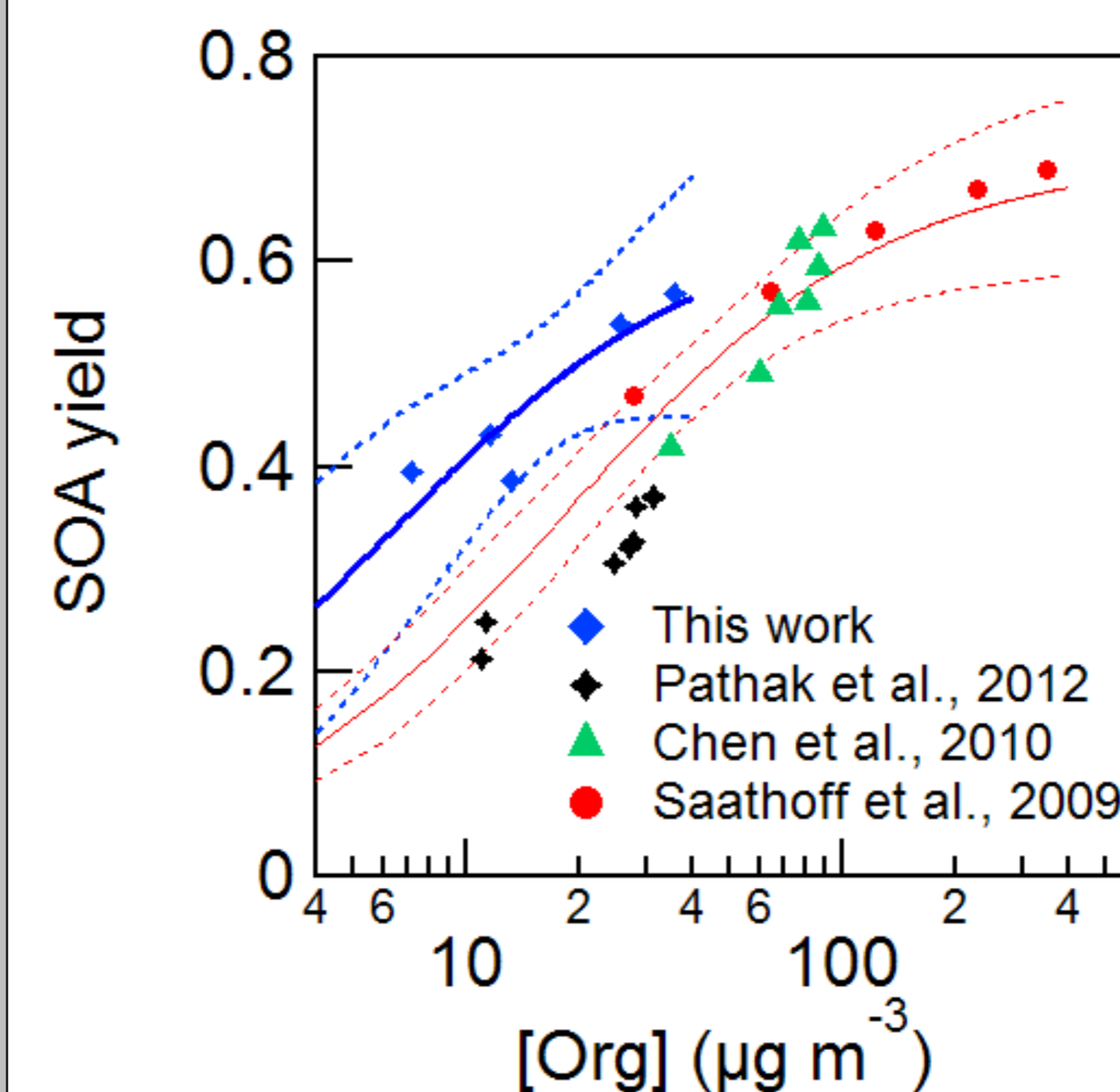
FR: flow reactor; SC: smog chamber

## Results: aerosol particle distribution and yield

### Example of the reaction limonene + $O_3 \rightarrow$ 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?



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

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

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)

## Conclusions and perspectives

### ➤ Conclusions

- Determination of  $k_{LIM+O_3} = (2.23 \pm 0.08) \times 10^{-16} cm^3 \text{ molecule}^{-1} s^{-1}$  and  $k_{\alpha-PIN+O_3} = (1.29 \pm 0.16) \times 10^{-16} cm^3 \text{ molecule}^{-1} s^{-1}$  in agreement with literature
- Determination of SOA yield for the reaction limonene +  $O_3 \rightarrow$  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 // Duncanu 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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