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Processus chimiques et nucléation dans l'ozonolyse du limonène

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Atmospheric aerosols

Definition and presentation

What are aerosols ?

Atmospheric aerosols (or particulate matter) are solid or liquid particles suspended in the atmosphere



Mean diameters ranging from about 1 nm to about 100 μm

Origin

Natural

Anthropogenic



Impact of aerosols

Chemical composition

*Inorganic
or
organic*

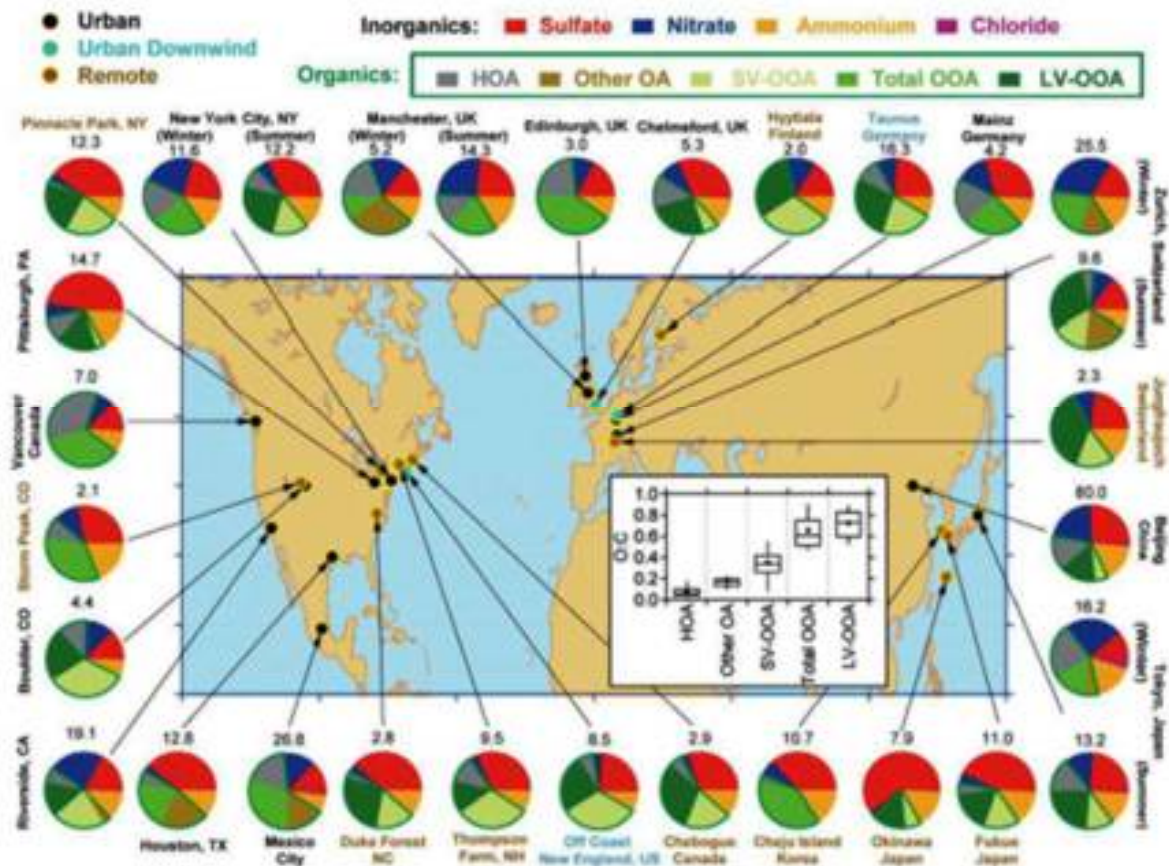
Primary aerosols

Volatile compounds

Secondary aerosols

Atmospheric aerosols

Chemical composition



Chemical composition of the submicron aerosol at different locations in the northern hemisphere (Jimenez et al., 2009)

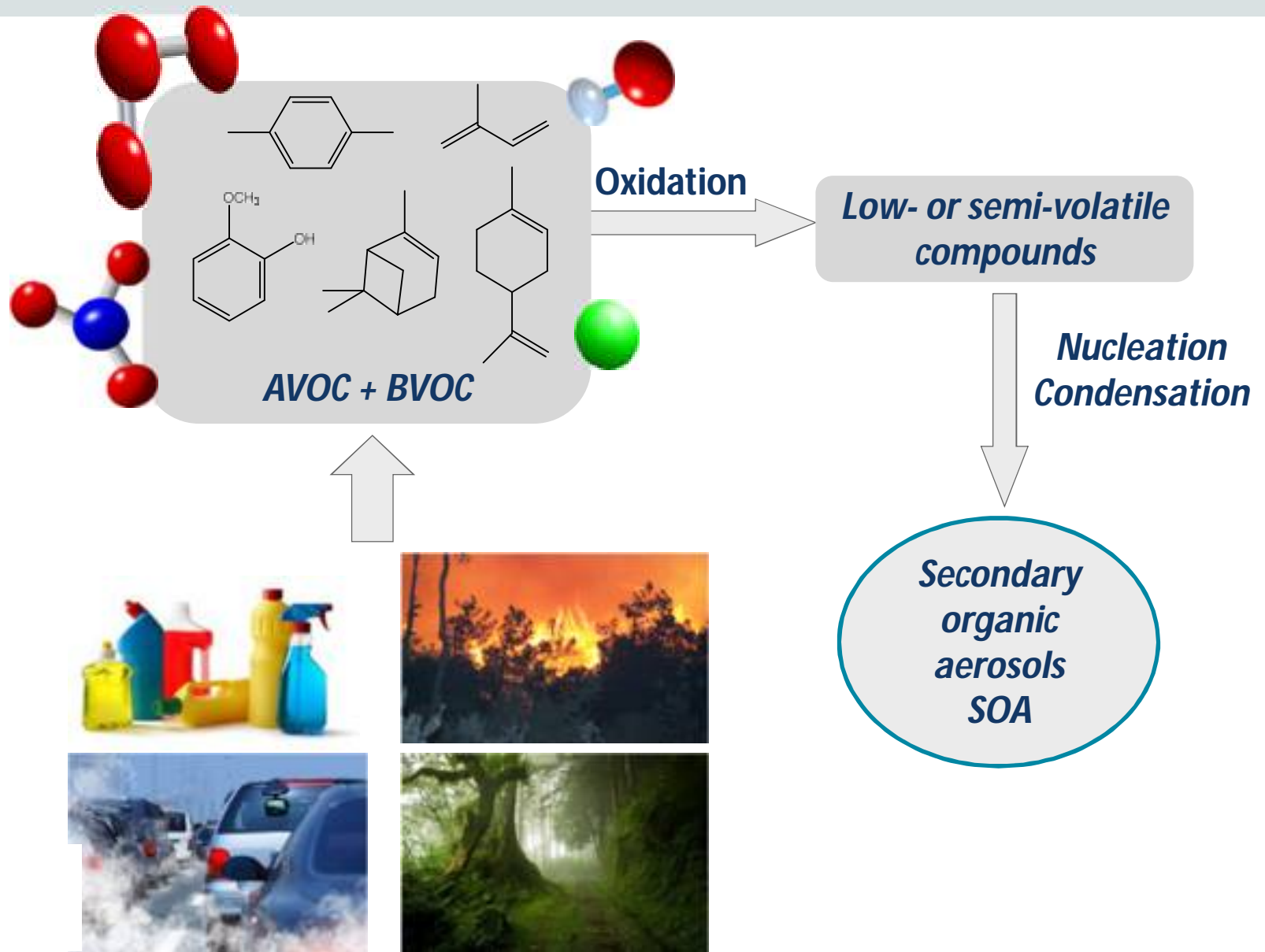
❖ Organic carbon accounts for a large part of the fine fraction of the aerosol

❖ Organic aerosols are mainly of secondary origin (Other studies: 15 - 90 % of the total mass of measured aerosols)

Secondary organic aerosols
SOA

Aérosols organiques secondaires

Définition et mécanisme de formation

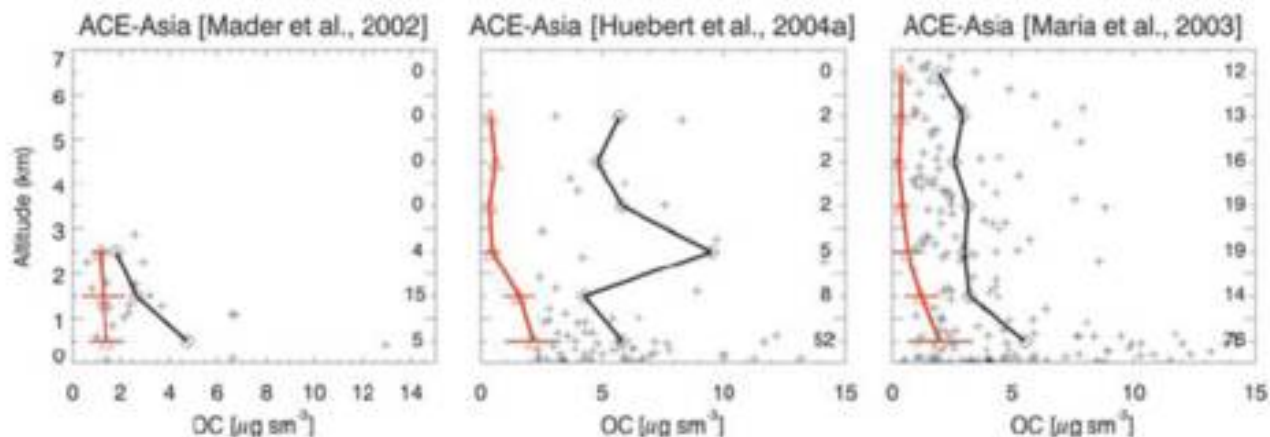


Problématique : Désaccords modèles-mesures

Comparaison AOS mesurés - modélisés

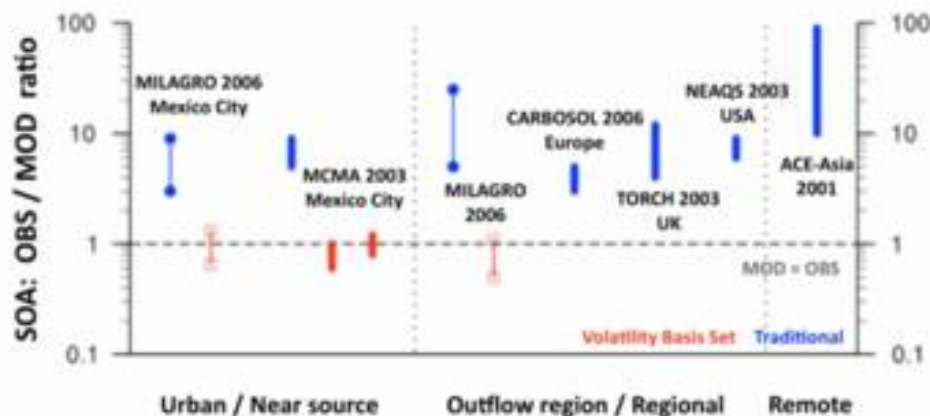
➤ Exemple de sous-estimation par les modèles

HEALD ET AL.: LARGE TROPOSPHERIC SOURCE OF OC AEROSOLS



Orange : modèle GEOS-Chem
Noir : mesures

Heald et al., GRL 2005



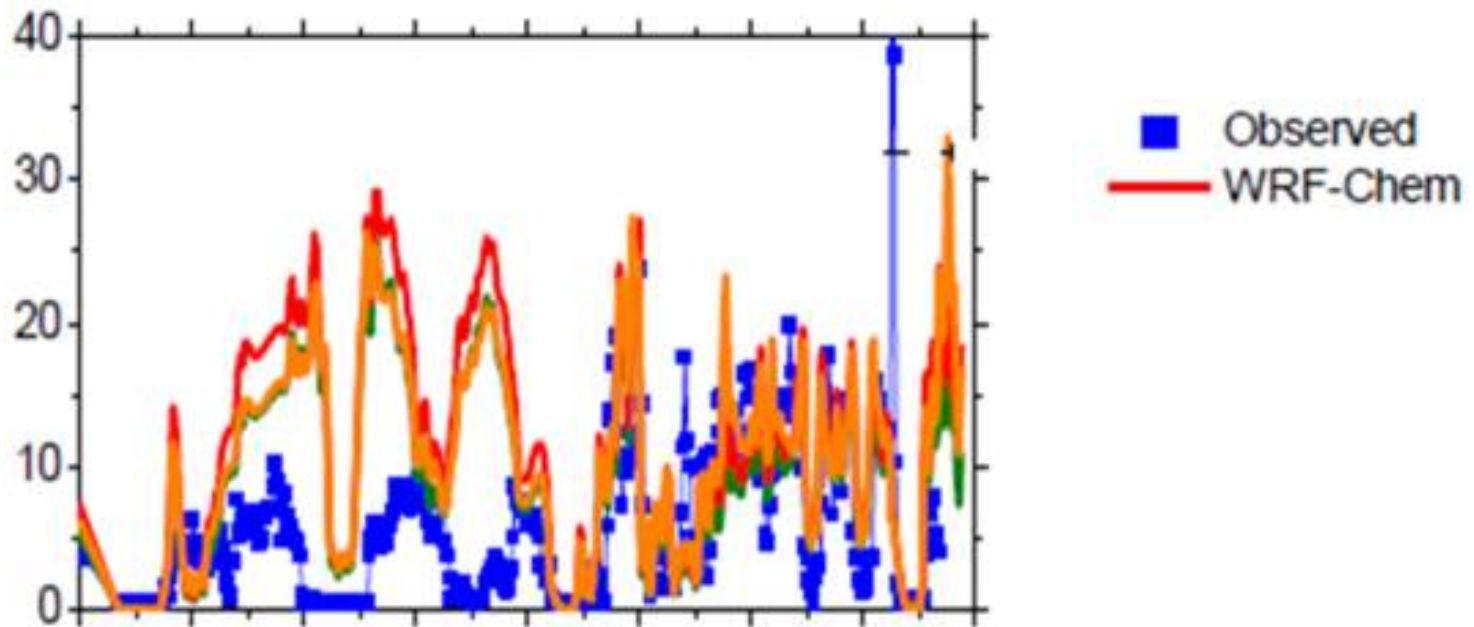
Hodzic et al., ACP 2010

Concentrations d'aérosol organique observé > concentrations calculées par le modèle

Problématique : Désaccords modèles-mesures

Comparaison AOS mesurés - modélisés

➤ Exemple de sur-estimation par les modèles



Comparaison entre les predictions du modèle WRF-Chem pour les aerosols organiques et les mesures faites à Mexico (Shrivastava et al., ACP 2011)

Concentrations d'aérosol organique observé < concentrations calculées par le modèle

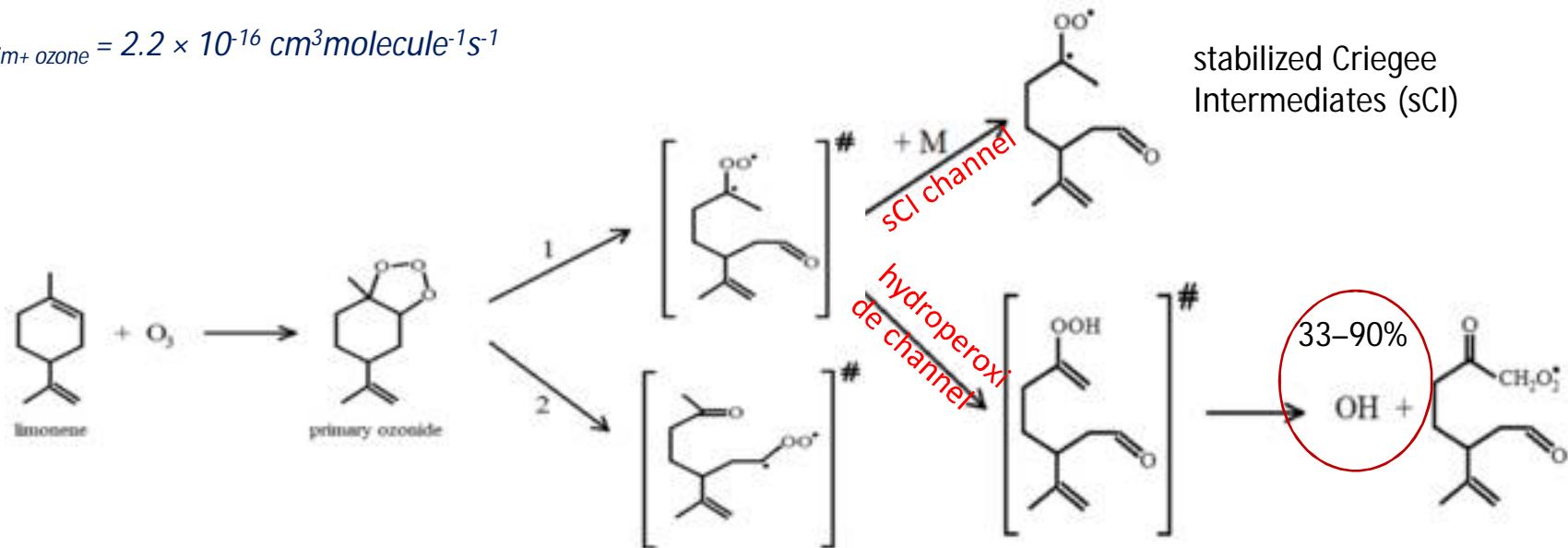
Problématique : Désaccords modèles-mesures

➤ Raisons possibles :

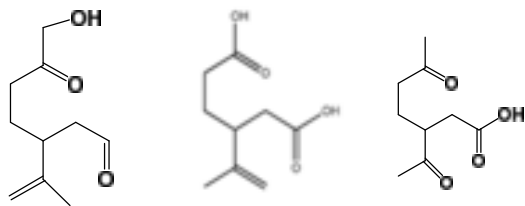
- ❑ *New sources of SOA discovered recently (ex: organosulphates)... which reduces the gap between [SOA] measured and calculated (Cui et al. 2014)*
- ❑ *SOA yield determined in the laboratory under conditions very far from reality: Presence of several compounds in the atmosphere, different conditions of T, RH, [compounds]*
- ❑ *Gas- and condensed-phase photolysis of VOCs not accounted for in chemistry models (Hodzic et al. 2015)*
- ❑ *Influence of anthropogenic air masses:
Several recent studies have suggested that anthropogenic emissions influence the formation of SOA from VOCs (Shilling et al., 2012, Carlton et al., 2010, Spracklen et al., 2011 ...)*

Limonene ozonolysis as a model

$$k_{\text{Limonene} + \text{O}_3} = 2.2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



Observed ozonolysis products: organic acids → SOA



sCI are reactive toward atmospheric species and can undergo bimolecular reaction with: H₂O, O₃, SO₂, organic acids, alcohols, carbonyl compounds...

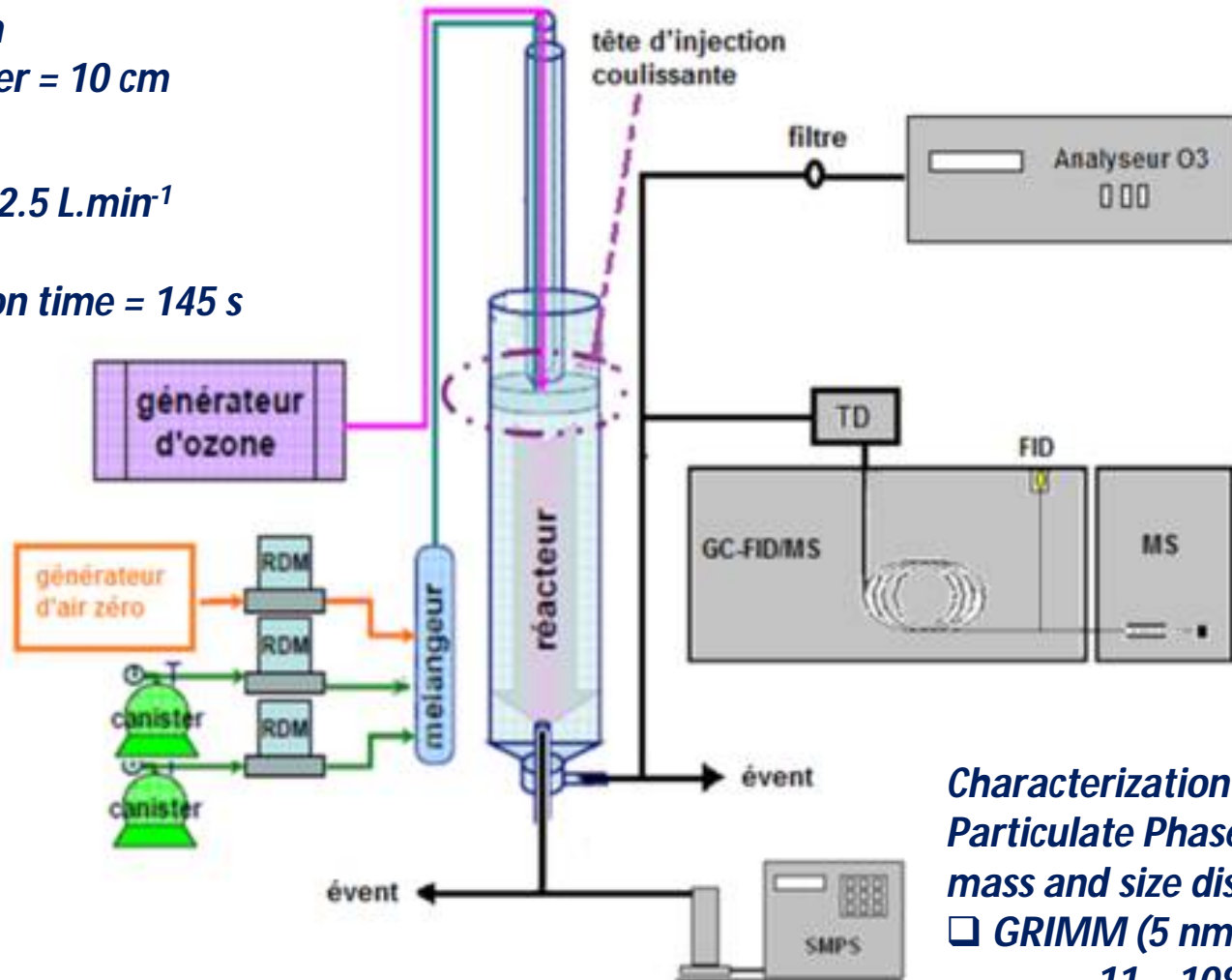
Many studies concluded that sCI play a key role in the SOA formation arising from the oxidation of BVOCs

(Bonn et al., 2014; Docherty & Ziemann, 2003; Heaton et al., 2007; Lee & Kamens, 2005; Yao et al., 2014)

Experimental setup: Laminar flow reactor

Height = 100 cm
Internal diameter = 10 cm

Total flow = $2.5 \text{ L}\cdot\text{min}^{-1}$
 $H = 90 \text{ cm}$
Fixed reaction time = 145 s



*Characterization of the
Particulate Phase: Number,
mass and size distribution.*

- GRIMM (5 nm - 350 nm / 11 - 1083 nm)
- TSI (10 nm - 1100 nm)

SOA formation from limonene ozonolysis

SOA yield : Flow reactor

$$Y = \frac{M_0}{\Delta HC}$$

M_0 : SOA mass formed

ΔHC : Mass consumption of VOCs

$$Y = 0,09 - 0,64$$

$$M_0 = 9 - 540 \mu\text{g}\cdot\text{m}^{-3}$$

Odum (1996):

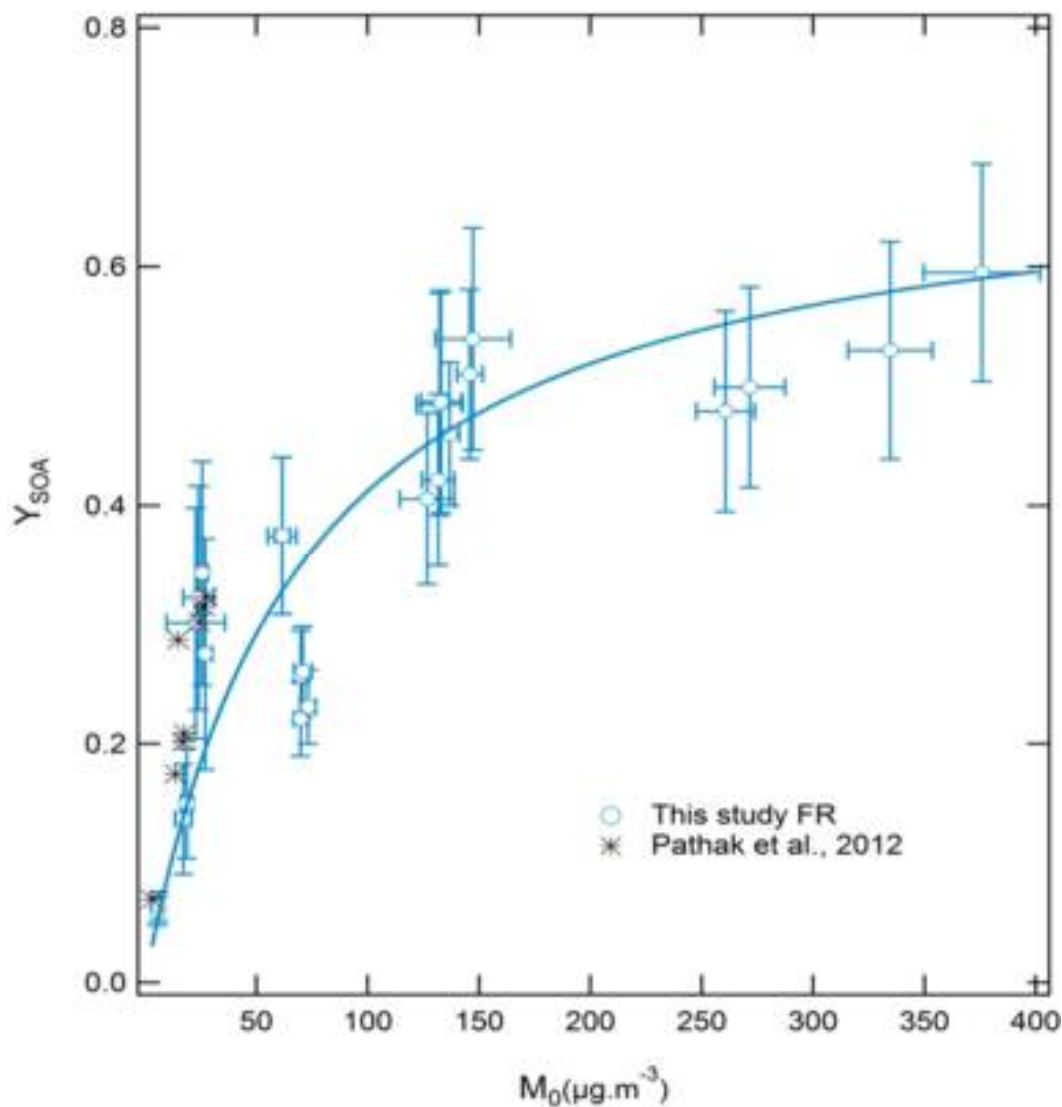
$$Y = M_0 \sum \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0}$$

α_i : Stoichiometric coefficient of formation of product i

$K_{om,i}$: Partitioning coefficient between gaseous and particulate phase

$$\alpha = 0.66 \pm 0.04$$

$$K = (1.5 \pm 0.3) \times 10^{-2} \text{ m}^3 \mu\text{g}^{-1}$$

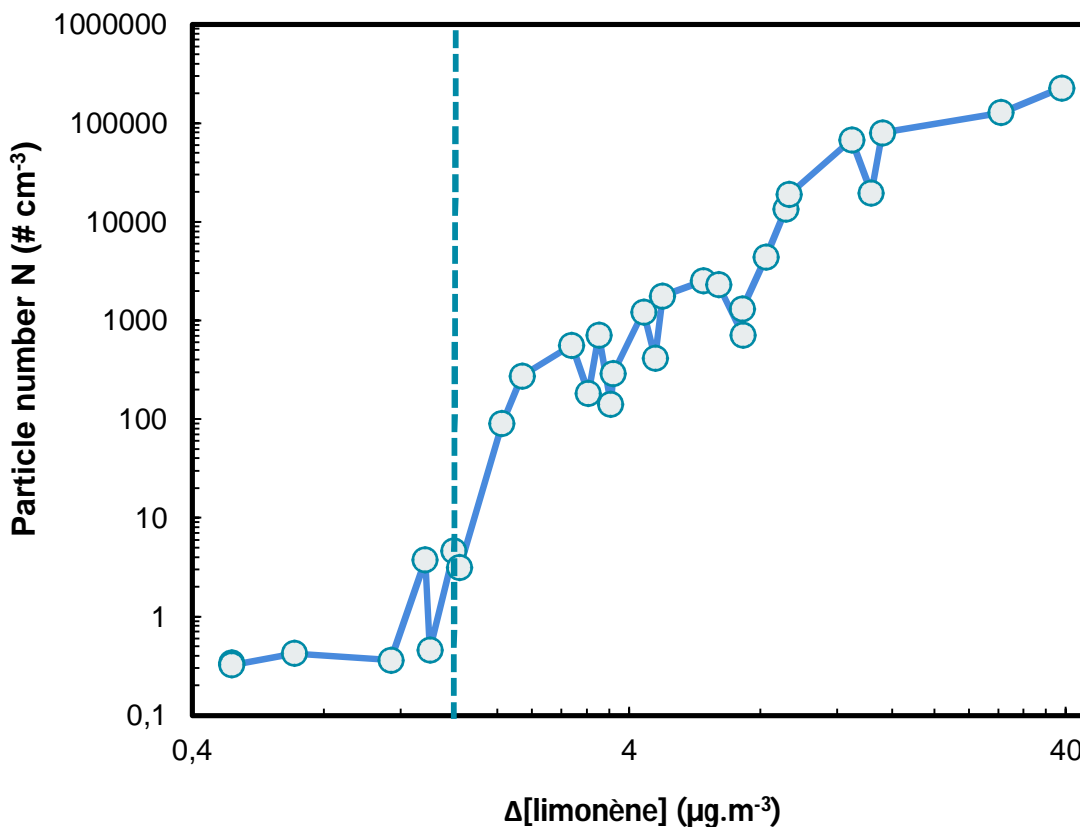


SOA formation from limonene ozonolysis

Nucleation threshold (NT)

- Corresponds to the minimum amount of limonene that must react to initiate nucleation
- **NT** → **Flow Reactor**
- Series of reactions with
 - $[lim]_0 = 340 - 420 \mu\text{g}\cdot\text{m}^{-3}$
 - Progressive increase in $[O_3]_0$: $6 - 120 \mu\text{g}\cdot\text{m}^{-3}$
 - Blank of particles $< 1 \text{ part}\cdot\text{cm}^{-3}$

$$NT = 1.8 \pm 0.2 \mu\text{g}\cdot\text{m}^{-3}$$



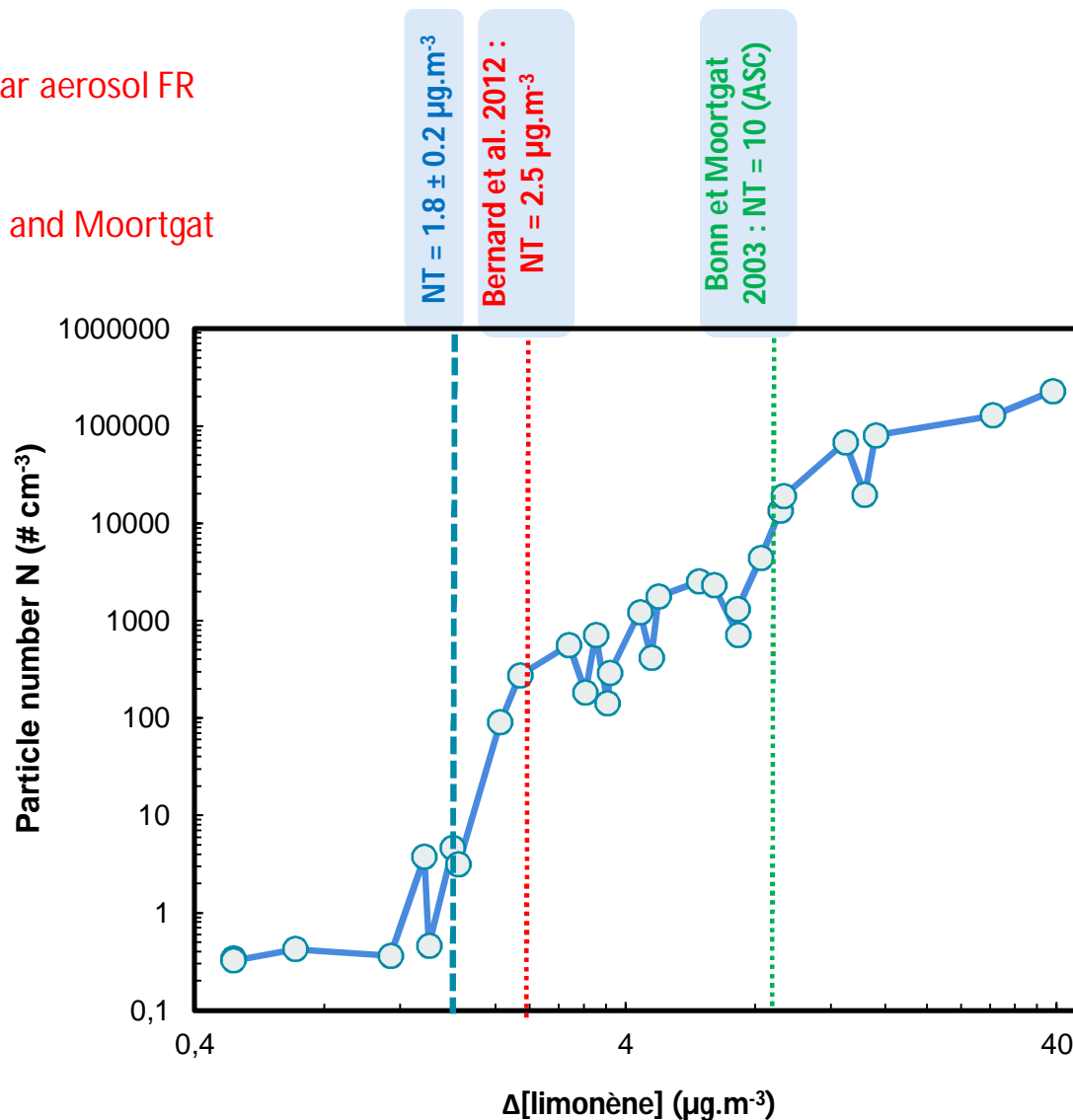
SOA formation from limonene ozonolysis

Nucleation threshold

❖ Good agreement with Bernard et al: similar aerosol FR

❖ Higher NT of about $\mu\text{g}\cdot\text{m}^{-3}$ found by Bonn and Moortgat

They used a smog chamber and a CPC with a higher particle size detection limit (10 nm) → thus precluding the detection of smaller particles

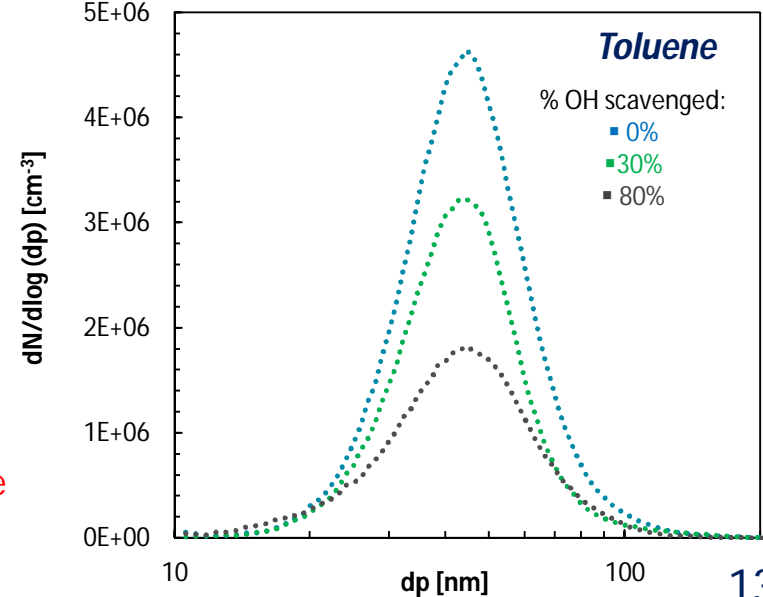
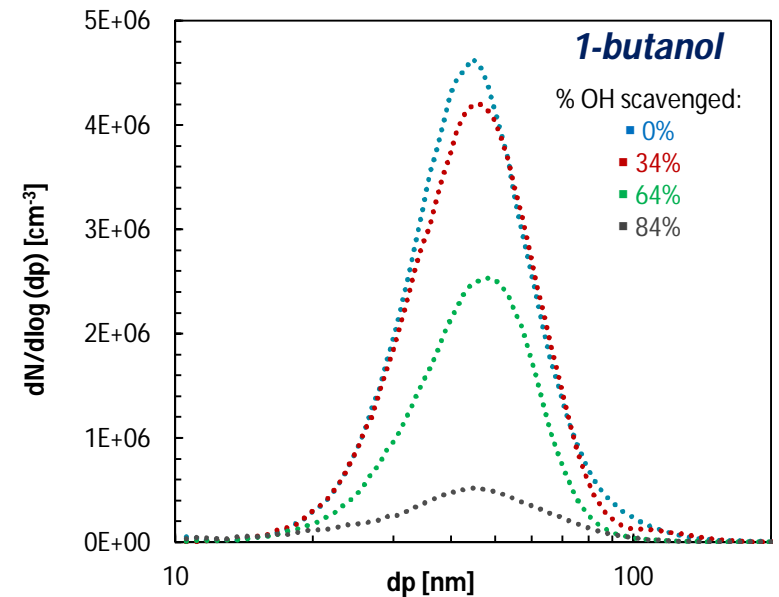
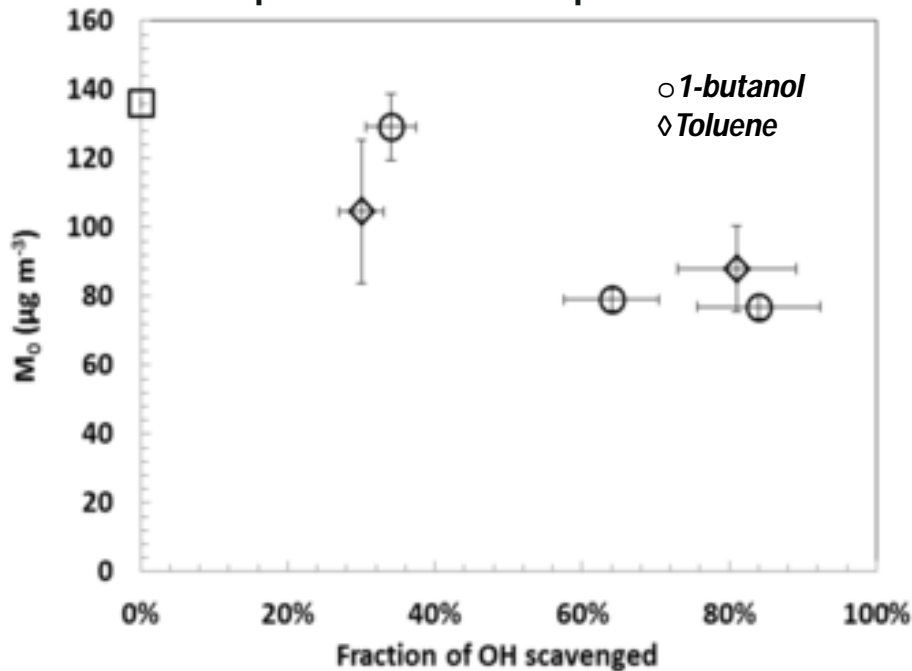


Influence of OH radical scavenger on SOA formation

Influence on particle mass and number size distribution

	[LIM] ₀ (μg·m ⁻³)	[O ₃](μg·m ⁻³)	% OH scavenged
1-butanol	≈ 900	200 – 2400	35 – 85
Toluene		250 – 850	30 – 80

Comparison with base experiment



- Rapid decrease of M_0 of roughly 40% for ~ 80% of OH scavenged
- Significant decrease of the particle number with increasing the scavenger concentration
- Similar observations for different [O₃]₀

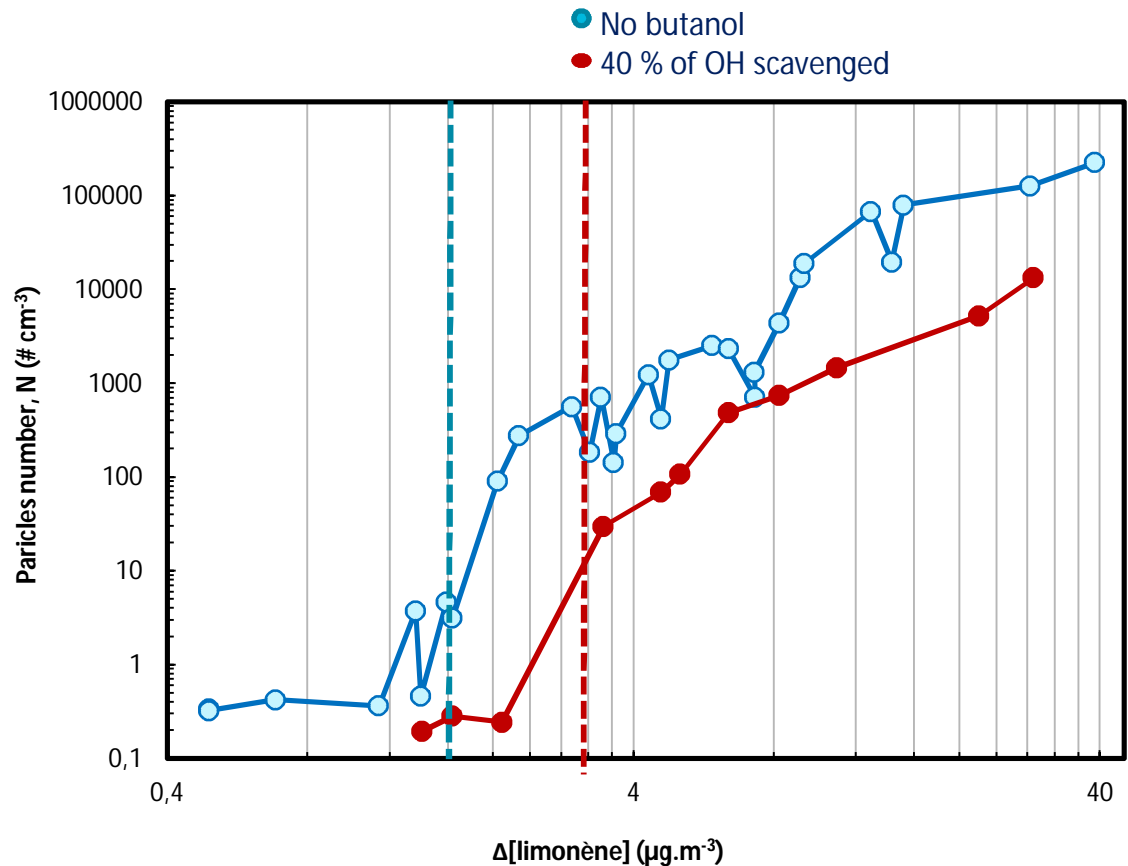
Influence of OH radical scavenger on SOA formation

Influence on Nucleation Threshold

- $[lim]_0 = 340 - 420 \mu\text{g}\cdot\text{m}^{-3}$

- Progressive increase in $[O_3]_0$: $6 - 120 \mu\text{g}\cdot\text{m}^{-3}$

❖ The presence of butanol as OH-radical scavenger thus clearly time-shifted the nucleation process:
 $1.8 \pm 0.2 \mu\text{g}\cdot\text{m}^{-3}$ to $3 \pm 0.3 \mu\text{g}\cdot\text{m}^{-3}$ when 40% of OH radicals are scavenged



Influence of OH radical scavenger on SOA formation

The presence of 1-butanol and toluene used as OH scavenger decrease SOA mass and number and delay the NT

1- They suppress the OH + limonene reaction and "replace" the corresponding reaction products by those from the OH + scavenger reaction:

~~Limonene + OH \rightarrow 0,08 - 0,41 SOA~~

1-butanol + OH \rightarrow Volatile products \rightarrow No SOA

Limonene + O₃ \rightarrow Y_{OH} = 0,67



consumption of \approx 30 ppb of toluene



50 $\mu\text{g}\cdot\text{m}^{-3}$ SOA (Hildebrandt et al. 2009)

2- they can modify the HO₂/RO₂ peroxy radical concentration ratio:

□ A few studies underlined the role of HO₂/RO₂ concentration ratio in the nucleation process

□ HO₂ yields from 1-butanol + OH and toluene + OH are expected to be of the same order of magnitude (from the literature) \rightarrow confirmed by MCM simulations: similar HO₂/RO₂ ratios (= 0.0031)

□ OH + SCAV: expected to increase the HO₂/RO₂ ratio and change the nature of peroxy radicals \rightarrow MCM simulations : 50% increase in HO₂/RO₂ from reactions without scavenger to reactions with 1-butanol and toluene

The change in reaction products may thus not be the only reason for the decrease in SOA

The increase in the ratio promotes HO₂-RO₂ reaction at the expense of RO₂-RO₂ reaction \rightarrow more volatile products (limonene hydroperoxides) \rightarrow less SOA

Influence of sCI scavengers on SOA formation

Influence on Aerosol Growth Curves

➤ **Aerosol growth curves** : aerosol mass produced as function of limonene consumption

➤ $[lim]_0 \approx 900 \mu\text{g.m}^{-3}$

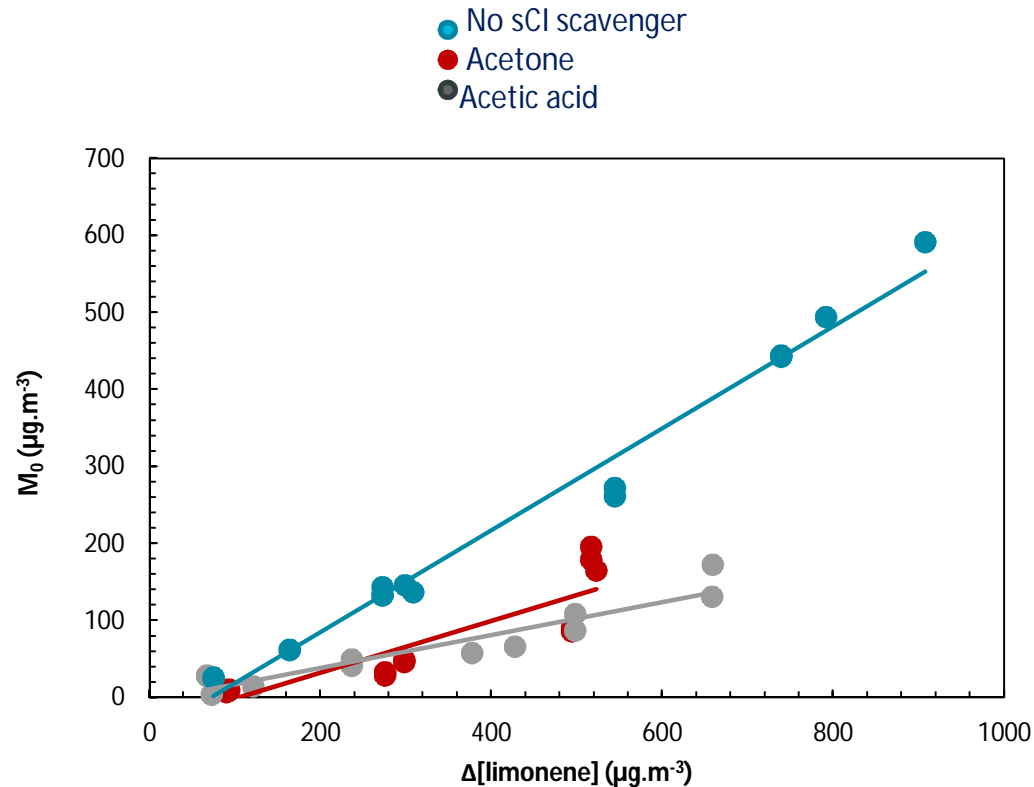
$[O_3]_0 = 200 - 2800 \mu\text{g.m}^{-3}$

$[AA]_0 = 0 - 17500 \mu\text{g.m}^{-3}$

$[AC]_0 = 0 - 10000 \mu\text{g.m}^{-3}$

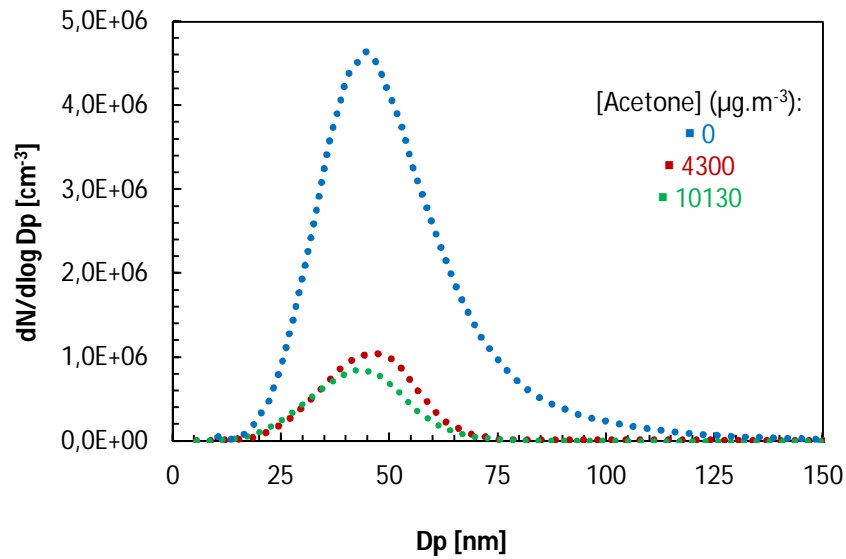
➤ **Linear increasing shape** : in agreement with literature studies.

➤ Adding $[AC]_0$ or $[AA]_0 \approx [Lim]_0 \rightarrow$ much less M_0 formed (more than a factor of 2) for a given amount of $\Delta[\text{limonene}]$ in presence of AC or AA compared to the experiments performed without sCI scavenger



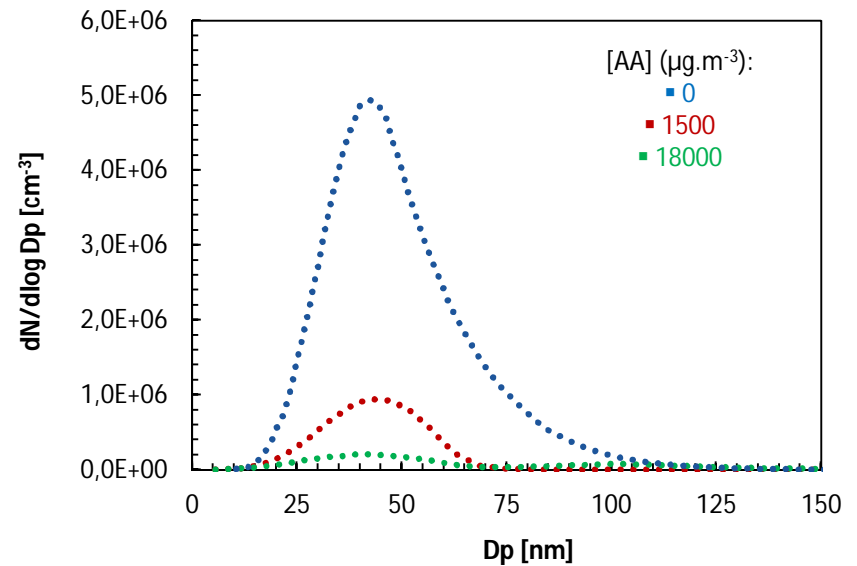
Influence of sCI scavengers on SOA formation

Influence on particle number size distribution



Strong reduction of the particle number concentrations:

a decrease of more than one order of magnitude.



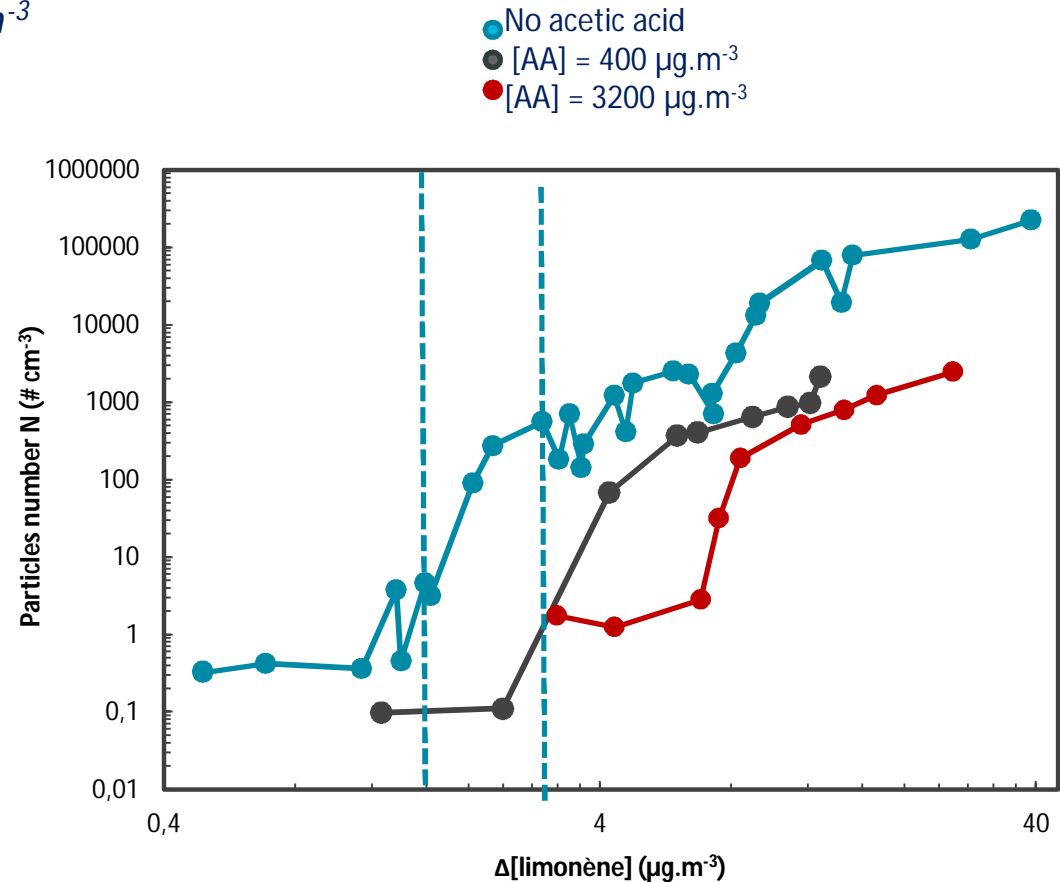
Influence of sCI scavengers on SOA formation

Influence on Nucleation Threshold

- $[lim]_0 \approx 450 \mu\text{g.m}^{-3}$
- Progressive increase in $[O_3]_0$: 6 - 120 $\mu\text{g.m}^{-3}$

$NT = 1.8 \pm 0,2 \mu\text{g.m}^{-3}$ to
✓ $3.7 \pm 0.4 \mu\text{g.m}^{-3}$ when $400 \mu\text{g.m}^{-3}$ of
AA was added
✓ $7.0 \pm 0.5 \mu\text{g.m}^{-3}$ when $3200 \mu\text{g.m}^{-3}$
of AA was added

❖ **The presence of acetic acid as sCI scavenger strongly delays the nucleation process.**



Influence of sCI scavengers on SOA formation

The presence of AA or AC decrease SOA mass and number and delay the NT

Reactions of AA or AC with OH radicals cannot be invoked

$$\frac{k_{\text{OH-AA}} \times [\text{AA}]_0}{k_{\text{OH-Lim}} \times [\text{Lim}]_0} = 0.02$$
$$\frac{k_{\text{OH-AC}} \times [\text{AC}]_0}{k_{\text{OH-Lim}} \times [\text{Lim}]_0} = 0.01$$



direct reaction with the C₁₀-sCI formed from limonene ozonolysis

β-pinene: Nucleation is induced by the secondary ozonide formed by association of the C₉-sCI with ozonolysis primary product (Bonn et al. 2002)

Formation of dimers and oligomers in the ozonolysis of limonene takes place through reactions implying sCI



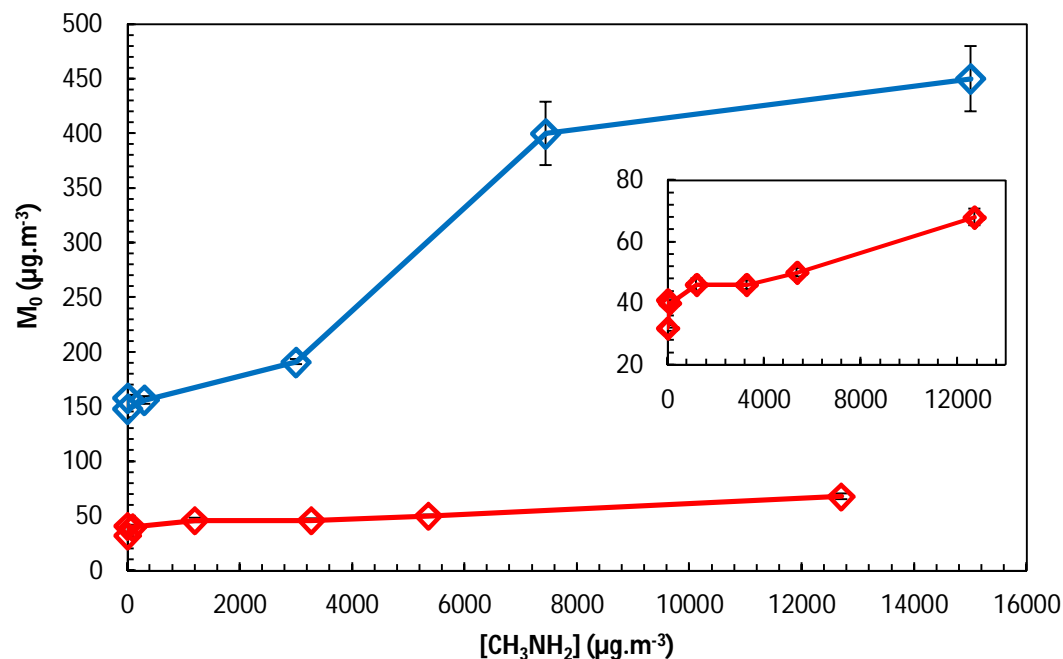
AA or AC as sCI scavengers → More volatile products → Less SOA

Influence of basic contaminants (methylamine) on SOA formation

Influence on total particle mass

Expériences en chambre de simulation atmosphérique (LPCA)

$[LIM]_0$ ($\mu\text{g}\cdot\text{m}^{-3}$)	$[O_3]$ ($\mu\text{g}\cdot\text{m}^{-3}$)	$[CH_3NH_2]$ ($\mu\text{g}\cdot\text{m}^{-3}$)
250	250	300 - 7500
100	100	100 - 12700



The addition of low $[CH_3NH_2]$ (with $[CH_3NH_2]_0 \approx [Limonene]_0$) does not modify the aerosol mass formed.

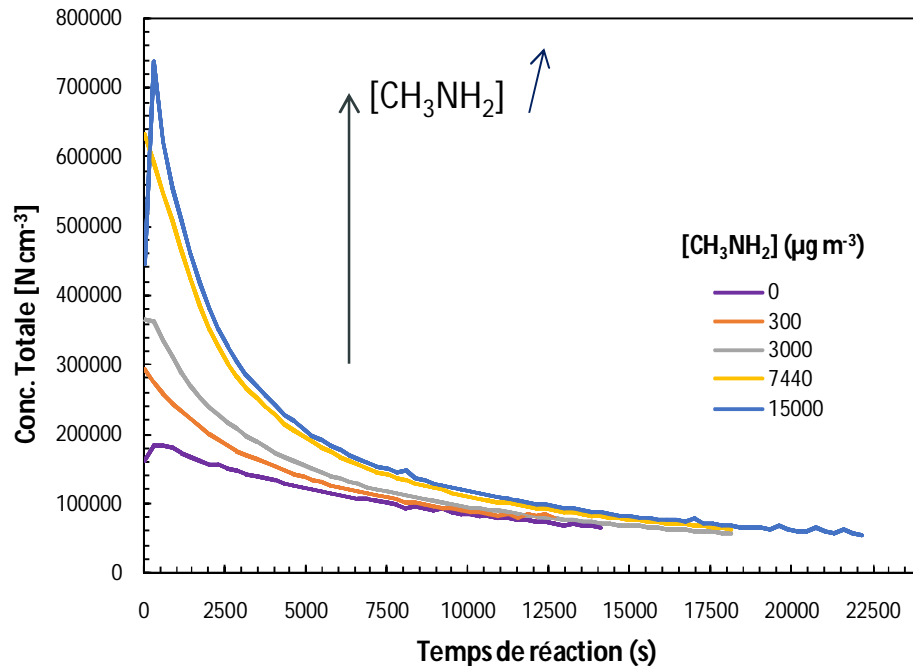
Increasing $[CH_3NH_2]$ increases M_0 significantly:
 $3 \times M_0$ obtained for $[CH_3NH_2]_0 = 50 \times [limonene]_0$

Influence of basic contaminants (methylamine) on SOA formation

Influence on total particle number

$[LIM]_0$ ($\mu\text{g}\cdot\text{m}^{-3}$)	$[O_3]$ ($\mu\text{g}\cdot\text{m}^{-3}$)	$[CH_3NH_2]$ ($\mu\text{g}\cdot\text{m}^{-3}$)
250	250	300 - 7500
100	100	100 - 12700

For both series:
Increasing $[CH_3NH_2]_0$ increases total particle number significantly



Influence of basic contaminants (methylamine) on SOA formation

The presence of methylamine increase SOA mass and number

Methylamine can interfere in different ways in limonene ozonolysis:

✓ Limonene + O₃ → organic acids in gas and condensable phase



❖ Acid – base reaction in gas phase:
between gaseous acid products and
methylamine



Induce nucleation and form clusters



❖ Reaction between methylamine and acidic particles



Condensation of amine into the acidic particulate
phase → formation of condensable salts
→ increase of SOA mass

✓ Methylamine oxidation by O₃ and OH radicals produce SOA (Y= 5 – 15 %)

Conclusion générale

- ✓ *Formation d'AOS dans l'ozonolyse du limonène :*
 - *Y et M_0 obtenus en réacteur à écoulement et en chambre de simulation en bon accord avec la littérature*
 - *Seuils de nucléation en bon accord avec la littérature*

- ✓ *Présence de piègeurs de radicaux OH*
 - *M_0 et N significativement réduits*
 - *Seuils de nucléation plus élevés*
 - *Effets attribués à une modification des produits de réaction et à une chimie des radicaux peroxy différente → Rôle de la voie hydroperoxide dans la formation des AOS*

- ✓ *Présence de piègeurs de sCl diminue significativement M_0 et N et retarde la formation de nouvelles particules → réactions des sCl avec les piègeurs → Rôle des sCl dans la formation des AOS*

- ✓ *Présence de composés basiques augmente la formation d'AOS*
 - *Réactions acide-base en phase gaz qui induit la nucléation et/ou en phase particulaire qui augmente M_0*
 - *Confirme des observations récentes d'espèces azotées dans l'AO en forêt boréale (Finlande)*

Thanks to

