

# Importance of the interconnection of the day- and night- chemistry of $\alpha$ -pinene - experiments in the ACD-C aerosol smog chamber

**Agata Kołodziejczyk**

Leibniz Institute for Tropospheric Research, Leipzig, Germany  
Atmospheric Chemistry Department (ACD) ✉ [agata@tropos.de](mailto:agata@tropos.de)



Atmospheric physics seminar, 19.11.2021



- Aerosol smog chamber experiments to investigate the aerosol transformation and its physicochemical properties;

## Importance of the interconnection of the day- and night- chemistry of $\alpha$ -pinene – experiments in the ACD-C aerosol smog chamber

### PRESENTATION CONTENT:

- Secondary Organic Aerosol (SOA) overview
- Aerosol Smog Chamber set-up (ACD-C)
- Interconnection of the day- and night- chemistry of  $\alpha$ -pinene project motivation
- Conducted experiments (experimental protocol)
- Secondary Organic Aerosol formation from  $\alpha$ -pinene oxidation
- Summary

# Atmospheric Aerosols - sources

Los Angeles<sup>[2]</sup>



A

Silesian Beskids<sup>[3]</sup>



C

Warsaw<sup>[1]</sup>



B

Eyjafjallajökull (Iceland)<sup>[3]</sup>



D

## Impact on:

- Radiation balance of our planet
- Climate changes
- Human health and quality of life<sup>[4]</sup>

Total PM emissions (primary and secondary) from different sources. The emission units are: Tg/year, while for BLZO it is TgC/year, for DMS TgS/year

Aerosol	Type of source: Natural (N) or anthropogenic (A) source	Emission scale <sup>[5,6]</sup>
Mineral Dust	N,A	1000 – 4000
Sea Salt	N	1400 – 6800
Volcanoes	N	50 (changing)
Dimethyl Sulfide (DMS)	N,A	10 – 40
Forest Fires	N,A	3 – 150
Antropogenic dust	A	290
Biogenic Volatile Organic Compounds	N	500 – 1200
<b>Total</b>		<b>3000 - 13000</b>

*Examples of different types of atmospheric aerosol*

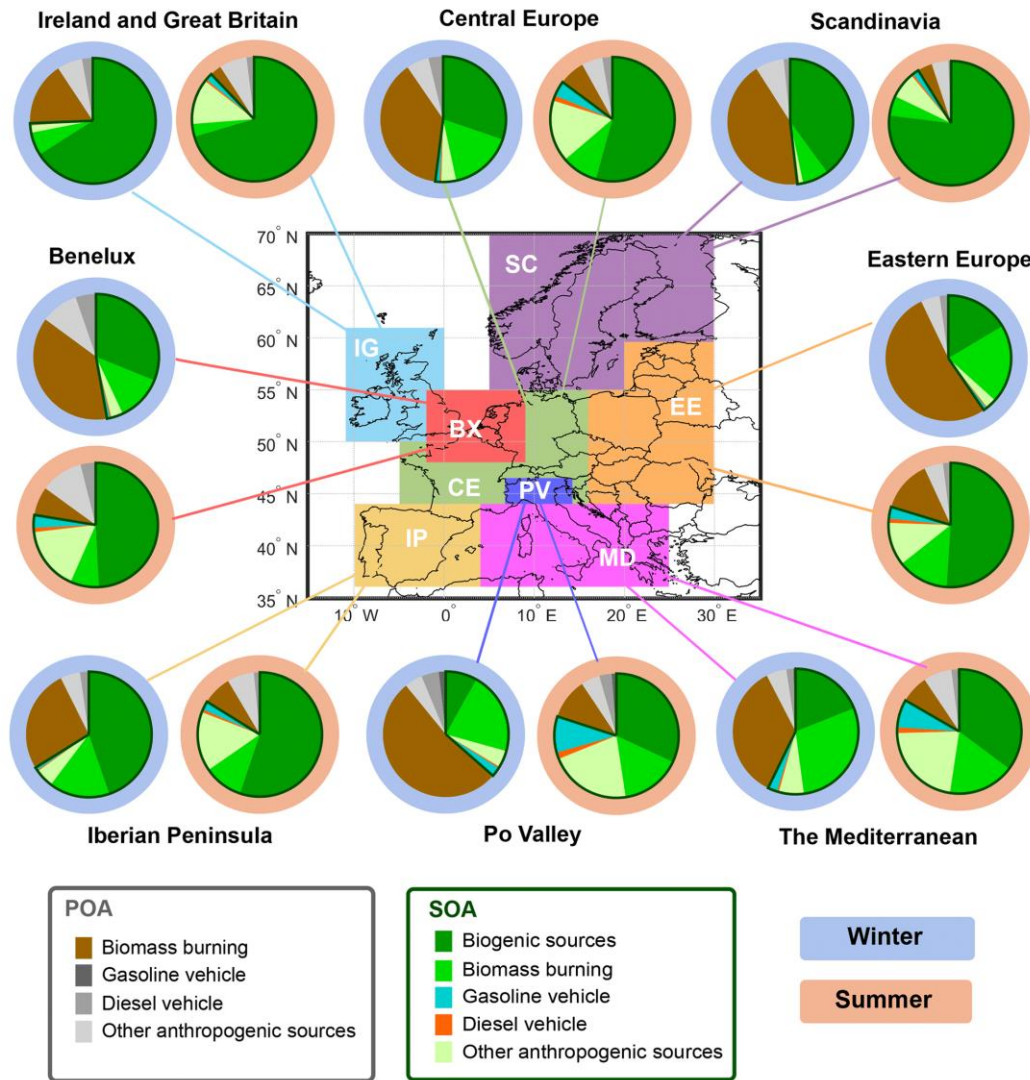
**TROPOS**

[5] John H. Seinfeld, Spyros N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 3rd Edition;

[6] Finlayson-Pitts & Pitts, Chemistry of the Atmosphere;



# Atmospheric Aerosols in Europe

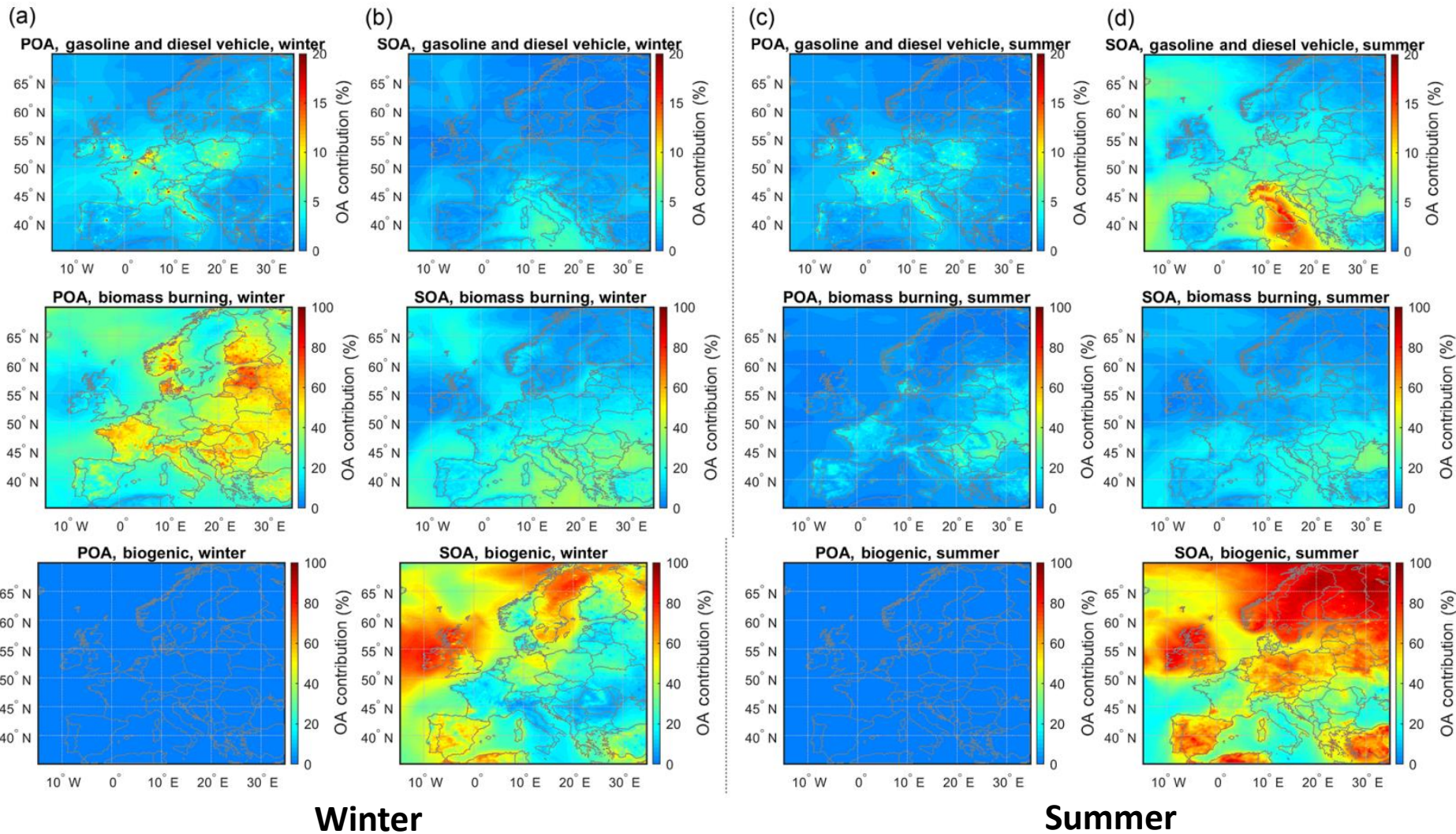


- In winter, the largest contribution over the whole domain comes from biomass burning from residential and agriculture activities (overall 43%);
- In summer, the biogenic SOA contributed up to 55 % of total OA in Europe;
- The contributions of gasoline and diesel vehicles to total OA were rather small compared to the other sources, with an average fraction of  $\sim 5\%$  (3.9 % in winter and 6.3 % in summer for the sum of POA and SOA)

**Modeled regional variations of primary and secondary organic aerosols sources in Europe in winter (December–January–February) and summer (June–July–August).<sup>[7]</sup>**

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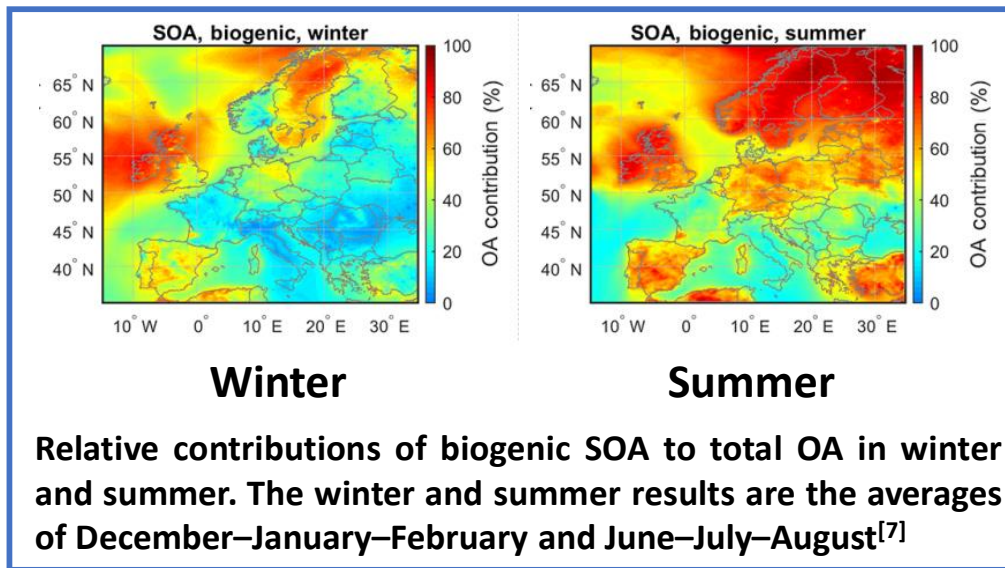
# Atmospheric Aerosols in Europe



Relative contributions of different sources (POA and SOA) to total OA in winter (a, b) and summer (c, d). The winter and summer results are the averages of December–January–February and June–July–August, respectively. OA from biogenic sources is all secondary so the POA panels for biogenic sources are empty.

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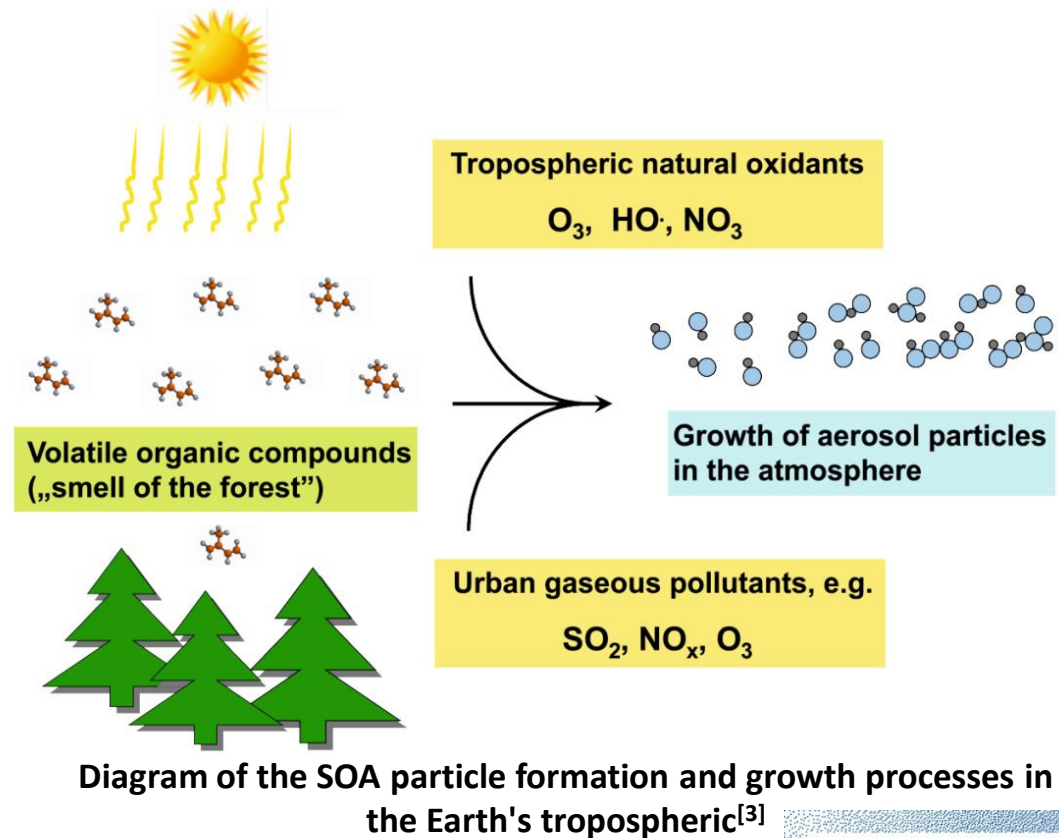




**Atmospheric oxidant and its average concentration<sup>[8]</sup>**

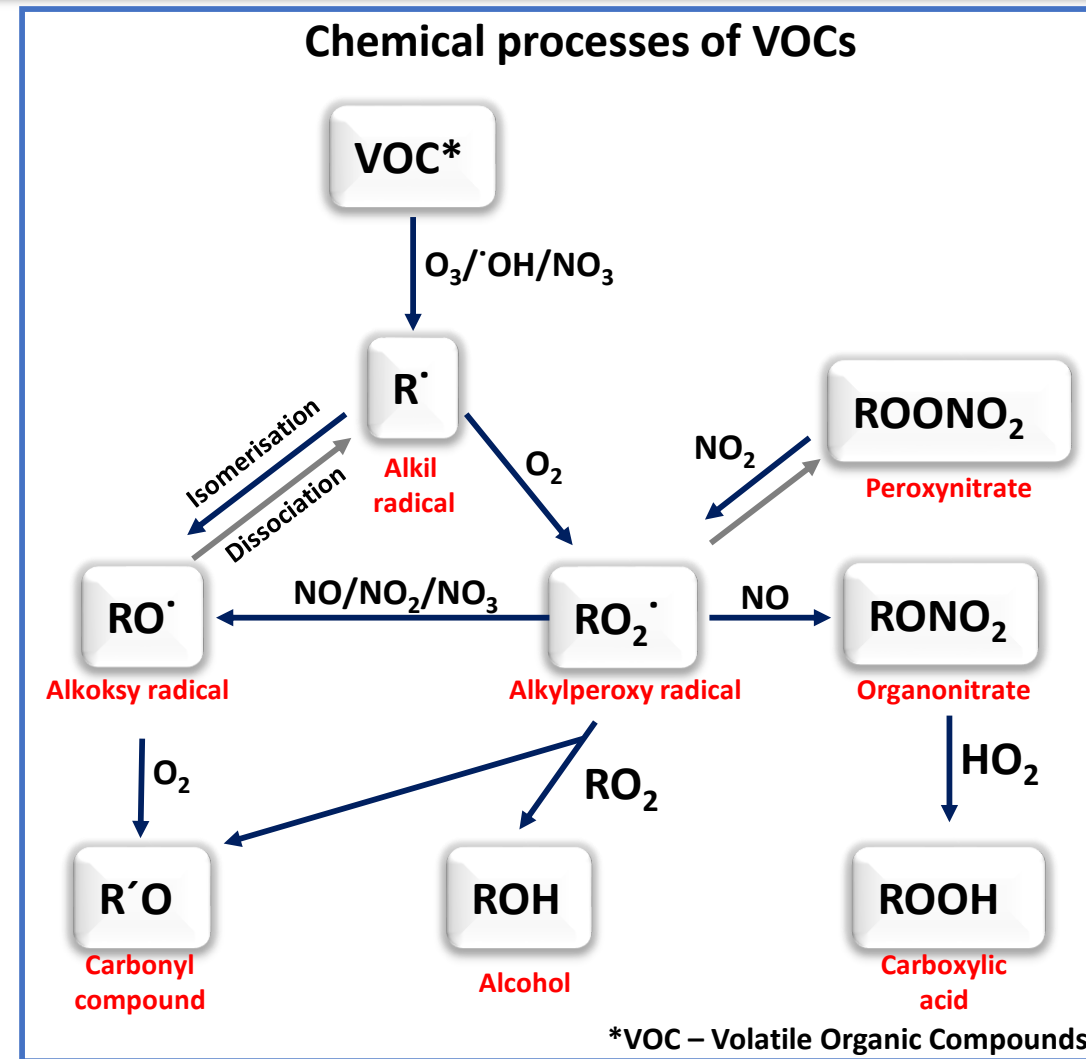
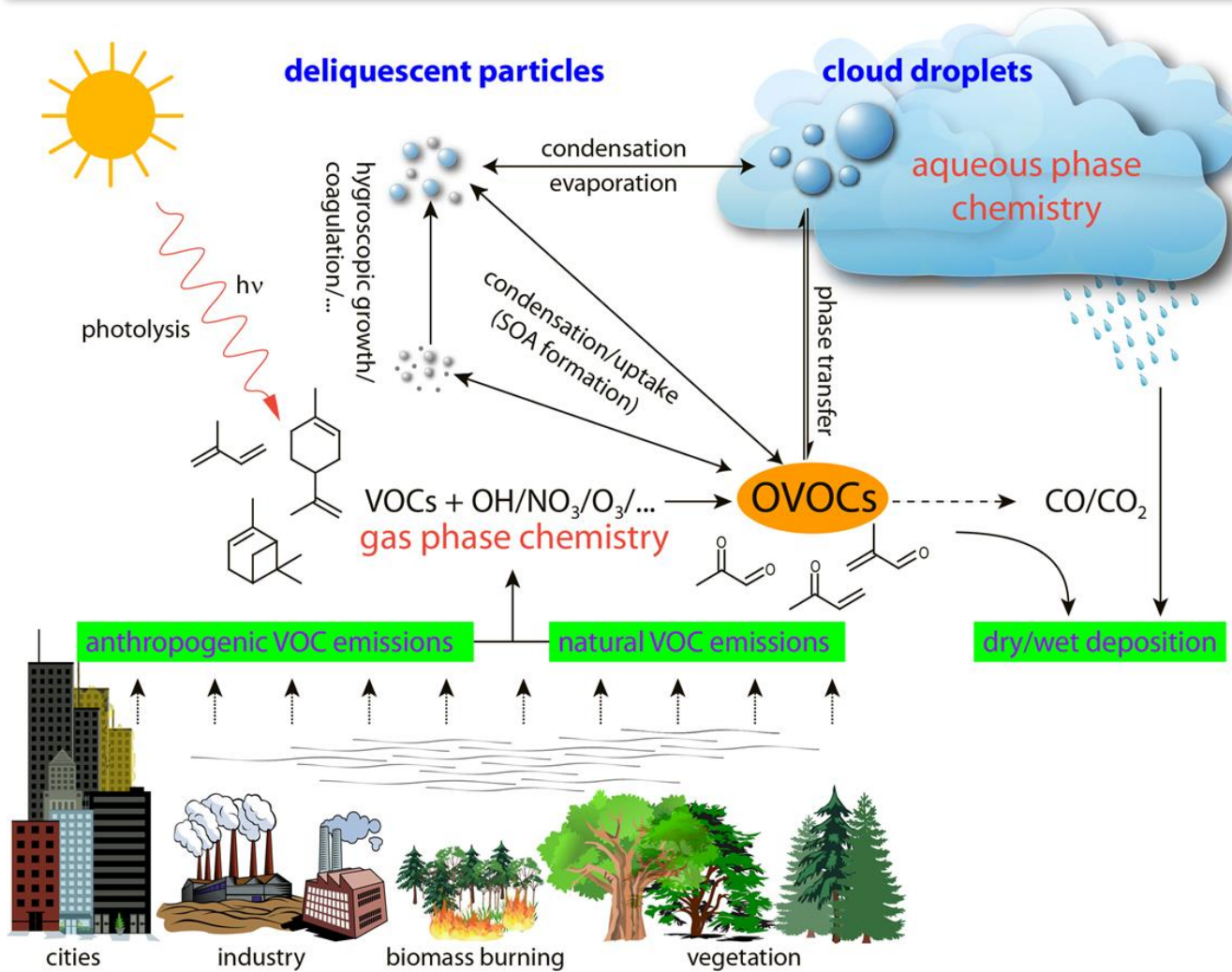
Oxidant	$k_{\text{Ox}+\beta\text{-pinene}}$	Average [Ox] (molecule/cm)
$\text{O}_3$	$1.5 \times 10^{-17}$	$7 \times 10^{11}$ (30 ppb) (24h average)
OH	$7.9 \times 10^{-11}$	$1 \times 10^6$ (0.04 ppt) (12h average)
$\text{NO}_3$	$2.5 \times 10^{-12}$	$2.4 \times 10^8$ (10 ppt) (12h average)

- Biogenic emissions: 500 – 1200 Mt C/year
- Oxidation of volatile organic compounds (VOCs) by OH,  $\text{O}_3$  and  $\text{NO}_3$  yields semi-volatile reaction products



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# Secondary Organic Aerosol Chemistry



Major processes in atmospheric organic chemistry. The fate of organic compounds in the atmosphere can be seen as competition between complete oxidation to CO<sub>2</sub> (fragmentation), functionalization also contributing to organic aerosols (OA), and deposition.<sup>[9]</sup>

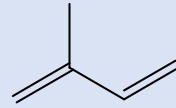
[9] M. Hallquist et al.: SOA: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, 2009

# Precursors of Secondary Organic Aerosol

## Biogenic SOA precursors

### Hemiterpene (C<sub>5</sub>H<sub>8</sub>)

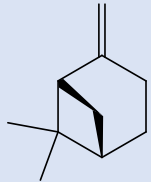
Estimated emission: 350 – 800 Tg/year



isoprene

### Monoterpene (C<sub>10</sub>H<sub>16</sub>)

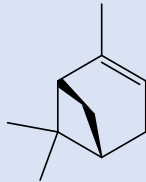
Estimated total emission: 127 – 177 Tg/year



$\alpha$ -pinene

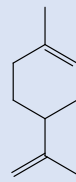
Estimated  
Emission  
(Tg/year):

45 – 70



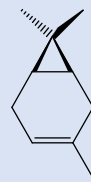
$\beta$ -pinene

15 – 25



limonene

7 – 15

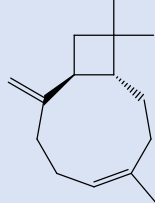


$\delta$ -3-carene

3 – 6

### Sesquiterpene (C<sub>15</sub>H<sub>24</sub>)

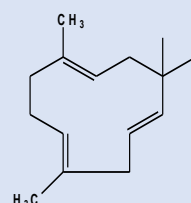
Estimated total emission: 18 – 25 Tg/year



$\beta$ -caryophyllene

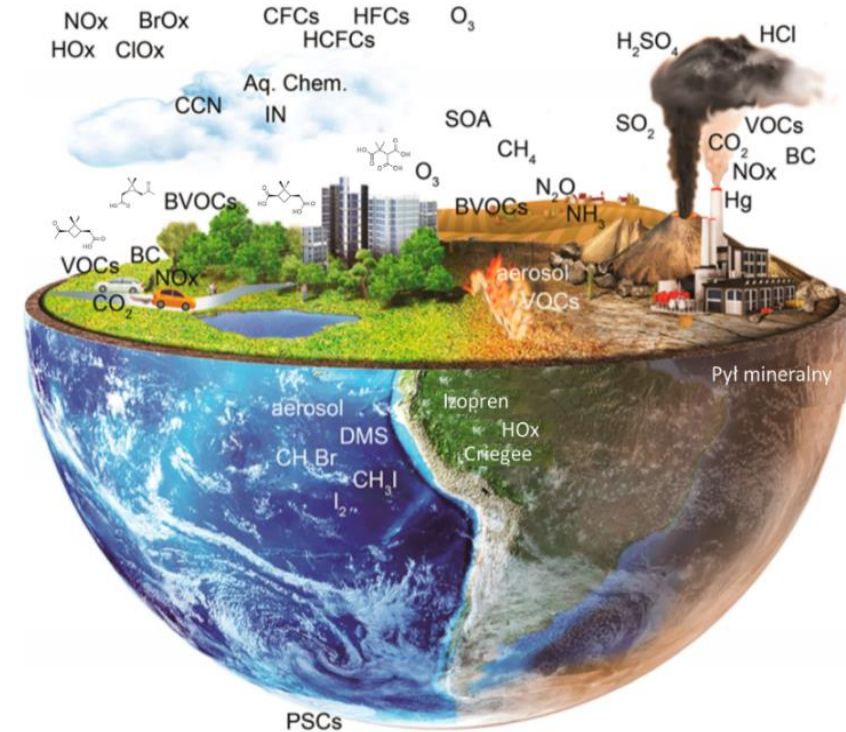
Estimated  
Emission (Tg/year):

4 – 7



$\alpha$ -humulene

2 – 3



Earth Atmosphere = Chemical reactor

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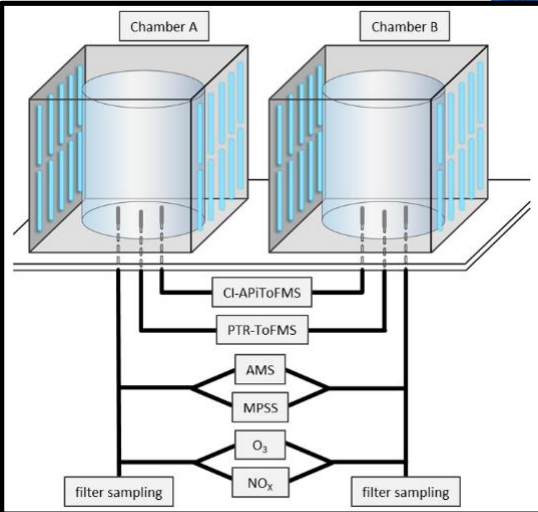
# Aerosol Smog Chamber

ACD-C with its twin chamber set-up is a research infrastructure with broad online and offline instrumentation to study:



Multiphase chemistry

SOA formation processes



- Two identical chambers (V = 19 m<sup>3</sup>, FEP foil)
- T-controlled (5–40 °C)
- 56 UV lamps (each)
- Equipped with state-of-the-art online instrumentation

VOC degradation mechanism



Toxicological effects of formed SOA



## Particle - phase

On-line measurements of:

- Particle size distribution
- Particle compositions
- Time series of Org, NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub> components



Aerosol Mass Spectrometer (AMS) [10]



Mobility Particle Size Spectrometer (MPSS)



ACD-C smog chamber

## Gas - phase

On-line measurements of:

- Precursor consumption
- Gas-phase organic composition
- Chemical formula of measured compounds

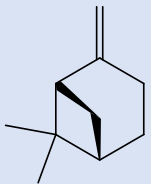


Proton-Transfer-Reaction Time of Flight Mass Spectrometer (PTR-ToFMS) [11]



Chemical Ionization-Atmospheric Pressure Time of Flight Mass Spectrometer (CI-API-TOFMS) [11]

Trace gas analysers:  
(Nox, O<sub>3</sub>, SO<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>)

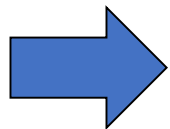


**$\alpha$ -pinene**

Estimated  
Emission  
(Tg/year):

45 – 70

- The chemistry that takes place during the day time influences the subsequent night-time chemistry and vice versa;
- In the evening when the OH radical production drops down, the VOCs and their oxidation products that remain in the atmosphere are subjected to the nighttime chemistry in which the  $\text{NO}_3$  radicals and ozone are most important;
- $\alpha$ -pinene is the second foremost release Biogenic Volatile Organic compound.



**The inter-connection of day- and night-time chemistry is a so-far unknown pathway of SOA formation**

### Main points:

- Understand the interconnection of day- and night-time  $\alpha$ -pinene chemistry

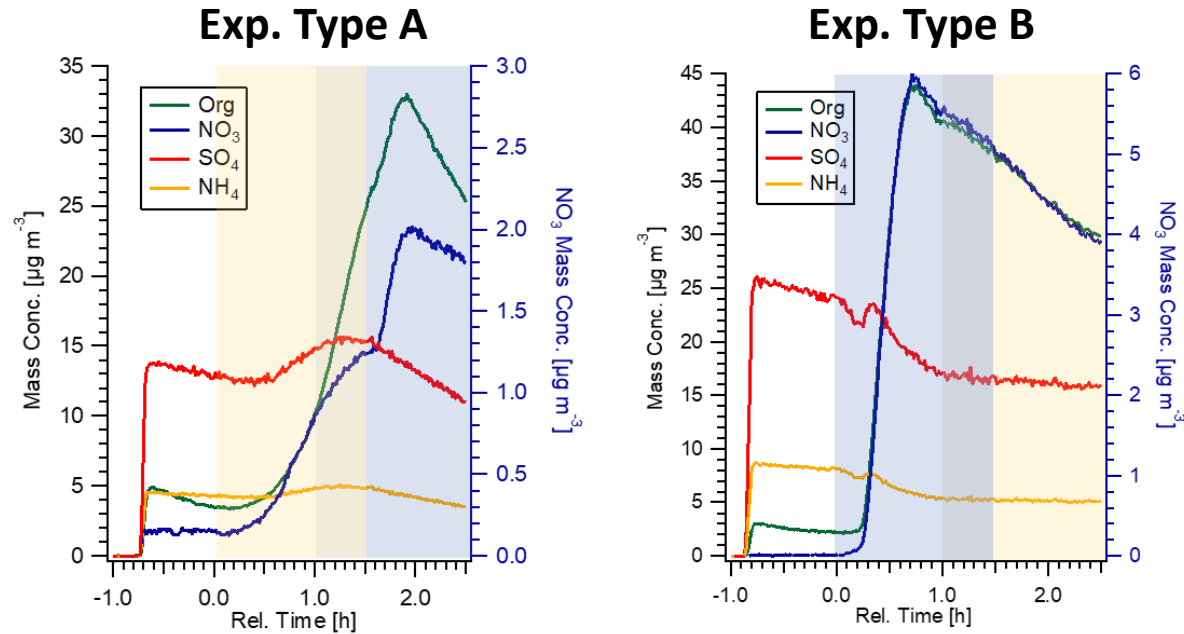
OH radical

$\text{NO}_3$  radical



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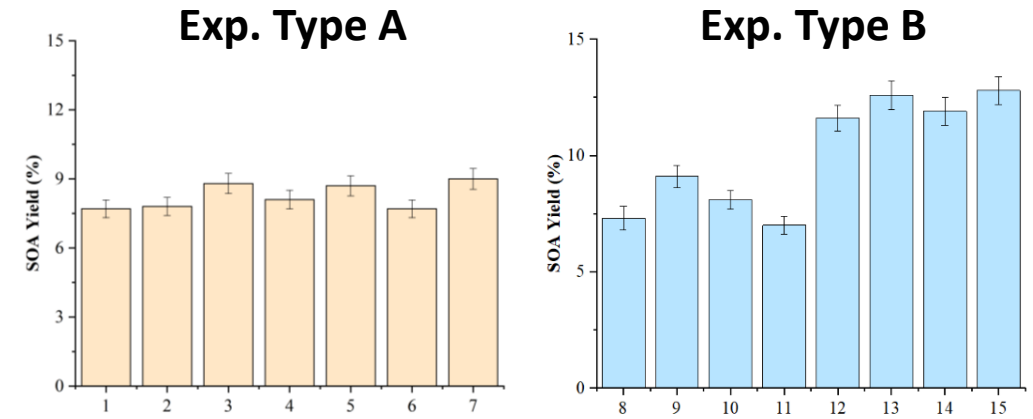




**Example of HR-ToF-AMS measurements of the  $\alpha$ -pinene reaction. Time series of AMS organic (Org), nitrate ( $\text{NO}_3$ ), sulfate ( $\text{SO}_4$ ) and ammonium ( $\text{NH}_4$ ) signals.**

- Exp. Type A: After day-time when 10% pinene is in the system (from 4 – 8 ppb) new particles are still produced;
- Exp. Type A: Organic mass is increasing together with increasing RH;
- Exp. Type B: SOA yield is slightly increasing together with increasing RH (from 8% to 12%);
- Exp. Type B: There is strong decay of organic mass in day-time period, which can be connected with volatilization process or further reaction of organonitrate group.<sup>[12]</sup>

## SOA Yield for conducted experiments

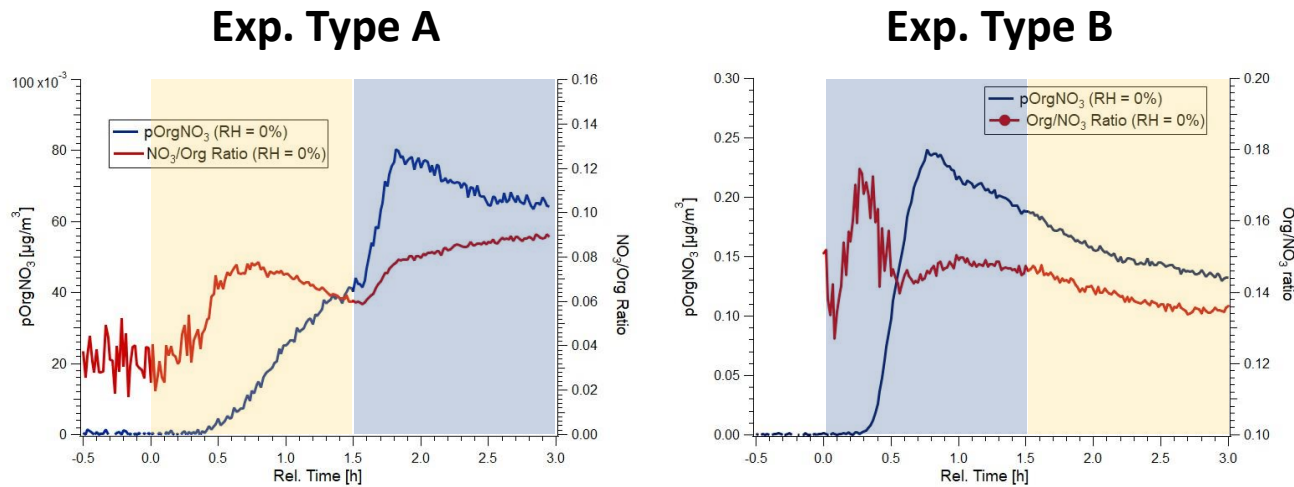


Precursor compound	Radical reaction	Literature reference
$\alpha$ -Pinene	$\text{NO}_3$	0.2–16 % (Hallquist et al., 1999); 4 or 16 % (Spittler et al., 2006); 1.7–3.6 % (Nah et al., 2016); 0 % (Fry et al., 2014); 9 % (Perraud et al., 2010); 0.3–6.9 % (Moldanova and Ljungstrom, 2000) 5.9 - 6.7 % (Mutzel et al. 2020)
	$\text{OH}$	21.2 % (Ng et al., 2007); 3.4 - 4.3 % (Mutzel et al. 2020)

# Particle-phase – Identification of Organonitrate formation

⇒ **D. K. Farmer et al. 2010:** “Organonitrates (ON) are important products of gas-phase oxidation of volatile organic compounds in the troposphere”

⇒ (Organonitrates: (ON, i.e.,  $\underline{RONO_2}$ ))



- Exp. Type A: ON are form, but during the dark conditions the increase is sharper and then stays fairly constant;
- Exp. Type B: the  $NO_3/Org$  ratio stays fairly constant during the  $NO_3$  reaction, which suggests that tertiary ON are not formed in the  $NO_3+\alpha$ -pinene reaction
- Exp. Type B: the loss of particle-phase ON via hydrolysis results a decrease in the  $NO_3/Org$  ratio due to the formation (and subsequent evaporation) of nitric acid.<sup>[13]</sup>

Kiendler-Scharr et al. (2016): “[...] determine the fraction of particulate organic nitrate ( $pOrgNO_{3frac}$ ) in the measured total nitrate”

$$pOrgNO_{3frac} = \frac{(1 + R_{OrgNO_3}) * (R_{measured} - R_{calib})}{(1 + R_{measured}) * (R_{OrgNO_3} - R_{calib})}$$

$$pOrgNO_{3mass} = pOrgNO_{3frac} * NO_{3total}$$

Ratios  $NO_2^+ / NO^+$ :

$R_{OrgNO_3}$  - organonitrate compounds (0.1)

$R_{measured}$  - measured ratio

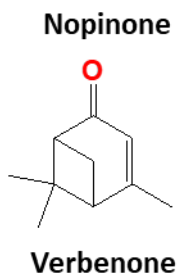
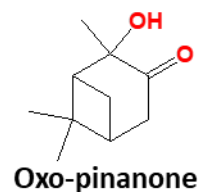
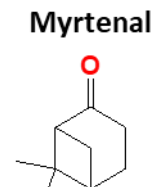
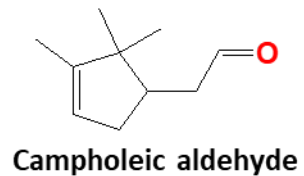
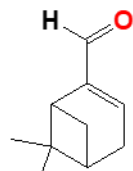
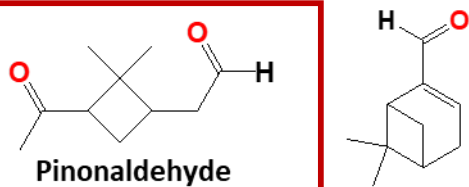
$R_{calib}$  - ammonium nitrate signal during AMS calibration.

Instrument depend (0.31)

## Quantified compounds

### Derivatize with DNPH

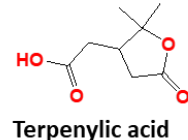
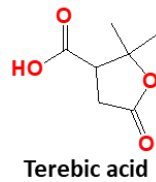
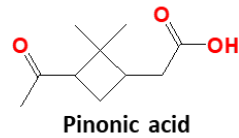
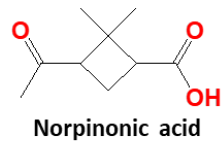
First generation product of  $\alpha$ -pinene oxidation



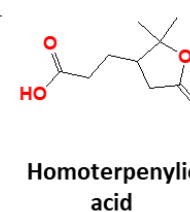
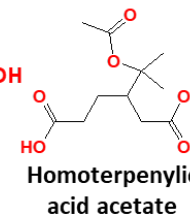
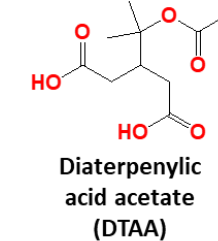
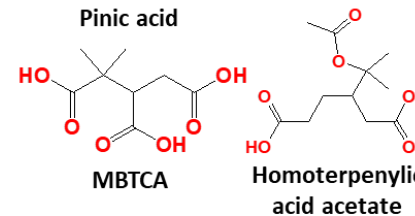
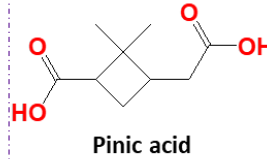
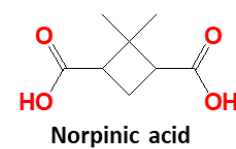
### Non-derivatized compounds

Further generation product of  $\alpha$ -pinene oxidation

#### Second-generation

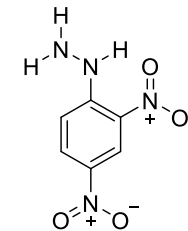


#### Three and more - generation

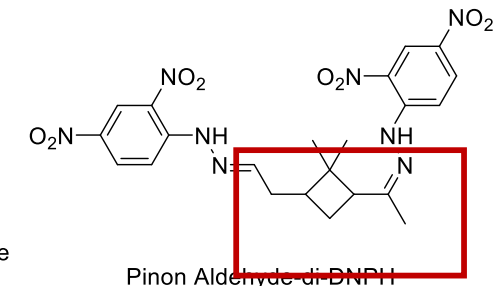


- Filter sample were taken after 1h of each reaction;
- All compounds were quantified using authentic standards;
- SOA- bond organic peroxides were quantified using UV-vis method<sup>[14]</sup>

### Derivatization agent

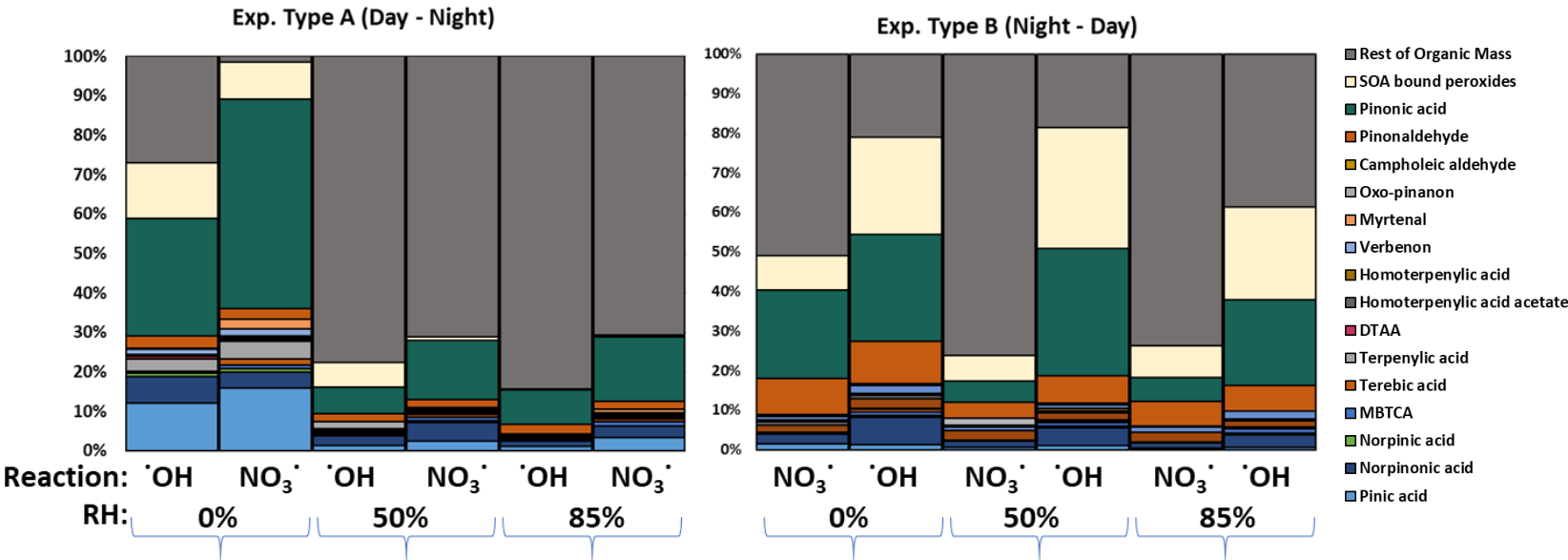


2,4-Dinitrophenylhydrazine (DNPH)





## Quantification results using LC-ToF-MS system



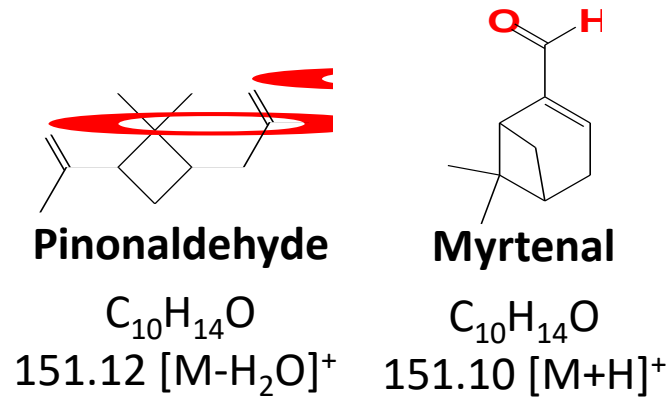
- Filter sample were taken after 1h of each reaction;
- All compounds were quantified using authentic standards;
- SOA - bond organic peroxides were quantified using UV-vis method<sup>[14]</sup>

- Important fraction in both type of experiment is **pinonaldehyde** (known as a first generation product of  $\alpha$ -pinene oxidation) and **pinonic acid** (known as a second generation product);
- For NO<sub>3</sub> radical reaction only 20% of fraction is identify, which can be connected with ON compound group;
- Compounds which cover smaller fraction shows interesting correlation only with one type of radicals (like MBTCA, Terebic acid, Homoterpenylic acid acetate);
- Exp. Type A: Surprisingly SOA-bound peroxides was not significant fraction when OH radical reaction was the starting periode;
- Exp. Type B: SOA-bound peroxides constitute almost 30% of fraction during the OH radical reaction;

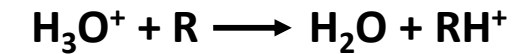


# Gas-phase – PTR-ToF-MS measurement

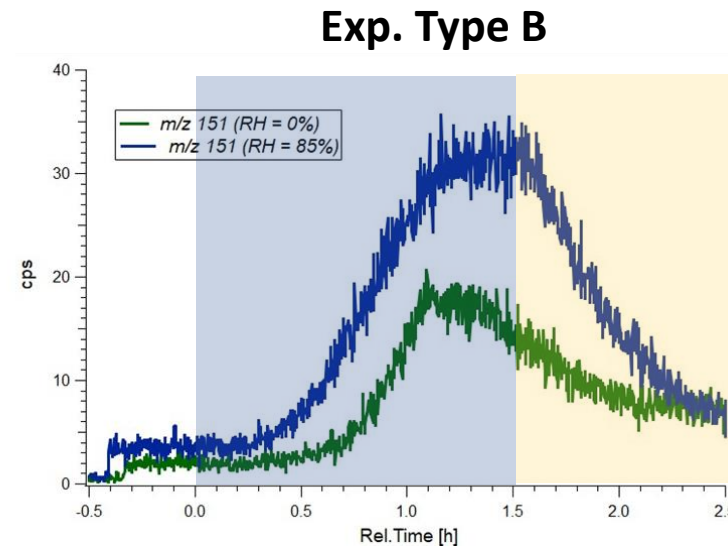
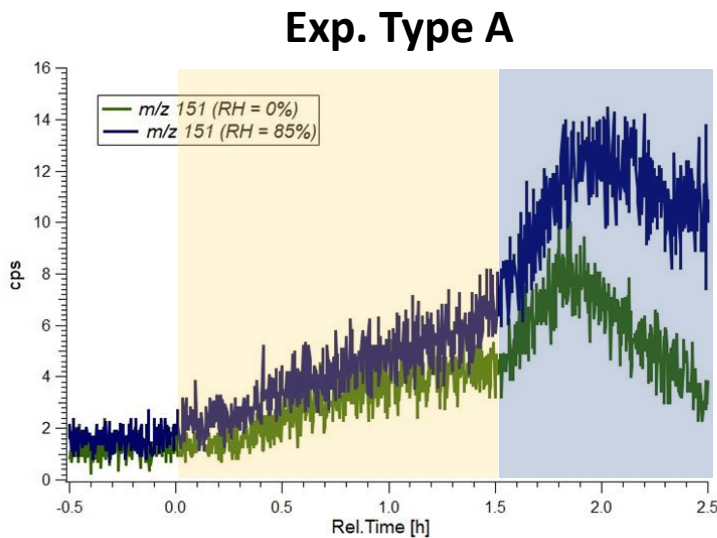
- Almost 20 masses was found to increase during the pinene oxidation reaction for both experiment Type;
- $m/z$  151 was found to be most intensive peak – usually described as pinonaldehyde ( $-H_2O$ ), but also for myrtenal<sup>[14]</sup>



**PTR-ToF-MS ionisation principal – Proton Transfer Reaction:**



For all compounds which have lower proton affinity than  $H_2O$  (691 kJ/mol)

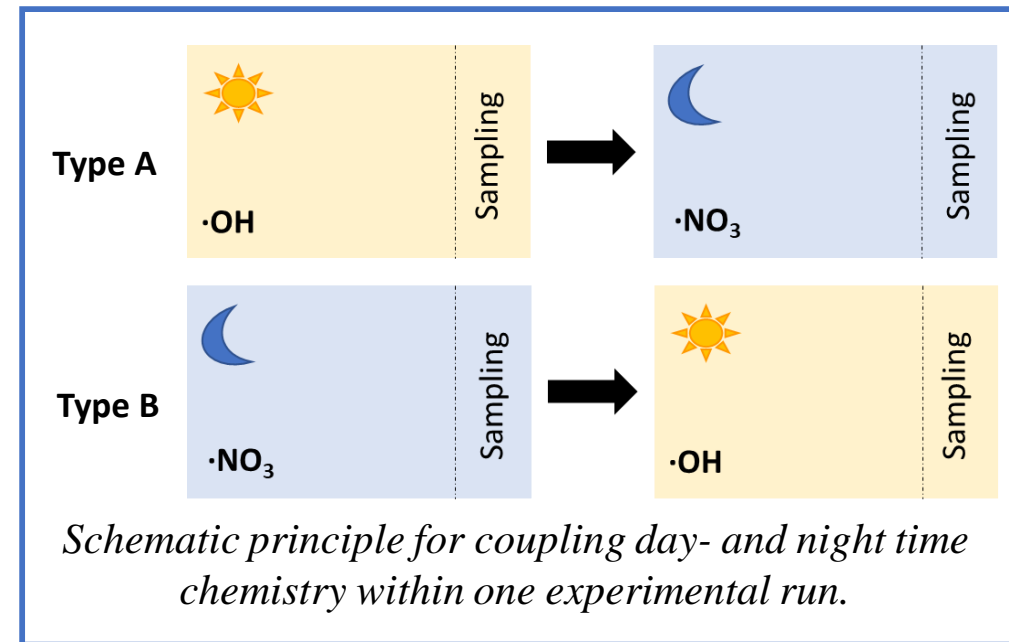


Time series of  $m/z$  151 signal recorded with PTR-MS for both Typ of experiments.

- $m/z$  151 with  $m/z$  169 do not correlate each other, that shows during the OH radical reaction more propable product correspond to  $m/z$  151 is myrtenal;
- For  $NO_3$  radical reaction pinonaldehyde is the most important first-generation oxidation product;

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- The interconnection of day- and night-time chemistry is complicated but crucial to understand the BSOA formation;
- Particles which are formed during the day-time and then react further in the night-time have different composition than particles formed in vice-versa process;
- SOA bond peroxides are an important group of compounds which are possibly formed from ON compounds (night-time chemistry);
- After the ON are created during the night-time process, they are lost via hydrolysis reaction, which is observed from a decrease in the  $\text{NO}_3/\text{Org}$  ratio (AMS measurements);
- Evaporation processes can be an important pathway of particle mass decrease, but this statement needs further studies;







**prof. Hartmut Herrmann**

Leibniz Institute for  
Tropospheric Research

**Group members of Atmospheric Chemistry Department of TROPOS**

**Thank you for you attention!**

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