

Chemical analysis of particulate and gaseous products from the monoterpene oxidation in the SAPHIR chamber during the EUCAARI campaign 2008

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Introduction

- The atmospheric oxidation of monoterpenes produces a number of multifunctional oxidation products which can condense on pre-existing particles.
- The chemistry of secondary organic aerosol (SOA) is complex and still largely unknown.
- The work package 1.2 of the EUCAARI project aims to study the processes of aerosol formation from the oxidation of realistic and complex biogenic volatile precursors.
- The EUCAARI 2008 campaign took place in June/July where formation and aging processes of organic aerosols were studied in the SAPHIR outdoor chamber in Jülich.
- The oxidation of different monoterpenes including aging processes within a time scale of two days was investigated.



Fig. 1: SAPHIR chamber in Jülich

Experimental

- The Boreal Mix was made of α -pinene, β -pinene, limonene, 3-carene and ocimene.
- In addition, two sesquiterpenes, α -farnesene and caryophyllene, were added in some experiments to the mixture (see Table 1).
- The oxidation was performed under natural atmospheric HO_x , light intensity and low NO_x conditions.
- The formed products were sampled using a denuder/PTFE filter technique at the end of the day one for the freshly generated products and at the end of the day two for the aged particles.
- In collaboration with the work package partners the different experimental parameters were comprehensively studied (e.g. aerosol hygroscopicity, volatility and product distribution).

Table 1: Experimental conditions

Experiment number	EUC08_1_1	EUC08_2_1	EUC08_4_1	EUC08_7_1	EUC08_7_2
Boreal Mix	50ppb	50ppb	50ppb	100ppb	Photochemical aging of particles from EUC08_7_1
	with ocimene	without ocimene	-	-	
Sesquiterpenes	-	-	5ppb	10ppb	
Filter number	3	5	9	15	16

Carbonyl compound analysis from denuder and filter samples

- Both the denuder and a half of the filter were extracted and subsequently derivatised with 2,4-dinitrophenylhydrazine (DNPH).
- After purification using solid phase extraction cartridges, the samples were analysed using HPLC/(-)ESI-TOFMS.
- The identification of the carbonyl-derivatives was based on the determination of the exact chemical formula using the highly sensitive TOFMS and the comparison to the retention times and mass spectra of derivatised authentic standards (e.g. endolim, nopinone, pinonaldehyde).

Acidic compound analysis from filter samples

- After extraction of the other half filter with methanol, the acidic products were analysed using UPLC/(-)ESI-IMS-QTOFMS.
- With authentic standards (e.g. pinic acid, norpinic acid, pinonic acid, norpinonic acid) quantitative results were obtained.

Results and Discussion

General observations

- Due to high blank values for formaldehyde and acetone in both the denuder and filter samples these compounds were not included in this discussion.
- Nopinone, a stable oxidation product of β -pinene, was not detected in both the gas- and particle-phases
- The slower reaction of β -pinene with ozone might be the reason for this observation.
- The most abundant acidic compound in the particle-phase was pinic acid.
- In general higher VOC concentrations resulted in a higher concentration of oxidation products.

Influence of ocimene

- Ocimene can react rapidly with ozone that provides additional OH radicals in the chamber.
- In addition ocimene reacts fast with OH radicals, effectively acting as an OH radical scavenger as well.
- In the experiments where no ocimene was added to the monoterpene mixture, higher concentrations of the first generation oxidation products were observed (see Figure 2).
- For the acidic compounds in the particle-phase it is hard to conclude the influence of ocimene.

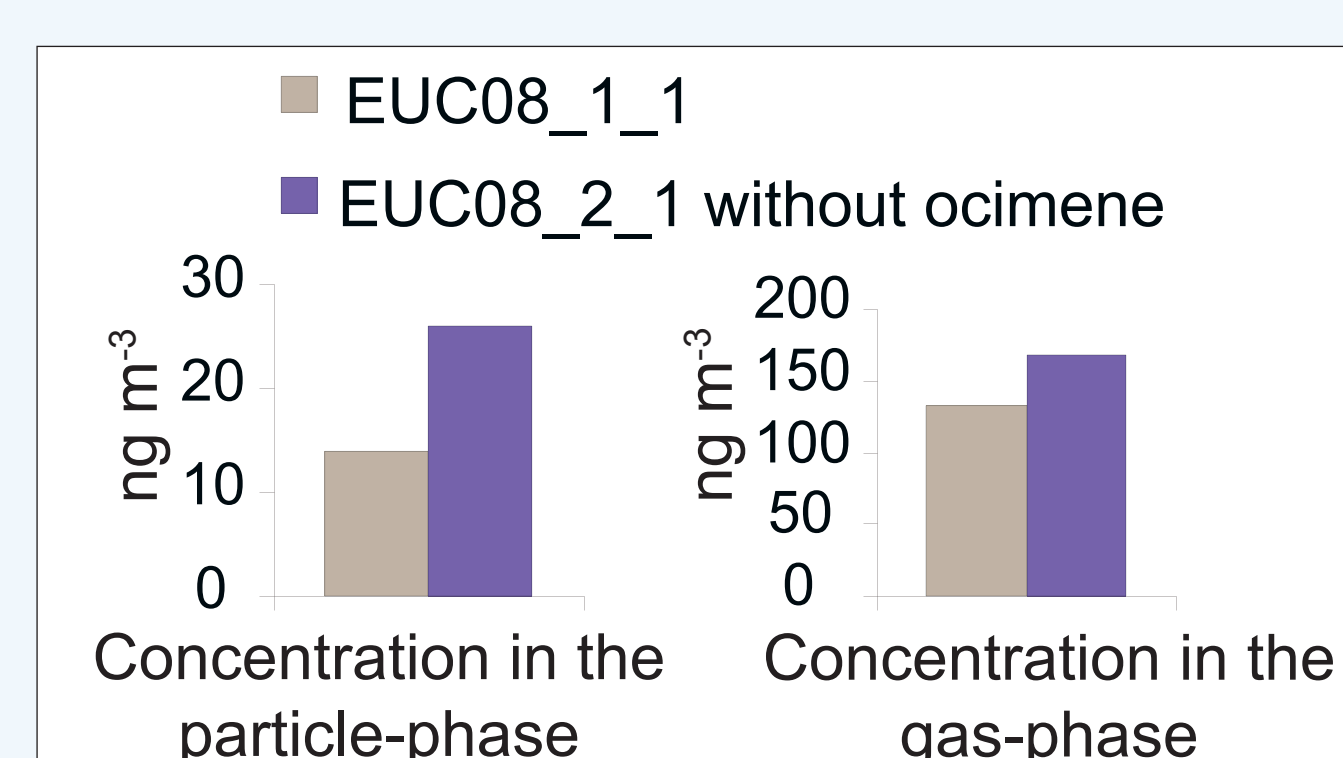


Fig. 2: The concentration of the 1st generation oxidation product pinonaldehyde in the particle- (left) and gas- (right) phases.

Influence of sesquiterpenes

- An oxidation product with one carbonyl group from sesquiterpene oxidation was detected in the filter samples from the experiments EUC08_4_1 and EUC08_7_1.

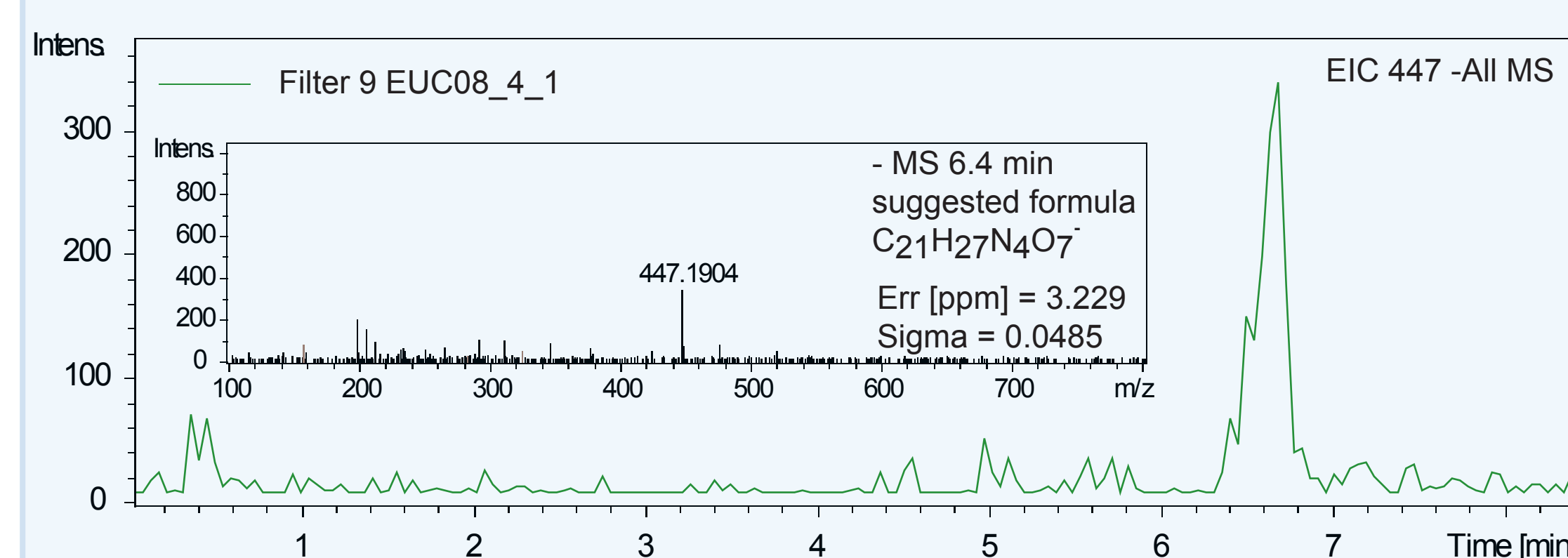


Fig. 3: Extracted ion chromatogram (EIC) of the derivatised filter sample from the experiment EUC08_4_1 with the TOFMS data of the m/z 447 compound.

- This compound was detected as its hydrazone derivative at m/z 447 ($\text{C}_{21}\text{H}_{27}\text{N}_4\text{O}_7$).
- The elemental composition of $\text{C}_{15}\text{H}_{24}\text{O}_4$ (MW 268) was determined based on the TOFMS data and the number of hydrazone groups (see Figure 3).

- Another sesquiterpene originating oxidation product was detected in the particle-phase at m/z 241 ($\text{C}_{12}\text{H}_{17}\text{O}_5$) with an intensity comparable to pinonic acid.
- The intensity of the first generation oxidation products decreased when sesquiterpenes were present in the VOC mixture, indicating their competing reaction with the monoterpenes.
- Table 2 summarises the concentrations of pinonaldehyde and endolim, which were determined in the particle-phase when sesquiterpenes were present.

Table 2: Influence of sesquiterpenes on particle-phase concentrations of 1st generation monoterpene oxidation products

Compound	Photooxidation experiment EUC08_7_1 with sesquiterpenes	Photooxidation experiment EUC08_3_1 without sesquiterpenes
Endolim	4 ng m ⁻³	43 ng m ⁻³
Pinonaldehyde	15 ng m ⁻³	22 ng m ⁻³

- The results shown in Table 2 are consistent with the experiments with ocimene where lower concentrations of pinonaldehyde were observed in the presence of ocimene.

Results of the Aging experiments

- Compared to the non-aging experiment EUC08_7_1 much higher concentrations of pinonaldehyde and endolim were observed after the photochemical aging experiment EUC08_7_2 (see Figure 4).
- This indicates a continuous production of pinonaldehyde and endolim during the aging process.
- For the particulate acidic compounds lower concentrations of oxidation products were found after the photochemical aging except pinonic acid which shows almost the same or higher concentrations than the corresponding non-aging experiment.
- The particulate pinonaldehyde concentration showed a similar trend to pinonic acid which indicates pinonaldehyde being a precursor for pinonic acid during the aging experiment.
- Pinic acid, which is believed to be a stable end product, is largely lost during the aging experiment.
- Only trace amounts of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) were detected in all samples, indicating the formation of different oxidation products.
- This observation is consistent with the suggested formation mechanisms of MBTCA which requires the presence of NO_x .
- Based on the results found here, no clear conclusions can be drawn for the influence of VOCs, concentrations used and photochemical aging.

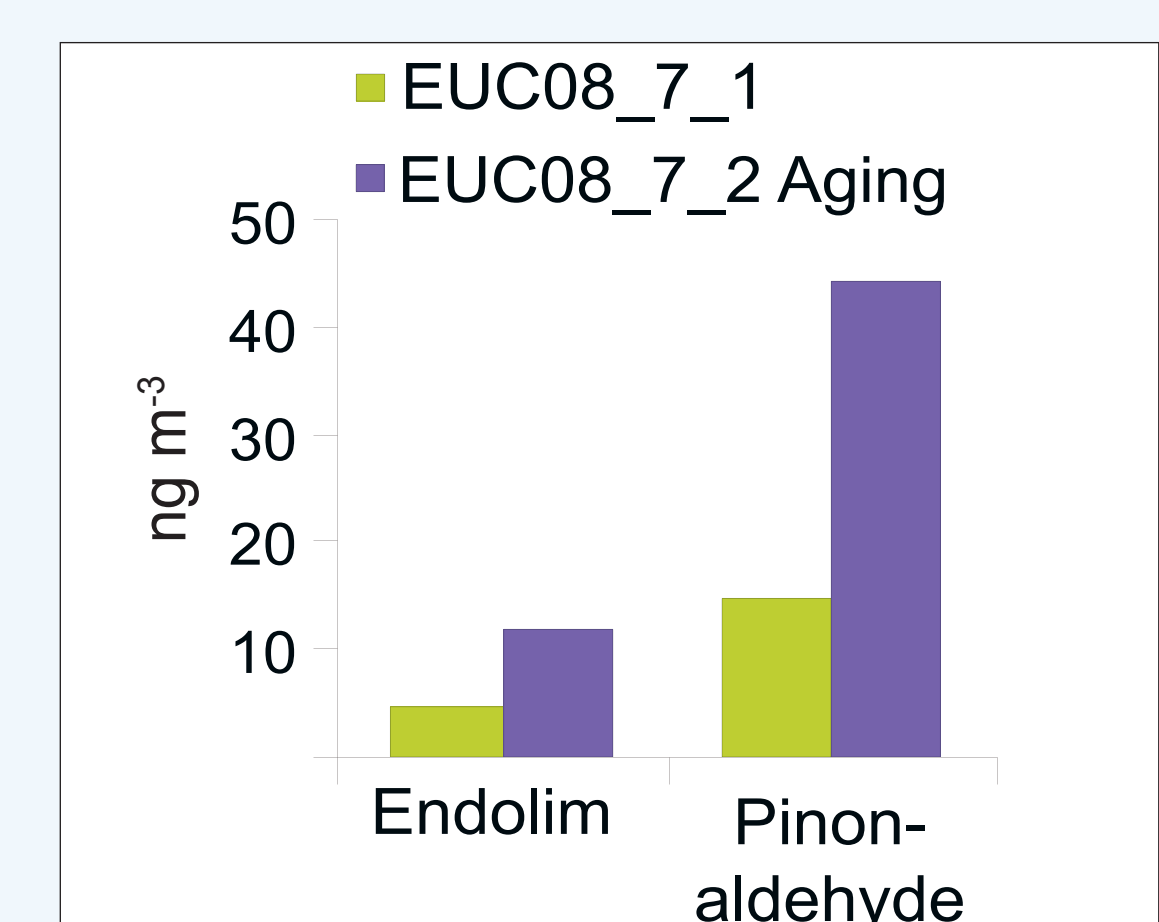


Fig. 4: The concentrations of endolim and pinonaldehyde in the particle-phase from experiments EUC08_7_1 (green) and the corresponding aging experiment EUC08_7_2 (blue).

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