

## INTRODUCTION:

A considerable lack of knowledge exists concerning the chemical composition of natural aerosols. Field observations over the past decade revealed that a significant fraction of ambient remote organic aerosol (OA) is highly oxidised (Kroll et al., 2011). The oxidation reactions (ageing) leading to formation of highly oxidised OA involve heterogeneous uptake of oxidants and multigenerational oxidation of vapours by OH radicals.

The objectives of this work are (i) to examine aging of SOA generated from a precursor mixture containing BVOCs (i.e.  $\alpha$  and  $\beta$ -pinene,  $\Delta_3$ -carene, and isoprene) that are most abundant at a remote boreal forest site Hyytiälä, Finland (Kourtchev et al., 2013) under several atmospheric conditions (e.g., UV radiation, OH radicals and acidic and neutral aerosol seed); (ii) to characterise the aged SOA using ultrahigh resolution mass spectrometry (UHR-MS); (iii) to investigate influence of different atmospheric conditions on oligomerisation of the organic components of the aerosol.

## RESULTS AND IMPLICATIONS:

### Direct Infusion MS Results:

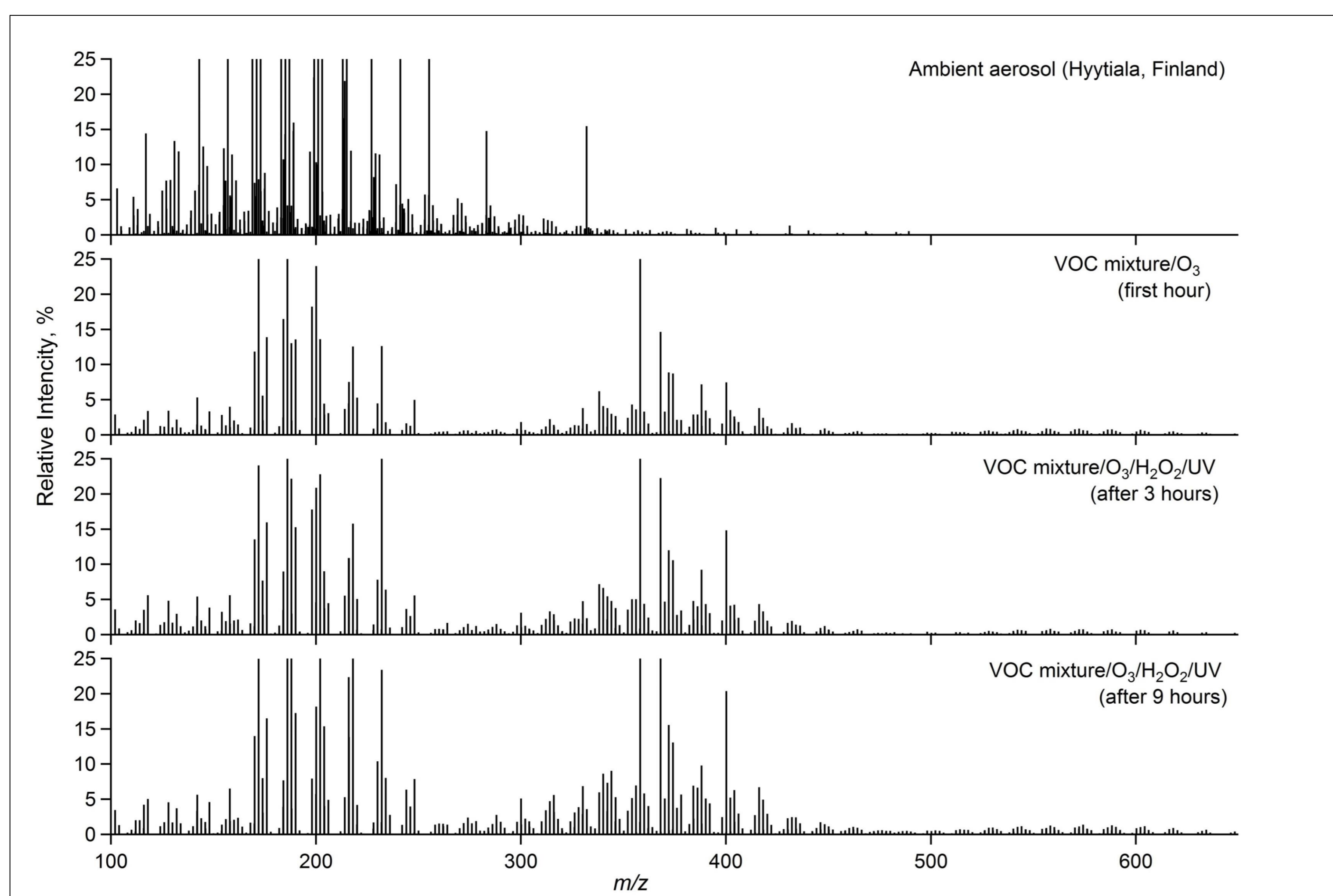


Figure 2. Direct infusion UHR-MS of the ambient and laboratory generated aerosol: ‘fresh’ SOA from the ozonolysis of the VOC mixture and OA ‘aged’ by H<sub>2</sub>O<sub>2</sub> and UV for 3 and 9 hours.

- The laboratory generated aerosol contained a large fraction of high molecular weight compounds that were not apparent in the ambient samples;
- Aerosol ageing at the current conditions did not significantly influence the occurrence of the dimers and trimers in the mass spectra (ions above 250 Da).

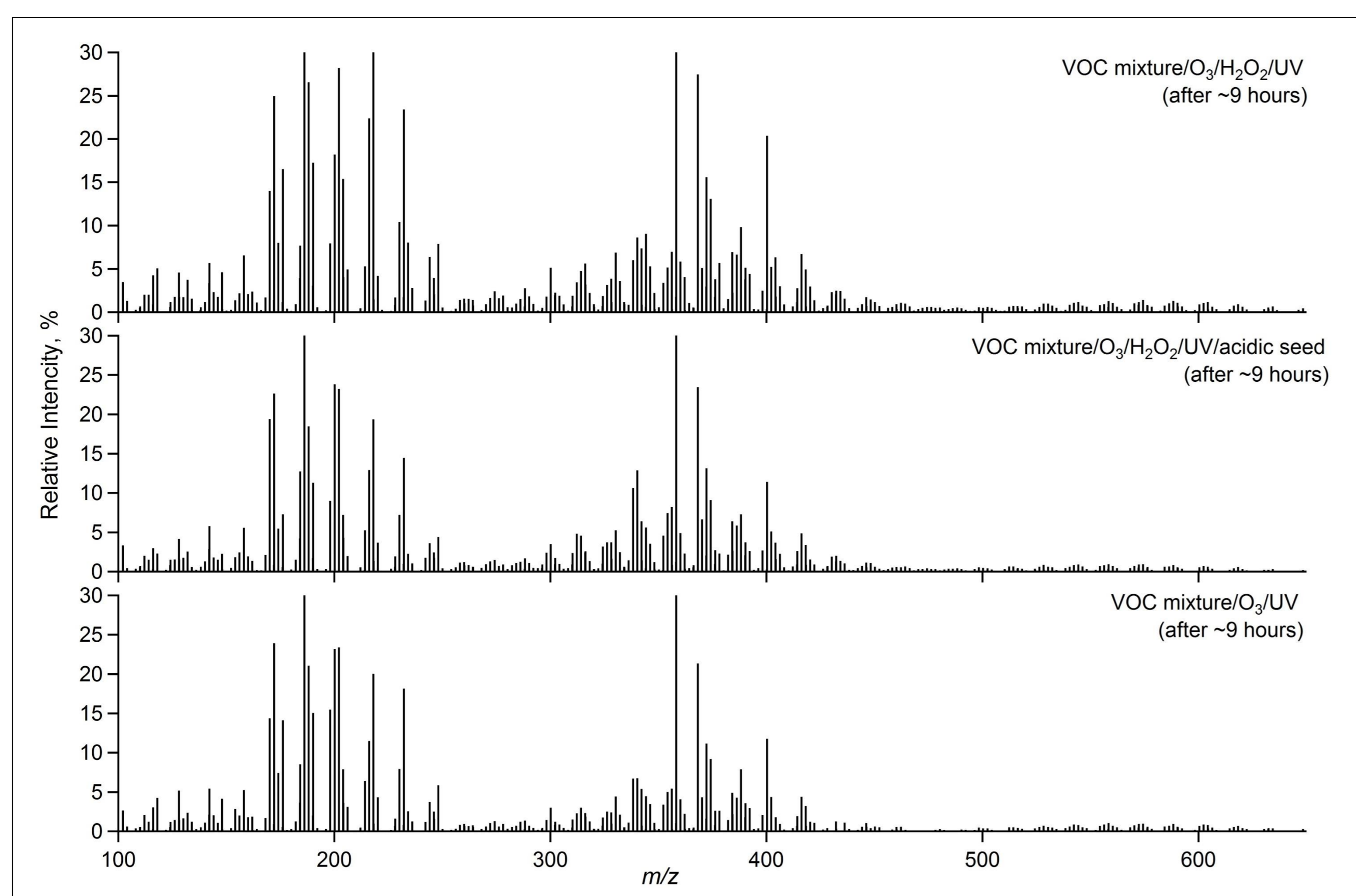


Figure 3. Direct infusion UHR-MS of the laboratory generated aerosol ‘aged’ for 9 hours under various conditions.

- No apparent difference in the mass spectral features of the dimers and trimers were observed.

## CONCLUSIONS:

- Aerosol aging under investigated conditions resulted in a slight shift of the distribution of molecules to the higher oxidation state;
- The LC/MS results indicated that one of the few dimers that were observed in the ambient aerosol (i.e.,  $m/z$  357) is not influenced by the aerosol ageing and exhibited different trend from the aged marker for oxidation of  $\alpha$ -pinene (i.e., MBTCA);
- The clear difference between the ambient and laboratory generated samples in the oligomeric region requires further investigation.

## REFERENCES:

Kroll et al., Nature Chemistry, 3, 133-139, 2011  
Kourtchev et al., Environ. Sci. Technol., 47, 4069-4079, 2013  
Müller et al., Atmos. Chem. Phys., 12, 1483-1496, 2012

## METHODS:

The experiments were carried out using 4.3 m<sup>3</sup> stainless steel CESAM atmospheric simulation chamber. The chamber was operated at 296 ± 2 K using a mixture of high purity oxygen and nitrogen at ~1 atm. SOA were formed from the reaction of VOC mixture containing  $\alpha$  and  $\beta$ -pinene,  $\Delta_3$ -carene, and isoprene (150 ppb total VOC) and ozone (450 ppb). For the OH<sup>•</sup> initiated ageing reactions, OH<sup>•</sup> were produced by H<sub>2</sub>O<sub>2</sub> photolysis using 4 kW Xe lamps. H<sub>2</sub>O<sub>2</sub> was continuously injected into the smog chamber after reaching the maximum concentration of the SOA produced from the ozonolysis reaction. For the seeded experiments, acidic aerosol seed was produced from an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. SOA samples were collected in three stages after: (a) reaching the maximum particle concentration (as measured by SMPS produced from the ozonolysis reaction of the VOC mixture, (b) ~3 hours and (c) ~9 hours of exposure of the SOA particles to the OH<sup>•</sup> and/or UV radiation.



Figure 1. CESAM atmospheric simulation chamber

- Depending on the SOA load of the sample, a portion of the filter was extracted in 5 mL methanol, filtered through 0.2  $\mu$ m PTFE filter and reduced by volume (to ~100  $\mu$ L);
- The extracts were analysed using an LTQ Orbitrap Velos fitted with a robotic nano-flow chip-based ESI source TriVersa NanoMate® and Accela LC system;
- The mass spectra were recorded in negative mode over the mass range  $m/z$  100-600 and  $m/z$  150-900 with a mass resolving power of 100,000 ( $m/\Delta m$ ) at  $m/z$  400.

## Carbon Oxidation State (OS<sub>C</sub>):

Carbon oxidation state OS<sub>C</sub> is shown to be strongly linked to aerosol volatility and thus is a useful parameter for classification of SOA (Kroll et al., 2011).

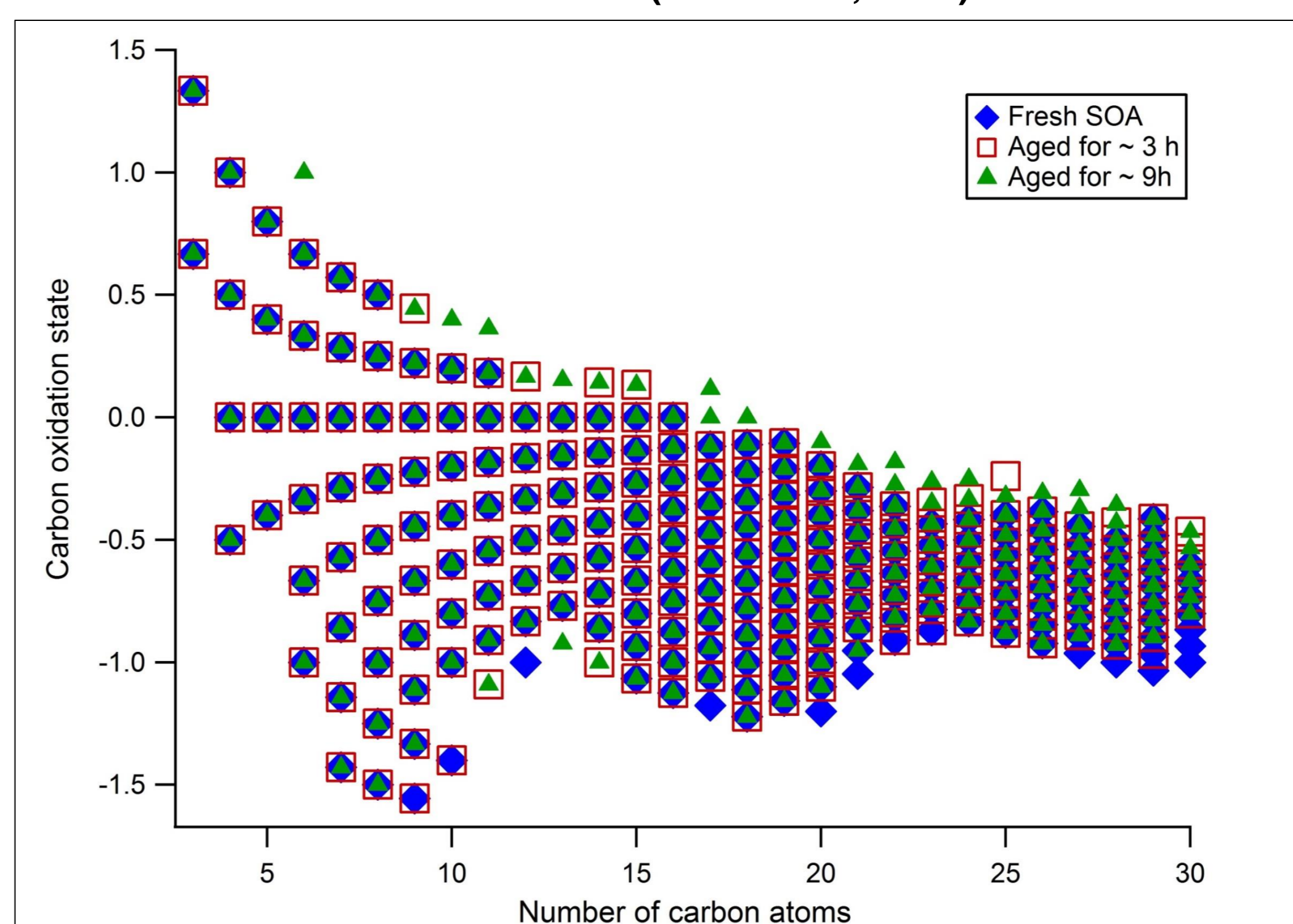


Figure 4. shows OS<sub>C</sub> plot for molecules in fresh and aged OA.

- No change in the compounds with a large number of Carbon atoms, associated with dimers and trimers are observed;
- On the other hand, a slight shift towards more oxidised state was observed in the aged OA.

## LC/MS results:

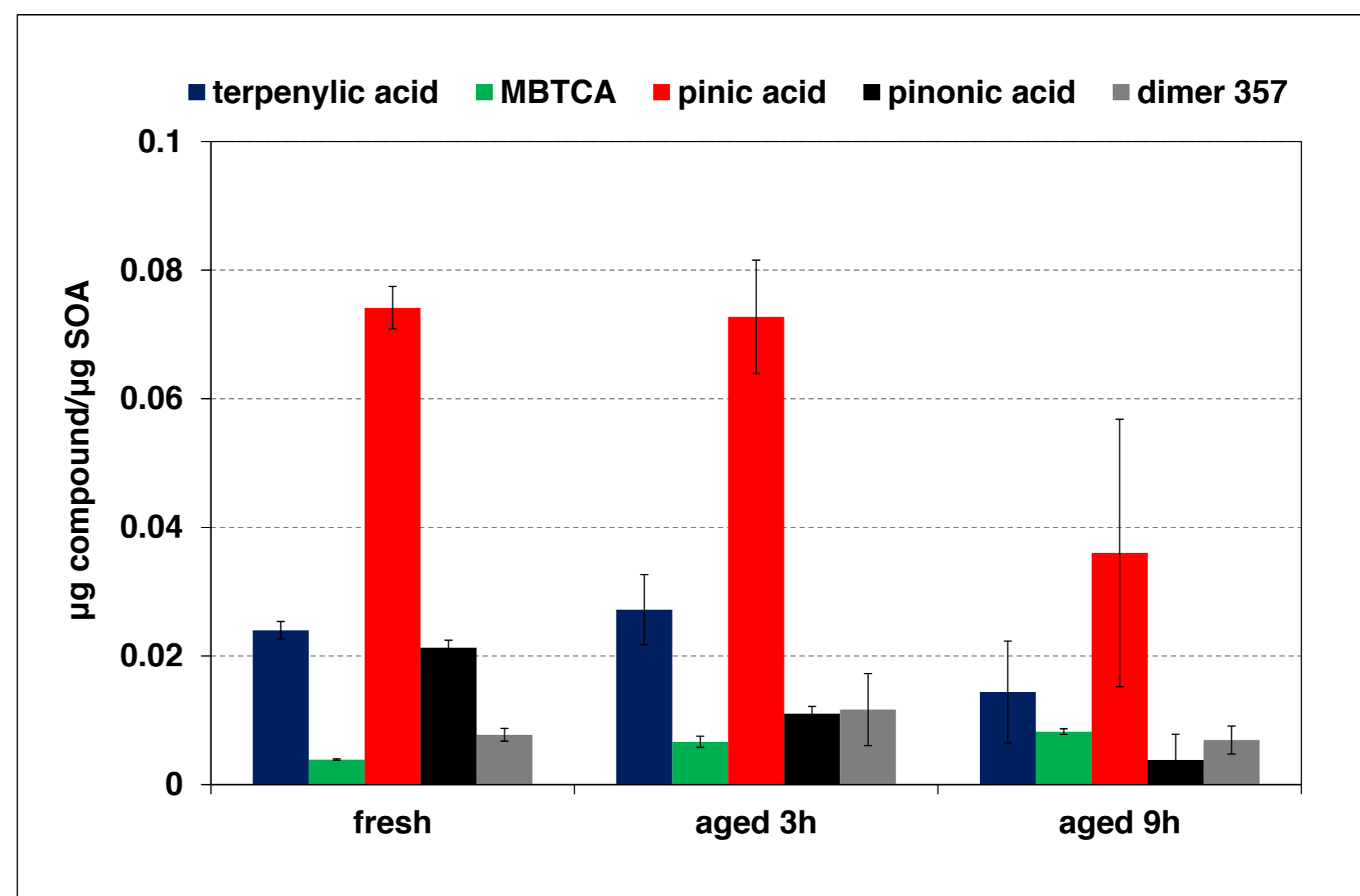


Figure 5. Ratio of marker compounds for ‘fresh’ (e.g., pinic acid and *cis*-pinonic acid) and ‘aged’ (e.g., MBTCA) to SOA in ageing experiment with UV, OH<sup>•</sup> and acidic seed. MBTCA is a known ‘aged’ marker for oxidation of  $\alpha$ -pinene (Müller et al., 2012).

- MBTCA/*cis*-pinonic acid ratio increases with time indicating consequent production of MBTCA and reacting away *cis*-pinonic acid;
- The dimer at  $m/z$  357 does not increase with the ageing time.

## Acknowledgments:

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