INTRODUCTION:
A considerable lack of knowledge exists concerning the chemical composition of natural aerosols. 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 ageing of SOA generated from a precursor mixture containing BVOCs (i.e. α and β-pinene, δ3-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:

METHODS:
The experiments were carried out using 4.3 m² 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 α and β-pinene, δ3-carene, and isoprene (150 ppb total VOC) and ozone (450 ppb). For the OH initiated ageing reactions, OH were produced by H2O2 photolysis using 4 kW Xe lamps. H2O2 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 (NH4)2SO4 and H2SO4. 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) ~8 hours of exposure of the SOA particles to the OH- and/or UV radiation.

Carbon Oxidation State (OSC): Carbon oxidation state OS_C is shown to be strongly linked to aerosol volatility and thus is a useful parameter for classification of SOA (Kroll et al., 2011).

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 and acidic seed. MBTCA is a known ‘aged’ marker for oxidation of α-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 387 does not increase with the ageing time.

Figure 1. CESAM atmospheric simulation chamber

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 H2O2 and UV for 3 and 9 hours.

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

REFERENCES:
Kroll et al., Nature Chemistry, 3, 133-139, 2011
Müller et al., Atmos. Chem. Phys., 12, 1483-1496, 2012