

Supporting Information for **“Online molecular characterisation of organic aerosols in an atmospheric chamber using Extractive Electrospray Ionisation Mass Spectrometry”** by P.J. Gallimore et al.

5

Experimental setup

The experimental apparatus used for production and classification of standard aerosols (section 2.1) and for the simulation chamber experiments (section 2.2) are shown below.

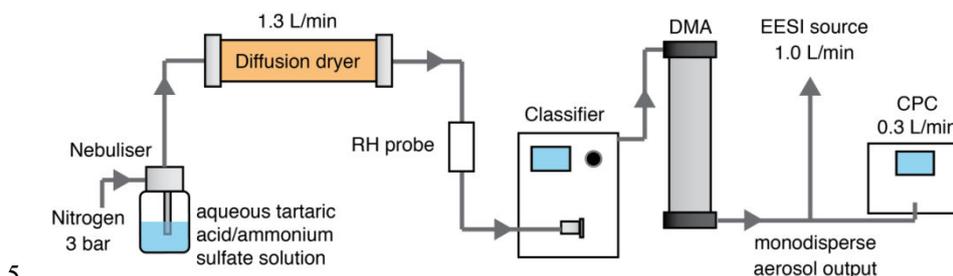


Figure S1: Aerosol flow setup used for producing, classifying and measuring the chemical composition of model aerosols to quantify the extraction process.

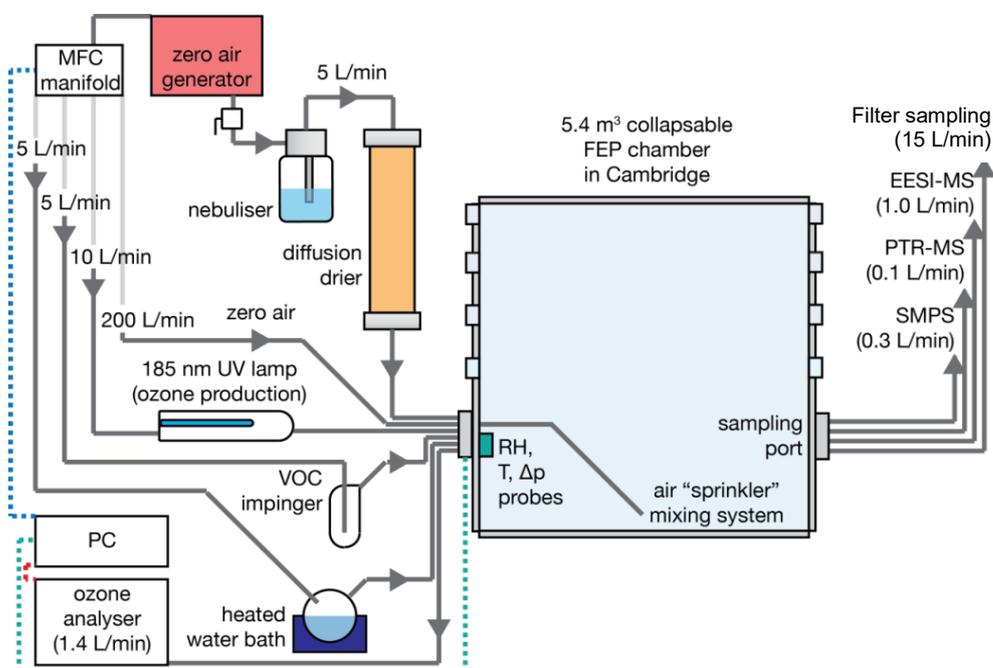


Figure S2: Operational details for the Cambridge Atmospheric Simulation Chamber (CASC), adapted from Gallimore et al., (2017b). The 5.4 m³ chamber enables study of secondary organic aerosol formation and aging processes in the laboratory; water vapour, seed aerosols, atmospheric oxidants and volatile organic compounds can be introduced under controlled conditions. A variety of instrumentation is attached to characterise the resulting chemistry, including a recently-developed extractive electrospray ionisation mass spectrometer (EESI-MS) to detect organic aerosol components.

Flow conditions in the EESI batch sampling system

This section considers the flow and mixing characteristics in the 10 L sampling reservoir (dimensions $\sim 92 \times 12$ cm) described in section 2.3. The 1 L min^{-1} “pushing flow” was introduced under laminar flow conditions (Reynolds number ~ 12). The total introduction of air was 3.5 L over
5 3.5 minutes, corresponding to a nominal distance of 32 cm along the flow tube. The extent of additional mixing beyond this volume displacement will be determined by molecular diffusion, described by Equation S1:

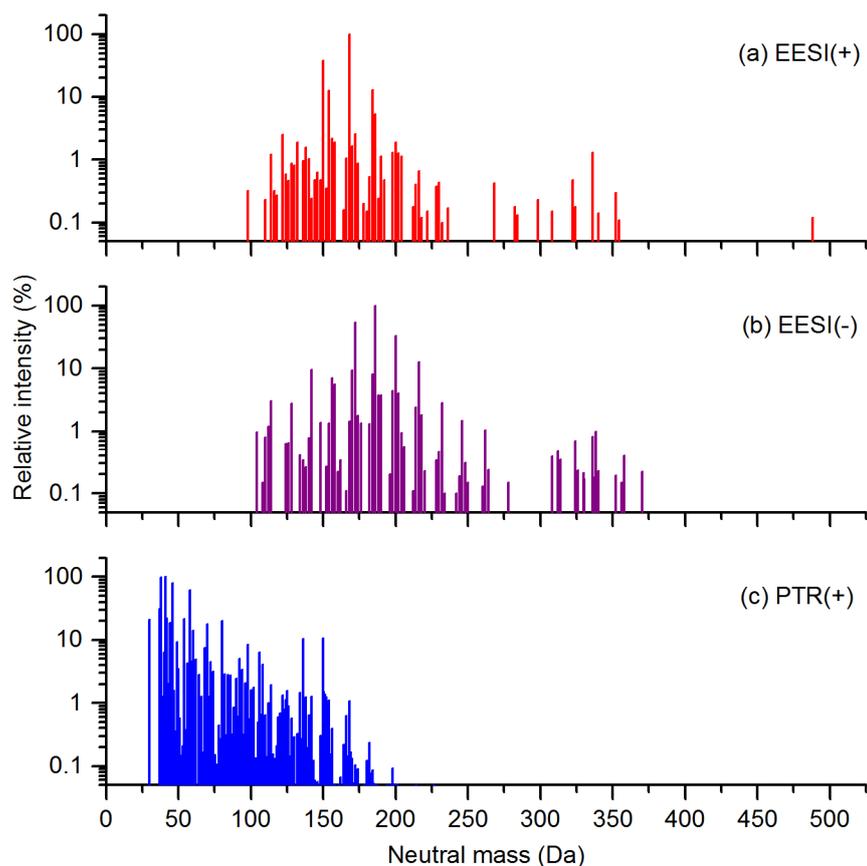
$$\tau = \frac{l^2}{D} \quad (\text{S1})$$

10 Where τ is the diffusion time, l is the diffusion length and D is the diffusion coefficient of air. Diffusion of accumulation mode particles will be negligible by comparison. For an introduction time of 3.5 minutes and diffusion coefficient $0.2 \text{ cm}^2 \text{ s}^{-1}$, the diffusion length is 6.5 cm. Therefore only the first $\sim 40\%$ of the tube length, furthest from the MS sampling, will be influenced by zero air introduction.

15

The EESI-MS signal is also relatively consistent across each 3.5 minute sampling period (Figure 3), confirming that this cycling does not significantly affect the sampled particle composition.

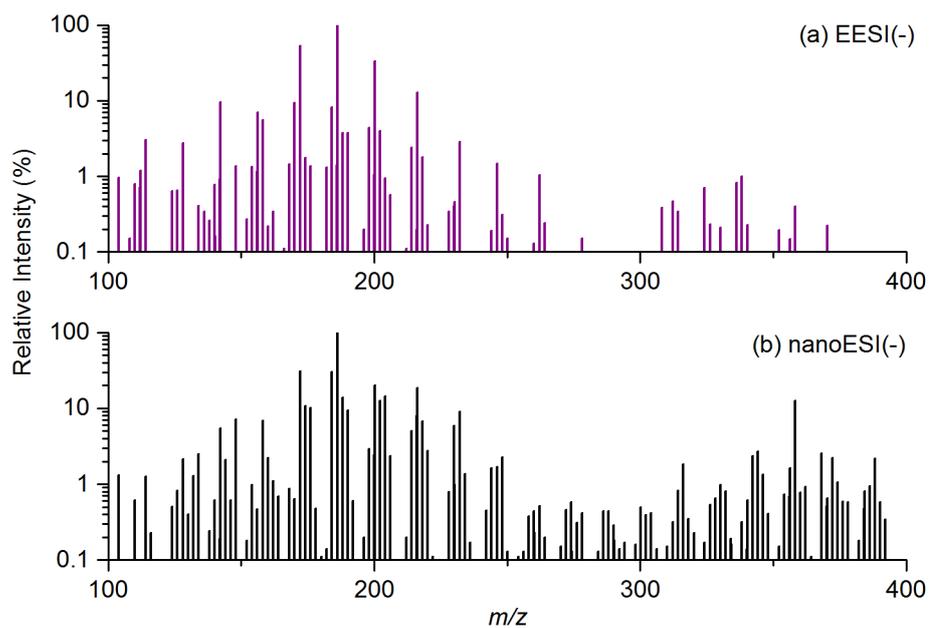
Mass spectra for EESI-MS and PTR-MS



5 **Figure S4: Mass spectra obtained during the dark ozonolysis of α -pinene under “medium” conditions (Table 1) using three online MS techniques: (a) EESI-MS in positive ionisation mode, (b) EESI-MS in negative ionisation mode and (c) PTR-MS using H_3O^+ as a chemical ionisation reagent. The ions have been assigned to molecular formulae and are plotted as neutral masses to aid comparison. Only PTR-MS ions corresponding to assigned α -pinene ozonolysis products are shown. Taken together, the three techniques enable online detection of a wide variety of organic compound classes and volatilities, from hydrocarbons such as α -pinene to highly oxidised carboxylic acids.**

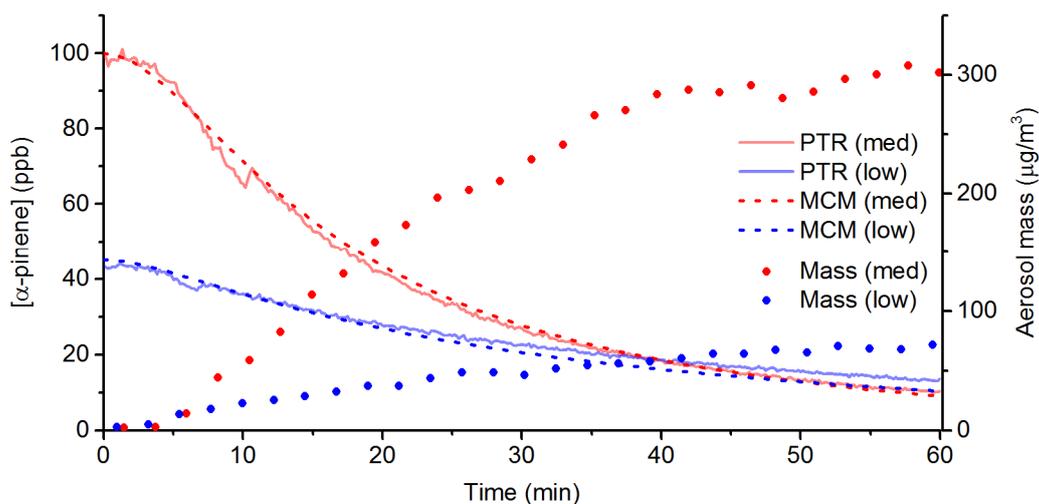
10

Comparison between EESI(-) and nanoESI(-) spectra

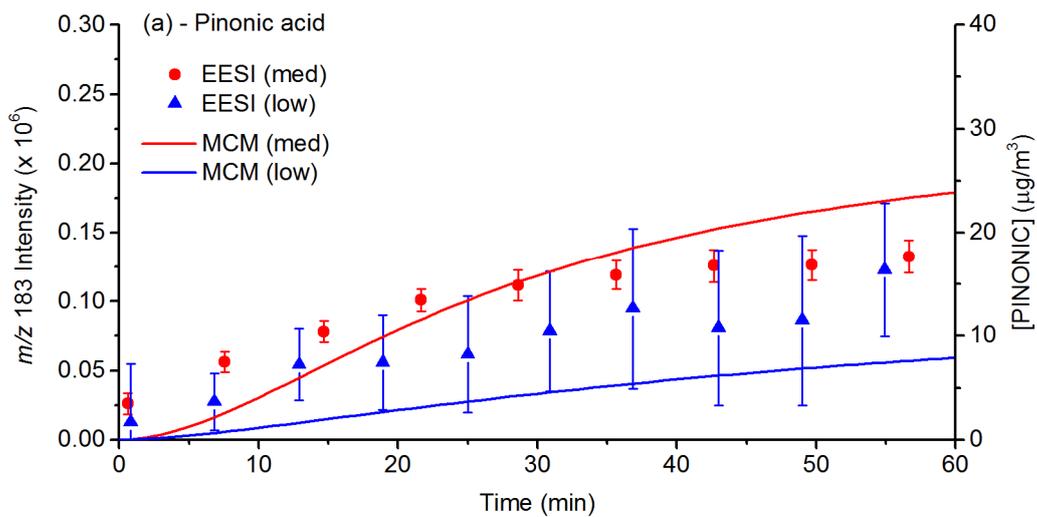


5 **Figure S5: Mass spectra obtained during the dark ozonolysis of α -pinene under “medium” conditions (Table 1) using (a) online EESI-MS in negative ionisation mode and (b) nanoESI-MS of SOA filter extracts. The online MS was acquired and the filter collected 1 hour after the start of ozonolysis in the chamber. The spectra are very similar in the monomer region (< 250 Da), but the oligomers detected are more numerous and possess slightly higher molecular weights in the nanoESI(-) spectrum.**

Comparison between measured MS intensities and MCM concentrations for oxidation products



5 **Figure S6:** α -pinene loss and SOA production during chamber experiments with varying $[\alpha\text{-pinene}]_0$, showing only the medium and low concentration conditions. Dashed lines: measured $[\alpha\text{-pinene}]$ from PTR-MS; Solid lines: MCM simulated $[\alpha\text{-pinene}]$; Points: measured aerosol mass from SMPS.



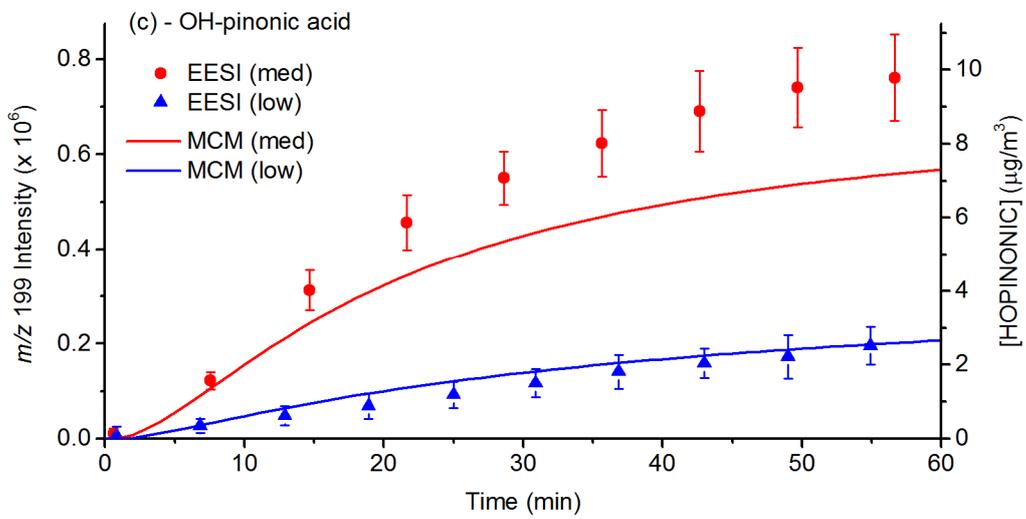
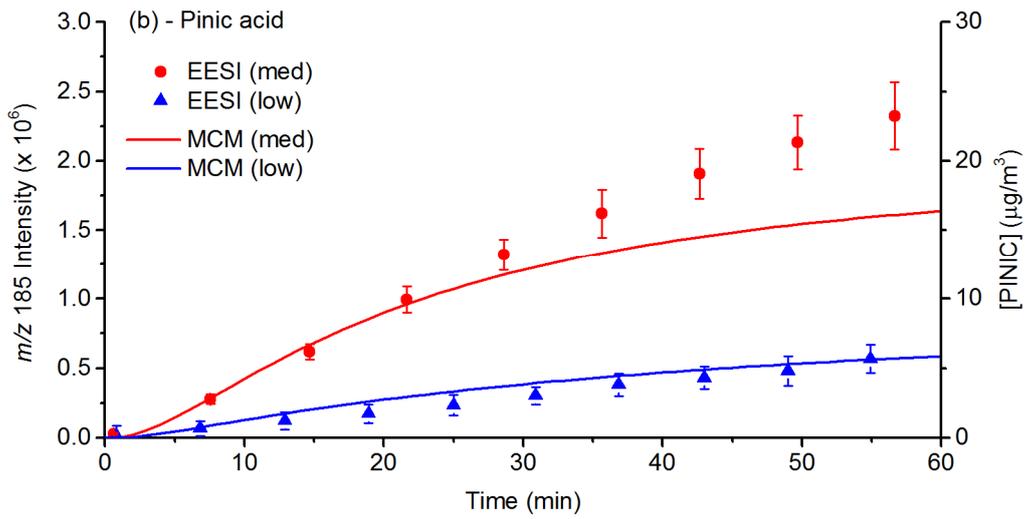
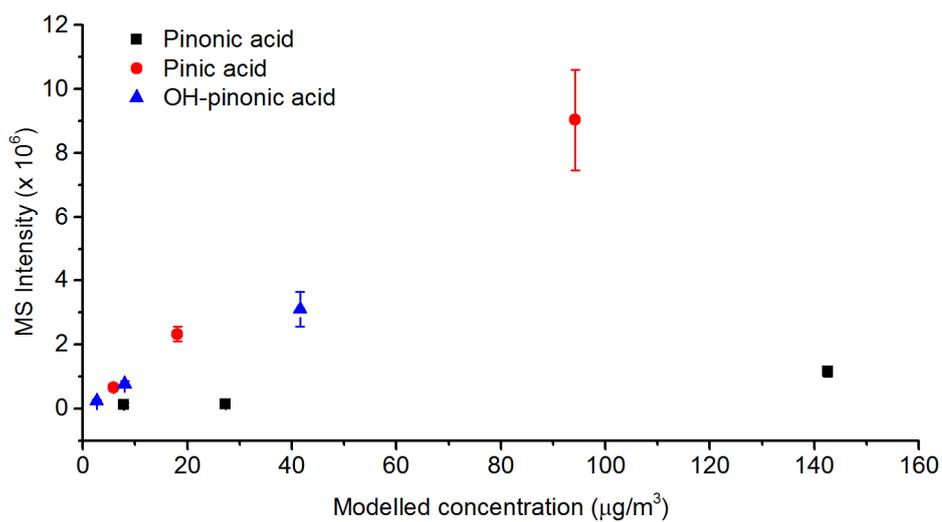


Figure S7: Comparison between EESI-MS intensities (left y-axis) and MCM simulated concentrations (right y-axis) for (a) pinonic acid, (b) pinic acid and (c) OH-pinonic acid, showing only the medium and low concentration conditions. The scales of the y-axes from Figure 7 have been divided by 4, so that the relative scaling between the m/z and MCM axes is consistent with Figure 7.



5 **Figure S8: MS intensity of pinonic, pinic and OH-pinonic acids as a function of predicted MCM concentrations. The data shown are for the measurements approximately 1 hour after the start of ozonolysis in Figure 7, where the rate of change of concentration slows and hence simulated and measured concentrations represent approximate final yields.**