Atmospheric
Chemistry
and Physics

Supplement of

Online molecular characterisation of organic aerosols in an atmospheric chamber using extractive electrospray ionisation mass spectrometry

Peter J. Gallimore et al.

Correspondence to: Peter J. Gallimore (pjg48@cam.ac.uk) and Markus Kalberer (markus.kalberer@atm.ch.cam.ac.uk)

Experimental setup

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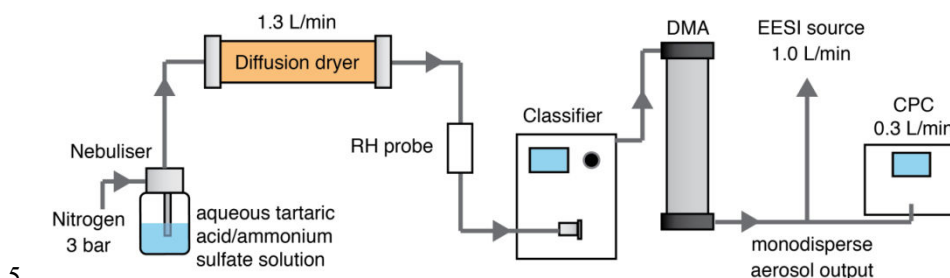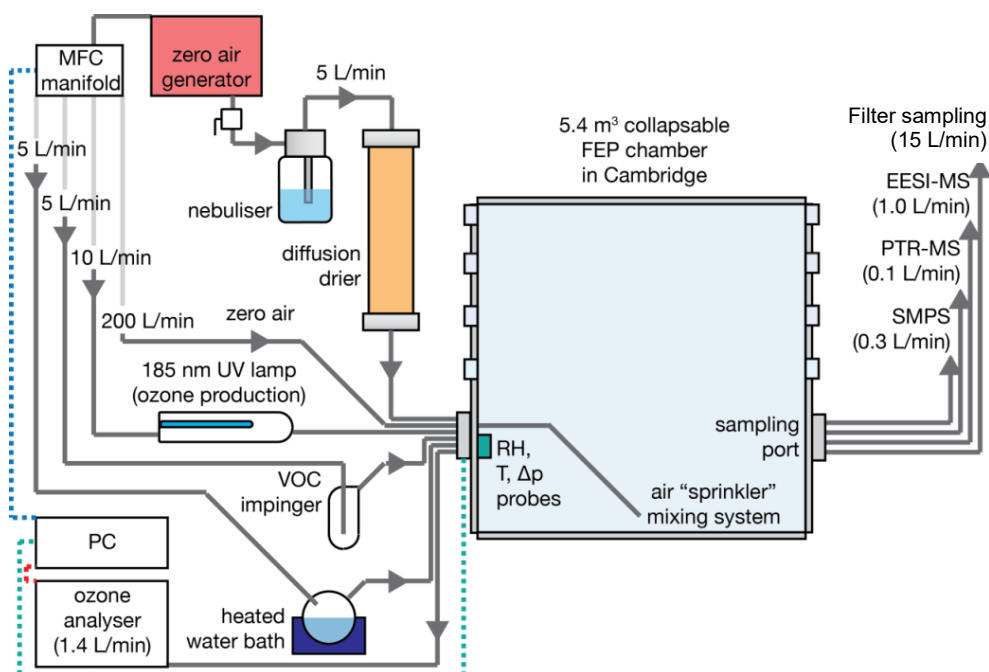

Figure S1: Aerosol flow setup used for producing, classifying and measuring the chemical composition of model aerosols to quantify the extraction process.

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 instruments are 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 ~ 92 ×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 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:

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

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 cm^2 s^{-1}, the diffusion length is 6.5 cm. Therefore only the first ~40 % of the tube length, furthest from the MS sampling, will be influenced by zero air introduction.

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.

3

Reaction scheme for MCM simulations

The reaction scheme for the degradation of α-pinene is based on the mechanism described in Saunders et al. (2003). All reactions involving the ozone-initiated oxidation of α-pinene and its products, including decomposition of reaction intermediates and secondary OH-mediated chemistry, were extracted from the MCM website (http://mcm.leeds.ac.uk/MCM) in June 2017. This mechanism extract comprises 313 explicit species.

We also included an auxiliary reaction to approximate the gradual introduction of ozone into the chamber (reaction S2):

$$\text{pre-O}_3 \text{ (g)} \rightarrow \text{O}_3 \text{ (g)} \qquad k_{\text{pre}} \qquad\qquad \text{(S2)}$$

Pre-O$_3$ does not participate in any other reactions, and is converted into O$_3$ on a timescale $\tau_{\text{pre}} = 1/k_{\text{pre}}$ = 3-30 minutes, adjusted to reflect the experimental timescale for ozone introduction for each experiment.

The simulations were initialised with all species concentrations set to zero, apart from: α-pinene (APINENE), which was set to 45, 100 and 500 ppb for the low, medium and high concentration experiments respectively, and pre-O$_3$ (PREO3) which was adjusted to simulate the observed [O$_3$]$_{\text{max}}$ in each experiment (Table 1).

Extraction efficiency of tartaric acid in mixed organic-inorganic aerosols
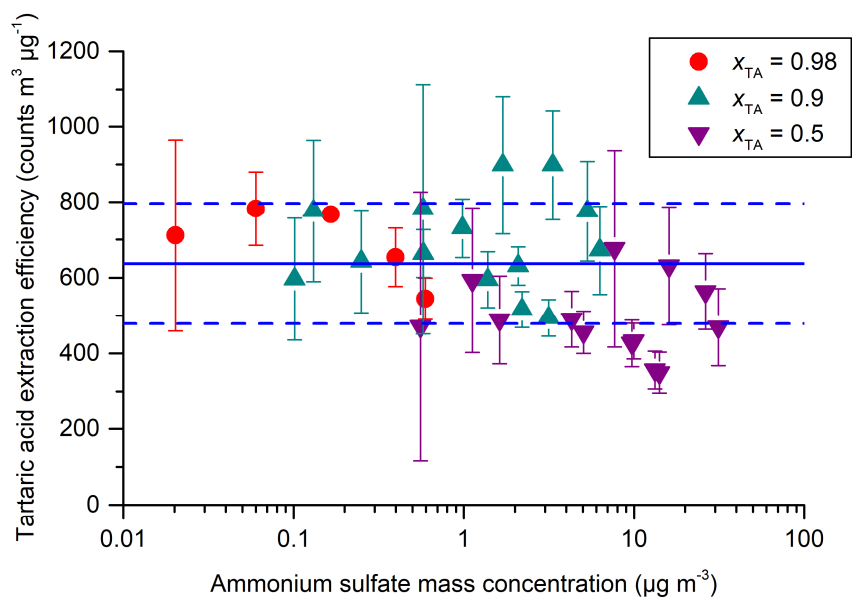
Figure S3: Tartaric acid MS signal, normalised by the tartaric acid aerosol mass, as a function of the ammonium sulfate aerosol mass. The blue solid and dotted lines represent the mean and standard deviation respectively of measurements on single-component tartaric acid aerosols ($x_{TA} = 1$).

5

Mass spectra for EESI-MS and PTR-MS
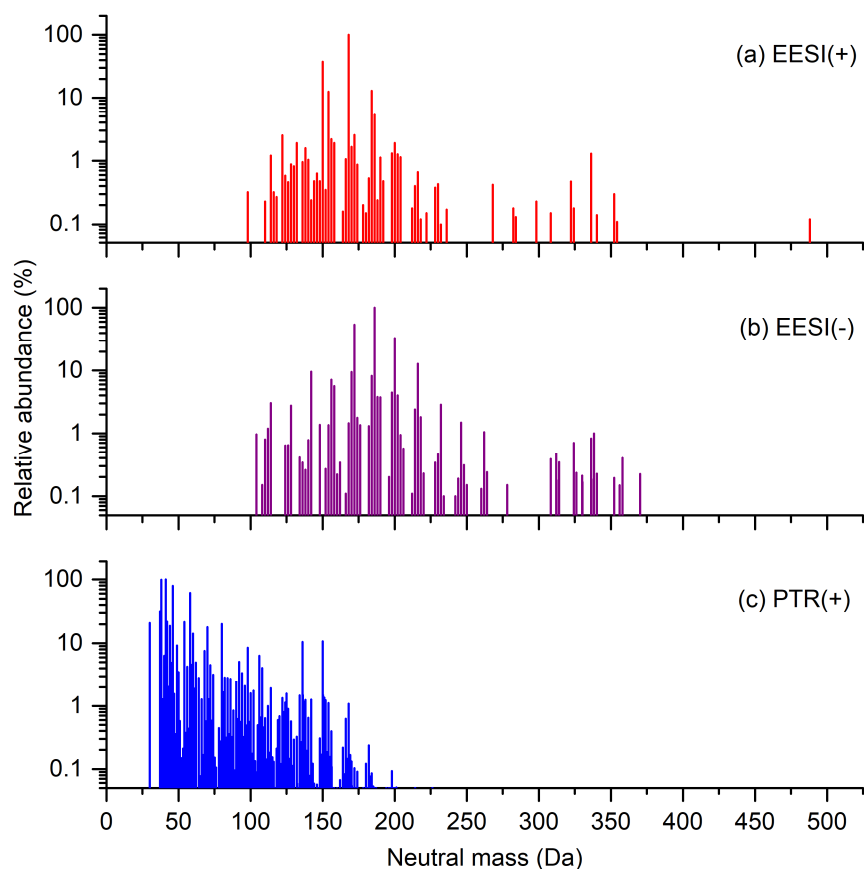
Figure S4: Mass spectra obtained during the dark ozonolysis of α-pinene under "medium" conditions (Table 1) using three online MS techniques: (a) EESI-MS in positive ionisation mode, (b) EESI-MS in negative ionisation mode and (c) PTR-MS using H_3O^+ as a chemical ionisation reagent. The ions have been 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.
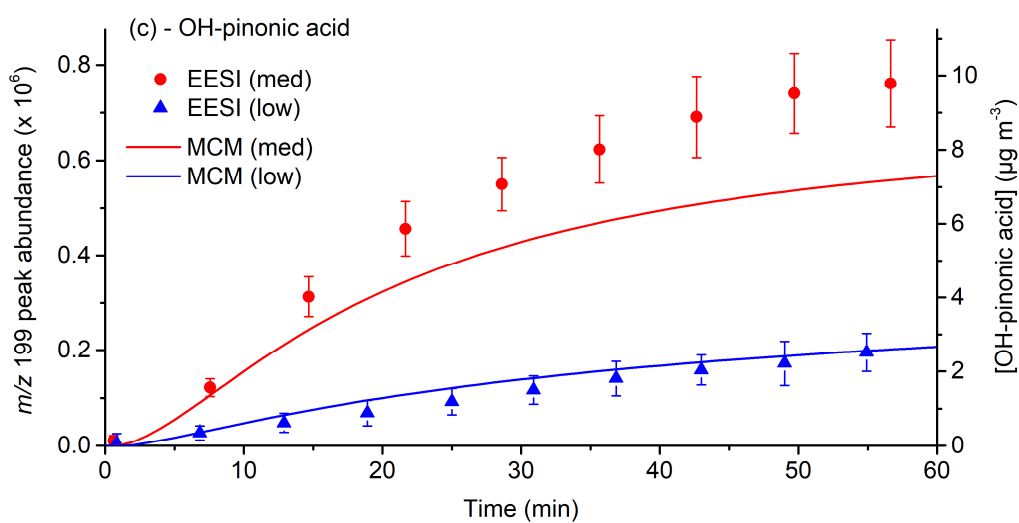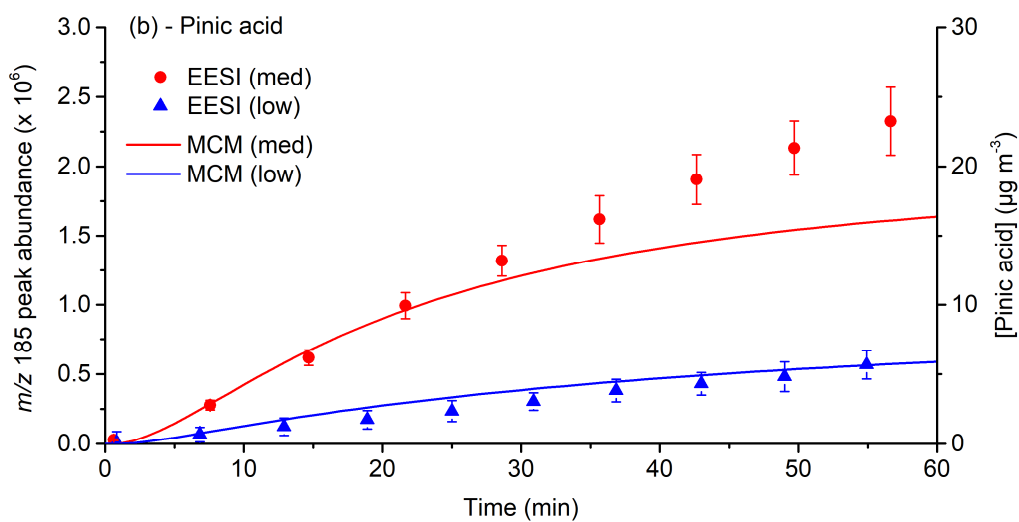
**Comparison between measured MS peak abundances and MCM concentrations for oxidation products**
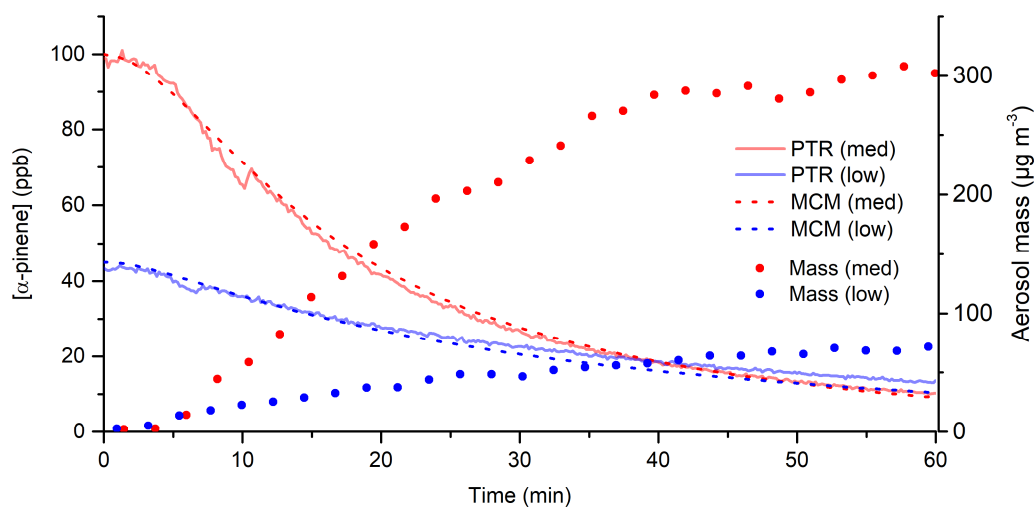
Figure S5: α-pinene loss and SOA production during chamber experiments with varying [α-pinene]₀, showing only the medium and low concentration conditions. Dashed lines: measured [α-pinene] from PTR-MS; Solid lines: MCM simulated [α-pinene]; Points: measured aerosol mass from SMPS.
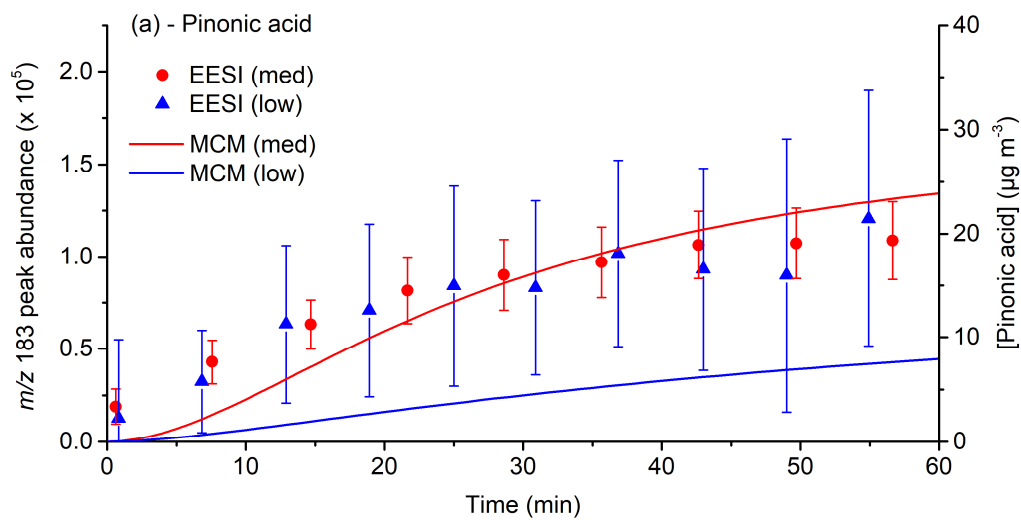
Figure S6: Comparison between EESI-MS peak abundances (left y-axis) and MCM simulated concentrations (right y-axis) for (a) pinonic acid, (b) pinic acid and (c) OH-pinonic acid, showing only the medium and low concentration conditions. The scales of the y-axes from Figure 8 have been divided by 4, so that the relative scaling between the *m/z* and MCM axes is consistent with Figure 8.
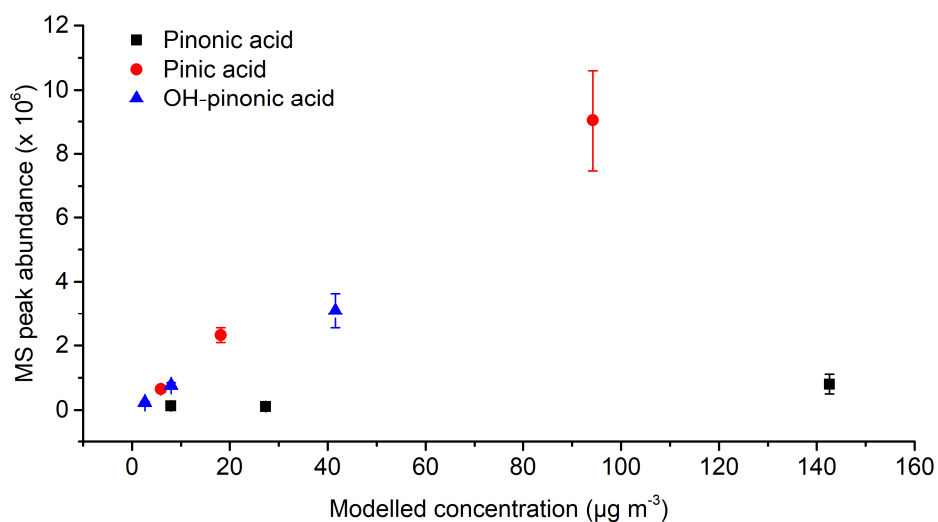
Figure S7: MS peak abundance of pinonic, pinic and OH-pinonic acids as a function of predicted MCM concentrations. The data shown are for the measurements approximately 1 hour after the start of ozonolysis in Figure 8, where the rate of change of concentration slows and hence simulated and measured concentrations represent approximate final yields.

References

Saunders, S. M., Jenkin, M. E., Derwent, R. G. and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, 2003.