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### Introduction

Various organic species are emitted to the atmosphere from vegetation. Biogenic hydrocarbons, especially monoterpenes play an important role in the formation of secondary organic aerosols (SOA) initiated by their atmospheric oxidation. It has been estimated that they contribute a significant mass to the total aerosol mass in the troposphere, ranging from 30 to 270 Tgy<sup>-1</sup> [Andreae and Crutzen, 1997].

The identification and quantification of reaction products from the oxidation process of terpenes in the gas phase has been receiving great attention over the past two decades. More recently, the aerosol formation during the oxidation process of terpenes in the atmosphere has also been investigated [Pandis *et al.*, 1991; Zhang *et al.*, 1992; Hoffmann *et al.*, 1997]. Although this process is believed to be a major source of SOA in the troposphere only limited number of experiments have been carried out to understand the quantitative and chemical nature of the produced aerosol [Griffin *et al.*, 1999; Winterhalter *et al.*, 2001]. Therefore understanding the nature of these species in both gas and particle phases is essential step towards assessing the climatic importance of these species.

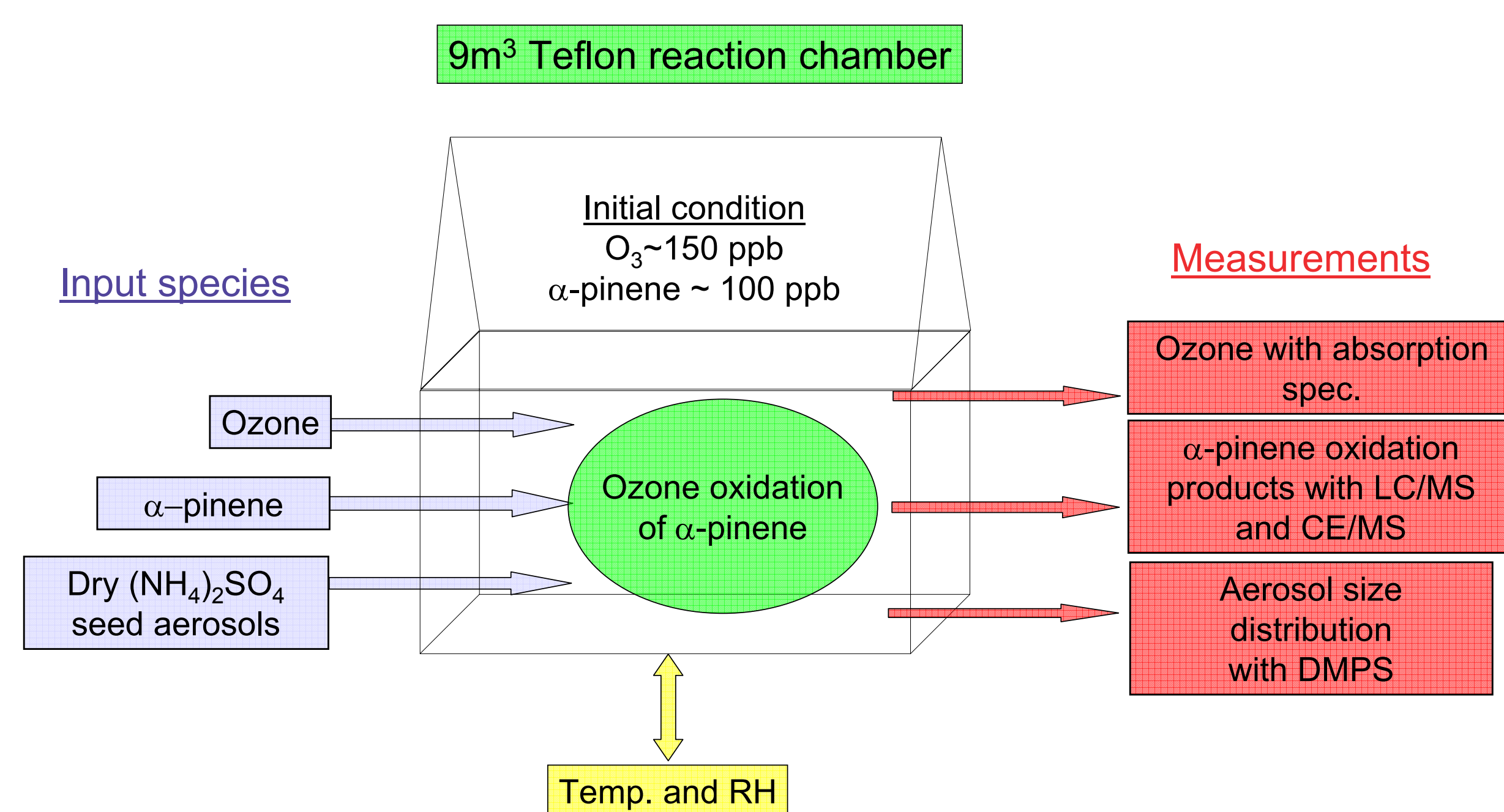


Fig. 1: Schematic diagram of the experimental setup

### Experimental Condition

Reactions were run in a 9 m<sup>3</sup> Teflon reaction chamber. Figure 1 shows the experimental setup. The initial concentration of  $\alpha$ -pinene was 56-94 ppbV. Ozone was produced by the photolysis of O<sub>2</sub> with Hg lamp and the concentration of ozone was ranged from 80-150 ppbV. The concentration of ozone was determined by UV absorption at  $\lambda=254$  nm. Ammonium sulphate seed aerosols were produced by a nebuliser and then dried with a diffusion drier prior to the entering the chamber. A bipolar charge neutraliser was used to neutralise the dried seed aerosol. The size distributions of particles in the reaction chamber as a function of time were measured by a differential mobility particle sizer (DMPS) and ultrafine differential mobility particle sizer (UDMPS). The seed aerosols and ozone are injected to the reaction chamber and mixed with a fan prior to the reaction with  $\alpha$ -pinene. After defining the initial concentrations of ozone and seed aerosols,  $\alpha$ -pinene was injected and mixed for further 5 minutes with a fan. The samples were collected on a PTFE filter (0.47 mm diameter, 1 mm pore size). Filters were extracted in 5ml of Milli-Q water for CE analysis. The samples were analysed with CE with an indirect UV method at  $\lambda=205$  nm and with a mass spectrometer detector. A buffer system containing 3 mM pyromellitic acid/6 mM DETA/5% methanol at pH 8.6 was used for CE indirect UV method and 10 mM ammonium acetate/0.4% methanol at pH9.1 with NH<sub>4</sub>OH was used for CE/MS method. A fused silica capillary was used for both method with internal diameter of 75  $\mu$ m and total length of 64.5 cm (effective length 56 cm) for CE indirect UV and internal diameter 50  $\mu$ m and total length of 85 cm for CE/MS, respectively.

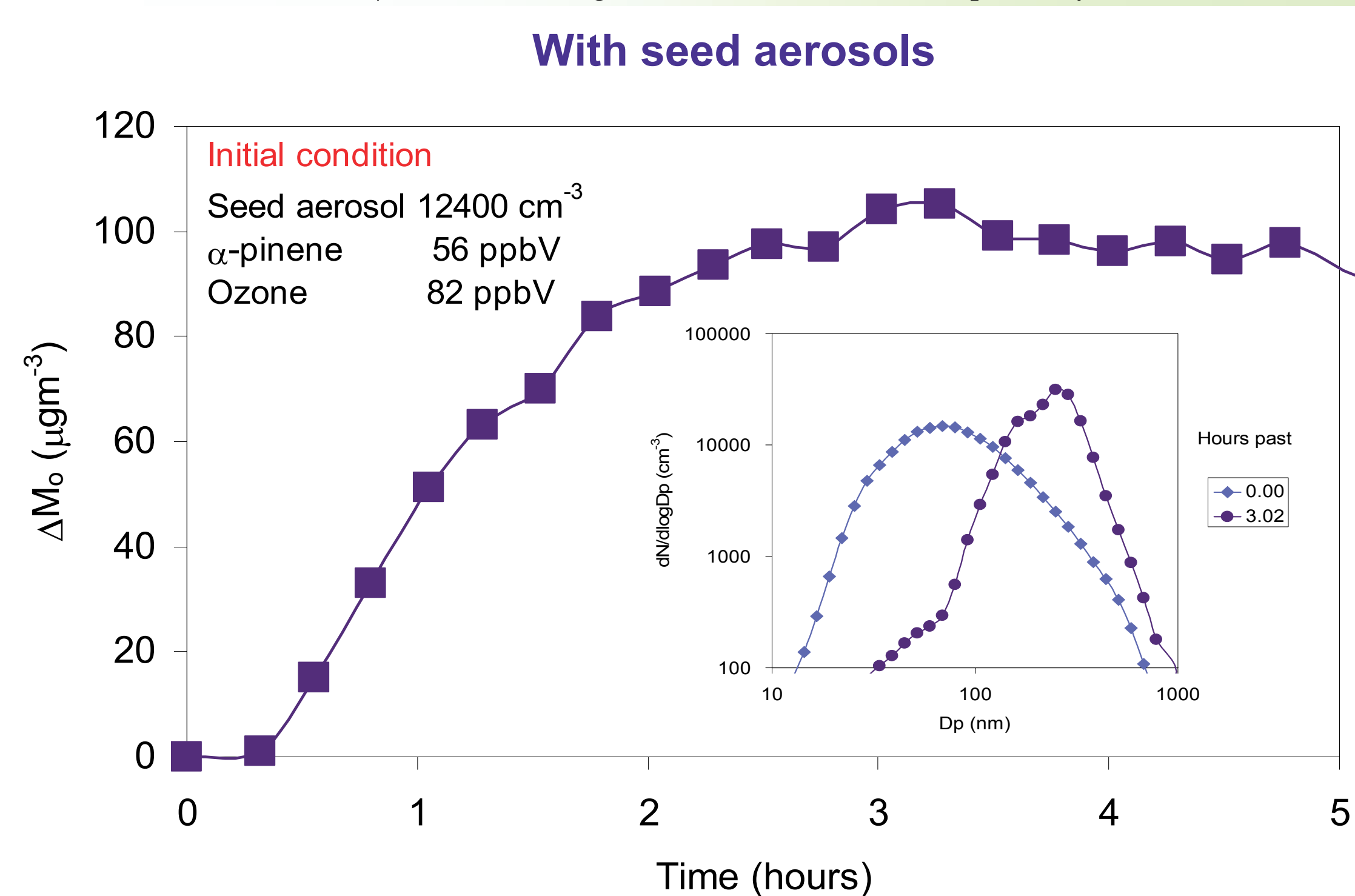


Fig. 2: Example of aerosol mass and size distribution change as a function of time with seed aerosols.  $DM_0$  is calculated from the change in aerosol size distribution.

### Results and discussion

Figure 2 and 3 show examples of increased aerosol mass ( $\Delta M_0$ ) and size distribution change as a function of time with and without seed aerosols, respectively. Increase in particle number, mass and mode diameter were observed shortly after  $\alpha$ -pinene was injected for both with and without seed aerosols case. In the presence of seed aerosols, condensation of organic vapour or newly formed ultrafine particles on the existing particles causes increase in particle size and mass. In a non-seeded aerosol experiment, burst nucleation forms a significant number of particles then followed similar evolution of particle size and mass as a seeded experiment. A maximum in  $\Delta M_0$  were reached about 3 hours after  $\alpha$ -pinene injection for both cases. Particle size distributions for both cases were poly-modal but they showed rather different characteristics. Although no clear explanation can be given without further characterising experiments, it may be due to the difference between a number of SOA formed at the time of  $\alpha$ -pinene injection and the speed of coagulation during the evolution of particles. Preliminary experimental results suggest  $\Delta M_0$  is strongly influenced by the initial experiment parameters but no clear relationship between each experimental parameter was observed from the results and further experiments are needed in order to understand the factor deciding  $\Delta M_0$  and yields.

Figure 4 shows a typical electropherogram. Only filter samples from experiments with seed aerosols were analysed at this time. CE analysis showed that major water soluble ionic products in the particle phase were pinic acid followed by norpinic acid. The concentrations of pinic acid and norpinic acid in the particle phase for the experiment shown in Figure 2 were 4.02 and 1.19  $\mu$ g m<sup>-3</sup>, respectively.

Figure 5 shows the mass spectrum of  $\alpha$ -pinene oxidation products from the experiment shown in Figure 3. High sensitivity of MS allows us to detect pinonic acid in samples which is usually not found in CE indirect UV method.

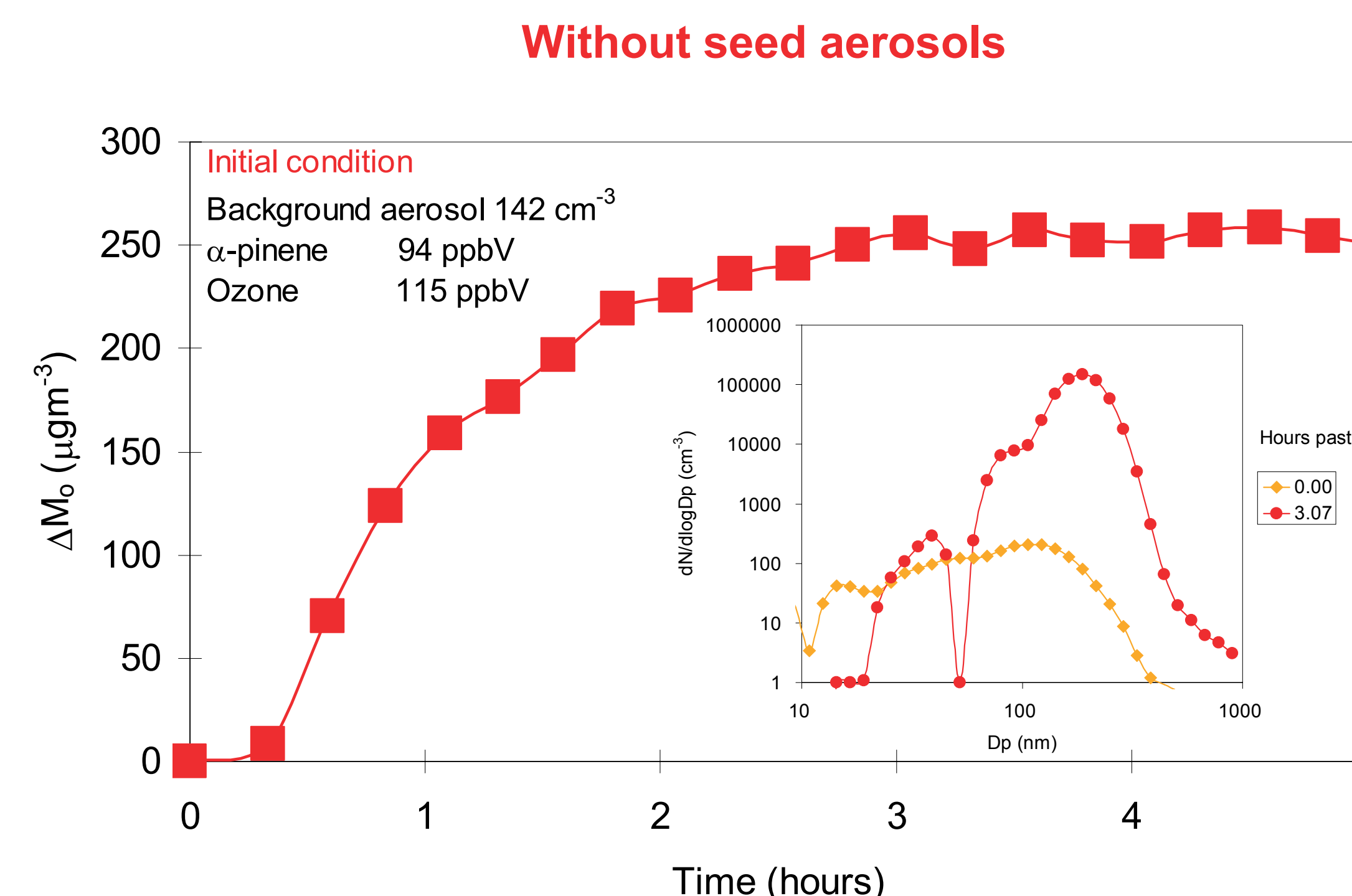


Fig. 3: Example of aerosol mass and size distribution change as a function of time without seed aerosols.  $DM_0$  is calculated from the change in aerosol size distribution.

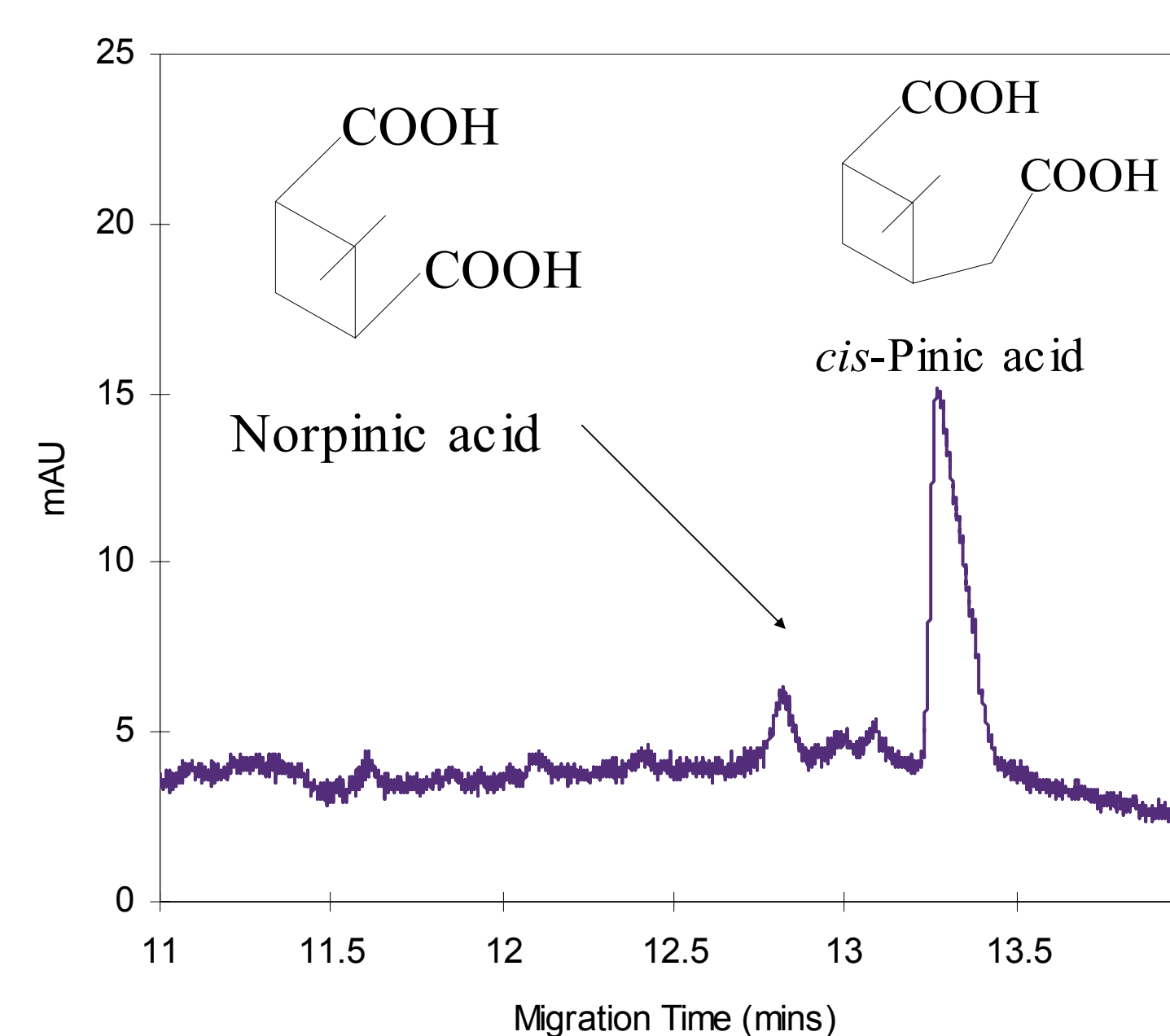


Fig. 4: Typical electropherogram of  $\alpha$ -pinene oxidation products

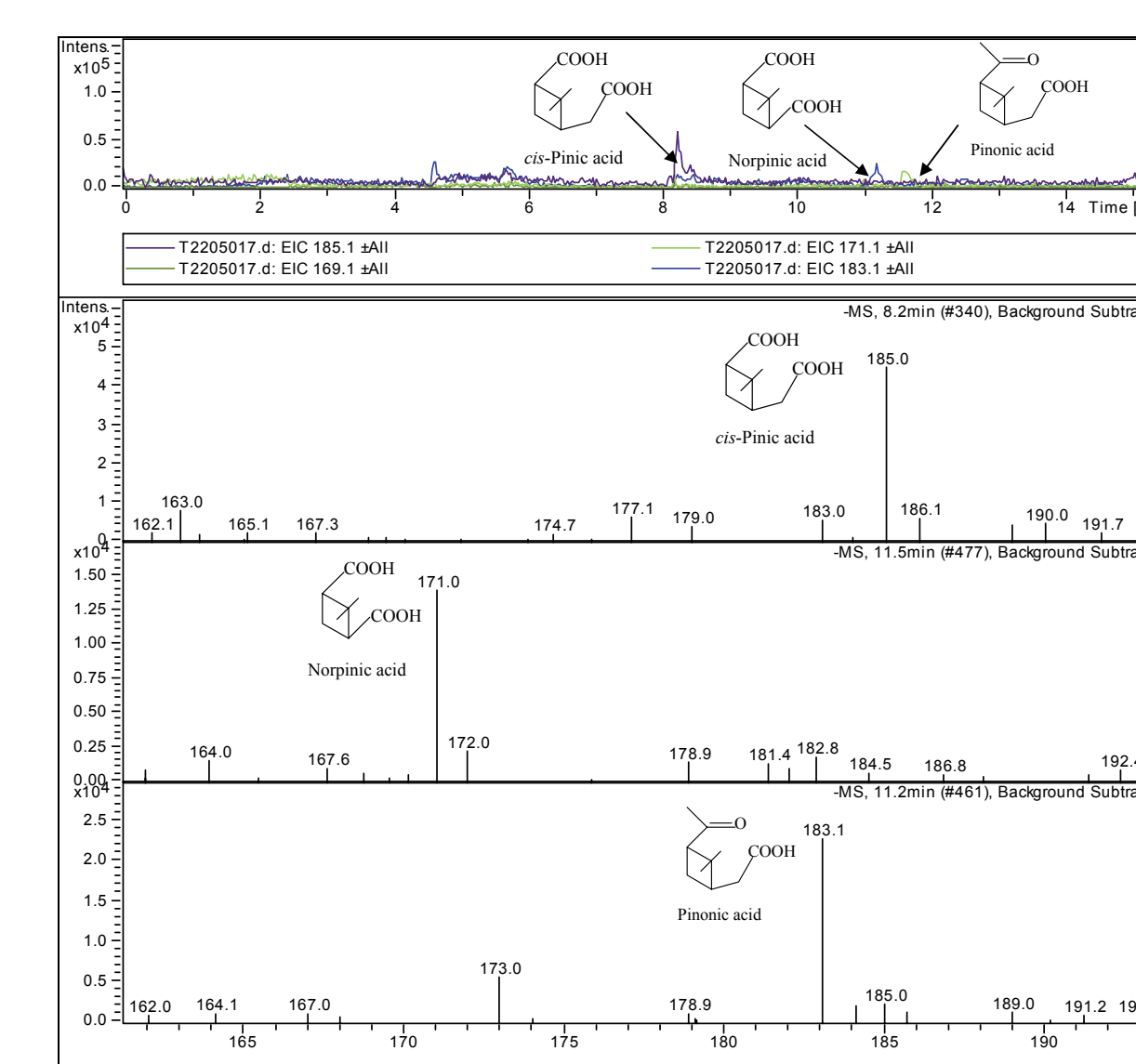


Fig. 5: Example of mass spectrum of  $\alpha$ -pinene oxidation products (7 Feb. 2002)

### Summary

In this study, some first results from chamber experiments for the characterisation of  $\alpha$ -pinene ozone oxidation products in the particle phase are presented. Evolution of particles ( $\Delta M_0$  and  $dN/d\log D_p$ ) as a function of time are shown for both seeded and non-seeded experiments. Further experiments are planned in order to characterise aerosol formation and evolution from  $\alpha$ -pinene oxidation. Oxidation products were analysed by CE and it is found that pinic acid and norpinic acid to be major ionic species in the particle phase. CE provides a fast and sensitive analysis for the ionic fraction of  $\alpha$ -pinene oxidation products and it will be coupled with MS for further product study.

### Future work

- Characterisation of experimental parameter dependency of particle evolution (temperature, RH, concentration of  $\alpha$ -pinene, ozone and seed aerosols)
- Determination of gas/particle phase partitioning ratio
- A new analytical method such as CE/MS
- Oxidation with OH and NO<sub>x</sub>

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