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Introduction

Atmospheric oxidation of monoterpenes is believed to play an important role in the formation of tropospheric ozone and secondary organic aerosols. Although this process is believed to be a major source of SOA in the troposphere our knowledge is still limited to understand the quantitative and chemical nature of the produced aerosol. Therefore understanding the nature of chemical species as well as their formation and conversion pathways in both gas and particle phases is an essential step towards in assessing the role of these species in aerosol chemistry and physics.

Experimental Condition

Reactions were run in a 9 m³ Teflon reaction chamber. The initial concentration of α -pinene was 100 ppbV. The concentration of ozone was in the range of 58-75 ppbV. The initial relative humidity of the chamber was 45 ± 5%. Ammonium sulphate and sulphuric acid seed particles were produced by a nebuliser. A bipolar charge neutraliser was used to neutralise the seed particles. 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 particles and ozone were injected to the reaction chamber and mixed with a fan prior to the reaction with α -pinene. After defining the initial concentrations of ozone and the size distribution of seed particles, α -pinene was injected and mixed for further 5 minutes with a fan. The samples were collected on a PTFE filter and a quartz fibre filter for CE-EIS-MS and thermographic analysis, respectively. A buffer system containing 20 mM ammonium acetate/10% methanol at pH 9.1 (adjusted by NH₄OH) was used for CE separation. Organic carbon (OC) content was determined by a thermographic method.

Size Distributions

The DMPS data is fitted to a log-normal size distribution in order to illustrate the change in size distributions through the experiments. Fig. 1A and 1B show the example of change in the particle number distribution (dN/dlogD_p) and Table 1 summarises the fitting parameters. The time zero is the initial size distribution of seed particles. For both experiments, the overall shape of the size distribution was still unchanged at the second scan (13 minutes after α -pinene injection). The size distributions from both experiments changed significantly by 30 minutes after the α -pinene injection due to the growth by a condensation process. The D_{pg} is nearly doubled with an ammonium sulphate seed particle and 1.4 times larger with a sulphuric acid seed particle. The σ decreased significantly with the both seed particles. As the mode diameter of ammonium sulphate seed particle was smaller than that of the sulphuric acid seed particle, the particles grew much faster and the shrinking of the size distribution from the condensation process was more pronounced than the sulphuric acid seed system. The size distribution continued to evolve after 30 minutes although the change was not as significant as the initial 30 minutes. The final D_{pg} for the ammonium sulphate seed system (168.6 nm) was slightly larger than that of the sulphuric acid seed system (156.2 nm). It is interesting to note that a small second mode started to evolve after 30 minutes with ammonium sulphate seed particles (D_{pg} ~ 80 nm) but not for the experiments with sulphuric acid particles. The nature of this mode is unclear and further study is needed in order to characterize this mode.

Chemical Analysis

The filter samples with only ammonium sulfate seed particles and sulfuric acid seed particles were also analyzed as blanks and no contamination was found from the seed particles and filters. It has been reported that some products from α -pinene ozonolysis form acetate adducts with HPLC-ESI-MS [Glasius *et al.*, 1999]. This was not observed with the CE-ESI-MS configuration. Fig. 2A and 2B show the typical base peak mass electropherogram with the ammonium sulphate seed particles and sulphuric acid seed particles, respectively. One noticeable difference is the small peak around 3.3 minutes in the electropherogram of sulphuric acid seed particle experiment (Fig. 2B). The extracted mass electropherogram reveals (Fig. 2C) compounds with m/z over 300. The absence of these m/z with the ammonium sulphate seed particles and no co-eluting compounds at this migration time suggest the sulphuric seed particle catalysed the formation of compounds with m/z over 300 although the formation of stable clusters in the ESI cannot be completely excluded as it has been suggested by some researchers [Hoffmann *et al.*, 1998; Glasius *et al.*, 1999]. Table 2 summarises the subsequent MS-MS experiments for further assessment of the products. It is found that m/z 167, 169, 185 and [M-H₂O] are the major fragments of fast migrating compounds with m/z over 300. Figure 3 summarises the measured and estimated concentration of OC and individual resolved species. It appears that the sulphuric seed particles produced more OC than the ammonium sulphate seed particles. The three most abundant compounds found with both seed particles are cis-pinonic acid (m/z 185), 172_1 (m/z 171) and 200_1 (m/z 199).

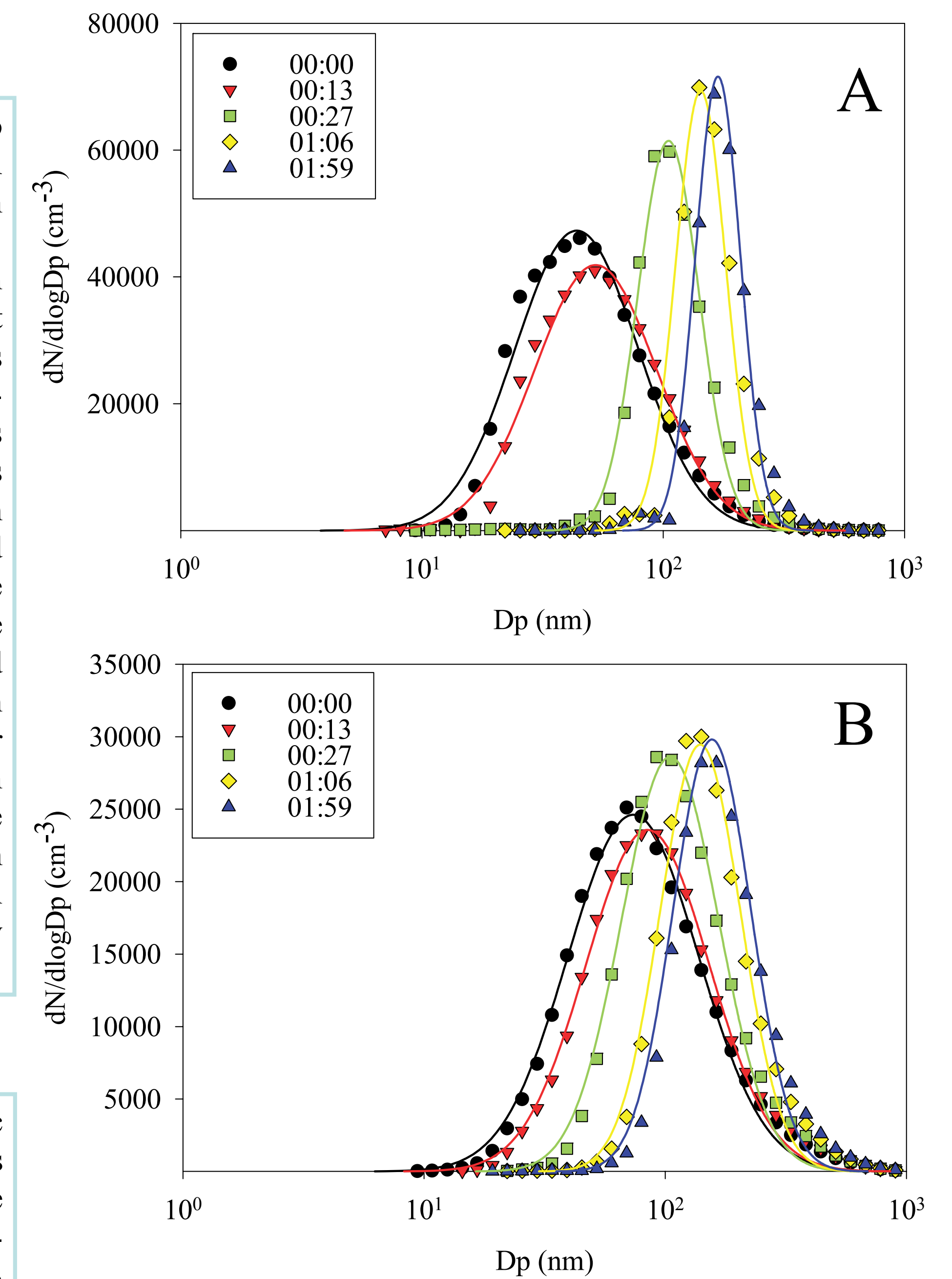


Fig 1: The particle number distributions as a function of time (A) with ammonium sulphate seed particles and (B) with sulphuric acid seed particles. The symbols represent the actual DMPS measurements and lines are the log-normal fittings.

Table 1: Log-normal fitting parameters of the size distributions for the experiment with (A) ammonium sulphate seed particles and (B) sulphuric acid seed particles.

Time (hh:mm)	(A) With sulphuric acid seed particle			(B) With ammonium sulphate particle		
	N (cm ⁻³)	D _{pg} (nm)	σ	N (cm ⁻³)	D _{pg} (nm)	σ
0:00	16631	73.7	1.86	30267	43.8	1.80
0:15	15081	84.5	1.80	26541	52.5	1.79
0:27	14442	104.8	1.59	19583	105.2	1.34
1:06	12352	139.7	1.47	18047	143.0	1.27
1:59	12056	156.2	1.45	16768	168.6	1.24

N: total aerosol number concentration, D_{pg}: geometric mean diameter, σ : geometric standard deviation

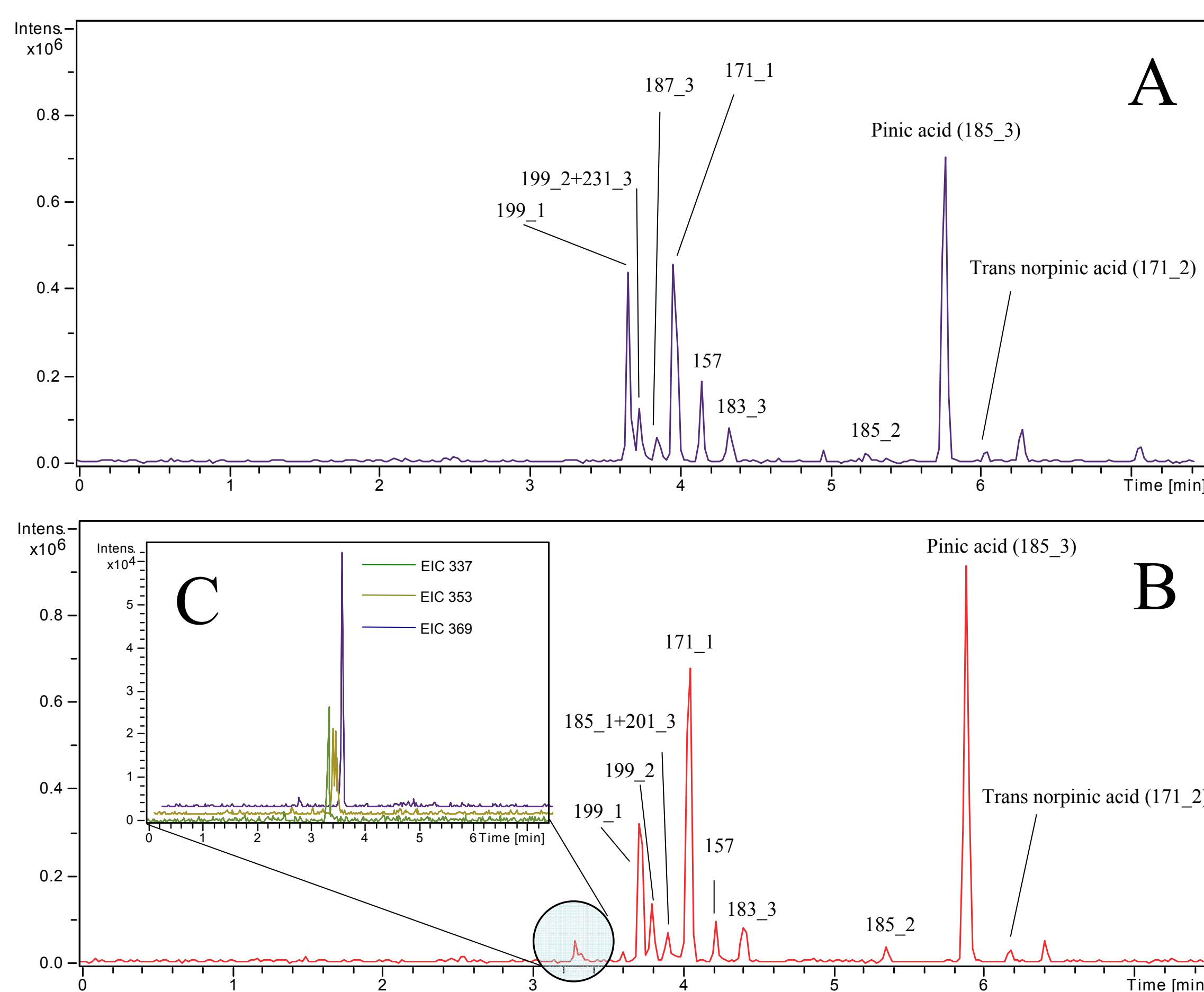


Fig 2: Typical mass electropherogram of α -pinene oxidation products (A) with ammonium sulphate seed particles and (B) with sulphuric acid seed particles.

Table 2: Summary of MSⁿ experiments.

Name	Precursor m/z peak no.	MS ² precursor (m/z)	Fragment 1 (-CO ₂) (m/z)	Int.	Fragment 2 (-H ₂ O) (m/z)	Int.	Fragment 3 (m/z)	Int.	Fragment 4 (m/z)	Int.	Fragment 5 (m/z)	Int.	Fragment 6 (m/z)	Int.
	337		293	w	319	s	167	s	169	m	185	m	275	w
		337→167	123	s										
		337→169	125	s										
		337→185												
		337→275												
		337→319	275	w	301									
	353		353→123		335	w	123	m	167	s	169	m	185	m
		353→167	123	s										
		353→169	125	w			123	m						
		353→185			167	s								
		353→335					353→335							
	369				351	m	141	m	167	s	169	s	185	s
		369→141												
		369→167	123	s										
		369→169					123	s						
		369→185	141	s	167	w								
		369→351	307	w	333	w								
	157		113	s										
	171_1		127	s										
Trans norpinic acid*	171_2		127	w										
Trans pinonic acid?	183_3		139	m	165	m								
Pincic acid*	185_3		141	s	167	m								
	187_3		169	s	125	s	127	m	145	m				
	187_4		169	s	125	s	127	m	145	m				
	197_1		153	s										
Hydroxy pinonic acid?	199_1		155	m	181	s	137	m	157	m				
Hydroxy pinonic acid?	199_2		155	m	181	s	137	m	157	m				
	215_1				153	s	199	m	235	w				
	215_2				157	s	199	m	235	w				
	231_3		187	s	213	w	145	s	167	s				
Trans pinonic acid?	367		323	w	349	s	185	s	199	s				

Int: Intensity, s: strong, m: medium, w: weak; *Authentic standard available

Acknowledgements

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Reference

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Hoffmann, T., R. Bandur, U. Marggraf, and M. Linscheid, Molecular composition of organic aerosol formed in the alpha-pinene/O₃ reaction: Implications for new particle formation processes, *Journal of Geophysical Research*, 103 (D19), 25,569-25,578, 1998

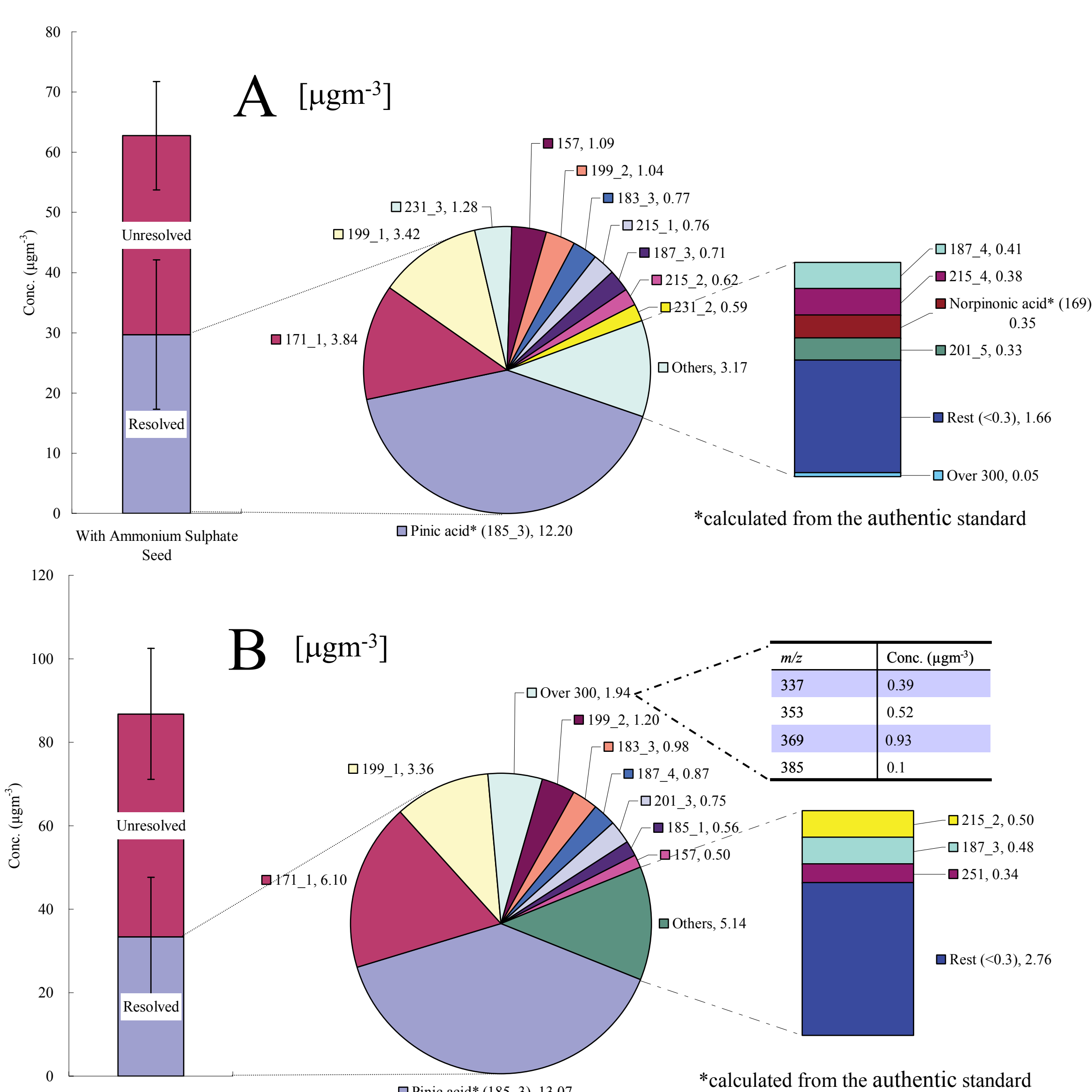


Fig 3: Estimated and calculated concentrations [$\mu\text{g m}^{-3}$] of α -pinene oxidation products (A) with ammonium sulphate seed particles and (B) With sulphuric acid seed particles.