

## Introduction

- Recent estimate suggests that biogenic secondary organic aerosol (SOA) contributes significantly to the total global particulate carbon load, ranging from 12 to 70 Tg SOA  $\text{y}^{-1}$  [Kanakidou et al., 2005].
- The  $\alpha$ -pinene and its oxidation products have received significant attention in the past due to its high emission rates from coniferous trees and its high SOA yields in chamber studies.
- Detailed organic speciation of summer time  $\text{PM}_{10}$  collected in Melbourne, Australia shows the presence of numerous monoterpene oxidation products from  $\alpha$ -pinene and  $\beta$ -pinene.
- In addition, two polar oxygenated compounds with molecular formulae of  $\text{C}_9\text{H}_{14}\text{O}_6$  and  $\text{C}_{10}\text{H}_{16}\text{O}_6$  were detected at higher levels. They are not reported previously.
- Because of their high abundance in summertime Australian samples, these compounds are proposed to be oxidation products of 1,8-cineole, which is typically emitted at high levels from common eucalyptus trees in Australia.
- 1,8-Cineole mainly reacts with OH radicals in the troposphere through H-abstraction mechanisms [Corchnoy and Atkinson, 1990].
- In order to elucidate the origin and the structures of these compounds, a series of 1,8-cineole oxidation experiments was conducted in an indoor aerosol chamber.

## Experimental Details

### Field Samples

- Figure 1 shows the location of the CSIRO Marine and Atmospheric Research (CMAR) Bay-side Air Quality Station (BAQS) at Aspendale in Melbourne, Australia. The site is located in a residential area 25 km south of the city of Melbourne.
- The site is influenced by vehicle emissions, marine aerosol, light industry and residential emissions (including emissions from wood heaters used for domestic heating between May and September).
- Samples from a  $\text{PM}_{10}$  high volume aerosol sampler were used for analysis. The high volume sampler (HVS) operated in this study was an Ecotech 3000 series with a Gold-Top  $\text{PM}_{10}$  inlet.

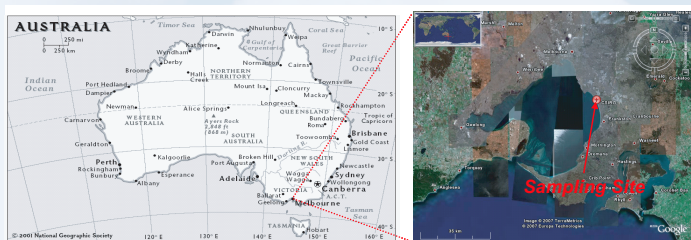


Figure 1. Map of Australia and the location of the CSIRO Bayside Air Quality Station at Aspendale

### Chamber Experiments

- A series of chamber experiments were carried out using 19 m<sup>3</sup> PTFE chamber. Table 1 summarizes the initial experimental conditions. Figure 2 shows the structure of 1,8-cineole.

Table 1. Initial experimental conditions used for this study. TME stands for tetramethylethylene.

Seed particles	System	Initial HC Conc [ppb]	Reacted HC [ppb]	Temperature °C	RH %
0.03/0.05M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>	TME/O <sub>3</sub>	100	25	22	50
0.06M Na <sub>2</sub> SO <sub>4</sub>	TME/O <sub>3</sub>	100	24	23	50
0.03/0.05M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>	CH <sub>3</sub> ONO/UV	150	28	22	52

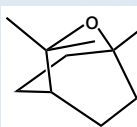


Figure 2. 1,8-Cineole

### Chemical Analysis

#### Gas-phase

- PTR-MS (Proton Transfer Reaction - Mass Spectrometry) for the online determination of hydrocarbon concentration.
- A NO<sub>x</sub> monitor for online NO and NO<sub>2</sub> determination.

#### Particle-phase

- Filters were extracted in methanol by ultrasonication.
- Dried under N<sub>2</sub> and reconstituted in 50/50 methanol/water (v/v).
- High Performance Liquid Chromatography simultaneously coupled to Electrospray Ionisation Time of Flight Mass Spectrometry (HPLC/ESI-TOFMS) and Electrospray Iontrap Mass Spectrometry (ESI-ITMS<sup>n</sup>).

## References

- Corchnoy, S. B.; Atkinson, R. Kinetics of the Gas-Phase Reactions of OH and NO<sub>3</sub> Radicals with 2-Carene, 1,8-Cineole, Para-Cymene, and Terpinolene. *Environ. Sci. Technol.* 1990, 24, 1497-1502.
- Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. Organic aerosol and global climate modelling: a review. *Atmospheric Chemistry and Physics* 2005, 5, 1053-1123.

## Results

- Figure 3 shows extracted ion chromatograms (EICs) from the analysis of an ambient sample and 1,8-cineole oxidation experiments. The retention times of 1,8-cineole oxidation products agreed very well with those from the ambient sample for both the  $\text{C}_9\text{H}_{14}\text{O}_6$  ( $m/z$  217) and  $\text{C}_{10}\text{H}_{16}\text{O}_6$  ( $m/z$  231) compounds.
- Figure 4 illustrates accurate mass and fragmentation experiment data for both the  $m/z$  217 and  $m/z$  231 compound. Neutral losses of 44 u (carboxylic group) and 60 u (acetate ester) were observed for both compounds.
- Based on the interpretation of the mass spectra and the structure of 1,8-cineole, a reference compound (diaterpenylic acid acetate (3-[1-(acetyloxy)-1-methylethyl]glutaric acid), MW 232) was synthesized and compared to the ambient and chamber samples.
- Its chromatographic and mass spectral behaviors agree extremely well (Figures 3 and 4), hence the  $\text{C}_{10}\text{H}_{16}\text{O}_6$  compound is positively identified as diaterpenylic acid acetate.
- The  $\text{C}_9\text{H}_{14}\text{O}_6$  compound is tentatively identified as diaterbic acid acetate (2-[1-(acetyloxy)-1-methylethyl]succinic acid).

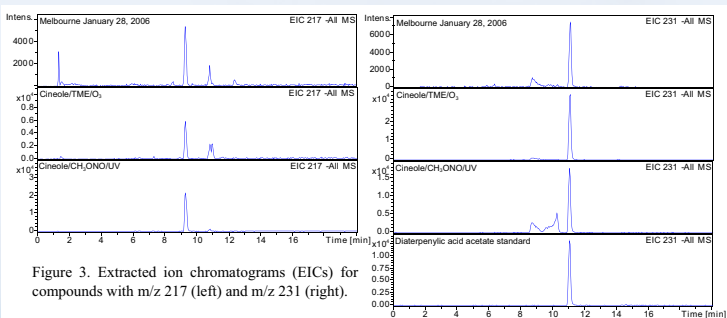


Figure 3. Extracted ion chromatograms (EICs) for compounds with  $m/z$  217 (left) and  $m/z$  231 (right).

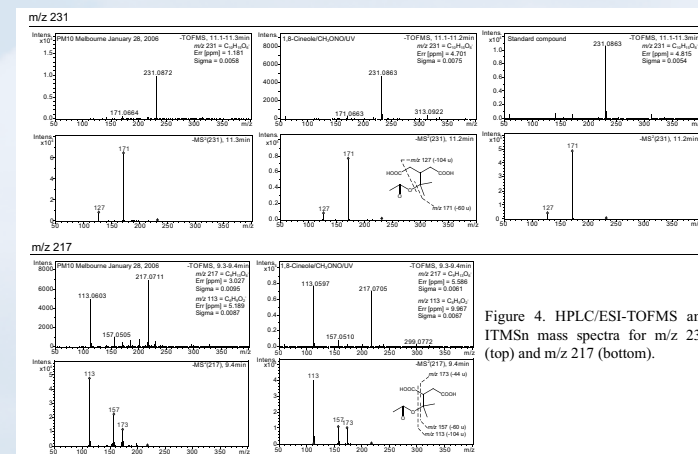


Figure 4. HPLC/ESI-TOFMS and ITMSn mass spectra for  $m/z$  231 (top) and  $m/z$  217 (bottom).

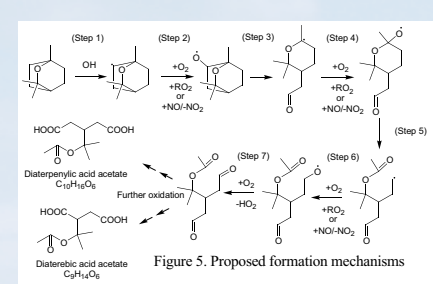


Figure 5. Proposed formation mechanisms

- Figure 5 presents the proposed formation mechanisms for diaterbic acid acetate and diaterpenylic acid acetate.
- The concentrations were as high as 47 ng m<sup>-3</sup> for diaterpenylic acid acetate and 30 ng m<sup>-3</sup> for diaterbic acid acetate in the ambient sample.
- The sum of these two compounds were approximately 9wt% of the laboratory produced SOA. The fraction of diaterbic acid acetate was higher for the high NO<sub>x</sub> experiment.

## Conclusions

- Two previously unreported monoterpene oxidation products were identified.
- The concentrations of 1,8-cineole oxidation products were much higher than typical  $\alpha$ -pinene oxidation products such as pinic acid and pinonic acid.
- The airshed of Melbourne is significantly impacted by SOA generated from regional biogenic emissions during summertime.
- In particular, the emission from eucalyptus trees contributes significantly to the SOA.
- Further study is necessary for better understanding of the impact of 1,8-cineole oxidation to the regional SOA loading where eucalyptus trees are common or widely planted.