

Aerosol-chamber study of the α -pinene / O₃ reaction: Influence of particle acidity on aerosol yields and products

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Motivation

Atmospheric aerosols often contain a substantial fraction of organic matter. The contribution of secondary organic carbon to the measured organic aerosol concentration remains a controversial issue. Atmospheric oxidation of monoterpenes is believed to play an important role in the formation of secondary organic aerosols (SOA). Although this process is supposed 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. The experiments will focus on possible effects of aerosol aqueous phase chemistry under acidic conditions following gas phase terpene ozonolysis. Such particle chemistry could lead to (i) an increase of SOA which might be important on a global scale and (ii) the formation of higher molecular weight products.

Chamber experiments are invaluable for understanding SOA formation. Therefore a new aerosol chamber is built.



Fig. 1: The new IFT aerosol chamber building

Set-up of the new aerosol chamber and planned experiments

As housing for the new IFT aerosol chamber a hall (Fig. 1) was completed in spring 2004. In this hall is built the new chamber facility. The chamber by itself is made of Teflon FEP film. The chamber has cylindrical geometry, a volume of 17.7 m³ and a surface/volume ratio of 2.1 m⁻¹.

The aerosol chamber is equipped with a humidifier, an ozone and a particle generator. Sixty UV lamps (100W Ever-sun Super, Phillips) are used to illuminate the aerosol chamber. To maximize the light intensity in the chamber, reflective aluminium sheeting covers the walls of the enclosure. A 6 kW heat exchanger controls the temperature of the insulated enclosure housing the Teflon chamber.

Outlets of the chamber are connected with a condensation particle counter (CPC), a continuous monitoring ozone analyzer and a particle sampling filter device with a fixed integrated annular denuder to avoid gaseous contamination of the deposited particles during sampling. The size distributions of particles in the aerosol chamber as a function of time are measured by a differential mobility particle sizer (DMPS). For time resolved rapid analysis of aerosol particles a condensational-growth and impaction system (C-GIS) will be used. C-GIS converts the aerosol into a hydrosol that can be readily drawn into a variety of systems for chemical analysis, cf. Fig. 4. An Agilent gas chromatograph (GC) with flame ionization detector monitors gas-phase hydrocarbon concentrations in the chamber.

First experiments in the new chamber will be the ozonolysis of β -pinene, limonene, cyclohexene and methylene cyclohexane. Aim is to study the influence of particles with different acidity on particle yields and particle phase products.

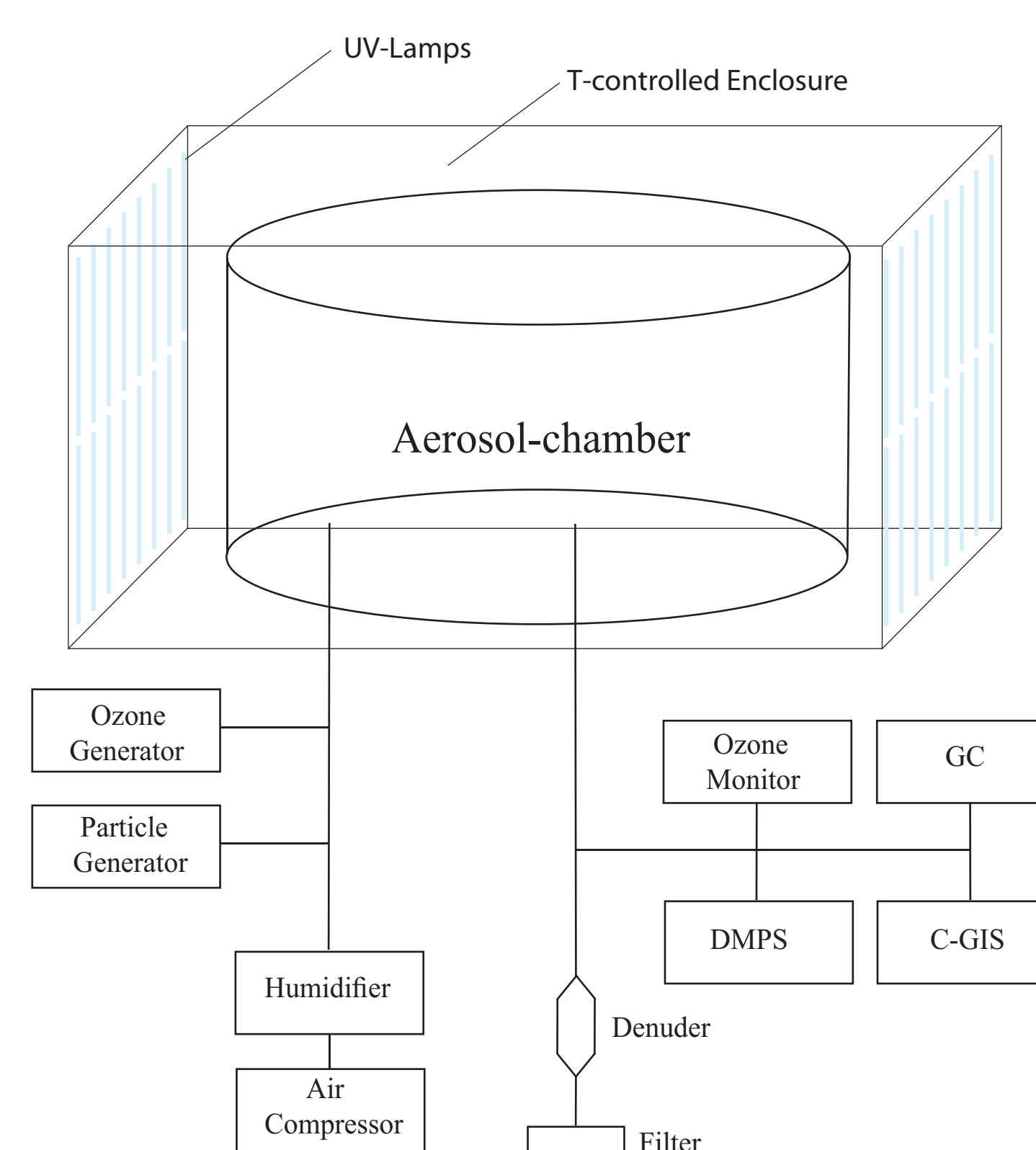


Fig. 2: Block diagram of gas- and aerosol-phase instrumentation of the new IFT aerosol chamber

Results

α -Pinene ozonolysis was carried out in the presence of ammonium sulfate or sulfuric acid seed particles in a 9 m³ Teflon chamber at mixing ratios of 100 ppbV for α -pinene and about 70 ppbV for ozone.

cis-Pinic acid (m/z = 185) and other species tentatively identified at m/z 171 and 199 were the major particle phase species for both seed particles although the product yields were different, indicating the influence of seed particle acidity.

Compared to the experiments with ammonium sulfate particles, almost 40% increase in measured OC concentration was observed from the experiments with sulfuric acid particles.

A number of compounds with $M_w > 300$ have been detected from the experiments with sulfuric acid seed particles suggesting an acid catalyzed formation of larger molecules in the particle phase (Fig. 3). This result indicates that particle acidity of atmospheric particles plays an important part in the heterogeneous reaction of SOA and may explain an unresolved fraction of organic aerosols in the atmosphere.

The C-GIS was tested in a few experiments. The results indicate that the C-GIS with subsequent analysis by capillary electrophoresis is possible with a time resolution of 15 min.

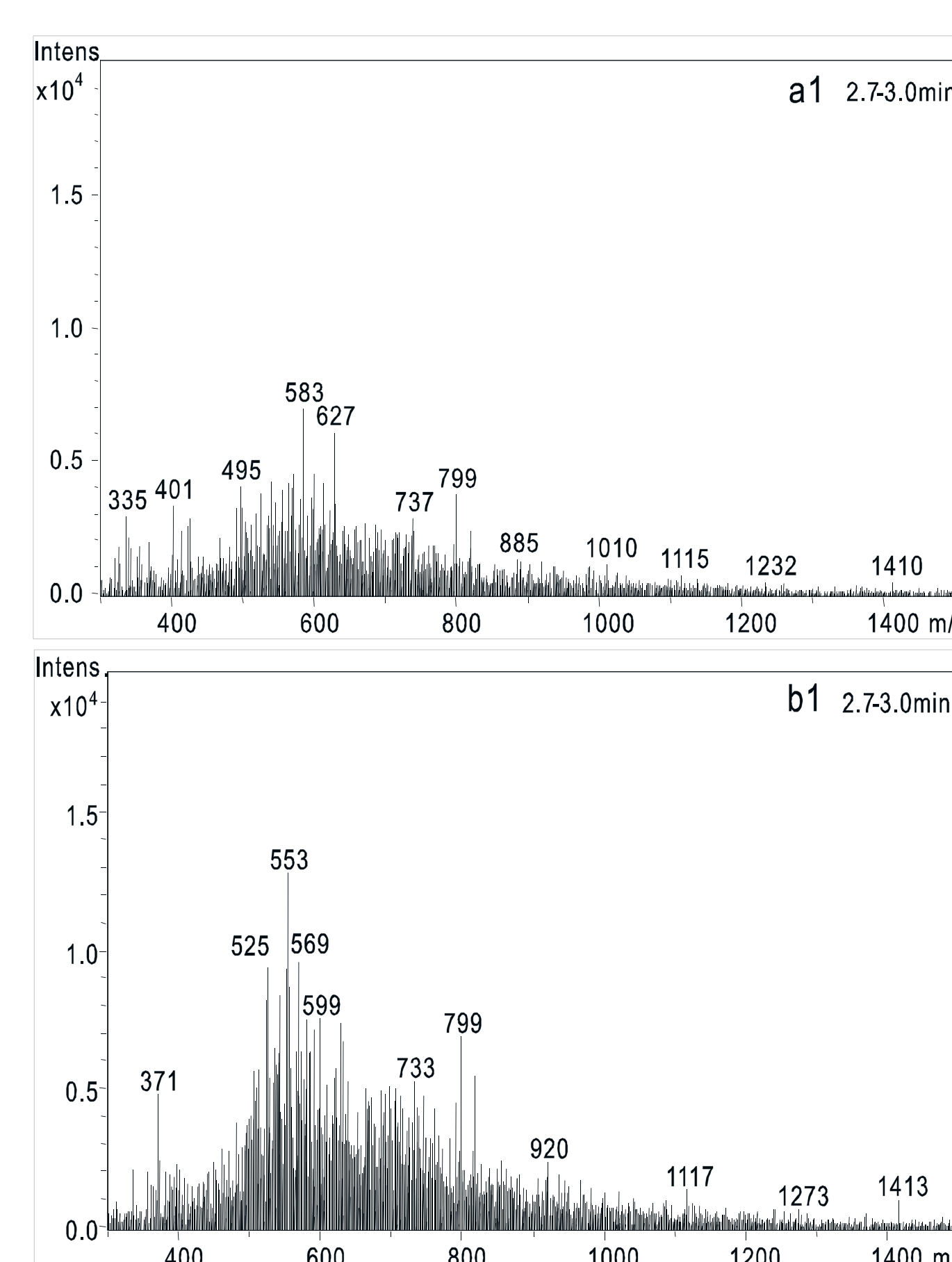


Fig. 3: Background subtracted mass spectra of peaks 2.7-3.0 min (CE-MS) for ammonium sulfate (upper part) and sulfuric acid (lower part). Note: small amount of oligomers and polymers are also found from ammonium sulfate seed particles.

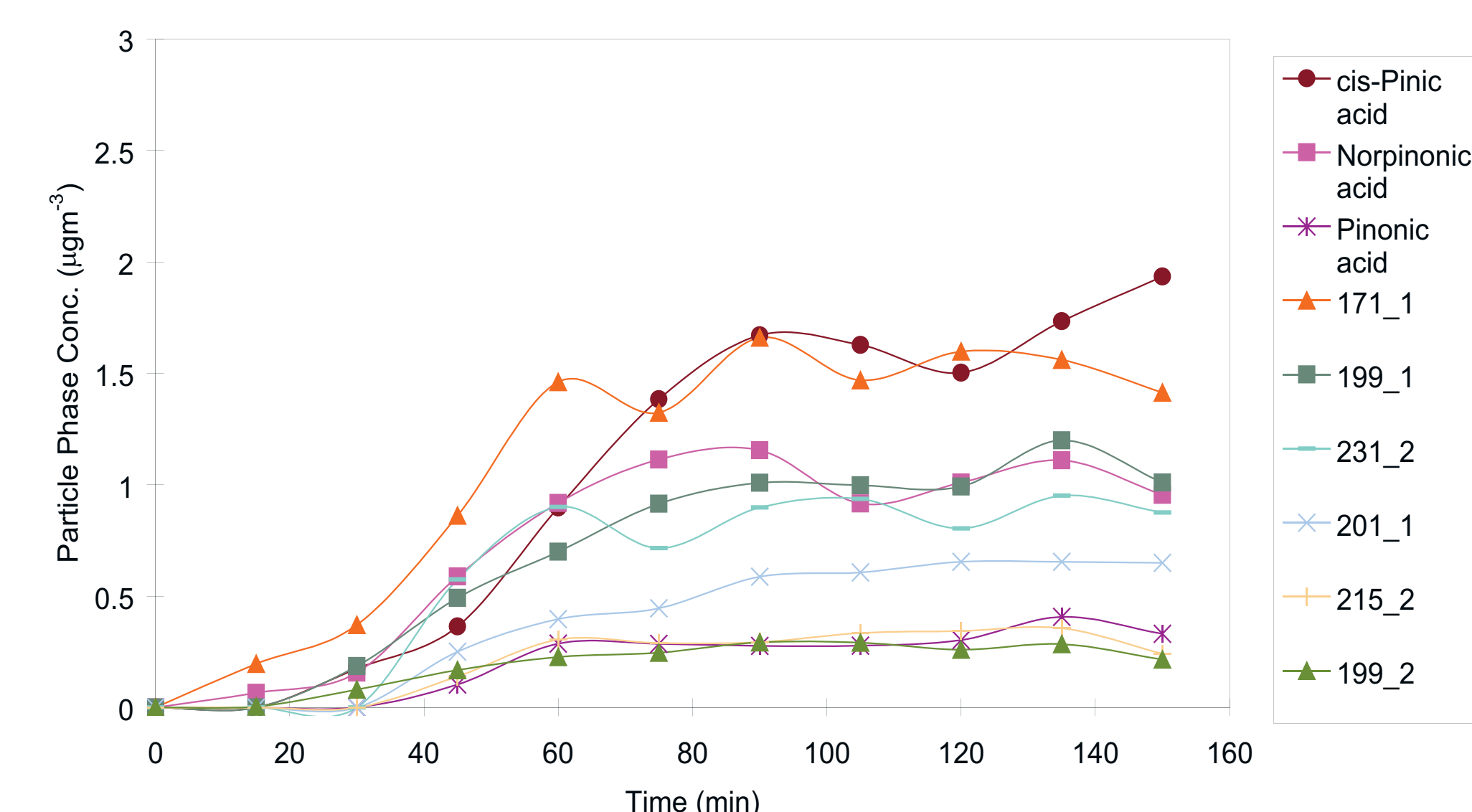


Fig. 4: C-GIS time series of most α -pinene oxidation products with sulphuric acid particles.

Acknowledgements

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