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Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols

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Abstract

Formation of carboxylic acids and dimer esters from α-pinene oxidation were investigated in a smog chamber and in ambient aerosol samples collected during the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX). Chamber experiments of α-pinene ozonolysis in dry air and at low NO_x concentrations demonstrated formation of two dimer esters, pinyl-diaterpenyl (MW 358) and pinonyl-pinyl dimer ester (MW 368), under both low and high temperature conditions. Concentration levels of the pinyl-diaterpenyl dimer ester were lower than the assumed first-generation oxidation products *cis*-pinic and terpenylic acids, but similar to the second-generation oxidation products 3-methyl-1,2,3-butane tricarboxylic acid (MBTCA) and diaterpenylic acid acetate (DTAA). Dimer esters were observed within the first 30 min, indicating rapid production simultaneous to their structural precursors. However, the sampling time resolution precluded conclusive evidence regarding formation from gas- or particle-phase processes. CCN activities of the particles formed in the smog chamber displayed a modest variation during the course of experiments with κ values in the range 0.06–0.09 (derived at a supersaturation of 0.19 %).

The pinyl-diaterpenyl dimer ester was also observed in ambient aerosol samples collected above a ponderosa pine forest in the Sierra Nevada Mountains of California during two seasonally distinct field campaigns in September 2007 and July 2009. The pinonyl-pinyl ester was observed for the first time in ambient air during the 2009 campaign, and although present at much lower concentrations, it was correlated with the abundance of the pinyl-diaterpenyl ester suggesting similarities in their formation. The maximum concentration of the pinyl-diaterpenyl ester was almost 10 times higher during the warmer 2009 campaign relative to 2007, while the concentration of *cis*-pinic acid was approximately the same during both periods, and lack of correlation with levels of of *cis*-pinic and terpenylic acids for both campaigns indicate that the formation of the pinyl-diaterpenyl ester was not controlled by their ambient abundance. In 2009, the concentration of the pinyl-diaterpenyl ester was well correlated with the concentration

of DTAA, a supposed precursor of diaterpenylic acid, suggesting that the formation of pinyl-diaterpenyl dimer was closely related to DTAA. Generally, the pinyl-diaterpenyl ester was found at higher concentrations under higher temperature conditions both in the smog-chamber study and in ambient air aerosol samples, and exhibited much higher concentrations at night relative to day-time in line with previous results.

We conclude that analysis of pinyl dimer esters provides valuable information on pinene oxidation processes and should be included in studies of formation and photochemical aging of biogenic secondary organic aerosols, especially at high temperatures.

1 Introduction

Biogenic secondary organic aerosol (BSOA) is formed through atmospheric oxidation and processing of naturally emitted volatile organic compounds (VOC) and comprises a major fraction of secondary organic aerosols (SOA) in ambient air (Hallquist et al., 2009). Aerosols affect climate through light scattering and by influencing the formation and lifetime of clouds (IPCC, 2007; Lohmann and Feicher, 2005; Andreae and Rosenfeld, 2008). To evaluate the climatic impact of atmospheric aerosols it is important to understand their chemical composition and sources as well as the chemical processes that form and transform them in the atmosphere.

Monoterpenes constitute an important group of biogenic VOC (BVOC) emitted from coniferous trees as well as other types of vegetation (Guenther et al., 1995). The atmospheric lifetime of monoterpenes is of the order of minutes to hours due to their fast reaction with hydroxyl radicals (OH), nitrate radicals (NO_3) and ozone (O_3) (Atkinson and Arey, 1998; Calogirou et al., 1999). The first-generation oxidation products of monoterpenes constitute a complex group of primarily carbonyl compounds, carboxylic acids, and organic nitrates (e.g. Yu et al., 1999; Glasius et al., 2000; Larsen et al., 2001; Hallquist et al., 2009; Camredon et al., 2010, Perraud et al., 2010; Fry et al., 2009), which can undergo further atmospheric processing such as oxidation (e.g., Szmigielski et al., 2007; Müller et al., 2011), formation of organosulfates (e.g., Surratt et al., 2008; Iinuma et al., 2007) and oligomerization (e.g., Tolocka et al., 2004; Kalberer et al., 2004). These processes (whether homogenous or heterogeneous) can incorporate otherwise volatile or semi-volatile compounds into the particle phase as less volatile products (Kroll and Seinfeld, 2008; Jimenez et al., 2009; Hallquist et al., 2009). Formation of oligomers, including dimers, from α-pinene ozonolysis products is an important SOA transformation process (e.g., Tolocka et al., 2004; Gao et al., 2004; Müller et al. 2008; Putman et al., 2012) that has been estimated to contribute as much as 50 % to non-volatile SOA mass (Hall IV and Johnston, 2010).

Dimers have often been identified according to their molecular weight determined by mass spectrometry, but based on previously proposed structures (Table 1) we suggest a more clear nomenclature where the names reflect the components of the dimer esters according to present understanding of their molecular structures. For example, the dimer of molecular weight (MW) 358 is called pinyl-diaterpenyl ester, the dimer of MW 344 is called diaterpenyl-terpenyl ester and the dimer of MW 368 is called pinonyl-pinyl ester, These three dimer esters have been recently observed in several smog-chamber studies of both α- and β-pinene oxidation (Müller et al. 2008, 2009; Camredon et al., 2010; Yasmeen et al., 2010; Gao et al., 2010).

Yasmeen et al. (2010) presented the first ambient measurements of the pinyl-diaterpenyl ester and diaterpenyl-terpenyl ester in particles collected during warm nights at K-Puszta, Hungary. However, it was unclear whether they were only detected during warm nights due to a temperature effect promoting ester formation at higher temperatures or due to photochemical degradation of the esters during daytime.

In this work we report concentrations and diurnal variations of first- and second-generation oxidation products of α- and β-pinene (listed in Table 1) in aerosol samples collected above a Ponderosa pine plantation in California, USA during the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX) 2007 and 2009. We investigated the influence of temperature on the formation of dimer esters and compared with results from dark smog-chamber ozonolysis of α-pinene under cool (15 °C) and warm (23–24 °C) conditions.

2 Experimental

2.1 Smog-chamber study

Experiments were conducted at the University of Copenhagen using a smog chamber setup consisting of a Teflon bag (Foiltech Gmbh) suspended from a metal frame in a temperature-controlled laboratory. The bag was shielded from light by dark curtains. Dimensions of the bag were 2.65 m × 2.95 m × 3.15 m ($H \times W \times L$), giving a volume of $\sim 25\,\mathrm{m}^3$ and a surface-area-to-volume ratio of $\sim 2\,\mathrm{m}^{-1}$. Stainless steel manifolds with inlet and outlet ports were mounted on two sides of the bag. All inlet and sampling lines reaching into the chamber were stainless steel. The temperature inside the bag was controlled by varying the temperature of the entire laboratory. O_3 was measured using a Thermo Electron Corporation Model 49i O_3 monitor and oxides of nitrogen (NO_x) were measured using a Thermo Electron Corporation Model 42i NO_x monitor. Temperature and relative humidity (RH) were measured inside the bag using a Rotronic Hygroclip HC2-C04 monitor. Initial O_3 concentrations, temperature, and RH for each experiment are given in Table 2. NO_x concentrations were 2 ppb or below in all experiments. RH was less than 1 %.

All experiments were performed in the dark. Particle size distributions were measured using a scanning mobility particle sizer (SMPS) system (TSI SMPS model 3936L72 consisting of a DMA model 3081 with a 3772 CPC operating with recirculating sheath air (10 : 1 $\mathrm{l\,min^{-1}}$ sheath-to-aerosol flow ratio). Size distributions (7–300 nm) were sampled every 3.5 min. No OH-scavenger or seed aerosol was added to the chamber in any of the experiments.

Aerosol samples were collected at 17 $\mathrm{l\,min^{-1}}$ for 15 or 30 min using 47-mm Teflon filters at chamber temperature. O_3 was removed from the sample stream by passing the aerosol through a potassium iodide coated annular glass denuder (URG-2000-30B) prepared following Williams and Grosjean (1990), and gas-phase organic compounds were removed in a similar manner using an XAD-4 coated glass denuder. The two denuders were placed in series in front of the filter. Filters were stored at −18 °C and under dark conditions until chemical analysis.

Prior to each experiment, the Teflon bag was cleaned; first it was flushed with O_3 and air and left with a high concentration of O_3 (ppm levels) for a couple of hours and afterwards flushed with dry clean air until the O_3 concentration was again below a few ppb. The chamber was then filled with high pressure dried purified air, and O_3 was added (O_3 Technology AB Model ACF-500) until an initial concentration around 100 ppb was reached (actual values are given in Table 2). 16 µl of α-pinene (Sigma Aldrich, $\geq 99\,\%$) was added to the chamber by injection into a clean air stream ($10\,\mathrm{l\,min^{-1}}$); this air stream was kept on for approximately 5 min to ensure proper mixing of the α-pinene and O_3. Further mixing in the bag was insured by pulses of high-pressure air into the bag. The initial concentration of α-pinene was estimated to be approximately 100 ppb based on the known volume of the chamber and the volume of α-pinene added ($M = 136.23\,\mathrm{g\,mol^{-1}}$, $\rho = 0.858\,\mathrm{g\,ml^{-1}}$).

Cloud condensation nuclei (CCN) activity of the particles formed in the chamber was measured using a continuous-flow CCN counter (Droplet Measurement Technologies CCN-100). The size distribution of the particles were first narrowed to monodispersity with a TSI DMA model 3081 before the particles were simultaneously measured for activated number concentration by the CCN counter and for total number concentration by a TSI CPC model 3010. Further details of the data acquisition methodology can be found in King et al. (2012). The temperature difference within the column of the CCN counter was set such that the supersaturation was 0.19 %. CCN activities were recorded for both experiments performed at 15 °C (sample temperature of the CCN column was 23 °C, experiment 2) and at 24 °C (sample temperature of the CCN column was 23 °C, experiment 3) for the entire course of the experiments. A fitting procedure was used to calculate activation diameters from measured activation curves, in which contributions from multiply charged particles were accounted for (Petters et al., 2007).

2.2 Field study

The BEARPEX campaign took place at a ponderosa pine (*Pinus ponderosa* L.) plantation owned by Sierra Pacific Industries adjacent to the University of California – Blodgett Forest Research Station (UC-BFRS; 38.90° N, 120.63° W, 1315 m elevation above sea level). High-volume filter samples (33 in total including two field blanks) were collected on 20 cm × 25 cm quartz fiber filters (Gellman QM-A) at 9.3 m on the main tower from 20–25 September 2007 (16 samples) and 26–31 July 2009 (17 samples). The 2007 sampling period was during early fall, with colder temperatures (11 ± 5 °C) than during the 2009 summer campaign (25 ± 4 °C, Table 3).

Samples were collected using a Thermo Anderson Total Suspended Particulate (TSP) high volume sampler with an SA-230-F impactor at a volumetric flow of 68 $m^3 h^{-1}$, as previously described by Bench and Herckes (2004). The impactor removed particles with diameters larger than 2.5 µm. The quartz filters were pre-fired by baking at 600 °C for 12 h and were stored in sealed foil lined plastic bags prior to use. After sampling with the quartz filters, they were immediately placed in pre-baked aluminum foil and stored frozen at −18 °C until analyzed. Field blanks were obtained by placing one filter in the sampler for ten minutes with the pump off around the midpoint of each sampling period. These filters represented two continuous five day periods, one in each year, with three filters per day that provided an uninterrupted time series with sufficient time resolution to separate the influence of local early morning biogenic emissions from the afternoon arrival of the urban plume from Sacramento and nighttime chemistry. Aliquots (115 cm^2) of these filters were used in this study.

2.3 Extraction and analysis

Filter samples were extracted in acetonitrile in an ultrasonic bath. The filters were removed and the solvent evaporated under a gentle flow of nitrogen. The sample was then re-dissolved in 3 % acetonitrile with 0.1 % acetic acid in water and filtered using a 0.21 µm syringe filter (Q-Max Syringe Nylon filters, Frisenette, Denmark).

Samples were analysed on a Dionex Ultimate HPLC equipped with a Waters T3 column (2.1 × 150 mm, 3 µm particle diameter) coupled through an electrospray ionization (ESI) inlet to a Bruker microTOFq quadrupole time-of-flight mass spectrometer (qTOF-MS) as previously described (Kristensen and Glasius, 2011). The HPLC mobile phase was acetic acid 0.1 % in water (v/v) (eluent A) and acetonitrile (eluent B) and a 50 min gradient elution was applied: Eluent B was kept at 3 % for 5 min, increased to 90 % in 25 min, kept at 90 % for 10 min, then increased to 95 % in 2 min, held for 6 min, and finally decreased to 3 % in 5 min. The injection volume was 10 µl and the flow rate was 0.2 ml min^{-1}. The ESI-qTOF was operated in the negative mode at the following conditions: nebulizer pressure 0.8 bar, dry gas flow 8.0 l min^{-1}, source voltage 4 kV, collision gas argon, quadrupole ion energy 5.0 eV, collision cell energy 10.0 eV and transfer time 100 ms.

Samples were calibrated to authentic standards of the following acids: *cis*-pinic acid, pimelic acid (98 %), and *cis*-pinonic acid (98 %) (obtained from Sigma-Aldrich) and terpenylic acid, diaterpenylic acid acetate (DTAA), and 3-methyl-butane tricarboxylic acid (MBTCA) (obtained from Y. Iinuma and O. Böge, Leibniz Institute for Tropospheric Research, Germany). Five-level calibration curves were constructed from 0.1 to 10.0 µg ml^{-1}. Due to a lack of authentic standards, diaterpenylic acid was quantified using an average of the terpenylic acid and DTAA calibration curves and the concentration of the three dimer esters (pinyl-diaterpenyl, diaterpenyl-terpenyl and pinonyl-pinyl) were determined from the average calibration curves of their precursors. Detection limits were 0.5–1.7 ng injected (see Kristensen and Glasius, 2011 for details).

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To rule out the possibility that dimer esters are formed during sample extraction and analysis, we performed a study of artifact formation of dimer esters. Solutions of suspected ester precursors (pinic acid, pinonic acid, terpenylic acid, MBTCA and DTAA, each about 10 µg ml^{-1}) were left at room temperature or at 5 °C for 4 days and analyzed. Very low concentrations of artefact dimer esters were observed, but these artefact dimer esters had a tendency to form sodium complexes in the electrospray source in contrast to naturally formed dimer esters. This resulted in different exact masses for natural and artifact dimer esters allowing them to be distinguished from one another. This shows that care should be taken when analyzing dimer esters, and the time from extraction to analysis should be kept at a minimum.

3 Results and discussion

3.1 Smog-chamber experiments

During the smog-chamber ozonolysis of α-pinene (at low RH and low NO_x), two dimer esters were observed: the pinyl-diaterpenyl ester (MW 358) composed of pinic acid and diaterpenylic acid units, and the pinonyl-pinyl ester (MW 368) composed of hydroxy-pinonic acid and pinic acid units. The supplemental information shows extracted ion chromatograms (EIC), MS and MS-MS spectra of these esters. The two esters were identified by their characteristic MS-MS fragmentation pattern. The MS-MS fragmentation of the pinyl-diaterpenyl ester observed in this study resembles the fragmentation pattern described by Yasmeen et al. (2010).

Figure 1 shows concentrations of pinic acid, pinonic acid, hydroxy-pinonic acid, terpenylic acid, DTAA, MBTCA, pinonyl-pinyl ester and pinyl-diaterpenyl ester as a function of time during the experiments. In all cases the concentrations increase during the first ~ 100–150 min and reach a maximum before decreasing towards the end of the experiments, similar to particle concentrations and most likely due to wall losses. Figure 2 shows the particle size and mass distributions of experiment 2 as a function of time (similar figures for experiments 1, 3, and 4 shown in supplementary material). The presented data has not been corrected for wall losses. Particle mass was obtained from SMPS data assuming spherical particles with an assumed SOA density of 1.23 g cm^{-3} based on previous work (Song et al., 2007).

The pinyl-diaterpenyl and pinonyl-pinyl esters were observed under both cold and warm conditions during the smog chamber experiments, reaching concentrations comparable to several first- and second-generation oxidation products (i.e. the first generation product pinonic acid, and the second generation products DTAA and MBTCA, Fig. 1). The pinyl-diaterpenyl ester showed somewhat higher maximum concentrations during the warm experiments (about 0.7 µg m^{-3}) compared to the cold ones (about 0.4 µg m^{-3}), while the pinonyl-pinyl ester showed no clear temperature dependency (maximum concentrations in the range 0.25–0.4 µg m^{-3}). The concentration of pinonic acid is lower in warm experiments compared to cold, since its vapor pressure favors presence in the gas phase at higher temperatures, while MBTCA shows higher particle-phase concentrations at higher temperatures, due to increased formation from OH initiated oxidation of pinonic acid in the gas phase followed by condensation (as observed by Müller et al., 2012).

Both dimer esters were observed within 30 min of addition of α-pinene, indicating that they are formed simultaneously with the formation of their structural precursors or shortly after, at our time-resolution. If condensed-phase reactions were important for initial ester formation at chamber conditions, a delay in the occurrence of esters compared to precursors would also be expected. Using on-line APCI-MS with high time-resolution, Müller et al. (2008) observed that intensity of esters increased even faster than the intensity of their monomer precursors in freshly nucleated aerosol in the α-pinene/O$_3$ system. The latter lead them to suggest that gas-phase ester formation could be important for homogeneous nucleation although the reaction mechanism has not yet been elucidated. A gas phase ester-forming mechanism could involve stabilized Criegee intermediates, formed by ozonolysis. The high O : C ratio of esters (0.47 and 0.36, respectively) points towards Criegee intermediates, since otherwise several oxidation steps would be needed to incorporate the high number of oxygen molecules implying a slower process than monomer formation. Heaton et al. (2007) observed almost immediate formation of dimers and higher order oligomers in a flow tube study of monoterpenes ozonolysis indicating that ester formation had almost no kinetic barrier and likely consisted of very few oxidation steps. Gas phase formation of pinyl-diaterpenyl and pinonyl-pinyl esters from Criegee intermediates would also explain why the esters were observed simultaneously with classical first generation products such as *cis*-pinonic acid. However, we did not observe dimer esters in concentrations above the detection limit in extracts from the gas-phase denuder samples. The saturation vapor pressure of pinic acid (9.5×10^{-6} Pa at 24 °C and 3.8×10^{-5} Pa at 15 °C extrapolated from Bilde and Pandis, 2001) is significantly above the limit (1.2×10^{-8} Pa) for it to be a nucleating species (Bonn and Mortgat, 2003).

We estimated the vapor pressure of the pinyl-diaterpenyl and pinonyl-pinyl esters using the p^0 calculator (Clegg et al. 2008) provided on the online Extended *AIM* Aerosol Thermodynamics Model homepage (http://www.aim.env.uea.ac.uk/aim/aim.php). Three structure based estimation methods for boiling point and vapor pressure of pure liquid organic compounds are used: first, Nannoolal et al. (2004) for boiling point using the vapor pressure by Moller et al. (2008), second, Nannoolal et al. (2004, 2008) for both boiling point and vapor pressure; third, Stein and Brown (1994) for boiling point and vapor pressure by Myrdal and Yalkowsky (1997). Using these three methods vapor pressures of 7×10^{-17}, 1×10^{-12} and 3×10^{-7} Pa, respectively, were obtained for pinyl-diaterpenyl ester at 298 K and vapor pressures of 4×10^{-15}, 5×10^{-11} and 8×10^{-7} Pa, respectively, are obtained for pinonyl-pinyl ester. These estimates differ by orders of magnitude illustrating the difficulty in estimating vapor pressures of large organic molecules. However, it seems reasonable to expect the vapor pressures of dimer esters to be significantly lower than for pinic acid, making them more likely candidates as nucleating species.

CCN activity of the SOA formed in the chamber is expressed in Fig. 3 in terms of the hygroscopicity parameter κ (Petters and Kreidenweis, 2007), which is calculated

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from the activation diameter measured at 0.19 % supersaturation. All κ values are in the range 0.06–0.09. Critical diameters as a function of time are given in Table S1. The CCN activities measured in this study fall within the range of those reported previously (Huff Hartz et al., 2005; VanReken et al., 2005; Prenni et al., 2007).

CCN activity displays only modest variation during the course of the experiments. However in Fig. 3 there is some indication that the rate of the changes depends on chamber temperature. At the higher temperature, κ decreases (i.e., CCN activity decreases) by a small but perceptible amount during the first 150–200 min of the experiment, whereas CCN activity remains relatively constant during this same time period at the lower temperature. The decrease in CCN activity at the lower temperature occurs only after 150 min have elapsed. This difference could possibly be attributed to slower initial aging at colder temperatures, leading to lower formation of esters and oligomers whose higher MWs imply lower CCN activity. This is consistent with the observation that the concentration of pinyl-diaterpenyl ester is higher in the condensed phase during the warmer experiments. Following the initial decrease in CCN activity, there is an increase in the activity under warm conditions (experiments 1 and 2), and there is a suggestion of an increase under cold conditions (experiments 3 and 4) after 250 min have elapsed. One explanation for this increase is further oxidative aging leading to higher O : C ratios, which has been shown in several studies to correlate with increased hygroscopicity (e.g. Jimenez et al., 2009).

In summary, the pinyl-diaterpenyl and pinonyl-pinyl esters are indeed formed rapidly in the ozonolysis of α-pinene and at concentrations comparable to some first- and second-generation products under both low and warm temperatures in chamber experiments. The rapid formation coincident with precursor formation suggests a gas-phase mechanism possibly involving Criegee intermediates, although due to the low time resolution of the filter samples no direct evidence was observed.

3.2 Field study

3.2.1 Pinyl-diaterpenyl ester

Monoterpene dimer esters were detected in ambient aerosols collected during two field campaigns in the Sierra Nevada Mountains of California (BEARPEX 2007 and 2009). In contrast to the recent study of Yasmeen et al. (2010), the pinyl-diaterpenyl ester (MW 358) of *cis*-pinic and diaterpenylic acid was observed in all BEARPEX night-time samples and even in daytime samples during 2009 (Fig. 4). A clear diurnal variation with night-time maxima was observed during BEARPEX, especially during 2007, when daytime levels were almost negligible. The estimated maximum concentration of the pinyl-diaterpenyl ester was about ten times higher during 2009 compared to 2007 (Table 3). The same tendency was observed for isoprene-derived organosulfates (Worton et al., 2011). The diurnal variation of the pinyl-diaterpenyl ester was less pronounced during 2009, and daytime levels grew to ten times the night maxima observed in 2007.

Scatterplots of the level of pinyl-diaterpenyl ester versus concentrations of the proposed precursors *cis*-pinic and terpenylic acids showed no significant linear relationship ($R^2 < 0.35$, $n = 30$, data not shown) for either acid, suggesting that the formation of the pinyl-diaterpenyl ester was not controlled by the ambient abundance of either *cis*-pinic or terpenylic acid. However, a scatterplot of the pinyl-diaterpenyl ester versus the concentration of DTAA during 2009 (Fig. S3) showed a high correlation ($R^2 = 0.86$, $n = 15$), indicating a possible relationship between the formation of the ester and DTAA. In addition to DTAA, the pinyl-diaterpenyl ester was also somewhat correlated with diaterpenylic acid ($R^2 = 0.54$, $n = 15$, Fig. S3), which has been hypothesized to form from the acid-catalyzed hydrolysis of terpenylic acid and DTAA (Yasmeen et al., 2010). During 2007 the pinyl-diaterpenyl ester also showed the best linear correlation with DTAA and diaterpenylic acid ($R^2 = 0.38$ and 0.47, respectively) of all the analysed α-pinene oxidation products (Fig. S3), though the correlations were much weaker than in 2009.

The correlations between the pinyl-diaterpenyl ester and DTAA in both campaigns and the lack of correlation with terpenylic acid could indicate that the diaterpenylic acid moiety involved in the ester formation is more likely to originate from the acid-catalyzed hydrolysis of DTAA, than from terpenylic acid as previously suggested by Yasmeen et al. (2010). This suggestion is also supported by a higher correlation between diaterpenylic acid and DTAA compared to terpenylic acid, which was observed in both the 2007 and 2009 campaigns. Based on these findings it is reasonable to postulate that the formation of the pinyl-diaterpenyl ester during the BEARPEX campaigns was closely related to the formation of DTAA.

It could be hypothesized that the factor of ten higher abundance of the pinyl-diaterpenyl ester during 2009 was caused by an overall increase in precursor acid concentrations between the September 2007 and July 2009 campaigns. Table 3 shows the average concentrations of the ester and the proposed acid precursors *cis*-pinic acid, terpenylic acid, DTAA and diaterpenylic acid. Both *cis*-pinic acid and DTAA were present at almost similar concentrations during both campaigns (7.6/7.1 and 5.0/6.5 $\mathrm{ng\,m^{-3}}$, respectively), while the concentration of terpenylic acid was actually higher in 2007 (15.2 $\mathrm{ng\,m^{-3}}$ in 2007 compared to 8.5 $\mathrm{ng\,m^{-3}}$ in 2009), possibly due to increased condensation at cooler air temperatures in 2007. Interestingly, the concentration of diaterpenylic acid was somewhat higher in 2009 compared to 2007 (1.2 and 0.6 $\mathrm{ng\,m^{-3}}$, respectively), which suggests more conversion of DTAA into diaterpenylic acid during the hotter 2009 campaign, although the concentration of DTAA was similar during both campaigns (6.5 and 5.0 $\mathrm{ng\,m^{-3}}$). The higher conversion of DTAA into diaterpenylic acid could also be related to the higher aerosol acidity observed in the 2009 campaign (Zhang et al., 2012). Even though higher temperatures could promote ester formation in the condensed phase, it is still difficult to explain the ten-fold increase in maximum concentration of the pinyl-diaterpenyl ester, based on concentrations of the precursor acids. Furthermore, no direct correlation was observed between the abundance of the pinyl-diaterpenyl ester and ambient temperature during either the 2007 or 2009 campaigns (R^2 = 0.12 and 0.09, respectively).

3.2.2 Pinonyl-pinyl ester

In addition to the pinyl-diaterpenyl ester (MW 358), an ester compound with MW 368 was also observed during the 2009 campaign. This compound was identified, based on its MS-MS fragmentation pattern, as an ester of hydroxy-pinonic acid and pinic acid. To our knowledge, this is the first reported observation of the pinonyl-pinyl ester in ambient aerosol samples.

In contrast to the pinyl-diaterpenyl ester, the pinonyl-pinyl ester was only observed in aerosol samples from 2009, and interestingly abundances of both esters showed similar variations between samples (Fig. 5). The pinonyl-pinyl ester showed a much better linear correlation ($R^2 = 0.78$, $n = 15$, data not shown) with the pinyl-diaterpenyl ester, than with its proposed precursors hydroxy-pinonic acid and *cis*-pinic acid ($R^2 =$ 0.31 and 0.37, respectively). This indicated that the concentration of the precursors were not solely responsible for controlling the formation of this ester, similar to the pinyl-diaterpenyl ester. The high correlation between the two observed pinene esters, the pinyl-diaterpenyl ester and the pinonyl-pinyl ester, indicates that other factors besides precursor concentrations are likely more important for governing ester formation and abundances.

3.2.3 Concentrations of α-pinene and its first- and second-generation oxidation products

During the 2009 campaign the α-pinene concentration was considerably higher (0.05–0.25 ppb) compared to the later part of the 2007 campaign when the filters were collected (0.02–0.1 ppb) (Worton et al, 2011; Bouvier-Brown et al., 2009). Consistent with this, we observe high concentrations of the first-generation oxidation product pinonic acid in 2009 relative to 2007 (11.0 and 6.1 ng m^{-3}, respectively, Table 2). However, despite the higher concentrations during the 2009 campaign, the α-pinene oxidation products *cis*-pinic acid and DTAA were observed at similar concentrations during both campaigns (Table 2). More efficient conversion of these compounds into esters, such as the pinyl-diaterpenyl and pinonyl-pinyl esters, and oligomers would help to explain the lower than expected concentrations of *cis*-pinic acid and DTAA observed in 2009. Quantification of the pinyl-diaterpenyl and pinonyl-pinyl esters indicate concentrations on the order of several ng m^{-3} (Table 2) and since other yet unidentified esters may also be formed from terpene-derived acids like *cis*-pinic acid, it is reasonable to hypothesize that ester formation could be a substantial sink of semi-volatile terpene-derived acids.

3.2.4 Photochemical aging

In the atmosphere, the composition and properties of aerosols continually evolve as they are aged through a range of chemical transformations that can occur in the gas and condensed phases. These oxidation reactions have been broadly defined into three categories: fragmentation, functionalization and oligomerization (Jimenez et al., 2009). Oligomerization reactions convert organic monomers in the aerosols into higher MW compounds (Rudich et al., 2007), such as the dimer esters observed in this study. The photochemical age of the collected aerosols in the two BEARPEX campaigns was estimated and compared with the observed ester content to investigate to what extent photochemical processing may affect the formation of the two observed esters (Fig. 6). Since the OH-initiated gas-phase oxidation of pinonic acid has been suggested to be the rate-limiting step in formation of the second generation product 3-methyl-1,2,3-butane tricarboxylic acid (MBTCA) (Zhang et al., 2010; Müller et al., 2011), the concentration of MBTCA indicates the degree of gas-phase OH photochemical processing. During 2007, some correlation ($R^2 = 0.40$, $n = 15$) between the pinyl-diaterpenyl ester and photochemical age was observed with both peaking during night-time (Fig. 6a). There was a better correlation between gas-phase photochemical aging and the concentration of pinyl-diaterpenyl ester in 2009 campaign ($R^2 = 0.57$, $n = 15$), while the correlation was lower for pinonyl-pinyl ester ($R^2 = 0.32$, $n = 15$) (Fig. 6b). The increased degree of photochemical aging in afternoon and night-time samples observed in both campaigns can be explained by the regular daily meteorological circulation patterns in the region of Blodgett forest. During daytime, air masses from the Central Valley and Sacramento metropolitan area move upslope and pass the sampling site. At night the flow pattern reverses and photochemically aged air masses move back downslope towards the Blodgett forest site (Murphy et al., 2006; Day et al., 2009). Worton et al. (2011) showed how this daily wind pattern affects local diurnal variations in concentrations of both gas- and aerosol-phase organic tracers.

Although comparison of the average MBTCA concentrations showed a higher average degree of gas-phase photochemical aging in the hotter 2009 campaign compared to the cooler 2007 campaign (8.9 ± 4.9 and $4.7 \pm 7.6\,\mathrm{ng\,m^{-3}}$, respectively) the low correlation between aging and ester content shown in Fig. 6b indicates that photochemical aging does not necessarily increase the formation of dimer esters, or that it facilitates further oligomerization of the dimer esters.

Another possible explanation is that the difference in relative humidity (RH) between the campaigns affects ester formation. In the 2007 campaign, RH was twice as high as in 2009 (Table 3). It was recently suggested that isoprene SOA mass is enhanced at low RH due to particle-phase esterification (Nguyen et al., 2011; Zhang et al., 2011, 2012). If low RH also enhances esterification of pinene oxidation products, this effect could contribute to explain the observed higher concentrations of dimer esters during the low RH campaign in 2009 compared to 2007. However, no significant correlation was observed between the ester concentrations and relative humidity during either of these campaigns (2007; $R^2 = 0.03$, 2009; $R^2 = 0.31$). In addition we did not observe a clear correlation between individual esters and acidity (sample average H^+ concentration from Zhang et al., 2012).

4 Conclusions

In this study, we showed that dimer esters of α-pinene ozonolysis products were formed in both laboratory chamber oxidation studies and in ambient air in a forested region at both low (about 10–15 °C) and high (about 25 °C) temperatures. Chamber results show that the dimer esters, such as pinyl-diaterpenyl and pinonyl-pinyl esters, were formed within the first 30 min of the experiment together with first-generation products, such as pinonic acid, but in contrast to the second-generation product MBTCA that forms from OH-oxidation of pinonic acid. Dimer esters may be involved in nucleation due to their estimated lower vapor pressures compared to monomers such as pinic acid. We observed that pinyl-diaterpenyl and pinonyl-pinyl esters are indeed formed in α-pinene oxidation at concentrations comparable to some first- and second-generation products at both low and warm temperatures in chamber experiments. Future laboratory work is needed to investigate the role of OH-initiated reactions of pinenes as well as the importance of RH on the formation of these dimer esters.

CCN activities of the particles formed in the smog chamber displayed a modest variation during the course of experiments. The κ values were in the range 0.06–0.09 (derived at a supersaturation of 0.19 %), which is consistent with results from other studies reported in the literature.

In ambient air samples from the 2007 and 2009 BEARPEX field campaigns in a forested mountain region in California, two dimer esters (pinyl-diaterpenyl and pinonyl-pinyl) were observed in day-time aerosol at estimated concentration levels comparable to known first-generation oxidation products of α-pinene. The pinyl-diaterpenyl ester was observed at even higher concentrations in all night-time samples. Maximum concentrations were about ten times higher during the warmer 2009 campaign compared to the cooler 2007 campaign. Overall the analyzed pinene oxidation products made up about 1 % of total organic aerosol mass. While variations in dimer ester concentrations could not be explained by variations in the concentrations of the proposed precursors, the abundances of the pinonyl-pinyl and pinyl-diaterpenyl esters were highly correlated, suggesting similar factors besides precursor concentrations were likely responsible for controlling ester formation in the atmosphere. The pinyl-diaterpenyl ester was also correlated with DTAA suggesting that ester formation may be related to DTAA formation. The concentration of MBTCA is indicative of the degree of oxidation by OH (of pinonic acid), and this, as well as ester concentrations, were higher during the warmer field campaign in 2009. The relationship between degree of OH aging and ester concentrations was not significant, suggesting that complex multistep processes control ester formation. The observed dimer esters may serve as markers of pinene SOA in future studies of SOA formation and levels.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/22103/2012/acpd-12-22103-2012-supplement.pdf.

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Table 1. Overview of compounds investigated in this study. References: (1) Claeys et al. (2009). (2) Yasmeen et al. (2010). (3) Szmigielski et al. (2007).

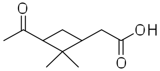
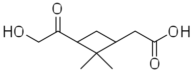
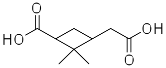
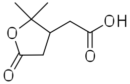
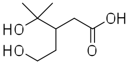
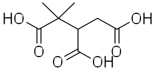
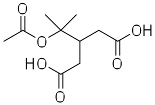
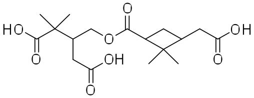
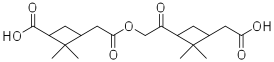
Compound (reference)	Suggested molecular structure	Molecular formula	$[M-H]^-$ ion (m/z)
Pinonic acid		$C_{10}H_{16}O_3$	183.101
Hydroxy-pinonic acid		$C_{10}H_{16}O_4$	199.104
Pinic acid		$C_9H_{14}O_4$	185.080
Terpenylic acid[1]		$C_8H_{12}O_4$	171.065
diaterpenylic acid[2]		$C_8H_{16}O_4$	175.105
3-Methyl-1,2,3-butanetricarboxylic acid[3] (MBTCA)		$C_8H_{12}O_6$	203.055
diaterpenylic acid acetate[1] (DTAA)		$C_{10}H_{16}O_6$	231.086
Pinyl-diaterpenylic ester MW 358		$C_{17}H_{26}O_8$	357.156
Pinonyl-pinyl ester MW 368		$C_{19}H_{28}O_7$	367.175

Table 2. Summary of the experimental conditions in the smog chamber.

Exp #	Date (d-m-y)	$[O_3]_0$ (ppb)	$[\alpha\text{-pinene}]_0$ (ppb)	T (˚C)
1	20-7-2011	116	100	23
2	25-7-2011	105	100	24
3	28-7-2011	116	100	15
4	29-7-2011	100	100	15

Table 3. Average concentrations of pinene oxidation products, average relative humidity (RH) and temperature during BEARPEX 2007 and 2009. Standard deviations are shown in brackets.

Campaign year	2007 ("cold")	2009 ("hot")
Temperature (°C)	11 (± 5.0)	25 (± 4.0)
Relative humidity (%)	70 (± 25)	39 (± 11)
Pinonic acid (ng m^{-3})	6.1 (± 0.6)	11.0 (± 5.6)
Pinic acid (ng m^{-3})	7.6 (± 4.0)	7.1 (± 3.0)
Terpenylic acid (ng m^{-3})	15.2 (± 6.9)[a]	8.5 (± 3.3)
diaterpenylic acid acetate (DTAA) (ng m^{-3})	5.0 (± 3.7)[a]	6.5 (± 2.7)
diaterpenylic acid (ng m^{-3})	0.6 (± 0.4)[b]	1.2 (± 0.7)[b]
3-methyl-1,2,3-butane tricarboxylic acid (MBTCA, ng m^{-3})	4.7 (± 7.6)[a]	8.9 (± 4.9)
Pinyl-diaterpenyl ester, MW 358 (ng m^{-3})	0.2 (± 0.2)[b]	3.7 (± 1.5)[b]
Pinonyl-pinyl ester, MW 368 (ng m^{-3})	n.d.	0.4 (± 0.2)[b]

[a] Quantified using response factor due to lack of authentic standards. [b] Quantified using surrogate standard due to lack of authentic standards – see experimental section for details. n.d: Not detected.

Fig. 1. Concentration profiles during smog-chamber experiments. ● Experiment 1 (23 °C), ■ Experiment 2 (24 °C), ▲ Experiment 3 (15 °C), × Experiment 4 (15 °C). No correction for wall losses has been applied.

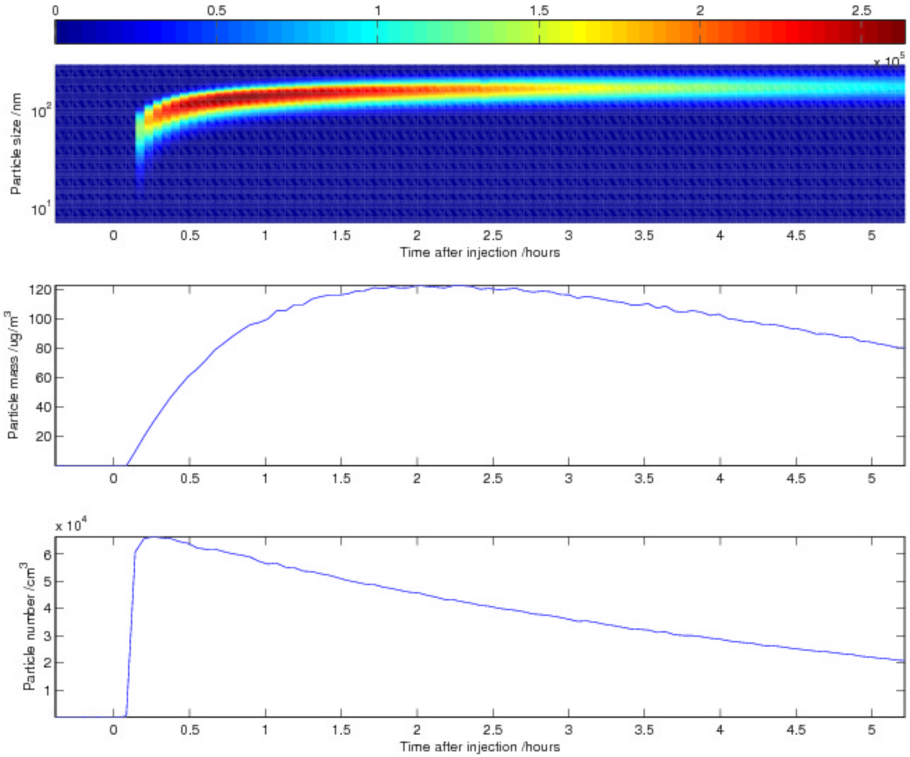


Fig. 2. Panel **(A)** shows the particle size distribution as a function of time measured with the SMPS system during smog chamber experiment 2. Panel **(B)** shows the inferred particle mass and panel **(C)** shows the integrated number concentration as a function of time. Similar plots for smog chamber experiments 1, 3 and 4 are provided in the supplementary material.

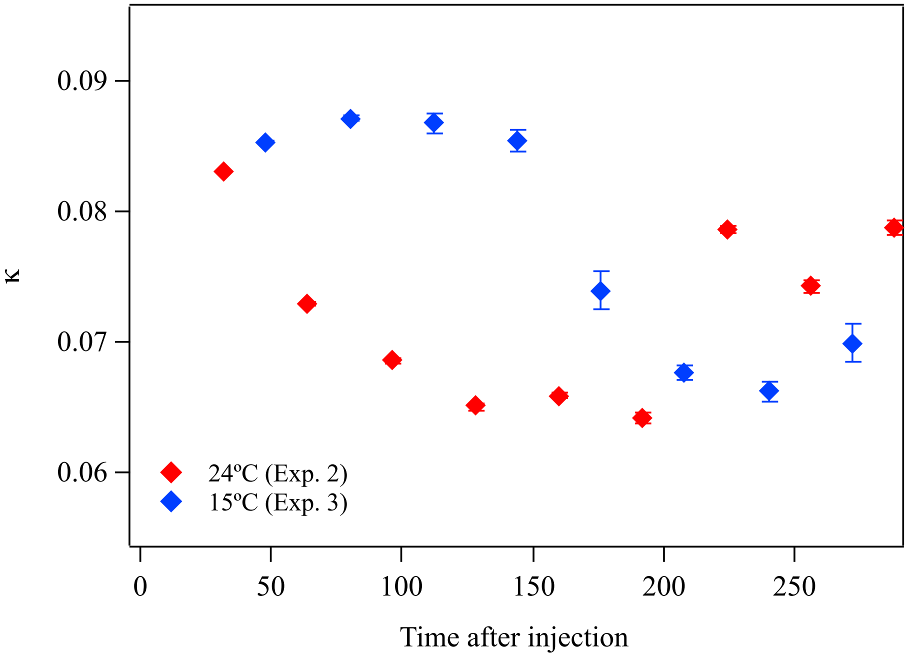


Fig. 3. Time series of the hygroscopicity parameter κ calculated from CCN activation diameters at 0.19 % supersaturation. Error bars are calculated from the error (two standard deviations) obtained from the fitting procedure used to derive activation diameters from the CCN activation curves.

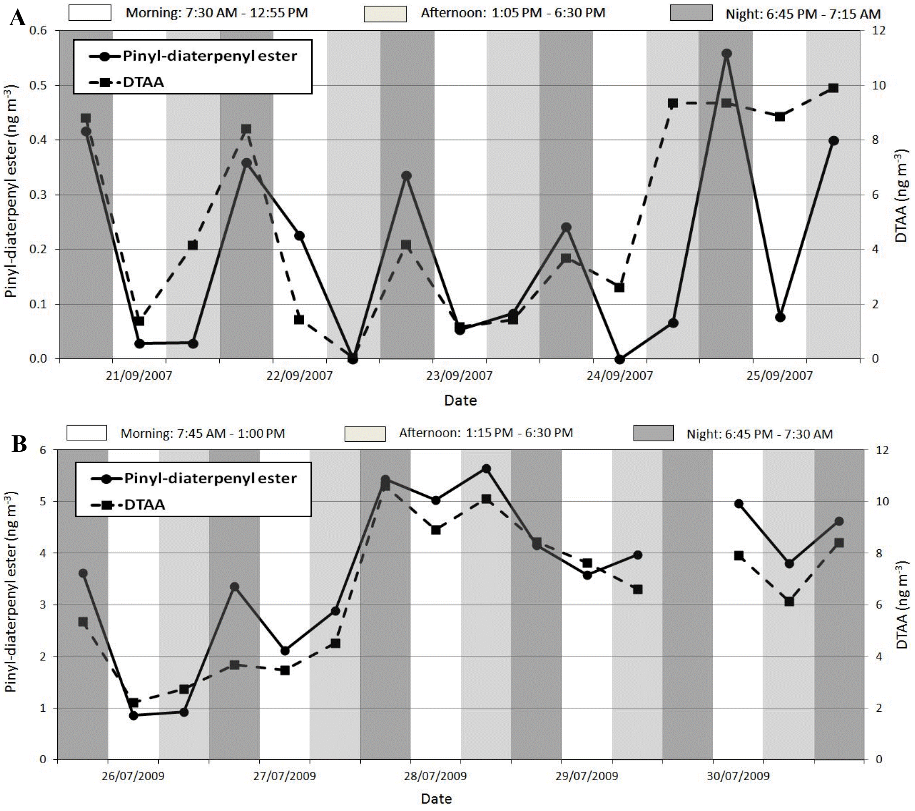


Fig. 4. Diurnal variation of the pinyl-diaterpenyl ester ● (ng m^{-3}) and diaterpenylic acid acetate (DTAA) ■ (ng m^{-3}) during the 2007 **(A)** and 2009 **(B)** campaigns. Note the different scales for pinyl-diaterpenyl ester in **(A)** and **(B)**. Night-time samples are highlighted in dark grey.

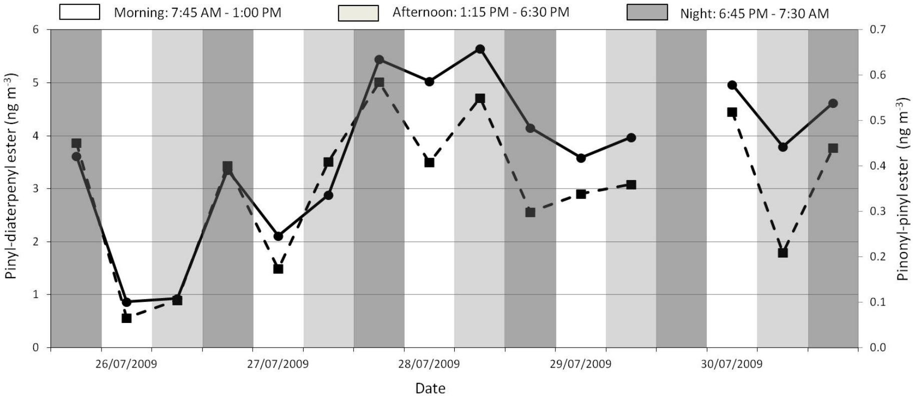


Fig. 5. Diurnal variation of the pinyl-diaterpenyl ester ● (ng m^{-3}) and pinonyl-pinyl ester ■ (ng m^{-3}) during the 2009 campaign.

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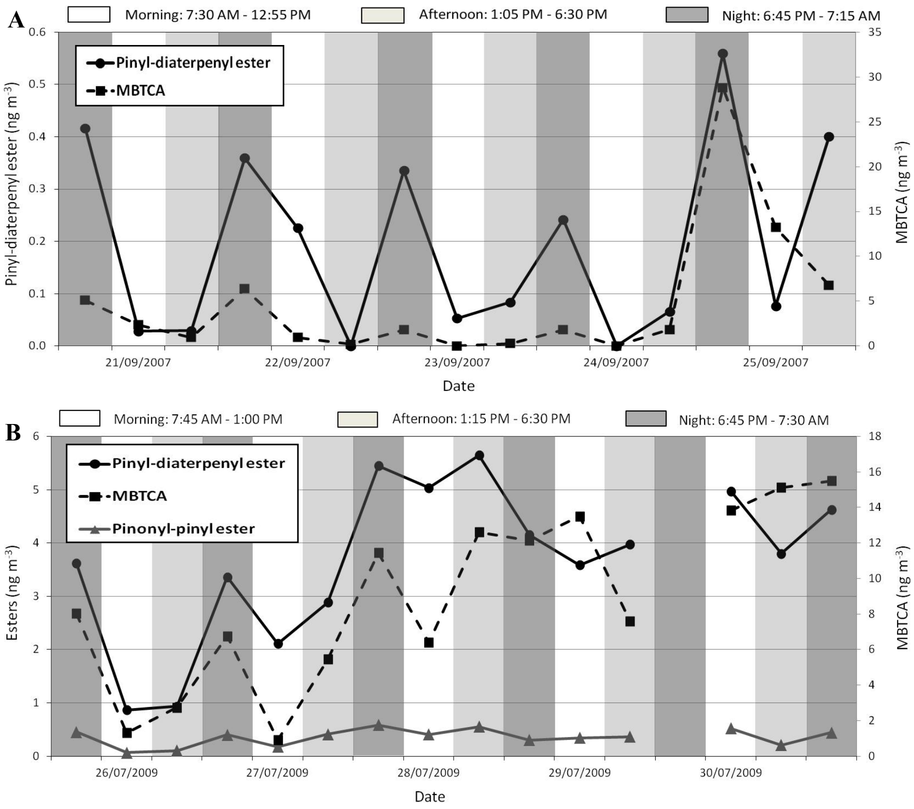

Fig. 6. Diurnal variation of the Pinyl-diaterpenyl ester ● (ng m^{-3}), pinonyl-pinyl ester ▲ (ng m^{-3}) and MBTCA ■ (ng m^{-3}) during the 2007 **(A)** and 2009 campaigns **(B)** period. Pinonyl-pinyl ester was only observed in 2009.