

Monoterpene pollution episodes in a forest environment: indication of anthropogenic origin and association with aerosol particles

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We used a monoterpene volume mixing ratio dataset measured from 12 June 2006 to 24 September 2007 and from 1 June 2008 to 3 March 2009 at the SMEAR II station to quantify the magnitude of anthropogenic monoterpene emissions aside from biogenic origins, to examine the anthropogenic sources, and to look at other associated pollutants. We discuss the relations between increased monoterpene mixing ratios and particle concentrations. We also characterize chemical properties of aerosol particles during two monoterpene pollution episodes in case studies. Out of 580 days analyzed, anthropogenic monoterpene pollution episodes were found on 341 (58.8%) days. The average monoterpene mixing ratio increased from 0.19 to 0.26 ppbv due to the presence of anthropogenic monoterpenes, which is equal to an increase of 36.8%. The observed anthropogenic monoterpenes were mostly from the Korkeakoski sawmill. Other gas pollutants might occasionally be emitted during the episodes, but did not show clear association with anthropogenic monoterpenes. Aerosol particle concentrations substantially increased during episodes, and monoterpene mixing ratios showed strong connections with Aitken mode particles both in number and volume concentrations. Particles associated with monoterpene episodes reached a CCN (cloud concentration nucleus) size. The chemical characterizations of aerosol particles in case studies show that the increase in aerosol particle mass was mainly from secondary organic aerosol.

Introduction

Monoterpenes (MT) present in the troposphere

affect the chemical composition of the lower troposphere and influence air quality (Aschmann *et al.* 2002, Atkinson and Arey 2003, Sakuly-

anontvittaya *et al.* 2008). Oxidation of monoterpenes leading to secondary organic aerosol formation affects aerosol loading, and further influences the climate system (Kulmala *et al.* 2004, Shantz *et al.* 2004, Heald *et al.* 2008). Identified MT sources include direct emissions of both biogenic and anthropogenic origin (Guenther *et al.* 1993, Kesselmeier and Staudt 1999, Granström 2005), but biogenic sources dominate the total MT emissions on a global scale (Guenther 1997). The global atmospheric budget of MT is uncertain due to large spatial variation and source uncertainty. The latest estimation of the global MT budget is $\sim 30 \text{ Tg Ca}^{-1}$ (Schurgers *et al.* 2009).

Biogenic emissions of MT are strongly light and temperature dependent, and therefore have seasonal and diurnal variations (Tingey *et al.* 1980, Bertin *et al.* 1997, Tarvainen *et al.* 2005, Roffael 2006). Many measurements were conducted to observe the direct biogenic emissions of MT by measuring the ecosystem-scale fluxes (Rinne *et al.* 2000, 2005), as well as vegetation emission rates by branch enclosure measurements (Guenther *et al.* 1996, Holzke *et al.* 2006, Ruuskanen *et al.* 2005, 2007).

Anthropogenic emissions of MT may originate from wood processing in forestry and the forest industry, due to processes of machining, logging, chipping, drying, debarking, sawing and pulping (Schade and Goldstein 2003, Granström 2009). Direct emissions of VOCs from sawmill activities have been studied for many years (Johansson and Rasmuson 1998, Stahl *et al.* 2004). Studies on emissions of MT from different forest industry processes have shown that the drying process is the dominant cause of the VOC emissions from sawmills, and monoterpenes are a major part of the VOCs emitted during drying, particularly in coniferous forest areas (Englund and Nussbaum 2000, Granström 2003).

The exact anthropogenic contribution to the secondary organic aerosol loading through MT oxidation products remains unknown (Kroll and Seinfeld 2005, Volkamer *et al.* 2006). An earlier study showed a connection between elevated MT mixing ratios and aerosol particle concentrations due to sawmill activities at the Hyytiälä site (Eerdekens *et al.* 2009). However, only one case was discussed, and no attempts to quantify the

magnitude of anthropogenic emissions derived from the total atmospheric MT loading over a longer period at this site have been reported. Also, the effects of the anthropogenic MT emissions on the physical and chemical characteristics of aerosol particles on a regional scale have not been studied in detail.

In this study, we present the MT mixing ratios measured at the Hyytiälä forest site along with meteorological parameters, trace gases, aerosol particle number size distributions, and aerosol mass spectrometry (AMS) data and use it to study the origin of the elevated MT mixing ratios observed at the SMEAR II station. We also investigate the magnitude of observed MT mixing ratios that originate from anthropogenic sources and the influence of increased anthropogenic MT emissions on the local air chemistry, and other possible associated pollutants during episodes. Finally, we investigate the possible influence of anthropogenic MT emissions on the physical and chemical properties of aerosol particles.

Material and methods

Measurement site

The measurements were a part of the EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality Interactions) (Kulmala *et al.* 2009) field observation campaign at the SMEAR II station [Station for Measuring Forest Ecosystem–Atmosphere Relations (for details see Hari and Kulmala 2005)] in Hyytiälä, Finland ($61^{\circ}51' \text{N}$, $24^{\circ}17' \text{E}$). The station provides continuous observations of aerosol particle size distributions, trace gas concentrations, and meteorological parameters including e.g. wind speed and direction, radiations in various wavelength bands, temperature, and relative humidity. The vegetation layer around the site is dominated by Scots pine with some Norway spruce, aspen and birch. In 2007, the average tree height was around 14–16 meters.

The VOC measurements were carried out from 12 June 2006 to 24 September 2007 and from 1 June 2008 to 3 March 2009. A wide range of VOC compounds was measured using

a proton transfer reaction mass spectrometer (PTR-MS) (Lindinger *et al.* 1998). The VOC measurements were conducted at the heights of 4, 14 and 22 meters during the whole measurement period, and additionally at the heights of 7 and 10 meters until October 2006. VOCs were measured in three-hour cycles from 24 March 2007 onwards. The three-hour cycles consisted of one-hour VOC mixing ratio profile measurements, one-hour ecosystem scale VOC flux measurements using the micrometeorological disjunct eddy covariance method, and one-hour shoot scale flux measurements using a dynamic chamber method. Two-hour cycles including only VOC mixing ratio profiles and ecosystem-scale VOC flux measurements were carried out before 24 March 2007. Inside the two- or three-hour PTR-MS cycles, the VOC background signals of PTR-MS, i.e. PTR-MS measurements of VOC-free air, were registered within the ecosystem-scale VOC flux measurement cycle. The PTR-MS was calibrated every week or every second week using VOC standard mixture gas, which was diluted by VOC-free air purified from ambient air by a zero air generator. The background signals of PTR-MS observed in the zero-air measurements were used to estimate the detection limits for all the VOC compounds, the detection limit for monoterpenes being 0.01 ppbv (Taipale *et al.* 2008). The calibration process and stability of the PTR-MS instrument, as well as the equations to derive VOC mixing ratios are described in detail by Taipale *et al.* (2008). The procedures to calculate the VOC volume mixing ratios were the same for the mixing ratio profile cycle and the ecosystem scale flux measurement cycle. Therefore, these two calculations are directly comparable.

The particle size distributions were measured by a Differential Mobility Particle Sizer (DMPS), which measures the size distribution as 38 size classes with mobility diameters in the range of 3–1000 nm (Aalto *et al.* 2001). An aerodyne Time-of-Flight Aerosol Mass Spectrometer (C-ToF AMS) (Canagaratna *et al.* 2007, Jimenez *et al.* 2010) was used to measure mass concentrations of species including sulfate, nitrite, chloride, ammonium and organic compounds in the submicron aerosol during a measurement campaign from 10 September to 16 October 2009.

The black carbon concentration was measured by an aethalometer (Virkkula *et al.* 2007).

Data processing

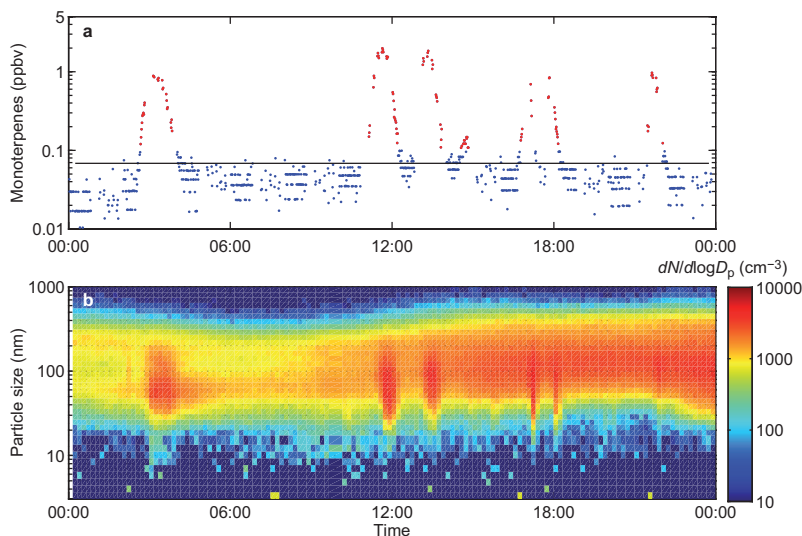
MT volume mixing ratios (MTVMRs) were calculated from the PTR-MS cycle of the VOC mixing ratio profile measurement for the whole measurement period. Also, MTVMRs were derived from the PTR-MS cycle of ecosystem-scale VOC flux measurements in 2007. The VOC flux measurements were conducted at the height of 22 meters. Therefore, we used MTVMRs from the height of 22 meters to keep data consistency. As the MT volume mixing ratio (MTVMR) data from 2007 contained the least amount of gaps inside the two- or three-hour PTR-MS cycles, the data from that year were used to identify and classify the MT episodes, and to estimate the duration of each episode. Data from other years were used to distinguish MT pollution episodes only.

The time resolution of the DMPS system is 10 min. We divided the DMPS particle size spectrum into three size modes: the nucleation mode in the particle size range of 3–25 nm, Aitken mode (25–100 nm), and the accumulation mode (100–1000 nm). We calculated the total number and total volume concentrations of aerosol particles in each size mode from the DMPS data. Total submicron particle volume concentrations were integrated from the DMPS size distribution assuming spherical particles.

Trace gas concentrations and meteorological parameters at SMEAR II were measured at several heights and averaged here over 30 minutes. We use the height of 16.8 m that agrees most closely with the observation height of MTVMRs by PTR-MS. Half-hour median values were calculated for all the data including particle number and volume concentrations and MTVMRs during the whole PTR-MS measurement period to perform a linear regression analysis involving all the parameters.

The PTR-MS measurements were not continuous over the whole period described here; there were several longer gaps. As the measurements were not fully continuous, the whole dataset used in this study for all the parameters includes only the data measured on the days with

Fig. 1. (a) Monoterpene volume mixing ratio on 8 March 2007. Blue and red dots are volume mixing ratios measured by PTR-MS. Monoterpene volume mixing ratios in the flux measurement cycle were averaged every minute. Horizontal line indicates average biogenic MTVMR (monoterpene volume mixing ratio). Red dots represent monoterpene volume mixing ratios during episodes. **(b)** Contour plot of particle size distributions measured by DMPS on the same day.



PTR-MS observations. In total, this whole dataset accounts for 580 days in 23 months.

Definition of a monoterpene pollution episode

It has been shown that the average biogenic MTVMR at the Hyytiälä station are dependent on temperature (Hakola *et al.* 2003, Tarvainen *et al.* 2005, Lappalainen *et al.* 2009). However, visual inspection of the entire MTVMR time series from Hyytiälä revealed peaks of extremely high volume mixing ratios. These episodes were chosen for more in-depth scrutiny. To accomplish this we needed to define what we consider a high-concentration monoterpene episode. For this purpose, MTVMRs measured on 8 March 2007 were plotted (*see* Fig. 1a). The estimated daily average biogenic MTVMR for the same day calculated from the data used by Lappalainen *et al.* (2009) was also included in the figure (horizontal line) to give an indication of the order of magnitude of biogenic-emitted MTVMRs. The estimated average MTVMR on this day was 0.06 ppbv. It is clear that the lowest measured MTVMRs are close to the estimated MTVMR. However, six periods of dramatically elevated MTVMRs reaching at the maximum 1.90 ppbv could be observed; this is over 30 times the estimated average MTVMR for this

day. We assumed that these elevated MTVMRs were not of biogenic origin, but a result of anthropogenic activities. In this study, we call these short periods with presumably anthropogenic MT occurrence ‘MT pollution episodes’.

These extremely high MTVMRs were so different from the rest of the measured MTVMRs, that they could be called outliers. To find these outliers, we applied the modified Thompson τ method (Wheeler and Ganji 1996, St-Onge *et al.* 2005). The measured MTVMR data from each day were taken as a sample for which the mean ($\bar{x}$) and standard deviation (S) were calculated. Then, for each measured MTVMR data point (x_i), the absolute value of the deviation was calculated with the equation

$$\delta_i = |x_i - \bar{x}| \quad (1)$$

The modified Thompson τ is calculated from the critical value of Student’s t as follows:

$$\tau = \frac{t_{\alpha/2}(n-1)}{\sqrt{n} \sqrt{n-2+t_{\alpha/2}^2}} \quad (2)$$

where n is the number of measured MTVMR data points during each day, $t_{\alpha/2}$ is the critical t value, for $\alpha = 0.001$. This high significance level was used to isolate the extremely high and to exclude the low MTVMR values. Thus, if a value was found to be an outlier (i.e. $\delta_i > \tau S$), we considered it an MT pollution episode in the

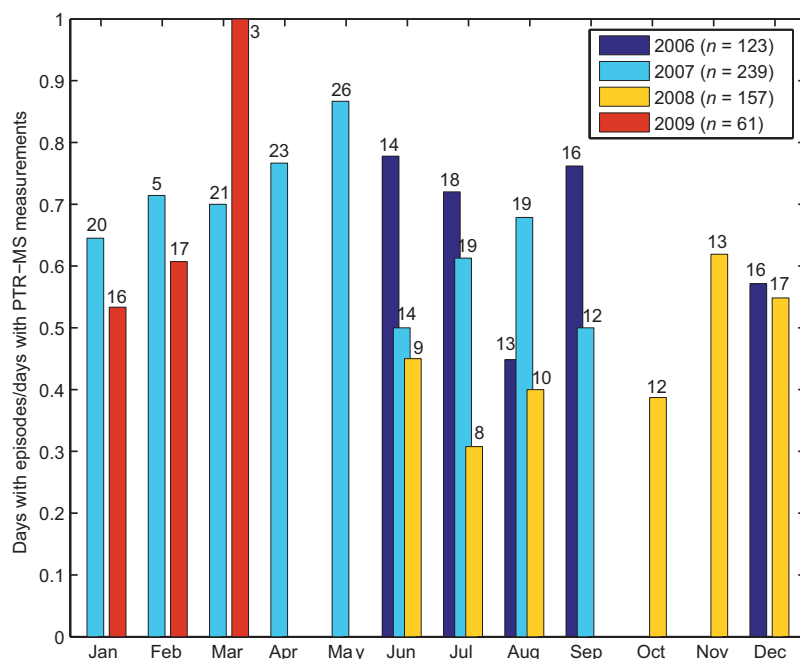


Fig. 2. The ratio of days with monoterpene pollution episodes to the days having PTR-MS measurements. Each color represents one-year data from 2006 to 2009. The numbers (*n*) in the legend are the sums of days with PTR-MS observations in each year. The numbers of days with episodes in each month are given above the bars.

daily measured MTVMR dataset, otherwise (i.e. $\delta_i \leq \tau S$) it was considered a non-episode biogenic MT emission. With this method, presumably all the MT pollution episodes of anthropogenic origin (peak and edge values during each episode on this day included) were captured (*see* red dots above the horizontal line in Fig. 1a). The modified Thompson τ method was applied to all the days with PTR-MS observations.

Results and discussion

Statistic of monoterpene pollution episodes

Out of 580 days analyzed, MT pollution episodes were found on 341 (58.8%) days. MT pollution episodes did not show any clear seasonal or annual distribution pattern (*see* Fig. 2).

The total duration of all the episodes in the whole dataset was calculated. Of all the days with MT pollution episodes, the sum of episode durations was equal to 6.1% of the total time with PTR-MS observations. This means that the average duration of an episode is ca. 90 minutes. It is, however, difficult to calculate the dura-

tion of each MT pollution episode, because the PTR-MS measurements were not fully continuous due to the sequences of PTR-MS cycles. We estimated the duration of each MT pollution episode found in the data of 2007. The longest continuous episode lasted ca. half a day which included several peaks of MTVMRs, while the shortest episode was only ca. half an hour in this dataset. The average measured MTVMR was clearly different on days with and without MT pollution episodes: 0.19 ppbv and 1.33 ppbv respectively; while for the whole measurement period it was 0.26 ppbv.

Connection between monoterpene volume mixing ratios, meteorological parameters, trace gases and aerosol particles

Meteorological parameters

In the whole dataset, the dominant wind direction was between west and south (Fig. 3a). However, the elevated MTVMRs during the episodes occurred when wind was mostly from the southeast 120°–140° (Fig. 3b). It can thus be con-

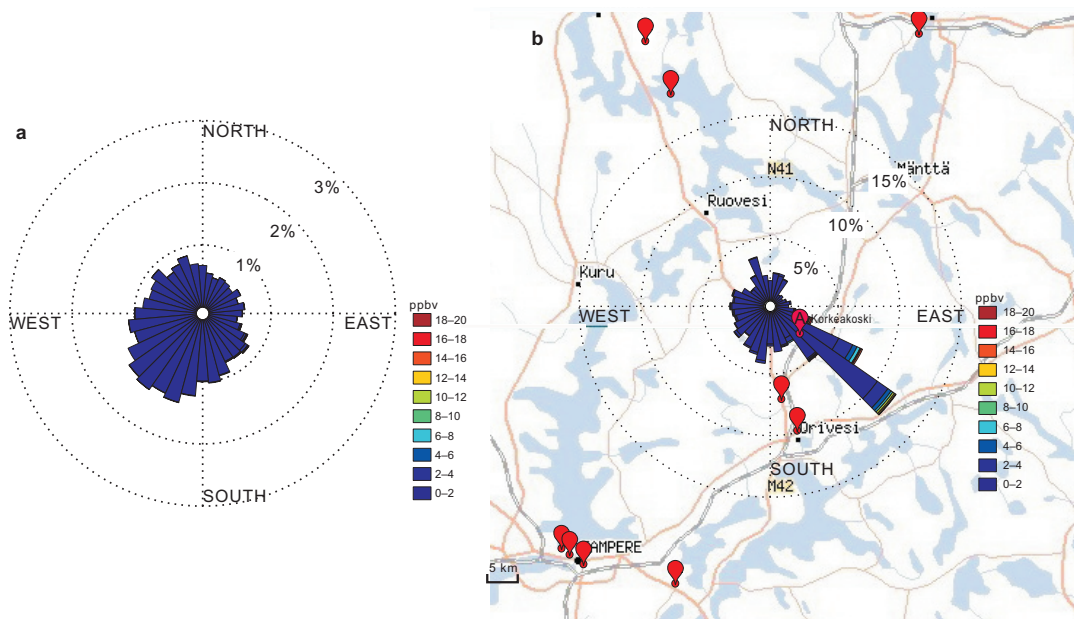


Fig. 3. (a) Wind directions for monoterpene volume mixing ratios (MTVMRs) in the whole dataset. (b) Wind directions for MTVMRs during monoterpene pollution episodes. Red balloons in the background map indicate sawmills around the SMEAR II station. The color bins inside the wind roses illustrate MTVMR ranges (ppbv). The map courtesy of ©Maanmittauslaitos 2010, and CSC PalTuli geospatial data service.

cluded that MTVMRs strongly depend on wind direction. In the whole dataset, winds came from between 120° and 140° during 5.4% of the total time. This direction is where the Korkeakoski sawmill is located (ca. 6 km from the SMEAR II station towards 130°). This sawmill is a likely source of elevated MTVMRs observed at the SMEAR II station, as MT and many other VOCs are intensively emitted from the wood cutting and drying processes. Also, some other possible upwind sources could be suggested. However, since MT in the air are short-lived, only those within a 50-km radius from the SMEAR II station can be considered (*see* red balloons in Fig. 3b). There are no other big sawmills within that distance towards southeast. Some other sawmills that are located to the north and southwest are much farther away from the measurement station than the Korkeakoski sawmill, thus their effect on MTVMRs should be much weaker. Therefore, the Korkeakoski sawmill factory is likely to explain most of the MT episodes observed at the SMEAR II station.

Other meteorological parameters such as wind speed, air temperature, relative humid-

ity, and global radiation had no clear effect on MTVMRs.

Trace gases

To investigate other possible associated gas pollutants and the local air chemistry during the MT pollution episodes, a linear regression analysis between MTVMRs and trace gas concentrations was performed for all the MT pollution episodes.

MTVMRs were not correlated with CO and ozone concentrations (R^2 of 0.05 and 0.04, respectively). In the whole dataset, the average NO_x concentration at the SMEAR II station was 1.42 ppbv which was insufficient for ozone formation (Seinfeld and Pandis 2006). Elevated MTVMRs may lead to ozone destruction, i.e. ozone concentrations decrease due to reactions with MT and other VOC compounds. However, the regression analysis did not reveal a possible link. No correlation could be seen between MTVMRs, SO_2 and NO_x concentrations. This possibly indicates that emissions of SO_2 and NO_x during MT pollution episodes are not as signifi-

cant as MT emission or those trace gases originated from different stages of wood processing at sawmills. Also, this further confirms that biomass combustion and coal industrial emissions are not causing the MT episodes.

Aerosol particles

To visualize a possible influence of MT pollution episodes on physical proprieties of aerosol particles, the DMPS particle size distributions observed on 8 March 2007 were plotted (*see* Fig. 1b). The DMPS spectrum shows elevation of Aitken-mode aerosol particle number concentrations (red in Fig. 1b) when MTVMRs are sharply elevated during six short periods during this day. Therefore, it is of interest to investigate the connection between elevated MTVMRs and aerosol particles during MT pollution episodes.

Monoterpenes vs. particle number and volume concentrations

No correlation between MTVMRs and nucleation-mode particle number and volume concentrations was found (*see* Fig. 4). However, MTVMRs correlated positively but weakly with Aitken mode particles during all episodes, the coefficients of determination (R^2) being: MTVMRs *vs.* particle number 0.27 (Fig. 4c), and MTVMRs *vs.* particle volume concentrations 0.28 (Fig. 4d). Correlation between MTVMRs and accumulation mode particle number concentrations was also weakly positive ($R^2 = 0.26$; Fig. 4e). However, MTVMRs showed weaker correlation with accumulation mode particle volume concentrations during the episodes.

One possible reason for the weak, positive correlation between MTVMRs and Aitken mode particles during the episodes was that primarily emitted particles were from the same sawmill source as the increased anthropogenic MTVMRs. No primary source of particle emission could be identified during wood drying process from sawmill, and particles were too small to be produced during mechanical wood processing. Two bark kettle units are used to generate power at the Korkeakoski sawmill, thus

particles may primarily be emitted from bark burning. Nevertheless, these primary particles do not fully explain the simultaneous particle increase seen at the SMEAR II station, as we did not find clear correlations between emitted MT and other trace gas concentrations during the MT pollution episodes.

Another explanation for the correlation might be that particles were formed and grew to Aitken sizes through nucleation and condensation processes during the MT pollution episodes. The outlet air temperature during a drying process in a sawmill is usually very high (Englund and Nussbaum 2000, Ståhl *et al.* 2004). Plenty of VOC compounds, including monoterpenes and sesquiterpenes, are emitted from the outlet of the dryer (Rupar and Sanati 2003). Studies have shown that particles can form via nucleation and grow up to several tens of nanometers in a few minutes due to e.g. sesquiterpene ozonolysis (Bonn and Moortgat 2003), and secondary organic aerosol concentrations significantly increase while air temperature decreases (Sheehan and Bowman 2001). Therefore, the particles could have formed via nucleation when the outlet air was cooling down after emission from the wood dryer. However, secondary nucleation taking place during atmospheric transportation was probably of minor significance, since practically no correlation between MTVMRs and nucleation mode particle number concentrations could be found. Nevertheless, particles grew to bigger sizes when the oxidation products of MT and other VOCs kept condensing on them. Therefore, when emitted MT and particles arrived at the SMEAR II station, we could find strong links between Aitken mode particles and anthropogenic MTVMRs not only in numbers, but also in volume.

Looking at the incoming solar radiation (*see* Fig. 4d) suggests that OH-oxidation did not drive the main oxidation process during the MT pollution episodes, as there was no clear connection between it and the particle concentrations.

MTVMRs showed weak correlation with accumulation mode particle volume concentrations, which is expected since the original volume of observed particles is already so large that additional condensation will not increase the volume as significantly as for the Aitken mode

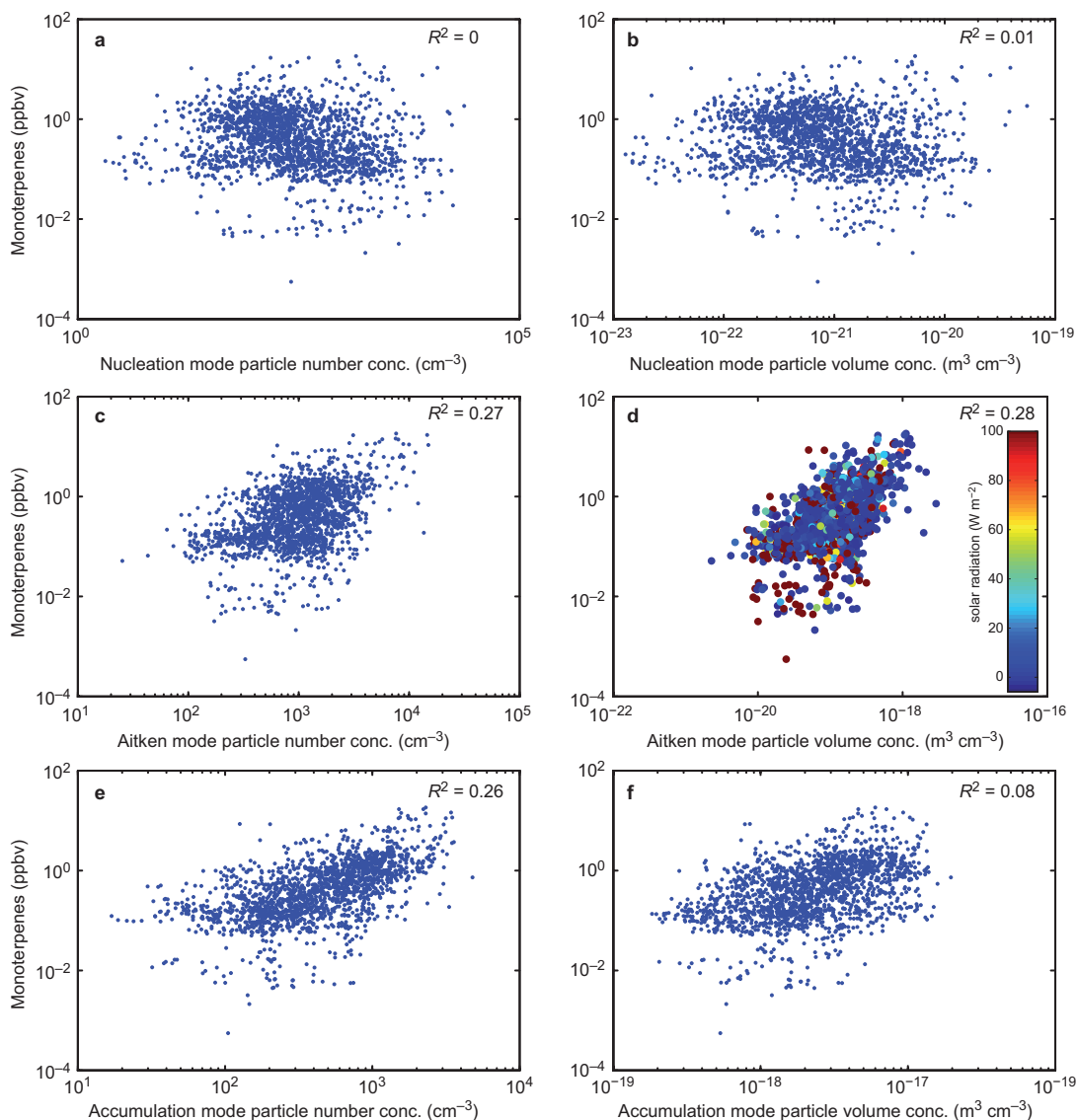


Fig. 4. Monoterpene volume mixing ratios *versus* particle number and volume concentrations in three size modes during all monoterpene pollution episodes. Correlation coefficients (R^2) are given in the plots.

particles, and it typically takes 1–2 days before particles formed via nucleation grow into the accumulation mode (Tunved *et al.* 2006).

Aerosol size distribution

The average particle size distributions during all the episodes as well as in the whole dataset were derived from DMPS data (Fig. 5). The size distributions were fitted with a log-normal

distribution function (Hussein *et al.* 2005) and depicted in the figure as solid lines. The suggested sub-modes are represented as dashed lines for each size distribution. The total average particle number size distribution is tri-modal with a main mode in the Aitken size range at 59 nm, a minor nucleation mode in the size at 21 nm, and a moderate accumulation mode at 177 nm (blue dots in Fig. 5a). The average particle size distribution calculated during all the MT episodes indicates a higher integral number of particles

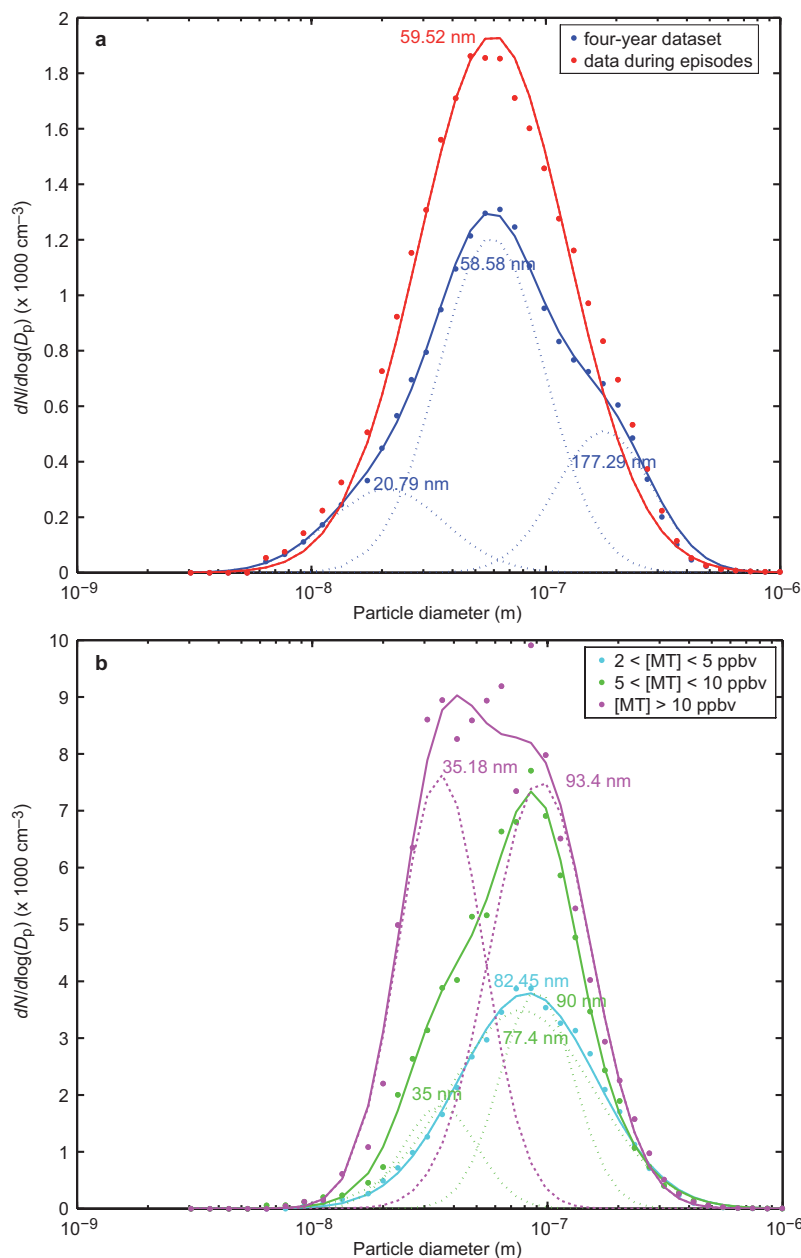


Fig. 5. (a) DMPS average size distribution during all monoterpene episodes and in the whole dataset. (b) DMPS average size distribution at three monoterpene volume mixing ratio ranges. The dots are calculated median values from DMPS, the solid lines are fittings for the measured DMPS data, and the dashed lines are sub-mode fittings for each size distribution. The numbers are the dominant sizes for each mode.

(red dots in Fig. 5a), and the only dominant particle size is found in the Aitken mode at 60 nm. Aerosol particles larger than ca. 50–100 nm in diameter are considered cloud condensation nuclei (CCN), which have potential to grow to cloud droplets (Komppula *et al.* 2005, Andreae and Rosenfeld 2008, Merikanto *et al.* 2009). Thus, particles emitted and formed in the emission plume of the sawmill may contribute to the

CCN loading in this area, at least during the MT pollution episodes.

To visualize the influence of different MTVMRs on the particle population during episodes, the average particle size distributions at three different MTVMR ranges: 2–5 ppbv (Range 1), 5–10 ppbv (Range 2), and > 10 ppbv (Range 3) were plotted (*see* Fig. 5b). Particle size distributions in each MTVMR range

were simply calculated based on the simultaneously measured MTVMRs, regardless of episode occurrence. We ignored particle size distribution for the MTVMR range of 0–2 ppbv, as most of the measured MTVMR values were in the rising and falling edges of the episodes. Only unimodal particle size distribution is distinguished in Range 1, with the dominant particle size of 82 nm. However, a trimodal size distribution is exhibited in Range 2 and bimodal in Range 3. The larger dominant sizes in these two distributions were 90 nm and 93 nm in Ranges 2 and 3, respectively. Meanwhile, particle number concentrations show a proportional increase with MTVMRs. This suggests that particles during the MT pollution episodes are primarily emitted along with MT or *in situ* nucleated at the sawmill in the very first minutes after emissions. The slight increase of the larger particle sizes in each size distribution suggests that particles grew by oxidation products of MT and other VOC compounds during atmospheric transportation. The smaller dominant sizes from the size distributions were 35 nm in Ranges 2 and 3. A possible reason is that particles in the smaller mode might be formed via nucleation during meteorological transportation in this extremely enriched VOC environment, while particles in the larger mode were primarily emitted or existing particles having grown due to condensation.

Case studies

The aerosol mass spectrometry (AMS) measurements were carried out on the days overlapping with PTR-MS observations, i.e. 1–15 October 2008. During that period, two strong MT pollution episodes were identified (Fig. 6b). The first MT pollution episode (Episode 1) occurred at ~21:00 on 3 October, and ended at ~10:00 on 4 October. The second episode (Episode 2) appeared at ~22:00 on 8 October, and ended at ~4:00 on 9 October. On 3 October just before Episode 1, a strong rain had taken place (see Fig. 6a), which resulted in a very low background particle number concentration (ca. 500 particles cm^{-3}). In this case, aerosol particles associated with high MTVMRs dominated in the total particle numbers at the SMEAR II station. Before Episode 2,

a strong new particle formation event occurred on October 7, and then a moderate new particle formation event at noon on October 8 (see the DPMS spectrum in Fig. 6d). The background aerosol particles (1850 cm^{-3}) were dominated by a large fraction of one day aged aerosol particles formed by new particle formation, and a small fraction of freshly formed aerosol particles before Episode 2. These two MT pollution episodes occurred in two distinguishable situations, which are of interest, and were thus selected for the case studies, in order to discuss the influence of the MT pollution episodes on the chemical properties of local and regional aerosol particles.

Three occasions included wind directions 120° – 140° (see Fig. 6a). Due to missing MTVMR data from the first two days, i.e. 1 and 2 Oct., we could not identify the MT pollution episode in the first occasion, even though several intensive aerosol particle bursts took place during this time. It is, however, clear that the MT pollution episodes occurred during the next two occasions when the wind directions were between 120° and 140° . No other episodes could be found for any other wind directions. This is consistent with our earlier result that the MT pollution episodes originated from the south-east, and were very sensitive to the wind direction. Several small air mass transitions happened during these two episodes which led to four intensive burst of both high MTVMRs and particle number concentrations captured in Episode 1, and two bursts captured in Episode 2.

MTVMR first sharply increased to 15.1 ppbv in association with 1700 particles cm^{-3} approximately at 21:30 in Episode 1, then next three MTVMR peaks reached 10.9 ppbv at around 01:00, 8.1 ppbv at 04:00, and 2.1 ppbv at 09:30 on the next day with associated particle number concentration peaks of 2600 cm^{-3} , 2100 cm^{-3} , and 1700 cm^{-3} , respectively (Fig. 6b). Episode 2 lasted around 6 hours, MTVMR first increased to 5.7 ppbv at around 22:30 on 8 October, and then elevated to 16.7 ppbv at around 02:30 on 9 October both in association with an intensive increase of particles. The simultaneously elevated particle number concentrations were 5500 and 12 000 particles cm^{-3} , respectively, which are ca. 4.5 times larger than the maximum during Episode 1. Aerosol particles were strongly corre-

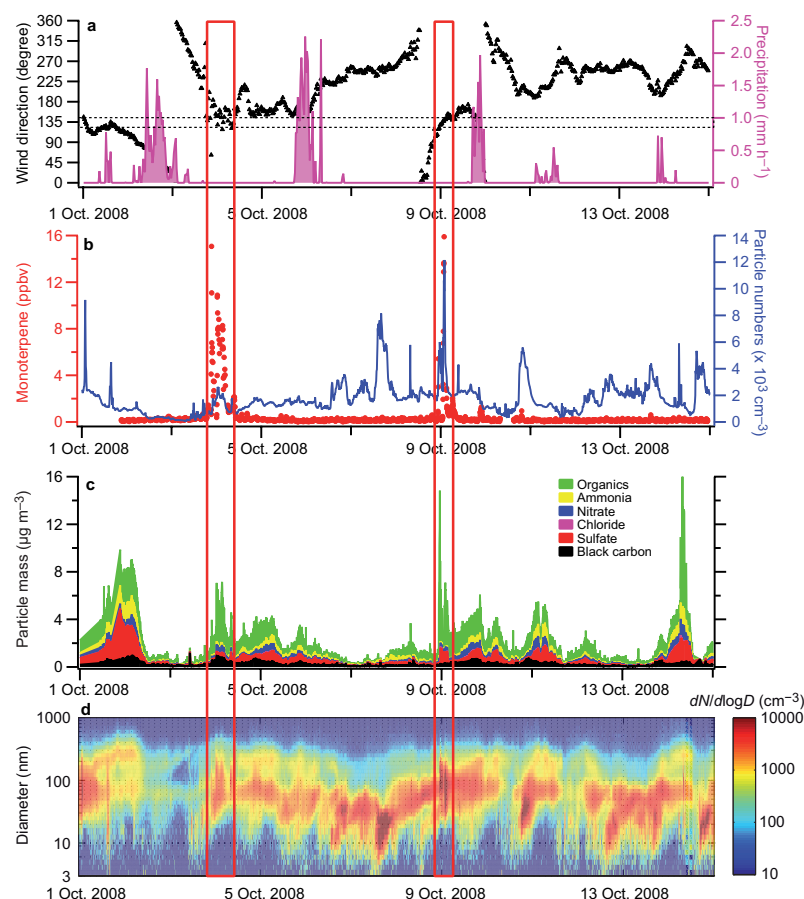


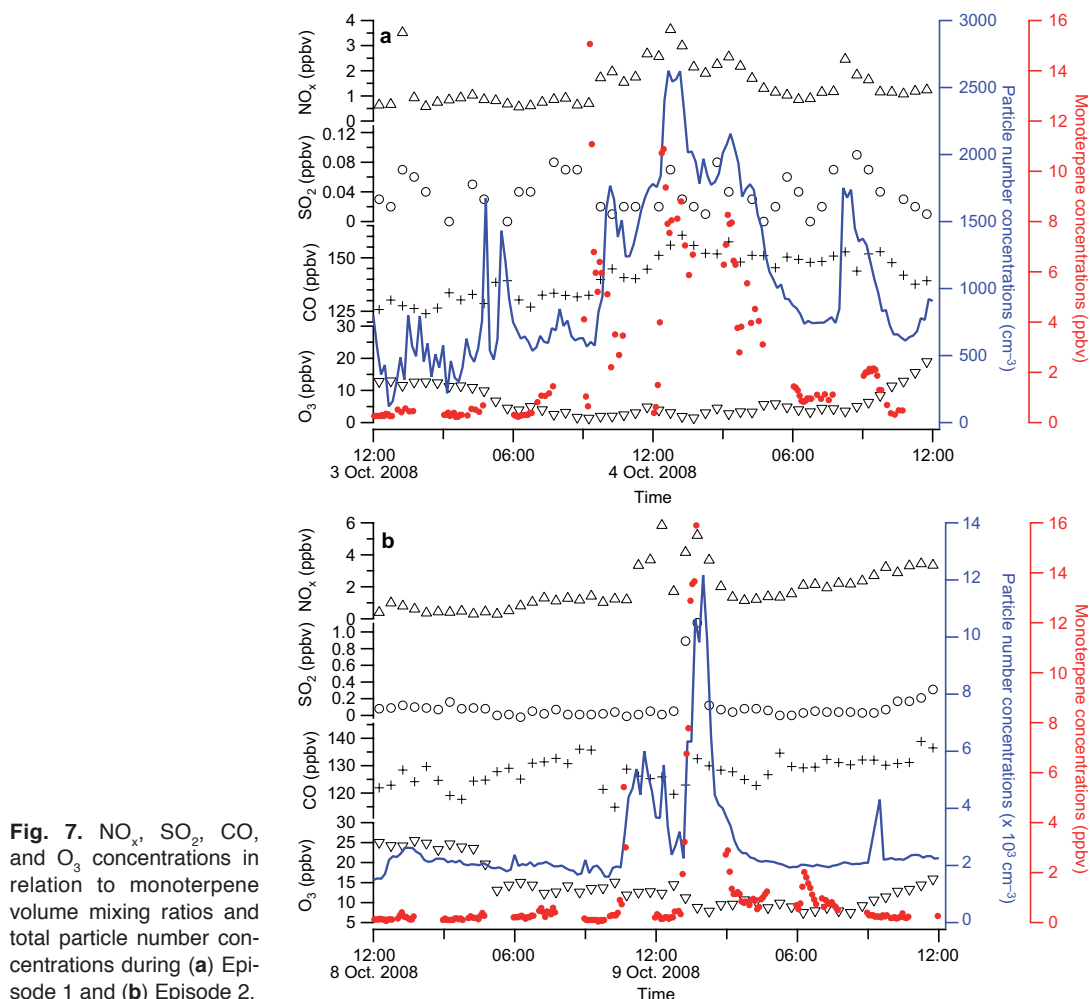
Fig. 6. Time series of (a) wind direction and precipitation (wind directions between 120° and 140° are marked by black, dashed rectangle; (b) monoterpene volume mixing ratios by PTR-MS and aerosol particle number concentrations by DMPS; (c) aerosol mass concentrations of the main species from AMS. (d) DMPS size distribution spectra from 3 to 1000 nm. All the four panels include data collected between 1 and 15 October 2008. The two monoterpene pollution episodes are marked with red rectangles.

lated with MTVMRs during these two episodes, as the coefficients of determination (R^2) between MTVMRs and Aitken mode particle number concentrations were 0.86 and 0.94 in Episodes 1 and 2, respectively.

Aerosol mass concentrations from AMS show simultaneous elevation during the two episodes (Fig. 6c). In Episode 1, the total mass concentration increased from 1.5 to 4.0 $\mu\text{g m}^{-3}$ in the first peak, and then reached 7.1, 7.2 and 4.6 $\mu\text{g m}^{-3}$ in the next three peaks, respectively. During Episode 2, aerosol mass concentration sharply increased to 14.9 $\mu\text{g m}^{-3}$ in the first peak, and then to 7.1 $\mu\text{g m}^{-3}$ in the second peak. The peak value of aerosol mass concentrations occurred before the peak value in particle number concentrations because the sizes of particles in the first peak were larger than in the next peak. Nevertheless, the coefficients of determination for MTVMRs vs. total aerosol mass

concentrations were 0.85 and 0.41 in Episodes 1 and 2, respectively. The total organics and black carbon masses demonstrate the clearest increase as MTVMRs elevated in Episode 1. The coefficients of determination for MTVMRs vs. black carbon, and for MTVMRs vs. total organics were 0.70 and 0.86, respectively. This may indicate that those particles were possibly from both primary emissions of power units and secondary formation and growth. In Episode 2, only the total organic mass concentration was correlated with MTVMRs ($R^2 = 0.3$). In both episodes, the total sulfate mass concentrations were strongly correlated with MTVMRs (coefficients of determination were 0.69 and 0.70 for Episodes 1 and 2, respectively).

During the two episodes, NO_x concentrations correlated strongly with MTVMRs ($R^2 = 0.88$ for Episode 1, and $R^2 = 0.69$ for Episode 2; see Fig. 7). SO_2 concentrations played no role in Epi-



sode 1, but SO_2 concentrations sharply increased from 0.1 ppbv to 1.0 ppbv at the second peak in Episode 2. Ozone concentrations changed very little during the two episodes. Nevertheless, the average ozone concentration in Episode 2 was around 15.0 ppbv, but only 5.0 ppbv in Episode 1. Assuming most of the particles associated with anthropogenic MT were formed via nucleation and further grew by ozonolysis products of MT and other VOC compounds during meteorological transportation, ozone concentration may explain the magnitude difference of particle number concentrations between these two episodes, as MTVMRs were similar during the first peak in both episodes. CO concentrations increased from 135.3 to 151.5 ppbv in Episode 1, but there was no clear change in Episode 2.

The background aerosol particle mass at the SMEAR II station was dominated by secondary organic aerosol, which was likely contributed by regional sources, such as biogenic SOA from tree emissions. Oxygenated organic aerosol (OOA) is the main fraction in the composition of aerosol mass at this site (Allan *et al.* 2006, Raatikainen *et al.* 2010). To visualize the temporal variations of aerosol mass during the days with episodes for these two case studies, the time variations of four selected organic mass fragments m/z 43, 44, 57, and 60 during these two episodes were plotted (see Fig. 8). During both episodes, m/z 43, and 44 were the main organic mass fragments which showed simultaneous elevation during the episodes. As m/z 44 provides estimation of the oxygen content of the organic groups in aerosol

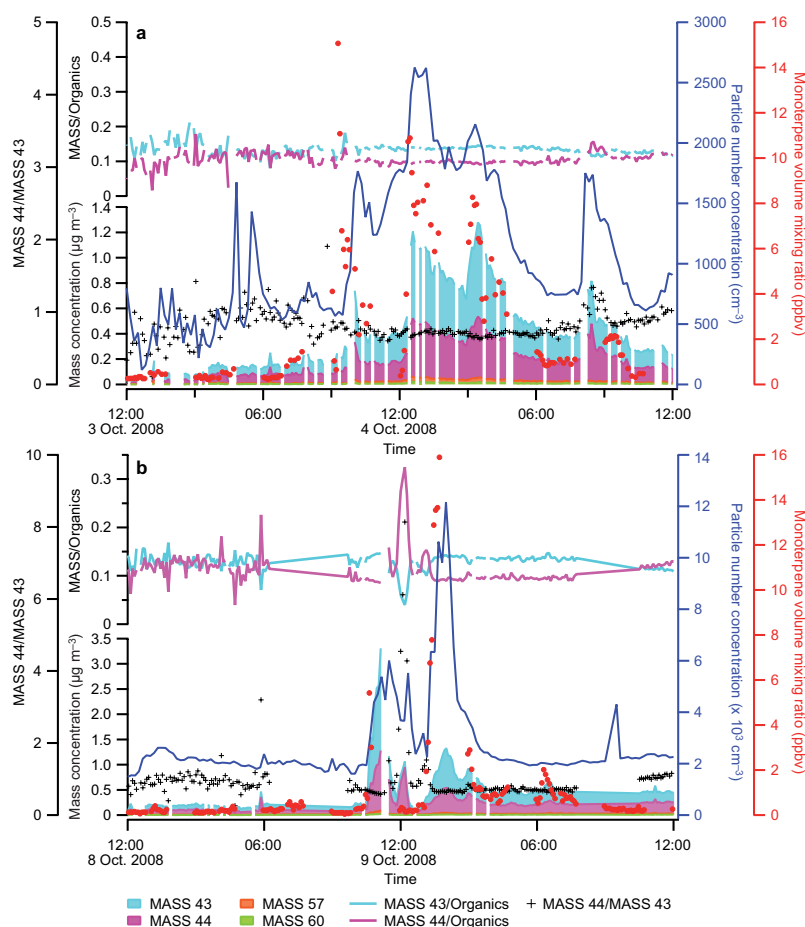


Fig. 8. Aerosol mass variations of m/z 43, 44, 57, 60 by AMS, and time series of MASS 44/MASS 43, MASS 44/Organics, and MASS 43/Organics ratios in relation to monoterpene volume mixing ratios and total particle number concentrations during (a) Episode 1 and (b) Episode 2.

mass and m/z 43 correlates well with total aerosol mass (Aiken *et al.* 2008), the ratios between m/z 44, m/z 43, and total organic mass were calculated for these two episodes. These three ratios did not show clear variations before, during, and after the episodes (Fig. 8). Even though the mass 44/mass 43 ratio was increased between the two peaks in Episode 2, we cannot conclude that those particles were from the MT pollution episode or some other local sources, because of the absence of MTVMRs during these two peaks due to the measurement cycles of PTR-MS.

Summary and conclusion

Here, we report MT pollution episodes at a boreal forest in Hyytiälä, southern Finland. On 341 (58.8%) days (out of the total 580 days), the

MT pollution episodes were registered. The sum of all the episode durations equalled 6.1% of the total PTR-MS measurement time. The observed anthropogenic MTVMRs reached at maximum 34.1 ppbv. The total average MTVMR measured at the SMEAR II station increased from 0.19 to 0.26 ppbv by taking the anthropogenic MT episodes into account, which roughly means that the average MTVMR from biogenic emissions was elevated by 36.8% because of the periodic influence of anthropogenic emissions at this site. The result suggests that the fraction and frequency of anthropogenic MT emissions due to forest industry is high enough to alter the local MTVMRs.

A significant wind direction dependence of high MTVMRs was found. This indicated that the origin of MT pollution episodes was mainly the Korkeakoski sawmill which is ca. 6 km to the southeast (130°) from the SMEAR II station.

Among other VOC compounds, MTs are the main pollutants from the Korkeakoski sawmill. Also some other gas pollutants might be emitted from the sawmill, but we did not find any clear connections between MTVMRs and other gas pollutant concentrations during the MT pollution episodes. However, the case studies showed that other associated pollutants may be occasionally emitted.

The co-appearance of MT and aerosol particles during MT pollution episodes suggests that the emissions from the Korkeakoski sawmill did not only cause the MT pollution episodes, but also had a noticeable effect on local aerosol loading. Measured aerosol particle size distributions during the MT pollution episodes indicate that the particles co-occurring with high MTVMRs were large enough to act as CCN.

The mass concentrations and chemical compositions of aerosol particles were characterized by using an AMS during two MT pollution episodes. Organic mass dominated the total aerosol mass concentrations. Organic mass fraction did not change significantly during the MT pollution episodes, which indicates that the aerosol particles linked to the MT pollution episodes had very similar composition to the regional background aerosol particles. Also, the ratios between m/z 44 and m/z 43 during the two episodes show close similarity to particles measured outside the MT pollution episodes.

In future, it will be of interest to conduct direct measurements of VOCs, chemical properties of aerosol particles and trace gases at the sawmill site to draw more straightforward conclusions on the magnitude of anthropogenic VOC emissions, as well as the effect of anthropogenic VOCs on the local air properties and chemistry.

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References

Aalto P., Hameri K., Becker E., Weber R., Salm J., Makela

- J.M., Hoell C., O'Dowd C.D., Karlsson H., Hansson H.C., Vakeva M., Koponen I.K., Buzorius G. & Kulmala M. 2001. Physical characterization of aerosol particles during nucleation events. *Tellus B* 53: 344–358.
- Aiken A.C., Decarlo P.F., Kroll J.H., Worsnop D.R., Huffman J.A., Docherty K.S., Ulbrich I.M., Mohr C., Kimmel J.R., Sueper D., Sun Y., Zhang Q., Trimborn A., Northway M., Ziemann P.J., Canagaratna M.R., Onasch T.B., Alfarra M.R., Prevot A.S.H., Dommen J., Duplissy J., Metzger A., Baltensperger U. & Jimenez J.L. 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* 42: 4478–4485.
- Allan J.D., Alfarra M.R., Bower K.N., Coe H., Jayne J.T., Worsnop D.R., Aalto P.P., Kulmala M., Hyotylainen T., Cavalli F. & Laaksonen A. 2006. Size and composition measurements of background aerosol and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer. *Atmos. Chem. Phys.* 6: 315–327.
- Andreae M.O. & Rosenfeld D. 2008. Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols. *Earth-Science Reviews* 89: 13–41.
- Aschmann S.M., Arey J. & Atkinson R. 2002. OH radical formation from the gas-phase reactions of O₃ with a series of terpenes. *Atmos. Environ.* 36: 4347–4355.
- Atkinson R. & Arey J. 2003. Atmospheric degradation of volatile organic compounds. *Chemical Reviews* 103: 4605–4638.
- Bertin N., Staudt M., Hansen U., Seufert G., Ciccioli P., Foster P., Fugit J.L. & Torres L. 1997. Diurnal and seasonal course of monoterpene emissions from *Quercus ilex* (L.) under natural conditions — applications of light and temperature algorithms. *Atmos. Environ.* 31: 135–144.
- Bonn B. & Moortgat G.K. 2003. Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons. *Geophys. Res. Lett.* 30(11), 1585, doi:10.1029/2003GL017000.
- Canagaratna M.R., Jayne J.T., Jimenez J.L., Allan J.D., Alfarra M.R., Zhang Q., Onasch T.B., Drewnick F., Coe H., Middlebrook A., Delia A., Williams L.R., Trimborn A.M., Northway M.J., DeCarlo P.F., Kolb C.E., Davidovits P. & Worsnop D.R. 2007. Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrometry Reviews* 26: 185–222.
- Eerdekens G., Yassaa N., Sinha V., Aalto P.P., Aufm'hoff H., Arnold F., Fiedler V., Kulmala M. & Williams J. 2009. VOC measurements within a boreal forest during spring 2005: on the occurrence of elevated monoterpene concentrations during night time intense particle concentration events. *Atmos. Chem. Phys.* 9: 8331–8350.
- Englund F. & Nussbaum R.M. 2000. Monoterpenes in Scots pine and Norway spruce and their emission during kiln drying. *Holzforschung* 54: 449–456.
- Granström K. 2003. Emissions of monoterpenes and VOCs during drying of sawdust in a spouted bed. *Forest Products Journal* 53: 48–55.

- Granström K. 2005. *Emissions of volatile organic compounds from wood*. Ph.D. thesis, Department of Environmental and Energy Systems, Karlstad University.
- Granström K. 2009. Emissions of sesquiterpenes from spruce sawdust during drying. *European Journal of Wood and Wood Products* 67: 343–350.
- Guenther A. 1997. Seasonal and spatial variations in natural volatile organic compound emissions. *Ecological Applications* 7: 34–45.
- Guenther A., Zimmerman P., Klinger L., Greenberg J., Ennis C., Davis K., Pollock W., Westberg H., Allwine G. & Geron C. 1996. Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements. *J. Geophys. Res.* 101(D1): 1345–1359.
- Guenther A.B., Zimmerman P.R., Harley P.C., Monson R.K. & Fall R. 1993. Isoprene and monoterpene emission rate variability — model evaluations and sensitivity analyses. *J. Geophys. Res.* 98(D7): 12609–12617.
- Hakola H., Tarvainen V., Laurila T., Hiltunen V., Hellen H. & Keronen P. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* 37: 1623–1634.
- Hari P. & Kulmala M. 2005. Station for measuring ecosystem atmosphere relations (SMEAR II). *Boreal Env. Res.* 10: 315–322.
- Heald C.L., Henze D.K., Horowitz L.W., Feddes J., Lamarque J.F., Guenther A., Hess P.G., Vitt F., Seinfeld J.H., Goldstein A.H. & Fung I. 2008. Predicted change in global secondary organic aerosol concentrations in response to future climate, emissions, and land use change. *J. Geophys. Res.* 113, D05211, doi: 10.1029/2007JD009092.
- Holzke C., Hoffmann T., Jaeger L., Koppmann R. & Zimmer W. 2006. Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots pine (*Pinus sylvestris* L.). *Atmos. Environ.* 40: 3174–3185.
- Hussein T., Dal Maso M., Petaja T., Koponen I.K., Paatero P., Aalto P.P., Hameri K. & Kulmala M. 2005. Evaluation of an automatic algorithm for fitting the particle number size distributions. *Boreal Env. Res.* 10: 337–355.
- Jimenez J.L., Canagaratna M.R., Donahue N.M., Prevot A.S.H., Zhang Q., Kroll J.H., DeCarlo P.F., Allan J.D., Coe H., Ng N.L., Aiken A.C., Docherty K.S., Ulbrich I.M., Grieshop A.P., Robinson A.L., Duplissy J., Smith J.D., Wilson K.R., Lanz V.A., Hueglin C., Sun Y.L., Tian J., Laaksonen A., Raatikainen T., Rautiainen J., Vaattovaara P., Ehn M., Kulmala M., Tomlinson J.M., Collins D.R., Cubison M.J., Dunlea E.J., Huffman J.A., Onasch T.B., Alfarra M.R., Williams P.I., Bower K., Kondo Y., Schneider J., Drewnick F., Borrmann S., Weimer S., Demerjian K., Salcedo D., Cottrell L., Griffin R., Takami A., Miyoshi T., Hatakeyama S., Shimono A., Sun J.Y., Zhang Y.M., Dzepina K., Kimmel J.R., Sueper D., Jayne J.T., Herndon S.C., Trimborn A.M., Williams L.R., Wood E.C., Middlebrook A.M., Kolb C.E., Baltensperger U. & Worsnop D.R. 2009. Evolution of organic aerosols in the atmosphere. *Science* 326: 1525–1529.
- Johansson A. & Rasmuson A. 1998. The release of monoterpenes during convective drying of wood chips. *Drying Technology* 16: 1395–1428.
- Kesselmeier J. & Staudt M. 1999. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *J. Atmos. Chem.* 33: 23–88.
- Komppula M., Lihavainen H., Kerminen V.M., Kulmala M. & Viisanen Y. 2005. Measurements of cloud droplet activation of aerosol particles at a clean subarctic background site. *J. Geophys. Res.* 110, D06204, doi: 10.1029/2004JD005200.
- Kroll J.H. & Seinfeld J.H. 2005. Representation of secondary organic aerosol laboratory chamber data for the interpretation of mechanisms of particle growth. *Environ. Sci. Technol.* 39: 4159–4165.
- Kulmala M., Suni T., Lehtinen K.E.J., Dal Maso M., Boy M., Reissell A., Rannik U., Aalto P., Keronen P., Hakola H., Back J.B., Hoffmann T., Vesala T. & Hari P. 2004. A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.* 4: 557–562.
- Kulmala M., Asmi A., Lappalainen H.K., Carslaw K.S., Poschl U., Baltensperger U., Hov O., Brenquier J.L., Pandis S.N., Facchini M.C., Hansson H.C., Wiedensohler A. & O'Dowd C.D. 2009. Introduction: European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) — integrating aerosol research from nano to global scales. *Atmos. Chem. Phys.* 9: 2825–2841.
- Lappalainen H.K., Sevanto S., Back J., Ruuskanen T.M., Kolari P., Taipale R., Rinne J., Kulmala M. & Hari P. 2009. Daytime concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors. *Atmos. Chem. Phys.* 9: 5447–5459.
- Lindinger W., Hansel A. & Jordan A. 1998. On-line monitoring of volatile organic compounds at pptv levels by means of protontransfer-reaction mass spectrometry (PTR-MS) — medical applications, food control and environmental research. *Int. J. Mass Spectrom.* 173: 191–241.
- Merikanto J., Spracklen D.V., Mann G.W., Pickering S.J. & Carslaw K.S. 2009. Impact of nucleation on global CCN. *Atmos. Chem. Phys.* 9: 8601–8616.
- Raatikainen T., Vaattovaara P., Tiitta P., Miettinen P., Rautiainen J., Ehn M., Kulmala M., Laaksonen A. & Worsnop D.R. 2010. Physicochemical properties and origin of organic groups detected in boreal forest using an aerosol mass spectrometer. *Atmos. Chem. Phys.* 10: 2063–2077.
- Rinne J., Hakola H., Laurila T. & Rannik U. 2000. Canopy scale monoterpene emissions of *Pinus sylvestris* dominated forests. *Atmos. Environ.* 34: 1099–1107.
- Rinne J., Ruuskanen T.M., Reissell A., Taipale R., Hakola H. & Kulmala M. 2005. On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem. *Boreal Environ. Res.* 10: 425–436.
- Roffael E. 2006. Volatile organic compounds and formaldehyde in nature, wood and wood based panels. *Holz als Roh- und Werkstoff* 64: 144–149.
- Ruuskanen T. M., Kolari P., Back J., Kulmala M., Rinne J., Hakola H., Taipale R., Raivonen M., Altimir N. & Hari

- P. 2005. On-line field measurements of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry. *Boreal Env. Res.* 10: 553–567.
- Ruuskanen T.M., Hakola H., Kajos M.K., Hellen H., Tarvainen V. & Rinne J. 2007. Volatile organic compound emissions from Siberian larch. *Atmos. Environ.* 41: 5807–5812.
- Rupar K. & Sanat M. 2003. The release of organic compounds during biomass drying depends upon the feedstock and/or altering drying heating medium. *Biomass & Bioenergy* 25: 615–622.
- Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M., Milford, J. & Guenther, A. 2008. Monoterpene and sesquiterpene emission estimates for the United States. *Environ. Sci. Technol.* 42: 1623–1629.
- Schade G.W. & Goldstein A.H. 2003. Increase of monoterpene emissions from a pine plantation as a result of mechanical disturbances. *Geophys. Res. Lett.* 30: 1380, doi: 10.1029/2002GL016138.
- Schurgers G., Arneth A., Holzinger R. & Goldstein A.H. 2009. Process-based modelling of biogenic monoterpene emissions combining production and release from storage. *Atmos. Chem. Phys.* 9: 3409–3423.
- Seinfeld J.H. & Pandis S.N. 2006. *Atmospheric chemistry and physics: from air pollution to climate change*, 2nd ed. John Wiley & Sons, New York.
- Shantz N.C., Aklilu Y.A., Ivanis N., Leaith W.R., Brickell P.C., Brook J.R., Cheng Y., Halpin D., Li S.M., Tham Y.A., Toom-Sauntry D., Prenni A.J. & Graham L. 2004. Chemical and physical observations of particulate matter at Golden Ears Provincial Park from anthropogenic and biogenic sources. *Atmos. Environ.* 38: 5849–5860.
- Sheehan P.E. & Bowman F.M. 2001. Estimated effects of temperature on secondary organic aerosol concentrations. *Environ. Sci. Technol.* 35: 2129–2135.
- Ståhl M., Granstrom K., Berghel J. & Renstrom R. 2004. Industrial processes for biomass drying and their effects on the quality properties of wood pellets. *Biomass and Bioenergy* 27: 621–628.
- St-Onge L., Archambault J.F., Kwong E., Sabsabi M. & Vadas E.B. 2005. Rapid quantitative analysis of magnesium stearate in tablets using laser-induced breakdown spectroscopy. *Journal of Pharmaceutical Science* 8: 272–288.
- Taipale R., Ruuskanen T.M., Rinne J., Kajos M.K., Hakola H., Pohja T. & Kulmala M. 2008. Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS — measurement, calibration, and volume mixing ratio calculation methods. *Atmos. Chem. Phys.* 8: 6681–6698.
- Tarvainen V., Hakola H., Hellen H., Back J., Hari P. & Kulmala M. 2005. Temperature and light dependence of the VOC emissions of Scots pine. *Atmos. Chem. Phys.* 5: 989–998.
- Tingey D.T., Manning M., Grothaus L.C. & Burns W.F. 1980. Influence of light and temperature on monoterpene emission rates from slash pine. *Plant Physiology* 65: 797–801.
- Tunved P., Hansson H.C., Kerminen V.M., Strom J., Dal Maso M., Lihavainen H., Viisanen Y., Aalto P.P., Komppula M. & Kulmala M. 2006. High natural aerosol loading over boreal forests. *Science* 312: 261–263.
- Virkkula A., Makela T., Hillamo R., Yli-Tuomi T., Hirsikko A., Hameri K. & Koponen I.K. 2007. A simple procedure for correcting loading effects of aethalometer data. *J. Air & Waste Manage Assoc.* 57: 1214–1222.
- Volkamer R., Jimenez J.L., San Martini F., Dzepina K., Zhang Q., Salcedo D., Molina L.T., Worsnop D.R. & Molina M.J. 2006. Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. *Geophys. Res. Lett.* 33: 17 811–17 815.
- Wheeler A.J. & Ganji A.R. 1996. *Introduction to engineering experimentation*. Prentice Hall, Englewood Cliffs, NJ.