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Spring recovery of photosynthesis and atmospheric particle formation

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We investigated springtime atmospheric particle formation in a Finnish boreal forest with respect to the spring recovery of photosynthetic capacity by using particle size distribution data together with a temperature-dependent state of photosynthetically active substances parameter, S. Spring is a period of exceptionally high particle formation event frequency and the events also produce a high number of aerosol particles. We found that the onset of the period of a high particle formation event frequency coincides with start of the spring recovery of the photosynthetic activity in the boreal coniferous forest. The highest particle formation frequency was found to occur with values of S close to 0 °C, which corresponds to a relative photosynthetic efficiency of about 30% of the maximum efficiency. The nucleation mode particle number concentration was highest with values of S between –3 °C and 0 °C, higher S resulting in lower average particle number concentrations. The increase in particle formation efficiency was also clearly reflected in the particle size distribution. Investigations in other atmospheric parameters important for nucleation revealed elevated ozone concentrations, but no clear other reason for the elevated particle formation activity. Therefore, we suggest that the particle formation peak is caused by biogenic volatile compound emissions from the boreal ecosystem that is undergoing spring recovery.

Introduction

It has been known now for a while that atmospheric aerosol particle production occurs frequently in various areas of the globe (e.g. Kulmala *et al*. 2004a). Especially forested areas have been shown to be a strong source of particulate material (Tunved *et al*. 2006), both in terms of producing new particles and thus increasing particle number concentrations, and in turns of increasing particulate mass concentrations by growing existing particles. Both these phenomena have been linked to emissions of volatile organic compounds (VOCs) emitted by the forest vegetation (therefore called biogenic VOCs or BVOCs) (Kulmala *et al*. 2004b). Studies have shown that even the smallest, recently-nucleated particles contain organic material (Kulmala *et al*. 2007); organic vapours have been proposed to be the main candidate to explain the majority of observed particle growth rate.

The range of organic vapours that could act as precursors for aerosol formation is limited by their vapour pressure: it has to be low enough so that the compound prefers the liquid phase. As implied by their name, BVOCs themselves are too volatile for this so they have to undergo a chemical transformation before forming aerosol. The vapour pressure can, in general terms, be considered to be decreased with increasing amounts of carbon atoms in the compound. Typically, VOCs with more than 6–7 carbon atoms are considered good aerosol precursors. Of biogenic emissions, terpenoids such as mono- and sesquiterpene oxidation products belong to this group. Trajectory studies of boreal forest air masses have quantitatively linked monoterpene emissions to the observed particle mass (Tunved *et al*. 2006).

Aerosol particles are a necessary prerequisite for cloud formation because they act as nuclei for condensing cloud droplets. Changes in cloud droplet number, and to a lesser extent in their composition, can cause changes in cloud albedo, lifetime and rainout, thereby affecting the Earth's radiative balance. This is called the aerosol indirect effect. By themselves, aerosol particles also scatter solar radiation, which adds another climatic effect. This is called the direct aerosol effect (e.g. Seinfeld and Pandis 1998).

The climatic influence of aerosol particles, the frequency and regional nature of atmospheric particle formation over vegetated areas and the clear linkage of particle formation to BVOC emissions prompted Kulmala *et al*. (2004b) to suggest a feedback mechanism between forests, aerosols and climate. This feedback involves the rising temperature (and possibly also rising CO_2 levels) that enhances photosynthesis in plants, leading to increased plant emissions (Bäck and Hari 2008), which in turn increases aerosol particle production and possibly leads to a cooling radiative forcing via both direct and indirect aerosol effect.

Particle formation events have been observed continuously and frequently at the SMEAR II measuring station in Hyytiälä, Finland, since 1996, when aerosol size distribution measurements using a Differential Mobility Particle Sizer commenced (Mäkelä *et al*. 1997). The data from these measurements show a clear annual pattern in particle formation event frequency, with a maximum in spring. The data show further a clear and often quite quick transition from winter, when no particle formation is occurring, to a very high formation activity in spring (Dal Maso *et al*. 2005). This springtime maximum has remained unexplained.

The above-mentioned link between biogenic emissions of organic compounds from trees and aerosol formation has raised a question of whether the high springtime particle formation activity is connected with the re-awakening of the biological activity of the forest vegetation. As one of the main aerosol formation precursor BVOCs, monoterpene, is produced in the chloroplast of plants, and photosynthesis is needed for some of the chief precursors, it is of interest to take a more detailed look at this link.

We studied the springtime onset of particle formation in the light of the photosynthetic activity of trees. For this purpose, we made use of the state of phosynthetic functional substances, *S*, introduced by Hari *et al*. (2008). *S* is a temperature-dependent parameter that can be used to predict the start of photosynthesis of trees. We compared the particle formation event frequency, the number concentration of small particles and the particle number size distributions as a function of this state parameter in order to investigate the link between the onset of particle formation and the onset of photosynthesis in a boreal forest. In doing so, we wish to shed light on the question whether such a link exists and at which stages of spring recovery photosynthetic activity starts to be reflected in atmospheric aerosol concentrations.

Materials and methods

Measurements

The measurement station SMEAR II (System for Measuring Forest Ecosystem–Atmosphere Relationships II; Hari and Kulmala 2005) is one of the three University of Helsinki stations dedicated to the investigation of the atmosphere–biosphere system. The station is located in a Scots pine forest in Hyytiälä, Finland (61°51´N, 24°17´E), 60 km northeast of the nearest city, Tampere, and 200 km northwest of Helsinki.

The SMEAR II station measures atmospheric gas concentrations, radiation and meteorological variables. A 73-m mast records continuous gas concentrations of NO_x, CO_2, CO, SO_2, O_3, and H_2O at six different height levels.

We analysed springtime data of aerosol number size distributions, CO_2 exchange data measured from chambers and air temperature data to elucidate the effect of the photosynthesis spring recovery on atmospheric particle concentrations.

Aerosol particle number size distributions are being measured with a pair of Differential Mobility Particle Sizer (DMPS) systems (Mäkelä *et al.* 1997, Aalto *et al.* 2001), consisting of a Differential Mobility Analyser (DMA) to size-classify the sampled aerosol particles, followed by a Condensation Particle Counter (CPC) to count the number of particles in each size bin. The DMPS system is measuring the lower (diameter 3–10 nm) and upper (10–500 nm) part of the particle size range every 10 minutes.

The measured aerosol size distributions were analysed to find out the days having a new particle formation (NPF) burst and days with no visible particle formation. The criteria for the selection were such that regional formation events with substantial growth were classified as burst days. Days with ambiguous status were flagged and removed from the data. A detailed description of the selection method and criteria can be found in Dal Maso *et al.* (2005).

We also utilized data from the continuous meteorological measurements. The measurement values used were taken at the lowest height that was closest to the aerosol measurement level possible.

State of functional substances, *S*

Comparing the measured aerosol size distribution features, especially the particle formation activity, with the measured photosynthetic activity is not a simple task. Measured carbon fluxes performed at the Hyytiälä station are representative of a respectively small area (of the order of a few hundred meters) when the eddy covariance method is used, whereas shoot-enclosure measurements provide essentially the photosynthetic activity of a single shoot. In contrast, the particle formation observed at the station is a regional phenomenon that is assumed to occur on a scale of tens to hundreds of kilometres (Kulmala *et al.* 1998, Dal Maso *et al.* 2007, Hussein *et al.* 2009).

In order to work around the scaling problem, we made use of studies about the dependency of photosynthesis on temperature. Already in 1980, Pelkonen and Hari (1980) suggested that the seasonal changes in photosynthesis are related to ambient temperature. Suni *et al.* (2003) found that the spring recovery of photosynthesis could be explained using a five-day backward average of air temperature. The concentrations and activities of enzymes, pigments and membrane pumps change during the annual cycle of photosynthesis. We call enzymes, pigments and membrane pumps functional substances. Hari *et al.* (2008) developed the approach of Pelkonen and Hari (1980) further and introduced the variable *S*, which describes the regularities in the functional substances connected with the annual cycle of photosynthesis. By using *S*, which has units of temperature, a simple linear relationship between the photosynthetic efficiency and ambient temperature history could be formulated. Kolari *et al.* (2007) investigated the dependence between the temperature history and photosynthetic efficiency further and found that the photosynthetic efficiency could be accurately predicted from temperature using a sigmoidal relationship.

The state of functional substances *S* relates to the temperature history as follows

$$\frac{dS}{dt} = \frac{T - S}{\tau},$$

where T is the ambient temperature and τ is a time constant, in practice representing the slowness of changes in the photosynthetic apparatus. Practically, S is calculated iteratively from an initial value in half-hour steps, starting from an initial value (in our case, the temperature at the start of year). When making comparisons with individual aerosol measurements, we performed a nearest-neighbour interpolation to the measured aerosol concentration. When making comparisons with daily measurements (such as whether a day was an event or not), a daily-mean value of S was used. In essence, S is a moving temperature sum, but one that can also decrease with time. This reversibility means that the photosynthetic activity can also decrease over time, which differentiates S conceptually from the accumulated temperature sum that is sometimes used to predict spring recovery-related events such as bud-burst or flowering.

As already mentioned, Kolari *et al*. (2007) presented a sigmoidal dependence between the relative photosynthetic efficiency (y) and the state of functional substances, as well as a linear one. The sigmoidal parameterization fits the data slightly better, but for simplicity's sake we will use the linear one in this study. The difference between the approaches is minimal. The functional dependence is given by $y = 0.065(S + 4.67)$, where y is the relative photosynthetic efficiency. Since the relative photosynthetic efficiency (actual efficiency divided by maximum efficiency) cannot be less than zero and also not larger than one, the formula is only valid in the interval [–4.67 °C, 10.71 °C]. The endpoints of this interval give the values of S for the onset of photosynthetic activity and the saturation of photosynthetic efficiency.

Results

Event probability

The peak in particle formation event frequency in spring has been known for some time. It has been observed at various stations inside the boreal forest area (e.g. Dal Maso *et al*. 2007, Kristensson *et al*. 2008). In order to investigate the onset of the intensive particle formation period in detail, we plotted the cumulative event number in spring as a function of the day of year. In such a plot, the spring onset of the particle formation period can be seen as a sharp rise in the cumulative event number when comparing with the calculated state of functional substances (Fig. 1). One can observe that the sharp increase in the cumulative event number often coincides with an increase in the value of state of functional substances.

The statistics of particle formation events are often presented on a month-by-month basis. We investigated the event frequency using a sliding event probability, P_e, that is defined by counting the number of event days in a time window and dividing this by either the width of the time window or by the number of days that are classified as either event or non-event days. The difference between the two described methods is that the second methods removes days of ambiguous status from the statistic.

We studied P_e, computed using a 21-day time-window, as a function of the day of the year as well as the monthly averages for the classified Hyytiälä data set until 2006 (Fig. 2). In winter, starting from November, particle formation events are rare. Around the start of February, the frequency of particle formation events started to increase and reached a peak value around mid-March. We also compared the averaged value of the state of functional substances with P_e. We found that the peak in particle formation event frequency occurred during the same period as when S was between –5 and + 10 °C, which is the value range where photosynthetic efficiency increases rapidly.

A similar figure can now be drawn, taking the state of functional substances as the independent variable. Instead of counting the number of particle formation events in a time window $2w$, we counted the number of events for which S was in the interval $[S - w, S + w]$, and divided this by the total number of days for which S was in the same interval, again also filtering out days with undefined status similarly to the daily probability case.

We studied the resulting event probability as a function of the state of functional substances S computed for the window size $w = 1$ °C (Fig. 3). We observed that the probability of having a particle formation event was at its minimum when S was below –10 °C. The particle formation probability started to rise sharply at values of S very close to those when the photosynthetic efficiency starts to differ from zero. The particle formation event probability rose to its maximum value at 0 °C when the photosynthetic efficiency reached 30% of its maximum value. The maximum photosynthetic efficiency corresponds to $S = 10.7$ °C. At $S = 2$–3 °C, the event probability had a minor minimum, but the S values of 5–7 °C again corresponded to an event probability almost as high as that of the first peak.

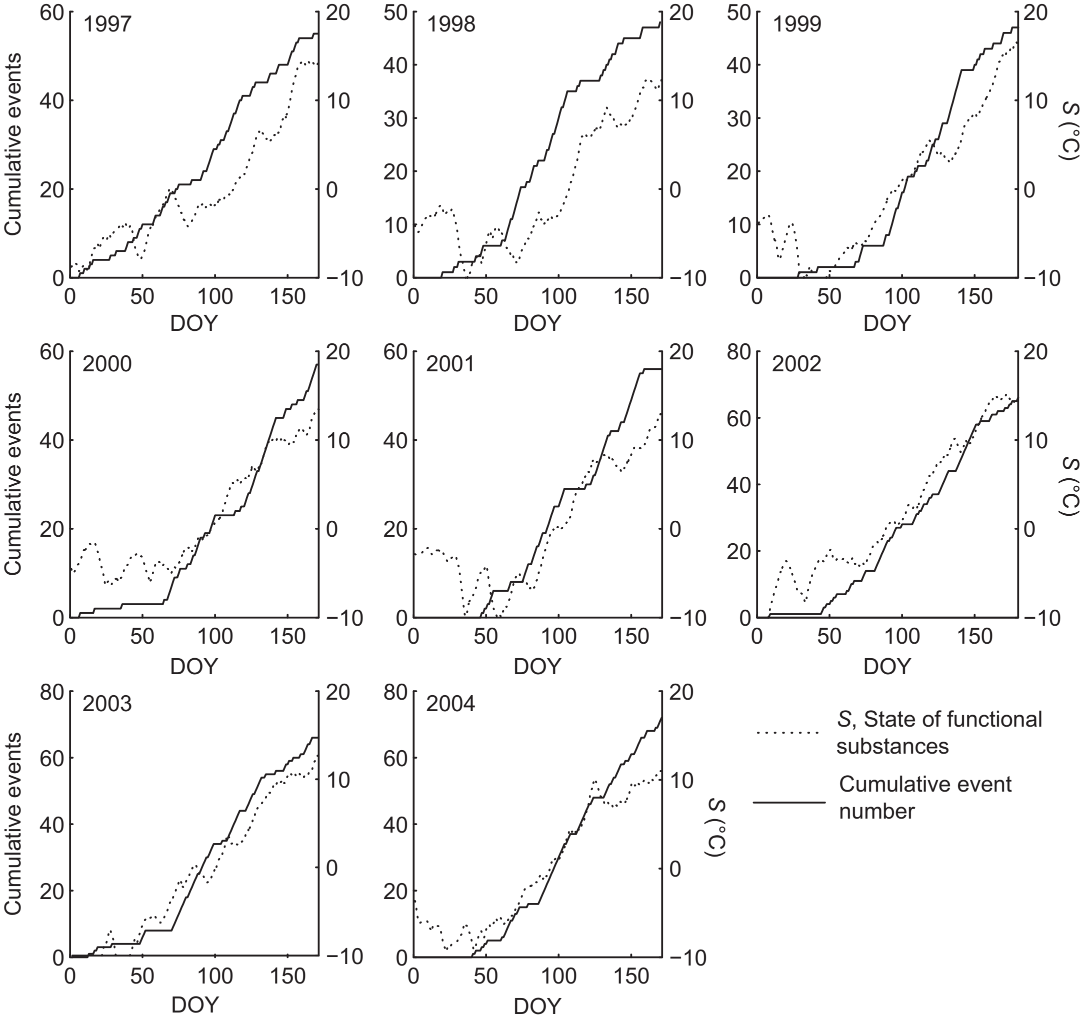

Fig. 1. The cumulative number of particle formation events at the Hyytiälä station for the years 1997–2004 (solid line). The dotted line shows the state of functional substances *S* for the same periods.

Nucleation mode particle number concentration

In order to get insight into particle formation in a more quantitative level, we also had a look at the springtime development of small particle concentrations. We integrated the measured size distributions from the smallest observable sizes to 25 nm, thereby obtaining the concentration of nucleation mode particles, N_{nuc}. As there are very few sources besides nucleation for particles in this size range, the resulting number can be used for quantifying the strength of the atmospheric nucleation process.

We studied the observed concentration range of nucleation mode particles (particles smaller than 25 nm) early in the year (Jan–May) for given values of *S* (Fig. 4). Only daytime measurements were taken into account, with daytime defined as that between 09:00 and 15:00 because this is also the time most particle formation events occur (Mäkelä *et al.* 2001).

The striking feature visible in Fig. 4 was the clear increase in nucleation mode particle concentration when the parameter for the state of functional substances rises above –3 °C. The average daytime nucleation mode concentration more than doubled for the *S* value in the range

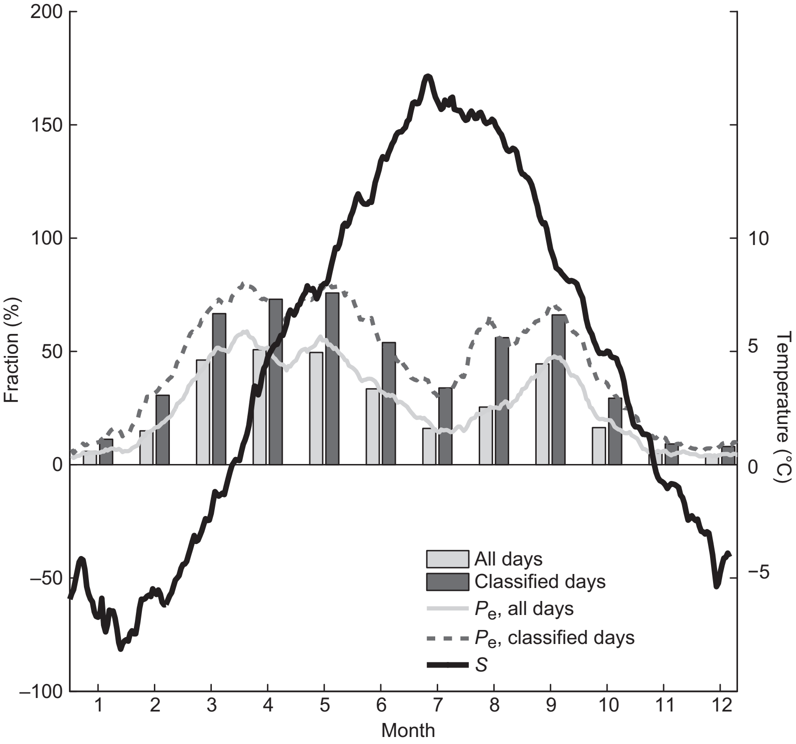

Fig. 2. The average annual variation of the state of functional substances *S* (scale on the right) and the probability of finding an event at a certain time of the year, for both month-by-month and three-week sliding average values. The grey line (sliding average) and grey bars (monthly values) represent values for which all days were included in the analysis. For equivalents indicated by the grey dashed line, undefined days (neither events nor non-events) were left out of the dataset for the probability calculation.

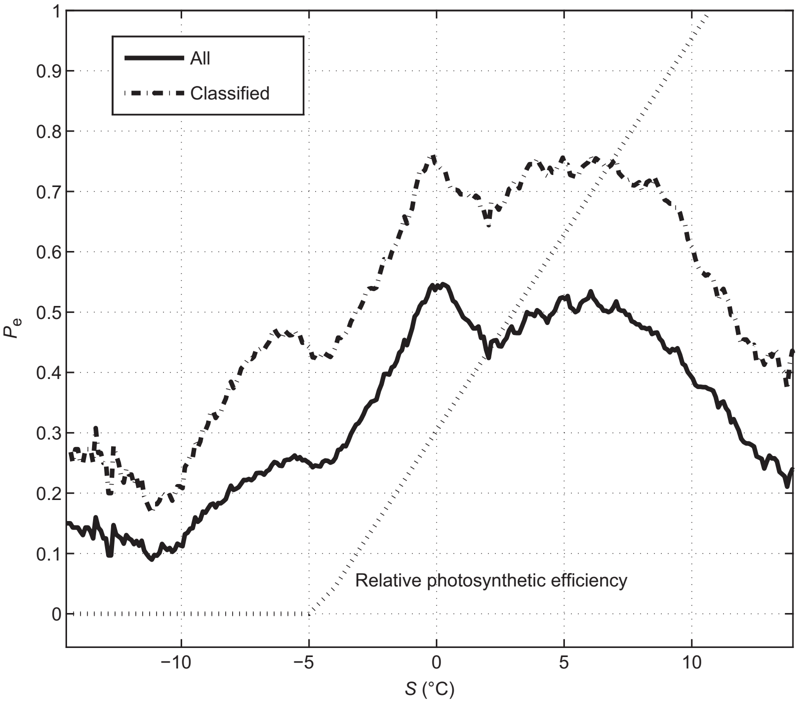

Fig. 3. The event probability as a function of the state of functional substances *S*. Only winter and spring (Jan–May) events were taken into account. The dotted line shows the parameterized relative photosynthetic efficiency, *y*, as given in Kolari *et al*. (2007), with a functional dependence $y = 0.065(S + 4.67)$. The solid and dashed lines represent two different ways of event classification analysis: the solid line shows the event probability when undefined days are omitted from the dataset, and the dash-dotted line represents data where these days were included.

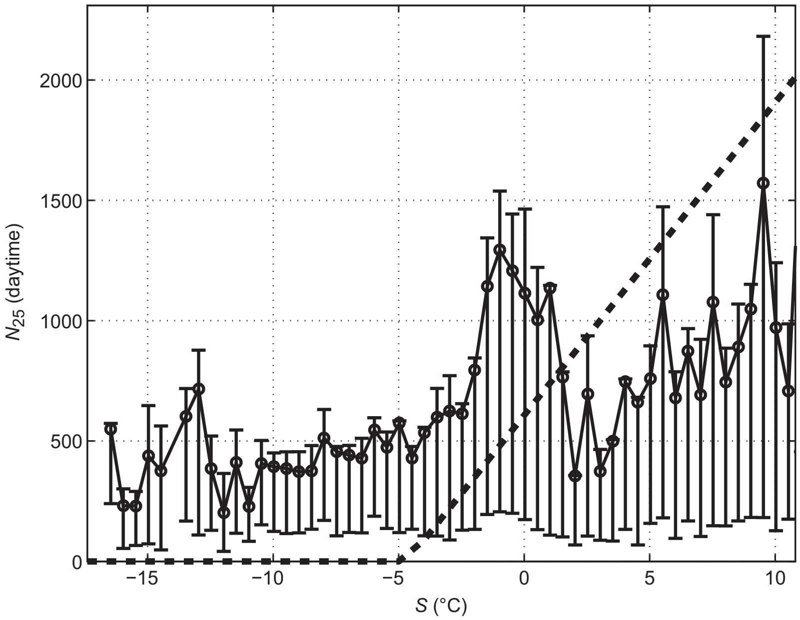

Fig. 4. The mean nucleation mode (particles smaller than 25 nm) concentration as a function of the state of functional substances *S*. The bars in the figure represent the 25th and 75th percentiles, while the circles give the mean value in the range [$S - \Delta S$, $S + \Delta S$], with $\Delta S = 0.5$ °C. For comparison purposes, we plotted again the photosynthetic efficiency as given in Kolari *et al*. (2007), scaled here by a factor of 2000 to fit it into the figure.

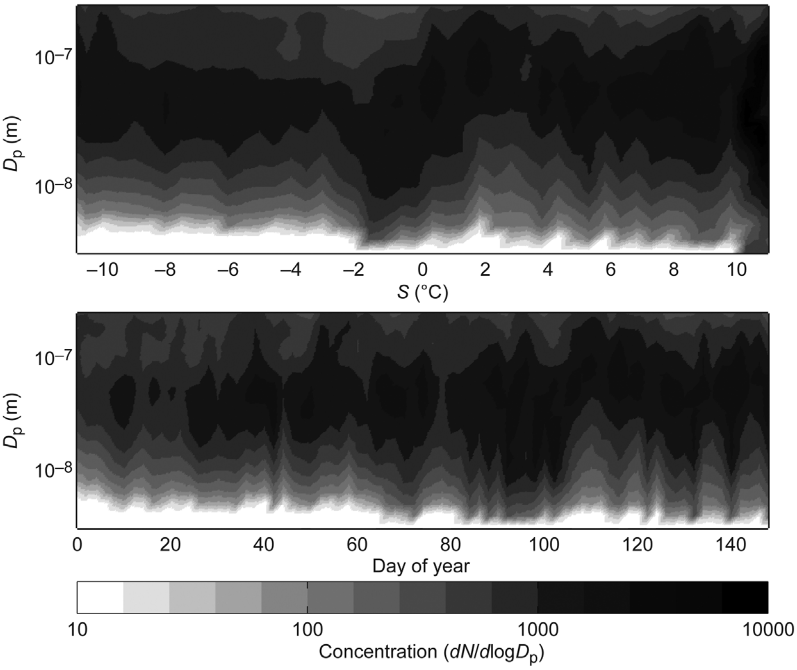

Fig. 5. The averaged particle size distributions as a function of the state of functional substances, (top panel) and the day of year (bottom panel). In the top panel, we give the state of functional substances in the *x*-axis, while the *y*-axis shows the particle size. The colour gives the particle concentration median, computed separately for all measured size classes. In the bottom panel, the *x*-axis is the day of the year instead of *S*, for springtime days.

[–3 °C, +1 °C] as compared with the concentrations for the wintertime *S* values. In contrast to the particle formation event probability, the concentration decreased again at higher values of *S*.

Studying the dependence of the particle size distribution on the state of functional substances is most convenient by using a surface plot of the size distribution (Fig. 5). In the surface plot, the most interesting feature could again be seen for the value range of [–3 °C, 0 °C]. We observed quite a distinct change in the average size distribution: the average size of the particles became smaller and their concentration increased. As the value of *S* increased, the size of the particles started to increase again and this continued until *S* reached the values of around 2–3 °C. No sharp transition could be observed as a function of the day of year, even though an increase in the average diameter could be observed between about the days 100 and 110.

Discussion

The analysis of the aerosol size distributions and concentrations as a function of the state of functional substances *S* yielded on one hand an expected result, namely that the particle formation frequency and the strength of the natural particle source was greater with increasing photosynthetic efficiency. On the other hand, we were surprised by the finding that the relationship between photosynthetic efficiency and particle formation was not linear, but more like a peak, occurring close to the time of the spring recovery of the forest and decreasing again after photosynthetic efficiency was close to its maximum.

Currently, the nucleation mechanism producing particles in the boreal forest area is a topic of intense investigation, but the exact nature of this mechanism has not yet been confirmed. It has been found that the particle formation rate can be expressed as a function of sulphuric acid concentration (Kulmala *et al*. 2006). On the other hand, measurements have shown that even very small particles contain organic compounds (O'Dowd *et al*. 2002). Oxidation products of VOCs most certainly are participating in the new particle growth, and probably also form the majority of the formed particulate volume and mass (Tunved *et al*. 2006). Studies performed in a plant chamber have shown that the growth rate of the particles is dependent mainly on the amount emitted organic carbon. On the other hand, the same studies have showed a great difference in the number and production rate of new particles, depending whether a single model VOC or real plants were used as a precursor producer (Mentel *et al*. 2009). This would indicate that the chemical composition of a precursor mix has an effect on the particle production mechanism. This effect may either be directly via the nucleation process itself (if organics are taking part), or via changing the atmospheric chemistry and thus affecting the nucleation precursor production.

There are a few possible explanations for the observation that *S* reaches its maximum at the values slightly below zero. We argue that the reason is in the photosynthetic recovery of the plants: that the VOCs produced at the start-up of photosynthetic production have more potential for atmospheric particle formation than the VOCs produced later in the year. In the following, we will examine this argument, as well as other possible explanations for this phenomenon.

The particle formation process depends on both the source strength of the new particles and the sink of recently-formed particles. The condensation sink (CS) has been identified as an important variable controlling particle formation in several studies (Hyvönen *et al*. 2005, Ljubotseva *et al*. 2005, Dal Maso *et al*. 2007). It is possible that meteorological processes cause a lower background particle concentration, and therefore also a lower sink, during the times when the plants are undergoing spring recovery. However, an examination of the data showed that this is not the case. We did not find lower values of CS in the *S* range that had high small particle number concentrations and high particle formation probabilities. Therefore, the increase in particle production in the spring recovery phase of the annual cycle is likely to be associated with the particle source strength and not the sink.

Particle production is very likely to follow from the atmospheric oxidation of some trace precursor, which may be a VOC, SO_2, or some other gas-phase species. Therefore, information can be gained by investigating the atmospheric oxidant concentrations. Lyubotvtseva *et al*. (2005) investigated the trace gas concentrations in different seasons and found that ozone was slightly elevated during springtime, and that event days generally had slightly higher ozone concentrations than non-event days. We investigated the ozone concentration as a function of *S* analogically to the number concentration of particles. We found that the ozone concentration exhibited a similar peak for the *S* values above –4 °C (Fig. 6). This peak was quite distinctive, even though the maximum was more local as compared with the particle number concentration maximum (Fig. 4).

The ozone peak could be explained by the transport from the upper layers of the troposphere, or by the increased photochemical production of ozone due to either increased radiation or higher VOC concentrations. VOCs act as fuel in the oxidation cycle of the atmosphere. It is probable that in springtime, all these factors play some role.

In contrast, when we investigated SO_2 concentrations as a function of *S*, we did not find a peak in the concentration, but actually a minimum in the concentrations at the values for spring recovery. This speaks in favour of the argument that particle production depends on the plant emissions: if the nucleation process were dependent only on the sulphuric acid concentration, then SO_2 should be higher at times of high particle formation frequency.

Ruuskanen *et al.* (2009) investigated the annual variation of the gas-phase VOC concentration by using a Proton Transfer Reaction Mass Spectrometry (PTRMS). The PTMRS is capable of measuring monoterpenes considered to be prime candidates for aerosol production. The measurements by Ruuskanen *et al.* (2009) showed that monoterpene concentrations are highest in summer and not especially high in spring. This leads one to suspect that while monoterpenes are quite probably taking significantly part in aerosol mass production, as found by Tunved *et al.* (2006), the aerosol number-forming (nucleation) process might be governed by other plant emissions. Results supporting this view were recently obtained by Mentel *et al.* (2009) who found that the aerosol number-forming potential of plant emissions rose with an increasing fraction of oxidised VOC (OVOC) emissions.

Summarizing, our findings indicate strongly that the spring peak observed in the frequency of particle formation, as well as in lower-troposphere particle number concentration, is connected to the recovery of the photosynthetic capacity of the boreal forest. A clearly defined peak in nucleation mode particle concentrations was observed when the photosynthetic capacity was between 25% and 50% of the full capacity. Ozone measurements showed that during the same range of the photosynthetic capacity, also ozone concentrations were elevated. This might at least partly be caused by the plant emission effect on the oxidation cycle. The particle formation efficiency does not seem to scale directly with the amount of emitted carbon. Therefore, it is likely that the chemical composition of early spring emissions have a larger aerosol producing potential than later emissions.

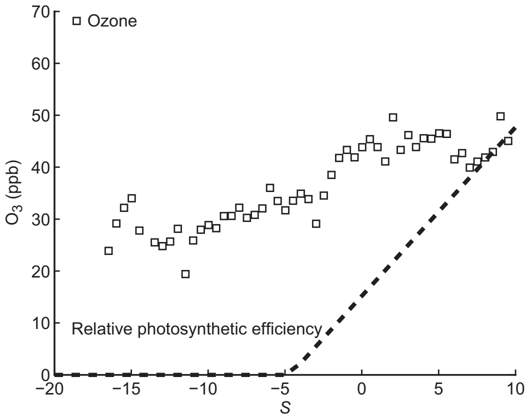

Fig. 6. The O_3 concentration measured at the Hyytiälä station as a function of the state of functional substances *S*. The dashed line shows the parameterized relative photosynthetic efficiency as given in Kolari *et al.* (2007), in arbitrary units.

Conclusions

We investigated aerosol particle concentrations in a boreal background site as a function of a temperature-dependent parameter *S*, called the state of functional substances. *S* has been shown to represent the annual cycle of the photosynthetic efficiency of pines. We found that the probability of finding a particle formation event is greatest for values of *S* slightly below 0 °C. When plotting nucleation mode particle concentrations, the peak could be seen very clearly. Examination of particle size distributions showed that the same value range of *S*, from about –3 °C to 0 °C, was associated with a significant drop in the particle size. All these factors indicate that the given range of the state of functional substances increases the strength of the particle formation process. Noteworthy is also that the strength of the particle source decreases again once *S* has reached values higher than a few °C.

We propose that the cause of the increased particle formation efficiency at the given range of the state of functional substances is caused by emissions from the forest vegetation, as it is recovering from the winter inactivity. Our finding of the state of functional substances and enhanced aerosol particle formation having a local maximum over a distinct *S* range leads us to believe that not only the amount of emissions, but also their chemical composition plays a part in the process. The exact chemical and physical mechanisms that lead to particle formation via nucleation are currently under investigation, and especially the participation of oxidised VOCs and sesquiterpenes might have a strong influence. This is also in line with recent studies in plant chambers (Mentel *et al*. 2009).

Our study shows that during spring recovery, plant emissions have a larger potential to form atmospheric aerosol particles than later in the year. Why and how these compounds with heightened aerosol forming potential are emitted remains a challenge for future studies. The exact nature of these emissions is currently unknown: they are probably highly reactive — and therefore short-lived — which makes concentration measurements challenging. Hopefully, the experimental difficulties can be overcome in the future, enabling a more detailed study of the links between vegetation spring recovery and atmospheric aerosol formation.

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