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Trends in new particle formation in Eastern Lapland, Finland: effect of decreasing sulphur emissions from Kola Peninsula

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Abstract

The smelter industry in Kola Peninsula is the largest source of anthropogenic SO_2 in the Arctic part of Eurasia and one of the largest within the Arctic domain. Due to socio-economic changes in Russia the emissions have been decreasing especially since the late 1990s resulting in decreased SO_2 concentrations close to Kola in Eastern Lapland, Finland. At the same time, the frequency of new particle formation days has been decreasing distinctively at SMEAR I station in Eastern Lapland, especially during spring and autumn. We show that sulphur species, namely sulphur dioxide and sulphuric acid, have an important role in both new particle formation and subsequent growth and that the decrease in new particle formation days is a result of the reduction of sulphur emissions originating from Kola Peninsula. In addition to sulphur species, there are many other quantities, such as formation rate or aerosol particles, condensation sink and nucleation mode particle number concentration, which are related to the number of observed new particle formation (NPF) days and need to be addressed when linking sulphur emissions and NPF. We show that while most of these quantities exhibit statistically significant trends, the reduction in Kola sulphur emissions is the most obvious reason for the rapid decline in NPF days. Sulphuric acid explains approximately 20–50 % of the aerosol condensational growth observed at SMEAR I and there is a large seasonal variation with highest values obtained during spring and autumn. We found that (i) particles form earlier after sunrise during late winter and early spring due to high concentrations of SO_2 and H_2SO_4, (ii) several events occurred during the absence of light and they were connected to higher than average concentrations of SO_2 and (iii) high SO_2 concentrations could advance the onset of nucleation by several hours. Moreover, air masses coming over Kola Peninsula seemed to favour new particle formation.

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1 Introduction

Both sulphur and primary particle emissions have been decreasing largely all over Europe (Kupiainen and Klimont, 2006; Vestreng et al., 2007; Smith et al., 2011), resulting in improved air quality, decreased acid fallout (Berge et al., 1999) and weakened direct radiative forcing by aerosols (Liepert and Tegen, 2002). The changes in indirect radiative forcing are more uncertain and complicated to address because the resulting decrease in CCN (Cloud Condensing Nuclei) concentrations due to the decrease in primary particle emissions can be at least partly compensated by secondary CCN production (new particle formation and growth) (Hamed et al., 2010; Makkonen et al., 2012). In the future, larger natural emissions of natural aerosol precursors due to warmer temperatures are likely to assist CCN production further (Makkonen et al., 2012; Paasonen et al., 2013).

The smelter industry in Kola Peninsula is not only the most important source of anthropogenic atmospheric SO_2 in the Finnish Eastern Lapland but also the largest or second largest source in the entire Arctic domain (Benkovitz et al., 1996; Prank et al., 2010), depending on the definition of the Arctic boundaries. During the past two decades, sulphur emissions from the Kola area have decreased distinctively, although they are still larger than those of entire Finland (Paatero et al., 2008). The SMEAR I station (Station for Measuring Ecosystem-Atmosphere Relations) (Hari et al., 1994) was established in 1991 to measure the impact of Kola sulphur emissions on the forests in Eastern Lapland. The station is located only 6 km from the Russian boarder (Fig. 1a). Värriö Subarctic Research Station is located about 800 m South of SMEAR I.

New particle formation (NPF) is tightly linked with SO_2: when in the atmosphere, SO_2 is oxidized to sulphuric acid H_2SO_4, which in turn is known to be the most important chemical component in new particle formation (Kulmala et al., 2004a; Sipilä et al., 2010; Kerminen et al., 2010). In the boreal forest zone, organic compounds are connected to new particle formation and growth (Kulmala et al., 2004b; Tunved et al., 2006; Paasonen, 2010). On the other hand, low values of condensation sink (CS), a measure

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on the ability of pre-existing aerosol particles to uptake condensable vapours (Kulmala et al., 2001), increase the probability for new particle formation. Thus, decreasing SO_2 concentrations decrease the probability of NPF by decreasing H_2SO_4 concentrations while at the same time decreasing values of CS caused by smaller sulphur and primary particle emissions tend to increase this probability.

Our main goal in this manuscript is find out whether NPF characteristics show any changes in Eastern Lapland over the last 13 yr and, if they do, is there any connection between their trends and the change in Kola emissions. More specifically, we aim to address the following questions: (1) is the signature from decreased Kola emissions observable in NPF characteristics and associated trends?, (2) what are the relative roles of the decreasing SO_2 concentration and decreasing value of condensation sink on NPF?, (3) how do changes in primary particle emissions, NPF and subsequent aerosol growth influence cloud condensation nuclei concentrations?, and (4) how the situation in Eastern Lapland differs from that reported for Western Lapland where the influence of Kola is expected to be much smaller. We will present long-term time series of SO_2 and aerosol particle number concentrations, NPF characteristics, as well as various other quantities related to NPF. We will also investigate how the seasonal distributions of these quantities have changed over the time and analyse the effect of air mass routes to NPF.

2 Materials and methods

The SMEAR I station (67°45′31″ N, 29°36′41″ E) (Fig. 1b) is built on the top of Kotovaara hill, 390 m a.s.l. The station is surrounded by a 60 yr old Scots pine (*Pinus sylvestris*) forest (Fig. 1c) and is located at the North side of the Värriö fell range, with peaks reaching from 500 to 550 m a.s.l. The highest fjeld North of SMEAR I is Nuortti (482 m a.s.l., furthermost, snow covered fjeld in Fig. 1c). Most of the area is dominated by Scots pine forests, in addition to which there are also large wetlands and deep gorges in the surroundings. The infrastructure of SMEAR I includes a small hut for the

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aerosol- and gas analysers (Fig. 1b) and a 16 m high weather mast. Some instruments have housings outside and also continuous chamber measurements of photosynthesis from the surrounding trees area conducted.

In this paper, we will use measurements of the aerosol number size distributions, SO_2 concentrations and meteorological variables. The aerosol size distribution is measured with a Differential Mobility Particle Sizer (DMPS) which classifies the particles according to their electrical mobility (related to particle diameter) (Aalto et al., 2001). The DMPS was installed to SMEAR I in autumn 1997 and the cut-off diameter was changed from 8 nm to 3 nm in 2005. SO_2 has been measured since autumn 1991 with a pulsed fluorescence analyser.

The days were classified into event, non-event and undefined days visually by looking at the daily aerosol size distributions. During an event day a new, growing mode appears below 25 nm (Dal Maso et al., 2005; Kulmala et al., 2012). During a non-event day there is no new mode below 25 nm whereas during an undefined day, although there is a new sub-25 nm mode it does not grow. The event days were further classified into classes I and II according to whether there was strong fluctuations in the mode concentration or diameter (class II) or not (class I).

As a proxy for gaseous sulphuric acid concentrations, two parameterizations exist (Petäjä et al., 2009; Mikkonen et al., 2011). In this study we used both. The first proxy is a linear parameterization developed by Petäjä et al. (2009) for a boreal SMEAR II site in Central Finland:

$$[H_2SO_4]_P = \frac{k_3 \cdot SO_2 \cdot \mathrm{Rad}}{\mathrm{CS}}, \quad (1)$$

where k_3 is a fitting parameter, SO_2 is the sulphuric dioxide concentration, Rad is the radiation and CS is the condensation sink. While either global or UV-B radiation can be used in calculating the proxy, we used global radiation due better data availability. The proxy given by Eq. (1) is physically well based, yet it is expected to be slightly inaccurate in environments where the value of CS is very low. This is because the pseudo-steady sulphuric acid concentration assumed by this proxy is achieved over

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the time scale CS^{-1}. In case of Värriö, this means that the proxy tends to overestimate sulphuric acid concentrations before the local noon and underestimate them in the afternoon. The second proxy for H_2SO_4 we used was a non-linear statistical proxy, developed by Mikkonen et al. (2011):

$$[H_2SO_4]_M = 8.21 \times 10^{-3} \cdot k \cdot \mathrm{Rad} \cdot [SO_2]^{0.62} \cdot (CS \cdot RH)^{-0.13}, \quad (2)$$

where k is a non-linear function of both temperature and atmospheric pressure and RH is the relative humidity. In this proxy, the role of CS is less important. The validity of the proxy given by Eq. (2) has not been tested for conditions typical for Värriö, so we apply it mainly as a tool to investigate the sensitivity of our results to the uncertainty in gaseous sulphuric acid concentration.

The trends of various parameters were calculated in the least-squares sense by fitting to logarithms of the measured and calculated data. These trends were then fitted to data model with a logarithmic trend component (relative trend) and 4-component stationary sinusoidal seasonal signal

$$\log(x) = a + bt + s_1 \sin\left(\frac{2\pi t}{1\,\mathrm{yr}}\right) + s_2 \sin\left(\frac{4\pi t}{1\,\mathrm{yr}}\right) + s_3 \cos\left(\frac{2\pi t}{1\,\mathrm{yr}}\right) + s_1 \cos\left(\frac{4\pi t}{1\,\mathrm{yr}}\right) + S \quad (3)$$

where x is the fitted parameter, a is a constant factor, b is the logarithmic trend, s_1 to s_4 are seasonal signal parameters and S is the residual noise term. In practice, the minimization of Eq. (3) in the least squares sense was obtained with Matlab routine lscov (Mathworks, Inc., 2010). In addition to this, we also used Mann–Kendall (Mann, 1945; Kendall, 1975) trend test for estimating the trends and their significances. Sample autocorrelation was not taken into account in any the fitting procedures.

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3 Results and discussion

3.1 Overview of new particle formation and growth in Värriö

3.1.1 General characteristics of new particle formation events

On average, 15 % of the days were event days during the time period 1998–2011. The average growth rate of particles during the event days was 2.7 nm h^{-1} and the corresponding formation rate of 8 nm-sized particles was 0.15 cm^{-3} s^{-1}. The mean formation rate of 3 nm-sized particles (2005–2011) was 0.24 cm^{-3} s^{-1}. There was a clear seasonal pattern in GR, the highest values being both during summer but almost as high also during winter (Table 1). On average, the highest values of J_3 were reached during April–May whereas J_8 peaked already earlier, in Feruary–April (Table 1). On average, there were 54 events per year, out of which 20 were class I events for which it was possible to determine both growth and formation rates. The event fraction had a bimodal yearly distribution with the maximum in the spring (March-April-May, ~ 0.26–0.28) and another local maximum in the autumn (September, ~ 0.22) (Fig. 2a). The non-even fraction on the other hand was highest in the winter (October–February, ~ 0.6–0.8 $month^{-1}$) (Fig. 2b). The undefined day fraction peaked in April (~ 0.4) and had a minimum in December (~ 0.12) (Fig. 2c).

The events started, on average, about 7 h after the sunrise (Fig. 3). The event starting times varied the most, and were also the earliest, during the spring. Between January and April, there was a clear connection between the event starting time and sulphur concentration levels: the events started on average 82 (93) minutes earlier when the SO_2 (H_2SO_4 proxy) concentration at the beginning of the event was at the highest 90th percentile as compared with the corresponding lowest median concentration levels. Taken together, these things suggest that the amount of sulphuric acid needed to trigger the NPF is reached typically earlier during the daytime in spring compared with the other seasons. The average sulphuric acid concentrations in Värriö were estimated to be highest during the late winter/spring as a result of high SO_2 concentrations com-

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bined with relatively low values of CS (Fig. 4). Few of the events started already when the sun was still below the horizon.

The NPF event frequency in Pallas, western Finnish Lapland, is generally slightly lower than in Värriö (Asmi et al., 2011). In addition, the annual event frequency distribution in Pallas is unimodal, with a peak in April and then gradually decreasing towards autumn (Asmi et al., 2011). In Pallas, the fraction of undefined days is on average about 0.14 month^{-1} lower and the number of non-events is on average 0.26 month^{-1} greater than in Värriö, but the yearly distributions from both sites resemble each other. The observed average values of GR and J are well in line with the previous studies from Finnish Lapland (Komppula et al., 2003; Dal Maso et al., 2007; Asmi et al., 2011), and slightly smaller than the corresponding values observed at SMEAR II, Southern Finland (Dal Maso et al., 2007; Nieminen et al., 2013). A similar seasonal behaviour of GR has been observed earlier in Värriö (Dal Maso et al., 2007) but in Pallas only summer maximum is seen (Asmi et al., 2011). The earlier onset of nucleation during spring has not been observed earlier in Northern Finland (Vehkamäki et al., 2004; Asmi et al., 2011). Vehkamäki et al. (2004) used the time when elevated concentrations of 8 nm particles were first observed, as the event start time, which shifts the spring event start times later since the growth rates are at their minimum in spring. We, in turn, estimated the formation time of 1.5 nm clusters assuming a constant GR below the cut-off size of DMPS. Since particle growth rates tend to increase with an increasing particle size in the sub 5–10 nm diameter size range (Hirsikko et al., 2005; Yli-Juuti et al., 2011; Kuang et al., 2012), the real starting times of the events might even be earlier than estimated here.

From March to July, the CS during event days was on average 67 % of the non-event day value. This is mostly a result of much lower accumulation mode concentrations during the event days. Also, the mean sulphuric acid proxy was 30 % higher during event days than during non-event days. Similar behaviour is also observed elsewhere in the boreal region (Petäjä et al., 2009). Also the global radiation was 60 % higher during event days than during non-event days. Contrary to the observations from Pal-

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las in Western Lapland or Hyytiälä in Southern Finland, sulphur dioxide on average increased early during the event day mornings reaching above 0.9 ppm and levelling to around 0.6 ppb in the evening, while during non-event days there was not as much daily variation and the concentrations were generally around 0.2 ppb lower. During the events observed during dark time (global radiation $< 20\,W\,m^{-3}$) the SO_2 concentration was on average two times higher than on an average event day. Also, lower temperatures seemed to favour new particle formation.

3.1.2 Trends in event characteristics and associated aerosol properties

When looking at the yearly number of event, non-event and undefined days, the new particle formation days have been decreasing by $-3.7\,\%\,yr^{-1}$ (Table 2). Moreover, there has been a radical decrease in class I event days ($-9.9\,\%\,yr^{-1}$) (Fig. 5a, Table 2), and a more subtle increase in the non-events ($+3.1\,\%\,yr^{-1}$) (Fig. 5b, Table 2). However, there was no trend in the class II events or in the undefined days (Table 2). If the class I events are divided further into class Ia, including very clear and undisturbed events, and class Ib, including the rest of the class I events, the decrease was most pronounced in the class Ia cases ($-16.7\,\%\,yr^{-1}$) (Table 2). During the last four years of this dataset, these events have been observed only during one year (2010). At Pallas, such a trend in NPF days was not observed (Asmi et al., 2011).

When the data are divided into two equally long periods, 1998–2004 and 2005–2011, the seasonal NPF distribution has changed markedly, especially in the case of class I events (Fig. 6a, b). In the first period the distribution was clearly bimodal, with a strong maximum in the spring and another smaller maximum in the autumn. In the later period the events were more evenly distributed and the autumn maximum had disappeared from both class I and II events (Fig. 6a, b). The decrease in the number of events is most pronounced in spring and autumn. In fact, the distribution of the latter period resembles more the one observed at Pallas (Asmi et al., 2011). The non-event days have increased throughout the year with largest increase during summer and autumn. The number of undefined days on the other hand has increased during

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late spring and decreased during late winter (Fig. 6c, d). The average number of class I events in Pallas is about 6 yr^{-1} (Asmi et al., 2011) which is close to the number of class I events observed in Värriö in the end of the time series. This could be an indication that previously the class I events that were observed in Värriö have been the result of both natural background as well as the extra boost from Kola emissions. The number of class II events, on the other hand did not change that much, but the seasonal distribution somewhat smoothened. Since class II events are not usually observed to start from the smallest size classes, we also hypothesize that the observation of class II event is connected to the amount of organic vapours rather than sulphur emissions from Kola since the contribution of organics to growth increases with increasing particle size (Riccobono et al., 2012; Riipinen et al., 2012).

Over the time period considered here, there was no significant trend in GR (Fig. 7a, Table 2), although in Hyytiälä there appears to be a significant positive trend (Nieminen et al., 2013). In Pallas high values of GR seem to be connected to high NPF event frequency (Asmi et al., 2011) but this was not seen Värriö. In the apparent formation rate of 8 nm particles, on the other hand, there was no significant trend. For 2005–2011 the trend in J_8 was very similar with both methods, −10.0 % yr^{-1} using the least squares method and −10.2 % yr^{-1} using the Mann–Kendall method (P = 0.06) (Fig. 7b, Table 2). For the apparent formation rate of 3 nm particles, the trend was not significant. However, during 2005 J_3 could be determined only from 8 events all of which were concentrated to April–June, when J_3 usually has the highest values. For years 2006–2011 the trend was significant and positive (Table 2).

The nucleation mode particle number concentration has increased about 4.3 % yr^{-1} (Fig. 8a, Table 2), whereas the total aerosol number concentration has decreased by 2.5 % yr^{-1} (Fig. 8b, Table 2). The decrease in the condensation sink (CS) is even larger, 7.7 % yr^{-1} (Fig. 8c, Table 2). The trends are very similar also when using the Mann–Kendall method (Table 2).

While decreasing sulphur emissions decrease the H_2SO_4 concentration and hence nucleation and growth, on the other hand it also leads into a decrease in primary emis-

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sions and hence decrease in the condensation and coagulation sinks. When CS decreases, more condensable vapours are left to the atmosphere, which can form new particles instead of condensing into pre-existing particles. Since the NPF event frequency is decreasing in Värriö, each NPF event must produce more particles than before as nucleation mode particle concentration is increasing. This can be seen in the increase of event-time J_3 (Table 2). However, since there was no significant trend in the apparent formation rate of 8 nm particles (J_8, Table 2), the particle production must have increased only in the smallest particle sizes. It is also possible that some of the increase in nucleation mode comes from an increased apparent particle production in the highest end of nucleation mode during class II events or undefined days. Contrary to our findings, Hamed et al. (2010) reported a clear decrease in J_3, as a result of reduced sulphur emissions and thus decreased number of nucleation days in Eastern Germany but on the other hand an increase in the subsequent growth of aerosol particles.

3.1.3 From formation to growth: trends in cloud condensation nuclei concentrations

In order to have climatic relevance, newly-formed aerosol particles need to grow to sufficiently large sizes. In moderately polluted environments, such as boreal forests, aerosol particles may act as cloud condensation nuclei (CCN) after reaching diameters between about 50 and 150 nm (Kerminen et al., 2005; Komppula et al., 2005; Sihto et al., 2011). Other sources for atmospheric CCN are primary emissions of CCN active particles and atmospheric aging (e.g. condensation growth or increase of hygroscopicity) of originally non-CCN active primary particles (Pierce and Adams, 2009; Kerminen et al., 2012).

We made linear fits to the logarithms of CN_{50}, CN_{80}, CN_{100} and CN_{150} (particles larger than 50, 80, 100 and 150 nm, respectively) concentrations. All of them showed a statistically significant decreasing trend over the study period (Table 2). The largest decrease was seen for particles larger than 80 nm ($-4.1\,\%\,yr^{-1}$), and the lowest one

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for particles larger than 150 nm ($-3.2\,\%\,yr^{-1}$) (Fig. 9, Table 2). Both CN_{50} and CN_{100} showed a trend of $-3.9\,\%\,yr^{-1}$ (Fig. 9, Table 2).

The trends in CN concentrations are well in agreement with the trend in the daily-mean CN_{100} concentration in Värriö reported by Asmi et al. (2013). Also, in their study, contrary to Värriö, the CN trends in Pallas were positive. In Värriö, the CN concentrations have been decreasing slower than the condensation sink (Figs. 8c and 9). Since the CN_{50} concentration has been decreasing with simultaneous increase in the nucleation mode particle concentration, we may conclude that the particle growth from the nucleation mode to > 50 nm is not very efficient in Värriö. On the other hand, the decrease in the CN_{150} has not been as large as the decrease in either CN_{50} or CS. This suggests that higher biogenic aerosol precursor emissions due to increased temperatures may have accelerated the growth of sub-CCN sized primary particles to CCN sizes, partly compensating the decrease in SO_2 and primary particle emissions (Paasonen et al., 2013; see also see the discussion in Sect. 3.2.1). One should, however, keep in mind that it is very difficult to separate between the three sources of CCN based solely on a time series analysis.

3.2 Association of the observed trends with sulphur emissions from Kola

Next we will investigate what kind of trends there are in sulphur dioxide and sulphuric acid concentrations and what are their contribution to the formation and growth of aerosols in Värriö.

3.2.1 New particle formation vs. sulphur species

SO_2 concentration has been decreasing by $10.9\,\%\,yr^{-1}$ 1998–2011 while for 1992–2011 the decrease was $5.2\,\%\,yr^{-1}$ (Fig. 10, Table 2). This decrease was not yet observable in the study made by Ruuskanen et al. (2003) where they used SO_2 data from 1992 to 2001. Likewise, in Sevettijärvi, close to Nikel and Zapoliarnyj smelters, the decrease in SO_2 was not very clear in the early 2000's (Virkkula et al., 2003).

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Sulphuric acid proxy calculated by Eq. (1) on the other hand has been decreasing in Värriö by 5.2 % yr^{-1} (Fig. 10, Table 2). According to Eq. (1) the lower the condensation sink is, the higher is the sulphuric acid concentration. Since CS has been decreasing by −7.7 % yr^{-1}, the resulting H_2SO_4 concentration without taking into account the SO_2 concentration, should be increasing. In Värriö, however, the decreasing SO_2 counteracts this. On the other hand, the lower the CS is, the longer it takes for vapors to condense on pre-existing particles, leading to possible overestimation in sulphuric acid proxy especially if calculated using Eq. (1). In Värriö the vapour lifetime with respect to condensing on particles (1 CS^{-1}) has increased from roughly 20 min to 1 h, hence it is possible that for the last few years the real sulphuric acid concentration is lower than the calculated value. Compared with Eq. (2), the parameterization by Petäjä et al. (2009) gives slightly higher values during winter–spring when CS is low (Fig. 4c). Also, the decrease in H_2SO_4 proxy is more distinct in the parameterization by Mikkonen et al. (2011) due to weaker dependence on CS (−8.0 % yr^{-1}) (Fig. 10, Table 2).

When we looked at the global radiation as a function of the NPF start time calculated using the apparent GR, HYSPLIT-back trajectories (Draxler and Hess, 1998) and SO_2 concentration, we saw that higher SO_2 concentrations seemed to favour earlier onset of NPF (Fig. 11). This was true especially when the radiation intensity was higher: the difference in NPF start time between times when SO_2 was low or high was on average 2–3 h when the mean global radiation one hour before and after the NPF start was higher than 300 W m^{-2} and about an hour when the global radiation was low (Fig. 11). This and the fact that earlier NPF start time after the sunrise is connected to high SO_2 concentrations (Fig. 3) clearly show the strong link between SO_2 and NPF in Värriö.

In general H_2SO_4 explains a large fraction of the growth of the newly-formed aerosol (∼ 20–50 %) (Fig. 12). The percentage is highest in spring (March–May) and autumn (August–September) with minimum in summer. This suggests that in fact at least some fraction of the effects of SO_2 and H_2SO_4 are related to the early condensational growth of the particles instead of formation of new particles. Also the 26.2 % yr^{-1} increase in J_3 (2006–2011) supports this. Considering that there has been a clear decrease in

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CS, it seems that during NPF there are not enough vapours to grow the particles into larger sizes. Both proxies give similar seasonal behaviour, but the parameterization by Petäjä et al. (2009) gives slightly higher percentages (mean 35.8 %) compared to the parameterization by Mikkonen et al. (2011) (mean 32.6 %). There is no visible inter-annual trend, although during the last few years the minimum percentage has been increasing. This is most likely due to the change in the event distribution; nearly all of the events from which GR can be calculated were observed during spring in the later period. In Pallas, approximately 5–40 % (Asmi, 2011) and in Hyytiälä less than 10 % (Boy, 2005; Fiedler, 2005) of the growth is explained by H_2SO_4 which is clearly much smaller fraction than in Värriö. In addition, the relative importance of H_2SO_4 is largest in late winter (February–March) and late summer (August) in Värriö.

The mean spring-summer (April–July) temperatures have increased in Värriö on average 1.3 °C (+1.9 °C increase in the median spring temperature) since 1998 (Fig. 13). Overall, the temperature increase in Värriö has been 0.05 % yr^{-1} (Table 2), corresponding an increase of 1.2 °C per decade. This increase in temperature might have increased the emissions of monoterpenes (Paasonen et al., 2013). Since organic vapours are important in the formation and especially growth of new aerosol particles, we would expect to see at least some correlation between the number of NPF events and temperature. Interestingly, during 1998–2011 there was no or very little correlation (R^2 = 0.13) with class I events and spring-summer (April–July) median temperature and this correlation was negative, but for class II events there was a clear positive correlation (R^2 = 0.41). This supports our hypothesis that an observation of a class II event is connected to organic emissions and not necessarily observed during high concentrations sulphuric acid originating from Kola since the particles have formed already elsewhere and the importance of sulphuric acid to the early growth has already diminished.

All in all, these results strongly suggest that sulphur dioxide and sulphuric acid have a very important role in NPF in Eastern Lapland, especially in the case of clear, undisturbed class I events.

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3.2.2 Connection with Kola emissions

Some studies have already shown that part of the NPF events observed at Värriö are induced by the high SO_2 concentrations associated with air masses coming over Kola (Pirjola et al., 1998; Komppula et al., 2003). All of these studies have however concentrated on rather limited dataset. E.g. Komppula (2003) estimated that during 21 months, roughly one third of the NPF events observed at Värriö were affected or caused by the Kola industry. No studies on the long-term effect of Kola emissions have been made so far.

The highest nucleation mode concentrations occurred when SO_2 concentrations were high. When dividing the data into "polluted" ($SO_2 \geq$ 95th percentile) and "clean" ($SO_2 \leq$ median) data, the yearly sum of SO_2 correlated very well with the yearly sum of nucleation mode particle concentration in the polluted data (Fig. 14 left side), whereas for the clean data the correlation was lower (Fig. 14 right side). Also, nearly all of the polluted data originated from the Kola sector, whereas for clean data the winds were mainly from the South-West direction.

One explanation for the decrease in class I events could be boundary layer dynamics during air mass transport from Kola. Usually the wind speed was lower in air masses coming over Kola than in air masses coming from South-West (Fig. 14). Since in lower wind speeds the turbulent mixing is reduced, in case of a NPF day this means that there are less fluctuations in the air and the event appears smoother and is therefore more probably classified as class I event (Dal Maso et al., 2005; Yli-Juuti et al., 2009).

There was a weak positive correlation between the yearly 95th percentile of SO_2 and yearly sum of events (both I and II). The correlation with non-events was much lower, $R^2 = 0.16$.

The majority of the events occurred when the wind direction was South-West. However, when comparing the relative wind direction distribution during event days, undefined days and non-event days, the wind direction was more frequently within the Kola sector (0–95°) during event days and especially during undefined days than dur-

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ing non-event days. In addition to wind direction, we used HYSPLIT-back trajectories (Draxler and Hess, 1998) to see how frequently the air masses arriving at Värriö had been over Kola during event days. We calculated the percentage of time that the air masses had arrived to Värriö over Kola for each month, during the whole time period 1998–2011 and during event days only. In order to be classified as arriving over Kola, the trajectory had to stay over the defined Kola area more than 50 % or 80 % of the last 36 h before arriving at Värriö. These studies showed that air masses came over Kola Peninsula more often on event days than on all days in late winter–early spring, summer and late autumn (Fig. 15). Similar, yet much weaker seasonality was also seen when taking into account only the local wind direction. The negative relative differences in winter (Fig. 15) are most likely due to very limited number of NPF events in winter.

The fact that the relative difference (percentage of air masses coming over Kola during event days compared with all days) stays positive nearly throughout the year could be an indication that of the many class II events originate over Kola, but due to transport times of a few hours to Värriö, we do not see the very formation of new particles in Värriö. Since the emissions from Kola have been decreasing, we expect that the area directly affected by the emissions over the smelters is also decreasing in size. This could explain the reason why we see the dramatic decrease in class I events, but not in class II events, which are thought to start new particle formation somewhere else than at the site of observation.

3.2.3 Possible socio-economic reasons for the observed trends

The main source of anthropogenic atmospheric SO_2 in Värriö is the industrial activity in the Murmansk Oblast region. Since the 1990s, the Murmansk region has slided into a socio-economic decline, which in turn has had an impact on the overall emissions of the region. From 1992 to 2011 the overall amount of atmospheric emissions has decreased from 617 thousand to 263.1 thousand tonnes per year (Federal State Statistic Service of Russia, 2013a). In particular, the overall amount of emitted SO_2 has decreased from 275.8 to 194.6 $kT\,yr^{-1}$ (from 2000 to 2012), and without filtering from

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245.3 to 176.6 kT yr^{-1} for the same period. For the period 2001–2012 the amount of SO_2 emitted primarily from combustion for energy production (heat and electricity) has also declined from 96.3 to 65.8 kT yr^{-1}. The amount of caught and deactivated SO_2 emissions has remained the same, being 134.7 and 135.2 kT yr^{-1} in 2001 and 2012, respectively (Federal State Statistic Service of Russia, 2013b).

Since the amount of deactivated emissions has not changed substantially, whilst the overall emissions have decreased, it is unlikely that this change is due to changes in filtering technology or deactivation methods. Rather, this change can be explained by socio-economic factors, such as changes in the political system, trends in economic development and/or demographic trends.

In the Murmansk Oblast, the regional gross domestic product (RGDP) has increased moderately from 55 135 to 260 264.7 millions of rubbles per year from 2000 to 2011 (Federal State Statistic Service of Russia, 2013c). Considering the overall level of inflation, the economy has been in decline, which is also explained by the developments of the sub-sectors of the economy. Retrieval of natural resources grew from 18.7 to 18.9 % of RGDP, process manufacturing declined from 21.8 to 15.5 % and production and distribution of energy, gas and water declined from 8.4 to 5.9 % from 2004 to 2011 (Federal State Statistic Service of Russia, 2013d). In addition, demographic trends are an important parameter that explains the reasons for the reduction in emissions. According to the Russian census, population in Murmansk region has decreased from 1 164 586 to 795 409 people during the period of 1989–2010 (Federal State Statistic Service of Russia, 2013e).

4 Conclusions

We have observed a dramatic decrease in the frequency of class I NPF events in Eastern Lapland, Finland, during 14 yr of aerosol size distribution measurements. The events have been decreasing throughout the year but especially during summer and

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autumn. We believe that the decrease in events is due to the gradual disappearance of the extra boost from Kola emissions and that the number of class I events observed in Värriö is now close to the natural background level, similar as observed in Pallas, Western Lapland.

The decreasing anthropogenic SO_2 and primary emissions have decreased the CS considerably, leading to an increase in the event-time J_3 and nucleation mode particle concentration. Thus, there are more nucleation mode particles per event. However, since most of the events have been lost during spring and autumn when the importance of sulphuric acid to the growth is the largest, even up to 50 %, and the organic emissions from the snow-covered trees especially during spring are minimal, the remaining sulphuric acid vapour concentrations are not high enough to grow the particles into potential CCN. On the other hand, enhanced secondary organic aerosol formation resulting from increasing temperature is not yet sufficient enough to compensate for this. Hence, the concentrations of apparent CCN are decreasing.

Events in general start earlier after sunrise during spring due to higher concentrations of SO_2 and H_2SO_4 as well as low CS. We observed also events in total lack of sunlight, and many of them were related to higher than average SO_2 concentrations. We also found that high SO_2 concentrations can advance the onset of nucleation by several hours especially if there is enough sunlight present.

There are several pieces of evidence showing that the observed decrease in the yearly number of events is connected to the reduction of air pollution from Kola Peninsula smelters. Firstly, when considering only data that exceeds the 95th percentile of SO_2, the yearly sum of SO_2 correlated very well with the yearly sum of nucleation mode particle concentration. These data are entirely associated with the Kola sector. For the clean data the correlation was much lower. Secondly, there was a clear positive correlation between the number of events observed in a given year and the yearly 95th percentile of SO_2. Finally, air masses coming over Kola Peninsula seem to favour NPF, especially during late winter, early spring and autumn. The relative difference between air masses coming over Kola on nucleation days compared with all days was several

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tens of percentages through late winter to autumn, exceeding over 100 % in February in the case of class I events. For class II events the relative difference is positive almost throughout the year. Overall, our results strongly suggest that sulphur species have a very important role in both NPF and subsequent growth and that the recent decrease in Kola sulphur emissions due to socio-economic changes in the Murmansk Oblast region has had a strong impact on the NPF in Eastern Lapland.

In the future, the trends in the NPF in Eastern Lapland will likely depend on the overall human activity in the Murmansk Oblast region, the general cleaning of the emissions by new filtering techniques and deactivation methods in there, and changes in natural biogenic emission. Until now, there has been no clear evidence on the cleaning of emissions in the Murmansk Oblast region. It is very likely that everywhere close to large sources of anthropogenic sulphur emissions with simultaneously low background aerosol concentrations, such as close to Arctic shipping routes, the trends in NPF are governed by these factors. Therefore, due to opening of new shipping routes and increased marine activity, it would be important to conduct more long-term measurements of NPF in the Arctic.

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Table 1. Monthly mean values (bolded) for GR, J_8 and J_3. The monthly 25th and 75th percentiles are shown below the means, respectively.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
GR [nm h^{-1}]	**3.1**	**3.5**	**2.1**	**1.8**	**2.5**	**3.8**	**4.4**	**3.7**	**2.8**	**2.2**	**2.9**	**2.1**
	1.8	2.4	1.1	1.1	1.2	2.6	3.2	2.9	2.2	1.6	2.3	1.2
	2.9	4.1	2.9	2.4	3.6	4.7	4.7	4.3	3.2	2.6	2.9	2.3
J_8 [cm^{-3} s^{-1}]	**0.05**	**0.19**	**0.20**	**0.21**	**0.16**	**0.13**	**0.17**	**0.11**	**0.12**	**0.08**	**0.11**	**0.04**
	0.02	0.04	0.04	0.05	0.05	0.06	0.07	0.06	0.06	0.03	0.05	0.02
	0.07	0.24	0.16	0.22	0.23	0.13	0.23	0.15	0.14	0.13	0.17	0.06
J_3 [cm^{-3} s^{-1}]	**0.07**	**0.11**	**0.17**	**0.45**	**0.32**	**0.16**	**0.23**	**0.19**	**0.18**	**0.13**	**0.09**	**0.04**
	0.07	0.03	0.07	0.13	0.07	0.12	0.10	0.07	0.06	0.04	0.07	0.02
	0.07	0.20	0.19	0.41	0.26	0.24	0.33	0.31	0.30	0.20	0.12	0.06

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Table 2. Trends for various parameters obtained using both least squares covariance method where the seasonal trend has been taken into account, as well as Mann–Kendall method (Sen's slope) without seasonality, as percentages per year. The slopes are for years 1998–2011, unless mentioned otherwise. The lower and upper 95th confidence intervals for the Sen's slopes are given for significant trends ($P < 0.05$), except for J_8 (2005–2011) where the confidence intervals are given in parenthesis, although $P = 0.062$.

Parameter	Slope (least squares cov.) [% yr^{-1}]	Sen's slope [% yr^{-1}]	Lower conf. interval for Sen's slope [% yr^{-1}]	Upper conf. interval for Sen's slope [% yr^{-1}]	P
SO_2 (1992–2011)	−5.2	−4.8	−5.5	−4.1	< 0.001
SO_2	−10.9	−11.3	−12.4	−10.2	< 0.001
H_2SO_4 Petäjä	−5.2	−6.2	−7.5	−4.9	< 0.001
H_2SO_4 Mikkonen	−8.0	−8.6	−9.5	−7.7	< 0.001
Nucleation mode	4.3	3.7	2.7	4.7	< 0.001
Total conc.	−2.5	−2.4	−3.0	−1.7	< 0.001
CN > 50 nm	−3.9	−3.9	−4.6	−3.1	< 0.001
CN > 80 nm	−4.1	−4.2	−4.9	−3.5	< 0.001
CN > 100 nm	−3.9	−4.0	−4.7	−3.3	< 0.001
CN > 150 nm	−3.2	−3.3	−4.0	−2.6	< 0.001
CS	−7.7	−8.0	−8.7	−7.4	< 0.001
Temperature	0.05	0.04	0.02	0.07	0.001
GR	1.5	−0.2			0.803
J_3 (2005–2011)	8.4	9.6			0.093
J_3 (2006–2011)	26.2	29.7	15.5	42.2	< 0.001
J_8	−1.3	−1.0			0.496
J_8 (1998–2004)	2.2	3.0			0.519
J_8 (2005–2011)	−10.0	−10.2	(−18.7)	(±0.0)	0.062
Event class I		−9.9	−14.2	−5.9	0.002
Event class Ia		−16.7	−24.4	−10.6	< 0.001
Event class Ib		−8.1	−13.6	−2.6	0.002
Event class II		1.1			0.661
All events		−3.7	−5.7	−0.5	0.025
Undefined		−0.6			0.701
Non-events		3.1	1.2	5.1	0.009

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Fig. 1. Location of SMEAR I (Värriö) station and three major mining cities in the Kola Peninsula **(A)**. The Polar Circle is also shown in the map. A photo of SMEAR I station **(B)** and an aerial photo of the surroundings **(C)**. The location of SMEAR I is circled with red.

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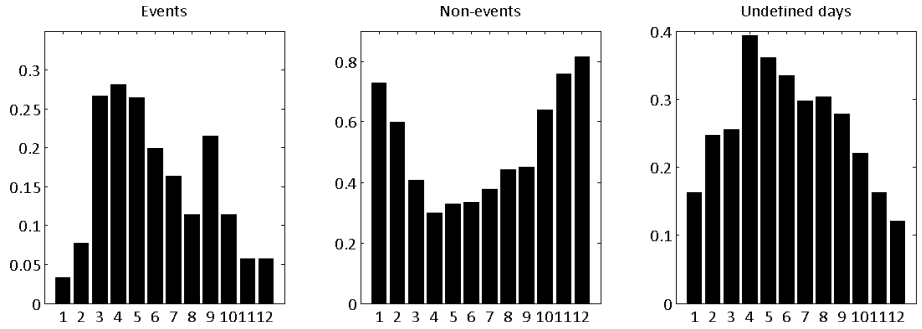

Fig. 2. Mean monthly event, non-event and undefined day fraction 1998–2011.

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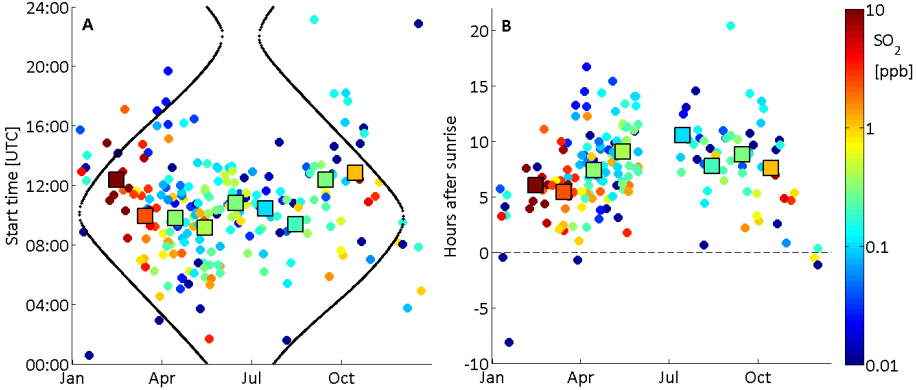

Fig. 3. New particle formation event start times as UTC **(A)** and hours after sunrise **(B)** at 1.5 nm as a function of SO_2 concentration (colour scale) for each event separately (circles). The filled rectangles represent the monthly averages for months with at least 10 events. The black curves denote the sunrise and -set times, respectively.

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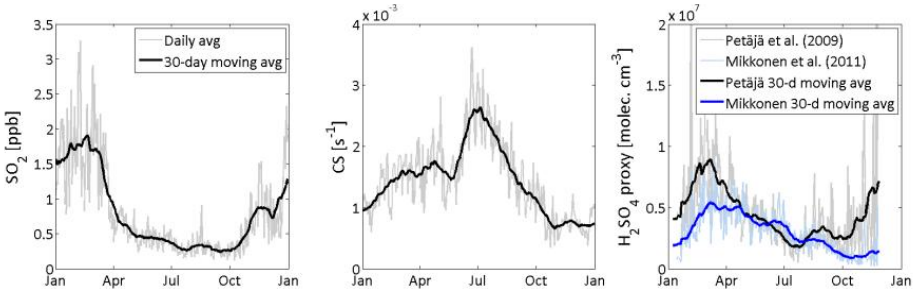

Fig. 4. The seasonal pattern of SO_2, CS and H_2SO_4 proxy.

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Trends in new particle formation in Eastern Lapland, Finland

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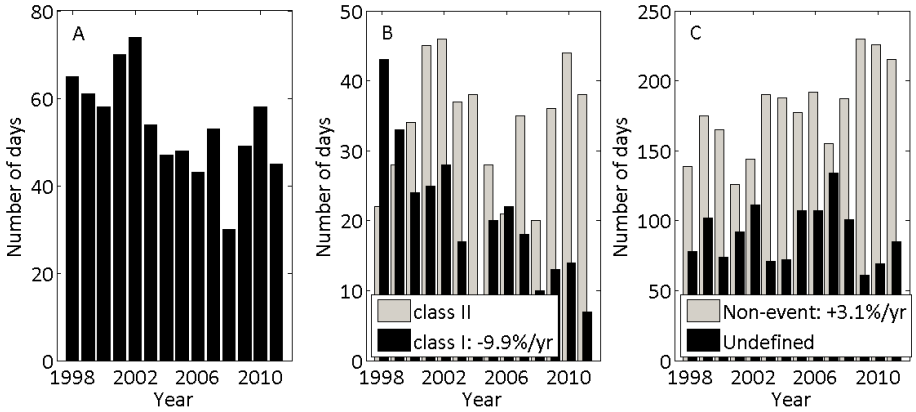

Fig. 5. Yearly number of event days **(A)**, divided into classes I and II **(B)** and yearly number of undefined and non-event days **(C)**.

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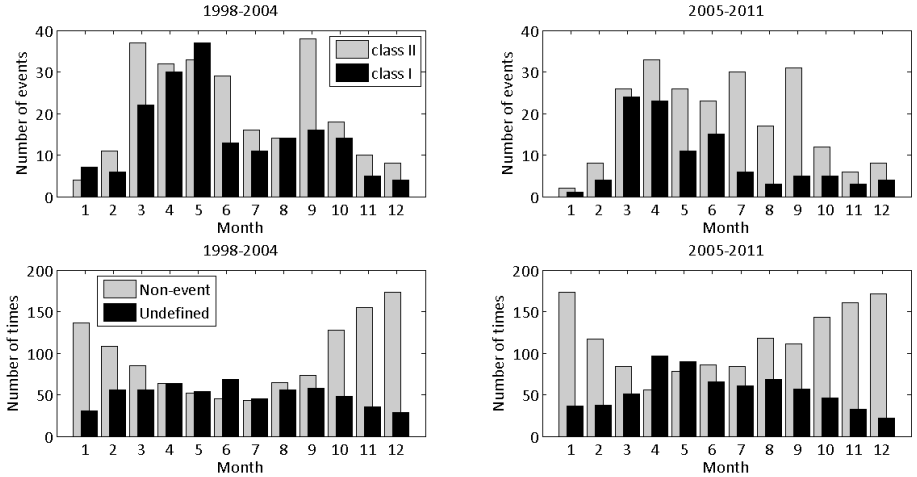

Fig. 6. The seasonal distribution of events, non-events and undefined days during 1998–2004 (leftmost panels) and 2005–2011 (rightmost panels).

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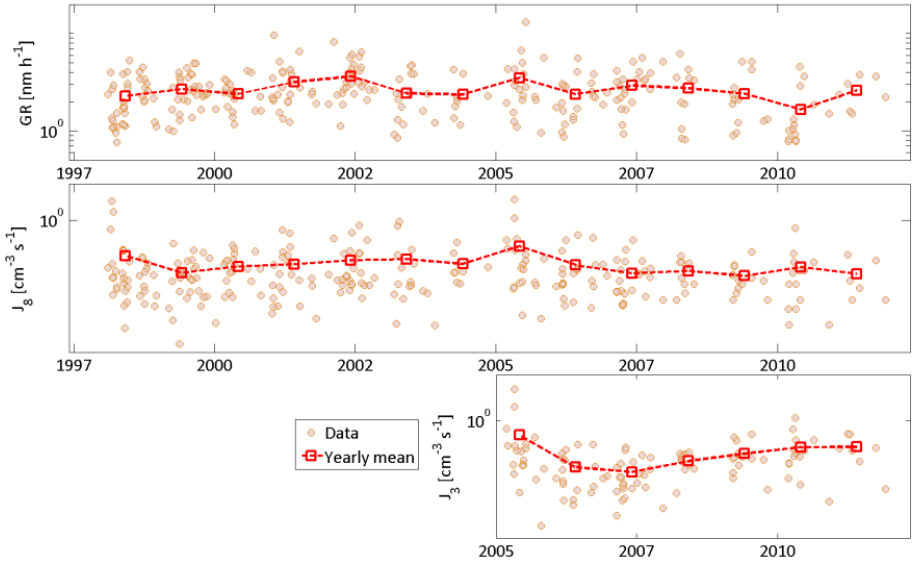

Fig. 7. Growth rate (upper panel) and formation rate of 8 nm particles (middle panel) 1998–2011 as well as formation rate of 3 nm particles (lower panel) 2005–2011. The yearly mean values are also shown.

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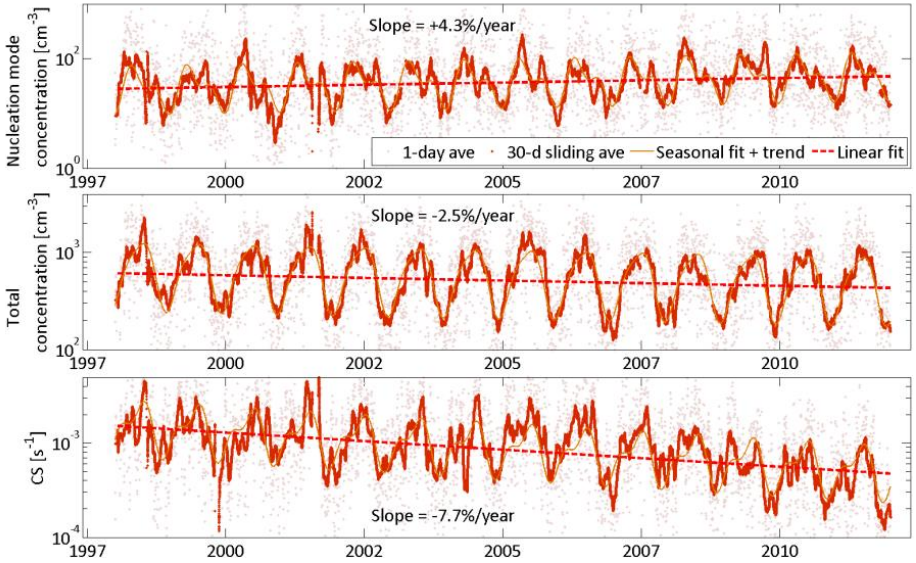

Fig. 8. Trends in nucleation mode and total concentration as well as condensation sink 1998–2011. The light red dots are 1 day averages, the solid dark red line is the 30 d sliding average, the thin orange line is the sinusoidal seasonal fit with the linear trend added and the red dashed lines are the linear fits.

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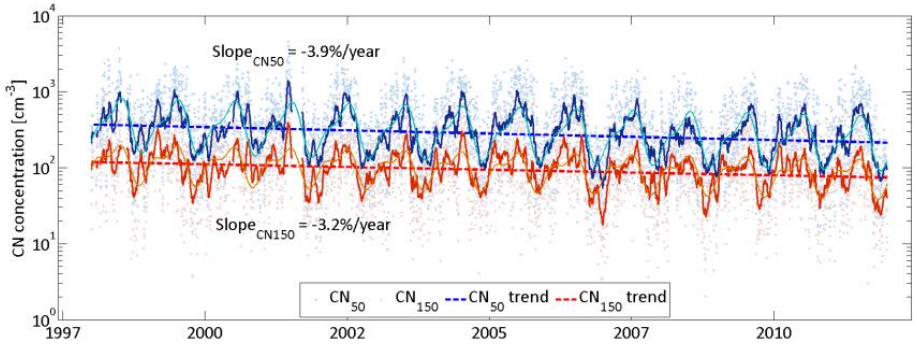

Fig. 9. Same figure as Fig. 8 but for trends in CN_{50} and CN_{150} concentrations 1998–2011.

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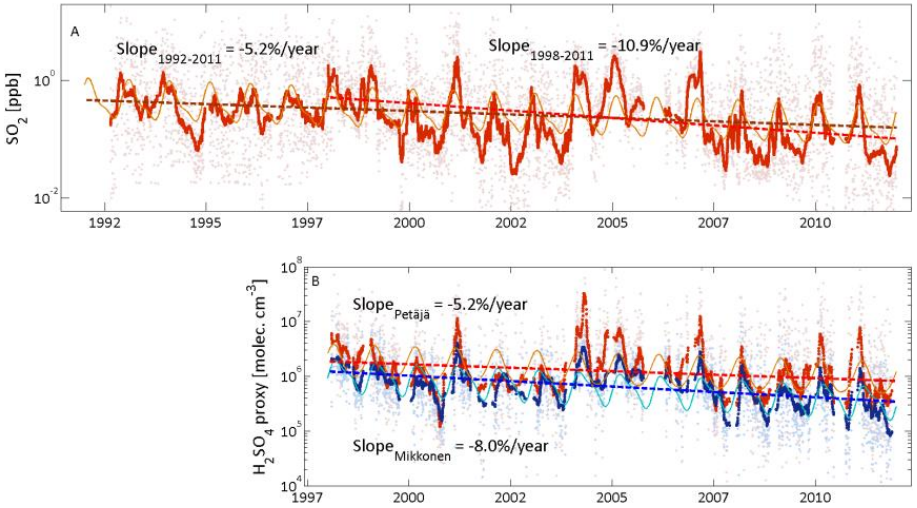

Fig. 10. 1 day averages (dots) and 30 day sliding average (thick line) of SO_2 (1992–2011) and H_2SO_4 proxy (1998–2011), for proxies Petäjä (red) and Mikkonen (blue), respectively. Sinusoidal seasonal fits with linear trend as well as linear fits to the logarithmic data are shown as well.

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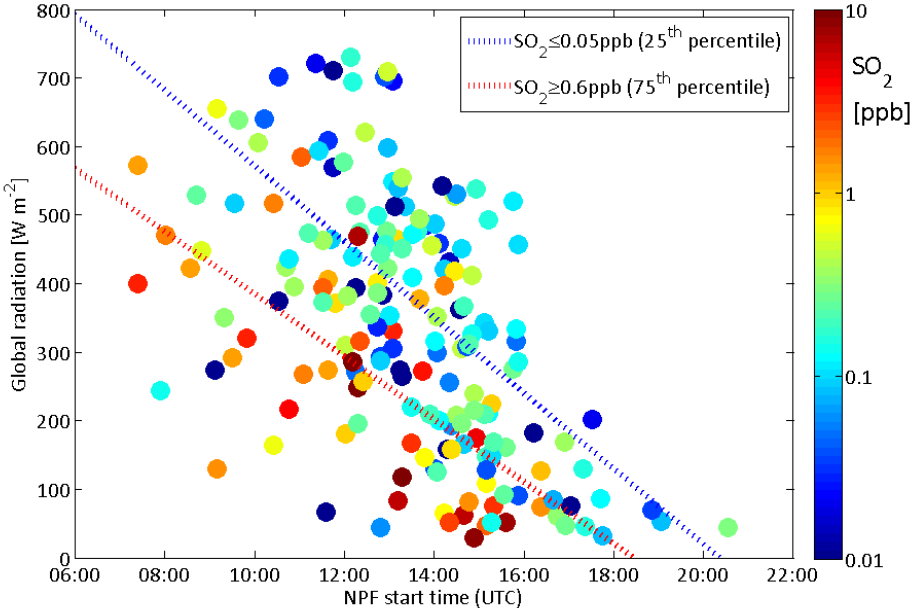

Fig. 11. NPF start time (UTC) as a function of global radiation and sulphur dioxide concentration (colorbar). Both are mean values one hour before and after the start of NPF. Linear fits for data when SO_2 concentration is less than 0.05 ppb or more than 0.5 ppb are shown with blue and red dashed lines, respectively. These values are the 25th and 75th percentile of SO_2 event-time concentration.

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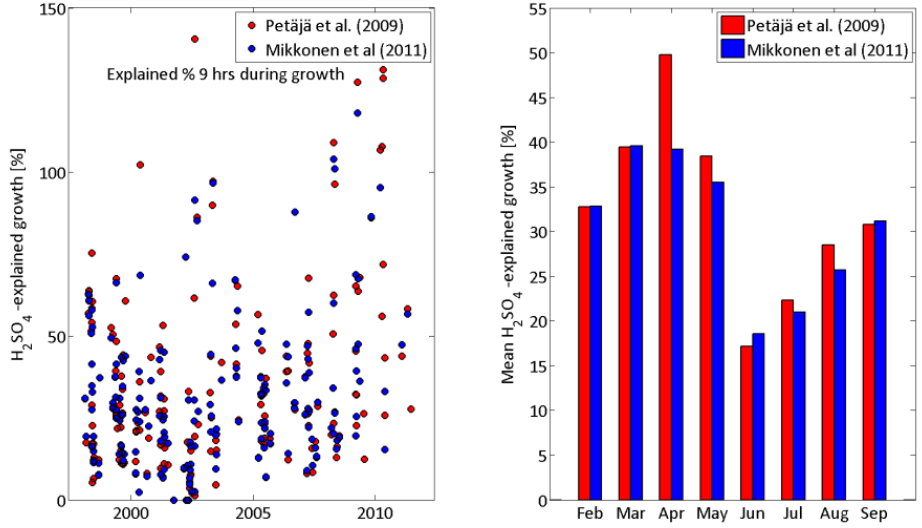

Fig. 12. The timeseries of the percentage which H_2SO_4 explains of the growth **(A)**, its yearly variation **(B)**. Months with less than 5 cases where the percentage has been calculated have been discarded.

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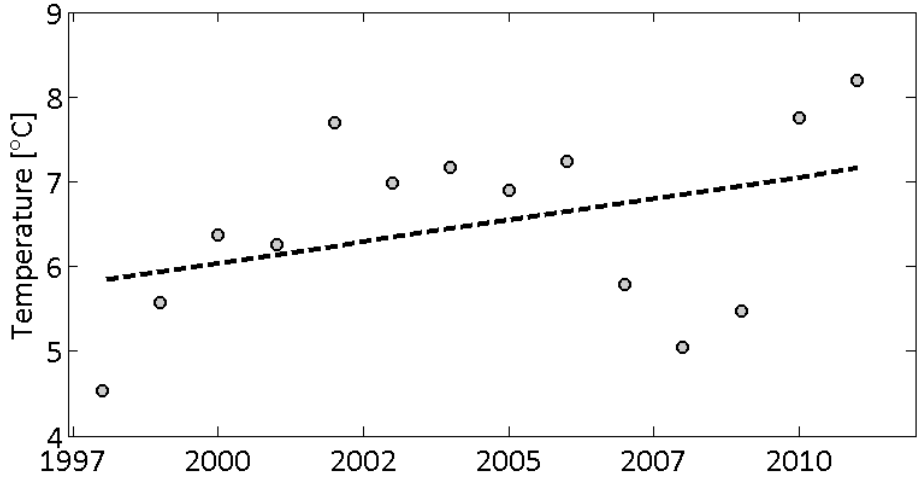

Fig. 13. Yearly April–July mean temperatures and a linear fit.

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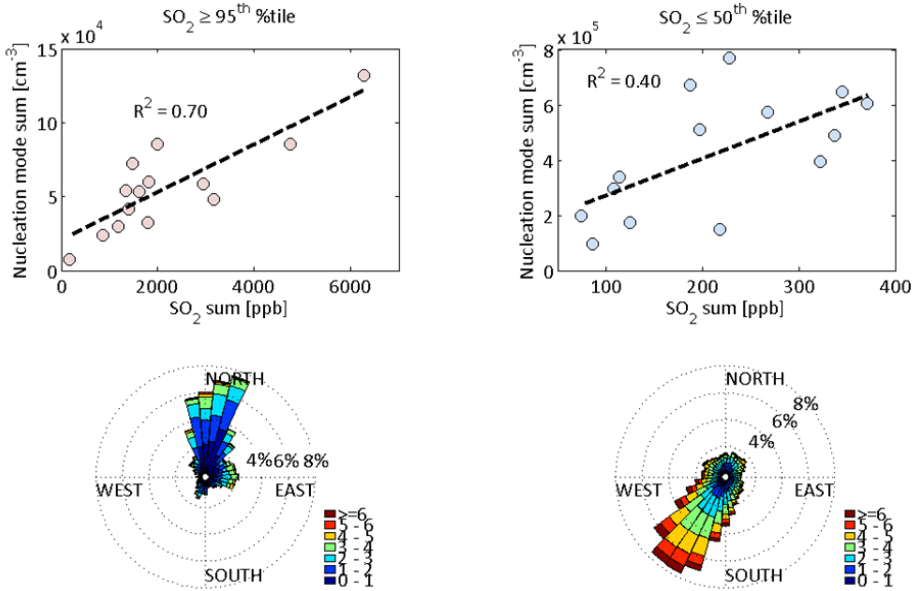

Fig. 14. Yearly sum of nucleation mode particle concentration as a function of yearly sum of SO_2 for polluted (SO_2 > overall 95th percentile) and clean (SO_2 < overall median) data and linear fits to them. Corresponding wind roses are plotted below. The color scale is the wind speed in m s^{-1} and the percentages shown in roses are fractions of the all (clean or polluted) data.

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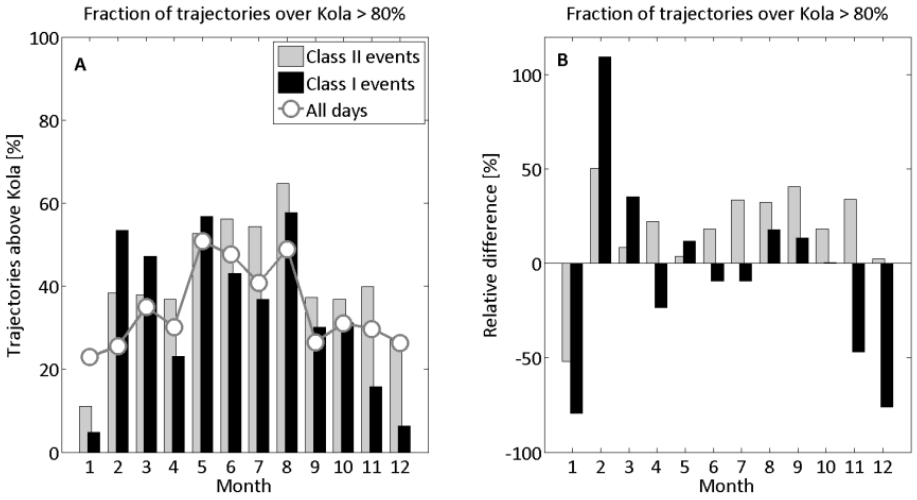

Fig. 15. Fraction of trajectories that come over Kola Peninsula so that the trajectory is over Kola more than 80 % of its time **(A)**, and respective relative differences between NPF days and all days for class I and II events **(B)**. Also the faction of time when trajectories pass over Kola before arriving at Värriö is shown for all days in **(A)**.

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