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Changes in the production rate of secondary aerosol particles in central Europe in view of decreasing SO₂ emissions between 1996 and 2006

A. Hamed¹, W. Birmili², J. Joutsensaari¹, S. Mikkonen¹, A. Asmi³, B. Wehner², G. Spindler², A. Jaatinen¹, K. Uhse⁴, A. Wiedensohler², K. E. J. Lehtinen^{1,5}, and A. Laaksonen^{1,6}

¹Department of Physics, University of Kuopio, P.O. Box 1627, 70211 Kuopio, Finland

²Leibniz Institute for Tropospheric Research, Permoserstrasse 15, 04318 Leipzig, Germany

³Division of Atmospheric Sciences, Department of Physical Sciences, P.O. Box 64, 00014, University of Helsinki, Finland

⁴Federal Environment Agency of Germany (UBA), Paul-Ehrlich-Strasse 29, 63225 Langen Germany

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



⁵ Finnish Meteorological Institute, Kuopio Unit, P.O. Box 1627, 70210 Kuopio, Finland

⁶ Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland

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Correspondence to: A. Hamed (amar.hamed@uku.fi)

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Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

In anthropogenically influenced atmospheres, sulphur dioxide (SO_2) is the main precursor of gaseous sulphuric acid (H_2SO_4), which in turn forms new aerosol particles (diameter $<10\text{ nm}$) through nucleation. As a result of socio-economic changes, East Germany has seen a dramatic decrease in anthropogenic SO_2 emissions between 1989 and present, as documented by routine air quality measurements in many locations. Using two different data sets of experimental particle number size distributions (3–750 nm) from the research station Melpitz (1996–1997 and 2003–2006) we have attempted to evaluate the possible influence of changing SO_2 concentrations on the frequency and intensity of new particle formation (NPF). Between the two periods SO_2 concentrations decreased on average by 65%, while the frequency of NPF events dropped by 45%. In addition, the average formation rate of 3 nm particles decreased by 68%. The trends were statistically significant, therefore suggesting a connection between the availability of anthropogenic SO_2 and the production of new particle number. A contrasting finding was the increase in the mean growth rate of freshly nucleated particles (+22%), suggesting that particle nucleation and subsequent growth into larger sizes are delineated with respect to their precursor species. Using three basic parameters, the condensation sink for H_2SO_4 , the SO_2 concentration, and global radiation intensity, we could define the characteristic range of atmospheric conditions under which particle formation events at the Melpitz site take place or not. While the connection between anthropogenic SO_2 , H_2SO_4 and NPF appears very plausible, our analysis yielded no significant evidence whether decreasing SO_2 concentrations did affect the production of cloud condensation nuclei (CCN).

1 Introduction

Aerosol particles play a key role in balancing the earth's radiation budget due to their light-scattering and cloud-forming properties (Haywood and Boucher, 2000)

ACPD

9, 15083–15123, 2009

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and through heterogeneous chemical reactions, the budget of photo-oxidants (Ravishankara 1997). In regional and global scales, aerosol particles have a potential to change climate patterns and the hydrological cycle (Ramanathan et al., 2001; Sekiguchi et al., 2003; Lohmann and Feichter, 2005). A better understanding of these aerosol-related effects, especially in relation to long-term climate projections, requires a more comprehensive knowledge on their sources, and atmospheric transformation processes. An important process controlling the number concentration of atmospheric particles is the formation of new ultrafine particles typically 1–2 nm in size, through gas-to particle conversion (e.g. Kulmala et al., 2004a; Jeong et al., 2004). Once thermodynamically stable, the new particles can grow through condensation and coagulation to sizes of 50–100 nm where they become active light scatterers and cloud condensation nuclei (CCN). From numerous observations worldwide it is now evident that atmospheric aerosol formation followed by condensational growth may occur in almost any part of the troposphere (Kulmala et al., 2004b).

Sulphuric acid (H_2SO_4) is considered as the most important species contributing to atmospheric particle nucleation (Weber et al., 1999; Kulmala, 2003). Its concentrations in tropospheric air, however, are typically not sufficient to account for the observed growth of fresh nuclei to sizes larger than 10 nm (Birmili et al., 2003; Wehner et al., 2005). Exceptions have been reported for the sulphur-rich urban atmosphere of Pittsburgh (Stanier et al., 2004). Other condensable vapours have been concluded to participate in the growth of nano-sized clusters, such as the oxidation products of volatile organic compounds (VOCs). According to the current understanding, sulphuric acid is likely to trigger nucleation whereas the oxidation products of VOCs govern the particle growth to larger sizes (Kulmala et al., 2007; Zhang et al., 2004; Laaksonen et al., 2008).

The major precursor of H_2SO_4 in the continental troposphere is sulphur dioxide (SO_2), which is oxidized during daytime by the hydroxyl (OH) radical. As a result of legislative emission control, the European levels of sulphur dioxide have undergone a substantial decrease over the last 2–3 decades (Manktelow et al., 2007; Beilke and

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Uhse, 1999). As a consequence of SO₂ reductions, the mass concentrations of sulphate aerosols have decreased as well (e.g. Spindler et al., 2004).

In the present work, our hypothesis is that the SO₂ reductions have also led to a reduced intensity of new particle formation and, consequently, to reduced number concentrations of secondary aerosols. In order to prove or disprove our hypothesis, we present two continuous data sets recorded in Melpitz, East Germany, during 1996–1997, and during 2003–2006, respectively. Events of new particle formation are identified and characterized, among others, by their frequency, and particle formation and growth rates. We examine the effects of sulphur dioxide and other parameters (in particular, solar irradiation and condensation sink) that are influential on the occurrence of new particle formation in the continental boundary layer, and show that between the two periods examined, a reduction in SO₂ levels has indeed most likely caused a reduction in the production of freshly nucleated particles. Finally, the effects of changing SO₂ on the production of cloud condensation nuclei (CCN) following nucleation events are evaluated and discussed.

2 Methods

2.1 Experimental data

Ambient particle number size distributions as well as a number of meteorological and gas phase parameters have been recorded at the atmospheric research station Melpitz (51°32' N, 12°56' E; 86 m a.s.l). The station is located near the village of Melpitz and about 46 km northeast from the city of Leipzig in Saxony (Eastern Germany). The region lies within densely populated central Europe, and is characterized by the presence of diffuse anthropogenic sources, such as vehicular traffic, agricultural and regulated industrial emissions. The surrounding of the station itself is flat grass land, where agriculture and wooded areas dominate up to a distance of several tens of kilometres around the station. The immediate neighbourhood of the station, however, is not used

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

for agricultural purposes except grass being mowed once a year. Details of the station can be found in Birmili and Wiedensohler (2000).

Particle size distribution measurements were carried out using twin DMPS systems (Differential Mobility Particle Sizers) with particle size ranges of 3–750 nm at Melpitz station during both periods (1996–1997 and 2003–2006). The instrument consists of Hauke differential mobility analyzers (DMA) and TSI CPC 3010 and UCPC 3025 particle counters (Birmili et al., 1999). The first DMPS measures particle size distributions between 3–20 nm and the second one between 15–750 nm. One measurement cycle lasts ten minutes. The same measurement technique and a very similar data processing method was used during both measurements periods.

Two size distribution data sets are used in this work, spanning the periods between March 1996 and August 1997, as well as between July 2003 and June 2006. Parts of these data sets were presented before, examining the environmental factors contributing to secondary new particle formation, the dependence of the particle size distribution on large-scale air masses, as well as the behaviour of the non-volatile particulate aerosol fraction (Birmili and Wiedensohler, 2000; Birmili et al., 2003; Engler et al., 2007). Our analysis also uses gas phase and meteorological parameters collected at the station, including SO₂, O₃, temperature, and global radiation. Table 1 summarizes all measured parameters, instruments, measuring ranges, and detection limits for different parameters at Melpitz station.

Gas phase and meteorological parameters from eleven observation sites were taken from routine observations by UBA (Federal German Environmental Agency, Dessau, Germany). All gas analyzers were regularly calibrated using calibration standards.

2.2 Nucleation event classification, and determination of particle production, condensation sink and growth rates

All days from the studied periods were classified into different categories, i.e., nucleation and non-nucleation days, depending on whether particle formation events were observed. During nucleation event days, an increase of the particle number concen-

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



trations in the nucleation mode connected with a clear growth of the newly formed particles for several hours can be observed clearly. If no formation of new particles has been observed, the day has been classified as non-nucleation day. If a day cannot be clearly classified as nucleation or non-nucleation day, it is classified as an “equivocal case”. The classification method of nucleation events we followed here is based on the method described in Hamed et al. (2007). In the resulting analysis and to minimize the uncertainty of the classification subjectivity, clear nucleation events and non-events were only taken into consideration. That also gives a good opportunity to investigate the reasons leading to nucleation events when compared with non-events days.

The aerosol condensation sink (CS) determines how rapidly molecules condense onto pre-existing aerosols and depends strongly on the ambient particle size distribution. To quantify condensation processes during new particle formation, we calculated the condensation sink by using the method described by Pirjola et al. (1998) and Kulmala et al. (2001). In practice, the vapor was assumed to have very low vapor pressure at the surface of the particle, and molecular properties were assumed similar to those of sulphuric acid.

From the DMPS data, we calculated the formation rate of 3 nm particles (J_3) following the method described by Sihto et al. (2006) and Riipinen et al. (2007). The growth rates of the nucleation mode have been estimated visually from daily size distribution contour diagrams. When quantifying the growth rate (GR) of the nucleation mode, a minimum growth time of three hours was required. If a continuous growth of the nucleation mode occurred, GR was estimated from periods lasting up to 8 h (Hamed et al., 2007).

2.3 CCN estimates from measurement data

In order to determine the production rates of CCN resulting from nucleation and growth of new particles, we applied the method of Laaksonen et al. (2005) to the size distribution data. Briefly, we calculated increases of particle number concentrations in the 50–750 nm, 100–750 nm, and 200–750 nm size ranges on nucleation event days. The

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

concentration increases in the given size ranges were simply determined from the differences in particle concentration at the moment when the nucleated mode reaches lower limit of the given size range, and at the time when the particle concentration in that size range reaches a maximum, or alternatively at 06:00 h LT of the following day if a maximum was not reached before. The termination of the calculation at this point is a practical necessity because of the interferences created by the morning rush-hour aerosol and by the start of vertical mixing. In this way we obtain conservative estimates for the increases of particle concentrations in the different size ranges.

In order to estimate the total CCN production, i.e. the production from primary and secondary sources, we calculated hypothetical particle source rates that are needed to support the average concentrations of particles in the given size ranges. In the steady state (SS), the particle source rate (P) equals the ratio of particle concentration (C) and the average particle residence time in air (t). For our calculations we adopted the residence time of 4 days for particles near the surface given by Balkanski (1991).

2.4 Estimate for CCN production from primary sources using emission inventory

One way of semi-independent estimates of the primary CCN production in a given area is to use existing emission inventories. The accuracy of emissions inventories are for this application, however, limited since they usually refer to particle mass rather than particle number, and typically include only sources that have been officially reported. Further limiting factors include the lack of longer time-periods, seasonal variations and detailed size distributions and chemical composition of the particulate emissions. We expect, however, that the primary CCN emission rates can be estimated within one order of magnitude on the basis of emission inventories.

The EMEP emission model database provides estimates of annual emissions of $\text{PM}_{2.5}$ on $50 \times 50 \text{ km}^2$ grid cells for the years 2000–2005 (Vestreng et al., 2007; Vestreng et al, 2006). By using these data and the source distributions of the emissions, we created a rough estimate of the primary emitted CCN from the period. The estimate is

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

based on the economic sectors of emissions from the EMEP database and typical literature distributions of different sources. For the years 1996 and 1997, with no specified EMEP emission model result available, we extrapolated the rates from year 2000 emission rates together with the trend of total PM_{2.5} emissions in Germany from 1996 to 2000. One of our central assumptions was that the PM_{2.5} emissions from different economic sectors represent, on average, a bimodal particle size distribution. In a first step, we distributed the mass emission to the two modes by a fixed (source-dependent) factor. Then the total modal particle number was calculated assuming a log-normal distribution leading to

$$N = \frac{6m}{\rho\pi} d_p^{-2} \exp(-4.5 \log^2 \sigma) \quad (1)$$

where N and m are the total number and mass of the emission in the size and source mode ($\text{m}^{-2}\text{yr}^{-1}$ and $\text{kg m}^{-2}\text{yr}^{-1}$), d_p is the geometric mean number diameter (or count median diameter, CMD) of the emission (m), ρ is the effective density of the particles emitted (kg m^{-3}), and σ is the geometric standard deviation of the emission mode. After this, the resulting number emission modes were summed up to a total emission size spectrum, which in turn was integrated to specific size ranges if needed. For the comparison with volume sources, the estimate of yearly area source of CCN from primary emissions is then multiplied by the presumed annual average height of the mixed layer in Melpitz site, 1 km in this case.

Table 2 describes the different emission categories we have used and the related factors used in calculation of the estimated number emission profiles. For traffic emissions (EMEP SNAP sector 7), we used an average number size distribution derived from diesel vehicles at maximum power (22f) (Morawska et al., 1998), resulting in CMDs of 70 nm and 420 nm with a relative mass ratio of 5% for the smaller CMD mode. For non-traffic emissions, we first assumed that EMEP sector S1 (energy production) can be represented by coal combustion plants with CMDs of 90 nm and 420 nm with mass ratio of 3% (22g), sectors S2 to S6 with mixed process plants with CMDs of 100 nm and 420 nm with mass ratio of 1% (extrapolated from Ehrlich et al. 2007, Figs. 3,

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



12 and 2e) and remaining sectors (other mobile emissions and agricultural emissions) were assumed to be unimodal coarse emissions with CMD of 5 m. In line with the very general nature of this analysis, we assumed that all the emission modes are constant in time and space, log-normal in shape with geometric standard deviation of 1.7 and no dynamic aging of emissions were considered. The particle density was assumed to be around 800 kg m⁻³ for traffic-derived particles and 1500 kg m⁻³ for all other particles.

3 Results and Discussion

3.1 Trends in atmospheric constituents

3.1.1 Sulphur dioxide (SO₂)

During the past twenty-five years European sulfur emissions have decreased continuously. The emission trend, however, varied considerably between individual countries. Between 1980 and 2000 particulate sulfate mass concentrations decreased by 50–70% in response to 90% reductions in emissions and measured concentrations of SO₂ in the United Kingdom, France and Germany (Löfblad et al., 2004). Germany, in particular, is a good example how industrial and domestic sulfur dioxide emissions were reduced according to the emission control policies (Gothenburg Protocol): The emissions decreased by 18% between 1980 and 1989 and by 85% between 1990 and 1999, respectively (Beilke and Uhse, 1999; Vestreng et al., 2007). It is essential to note that the decrease in East German emissions after 1989 can be largely ascribed to the de-industrialization process after Germany's reunification (Lintz et al., 2005). Since 2001, the national government has also encouraged the consumption of low-sulfur fuel in the road transportation by a tax discount. In East Germany the main pollution sources were associated with carbo-chemical industry (i.e. chemical industry based on processing lignite, brown coal as a raw material) as well as unregulated power plants. These industries clustered in the areas around Halle, Leipzig, and Cottbus, and indeed the Melpitz

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

research station was erected in 1991 with the aim to monitor mid-term changes within this region. In the 1980s the contribution of power plants to total ambient SO₂ was 75%, which doubtlessly enhanced the formation of acidic secondary aerosols (Marquardt et al., 1998; Krüger et al., 2004). In the late 1980s, average SO₂ and PM mass concentrations of more than 150 g m⁻³ could be measured around Leipzig, Halle, and Cottbus, while after 1990, the levels decreased rapidly to ca. 5 and 20–30 g m⁻³, respectively, after 2000 (Spindler et al., 2004). The last “dirty” carbo-chemical plant in the Leipzig region (Espenhain works), dedicated to the pyrolysis of lignite, closed in late 1996.

In general, the reduction of emissions in the majority of European countries between 1990 and 2004 was more than 60%, while it was over 80% for a quarter of the countries (Vestreng et al., 2007). The absolute reductions obtained between 1990 and 2004 were the largest for Germany, the Russian Federation, United Kingdom, and Ukraine. The estimated reduction within these four countries was larger than the reductions from all the other European countries together.

Myhre et al. (2004) showed that emission changes of SO₂ between 1985 and 1996 impacted the geographical distribution of the radiative forcing of the direct aerosol effect substantially. Krüger et al. (2004) showed that toward late 1990s, the PM and SO₂ emission reduction in Central Europe (particularly in East Germany and in Poland) caused the reduction of the indirect aerosol effect and therefore of the cloud reflectance (Vestreng et al., 2007). Fagerli et al. (2006) showed that the reductions have a pronounced impact on the sulphur deposition pattern in Europe although SO₂ emissions have been reduced substantially since the 1980s. Further reductions are planned to help reduce fine particulate matter mass concentrations in Europe, which have been linked to adverse health effects.

The trend in sulfur dioxide concentrations was determined on the basis of local measurements at Melpitz. Figure 1a shows SO₂ trends measured at Melpitz as well as regional measurement stations near Melpitz between 1991 and 2008. The series are 60 d floating averages of daily average values between 10:00 and 14:00 h. The Melpitz

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

values appear to be well representative of the regional SO₂ background. Data were obtained from UBA network.

Figure 1b shows monthly averaged SO₂ concentrations measured in Melpitz for the periods 1996–1997 and 2003–2006 (these periods cover our particle size distributions measurements). As indicated also by Fig. 1a, the SO₂ levels appear to have decreased between the two periods, in concurrence with the results of Vestreng et al. (2007). The overall reduction between averages from the two periods is 65%.

3.1.2 Nucleation event frequency and particle formation rate

Figure 2a shows the monthly average frequency of nucleation event days during the 1996–1997 and 2003–2006 periods. The results show in general that in the earlier dataset (1.5 yr) 50% of the measurement days were nucleation days whilst only 30% were so in the newer dataset (2003–2006). Non-nucleation days accounted for 39% of the days in the earlier dataset and for 54% in the new one. Equivocal cases, i.e. days for which we were not able to decide with confidence whether nucleation took place or not, accounted for about 11% and 16% of the old and new datasets, respectively. From the event frequency plot, it is clearly seen that the highest frequencies for nucleation events in 2003–2006 were observed from late spring to late summer, i.e. from June till September while in 1996–1997 the maximum frequency was 80% in June. Wintertime (December–February) notably was poor in terms of nucleation events, with an average event frequency of ~10% for 1996–1997 and ~3% for 2003–2006. Moreover, the total decrease in the numbers of nucleation days from years 1996–1997 to years 2003–2006 was about 45%. Figure 2b shows the 3 nm particle formation rate (J_3) determined for the particle formation events. For the older data series the formation rate values were clearly higher than for the 2003–2006 data series. The relative difference of average J_3 values between the two periods was about 68%.

The annual event frequency can be biased by the weather conditions in a particular year. The solar radiation levels are a good measure for the differences between the years from nucleation point of view as photochemical reactions drive the formation of

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

condensable species needed for nucleation to occur (Stanier et al., 2004; Birmili and Wiedensohler, 2000; Wehner and Wiedensohler, 2003; Hamed et al., 2007). We have therefore scrutinized both measurement periods for any meteorological differences by comparing the measured intensity of solar radiation (SR). Figure 3a shows the comparison of the radiation intensity between the two periods. No significant difference in SR is apparent during the months of highest nucleation event frequency (spring and summer) between the two periods. However, higher nucleation frequencies and rates in 1996–1997 may have been somewhat affected by more sunny weather in the winter months, whereas during the autumn months the 2003–2006 nucleation frequencies and rates may have been relatively more boosted.

Condensation sink (CS) for sulfuric acid and other condensable gases can have a preventing influence on nucleation. Figure 3b shows CS in different seasons for both time periods. It can be seen that CS was higher in 1996–1997 during spring and summer whilst no remarkable difference is apparent in winter and autumn. The CS may therefore have diminished the differences in nucleation frequencies and rates between 1996–1997 and 2003–2006.

3.1.3 Sulphuric acid

Sulphuric acid is an oxidation product of sulphur dioxide. It is generally thought of as the primary compound responsible for atmospheric nucleation although other species such as ammonia or organics might be involved as well (Weber et al., 1999; Kulmala, 2003; Zhang et al., 2004; Laaksonen et al., 2008). Since direct measurements of gas-phase sulphuric acid have not been performed at Melpitz, we calculated a proxy instead. The limiting step for the formation of H_2SO_4 is the reaction of SO_2 with the OH-radical. It has been shown that atmospheric OH concentrations correlate well with solar UV radiation (Rohrer and Berresheim, 2006). As UV radiation has not been measured continuously at Melpitz, we used the global intensity of solar radiation (SR) as a best replacement. The most important sink for gas-phase H_2SO_4 is the surface of existing atmospheric aerosol particles, onto which H_2SO_4 molecules condense rapidly. It is the

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

CS that determines the corresponding rate of mass transfer, and this depends on the size distribution of existing particles. Assuming that the formation and loss of the acid are in steady-state, we obtain a proxy for gas-phase sulphuric acid concentration given by $[\text{SO}_2] \times \text{SR} / \text{CS}$. (Kulmala et al., 2005).

As shown in Fig. 4a for the older data set the SO_2 concentration values were clearly higher than for the 2003–2006 data set in all seasons with remarkable difference in spring and summer. However, we should note that in winter times the number of data points for SO_2 were not statistically significant (48 and 30 data points for years 1996–1997 and 2003–2006 respectively; see below for statistical tests). Figure 4b shows that the proxy values have decreased concurrently with SO_2 , and as changes in SR and CS clearly do not explain this decrease (with the possible exception of autumn differences; see Sect. 3.1.4 below). We conclude that the reduced sulphur dioxide levels not only coincide with but are the cause of the decreased sulphuric acid proxy values.

As the decrease in the H_2SO_4 proxy is mostly caused by the observed decrease in SO_2 , a corresponding decrease in the number of newly formed particles is expected if sulfuric acid is a critical species controlling the formation of new particles. Experimentally, the number of newly formed particles decreased between both periods as well (cf. Fig. 2a,b). However, it needs to be remembered that the precise balance of H_2SO_4 is influenced by further unknown variables, such as the concentrations of the OH radical.

A modelling study of new particle formation events in Pittsburgh suggested that SO_2 reductions can either increase or decrease the frequency of nucleation (Gaydos et al., 2005). They suggested that reductions of sulphur dioxide and the resulting sulphate by up to 40% actually increase the frequency of nucleation events in summer. This was explained by decreasing sulphate concentrations allowing higher gas-phase ammonia concentrations and, since they assumed a ternary (sulfuric acid – ammonia – water) nucleation mechanism, ammonia concentrations appeared to be a limiting factor for the events. In wintertime they could not see such an effect; the modelling predicted fewer nucleation events along with decreasing SO_2 concentrations (Gaydos et al., 2005).

In contrast to the experimental particle formation rates, the growth rates of the fresh

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

particles to bigger sizes increased by roughly 22% from 1996–1997 to 2003–2006. Growth rates were higher in 2003–2006 (see Fig. 5a) and the difference was statistically significant in spring and in summer (see Sect. 3.1.4). Therefore, the mean particle growth rate has increased inversely to SO₂ concentrations, the H₂SO₄ proxy, and the formation rate of new particles. This observation is a clear indication of other species than H₂SO₄ being involved in the particle growth (Kulmala, 2003). It has been indicated that monoterpene oxidation products drive the growth of freshly nucleated particles in boreal forest areas (Tunved et al., 2006; Laaksonen et al., 2008). VOCs are also abundant in Central Europe (Müller et al., 2002; Alves et al., 2006), and it is likely that their low-volatility oxidation products contribute to particle growth (Wehner et al., 2005). The question whether VOC concentrations have increased over our observation period at Melpitz cannot be answered with certainty. Biogenic VOC emissions are temperature dependent, and as the average nucleation day temperatures in 2003–2006 were higher than in 1996–1997 (see Fig. 5b), it could be that oxidation products of biogenic VOC's have contributed to the increased growth rates. Ozone is responsible for the formation of condensable species directly through reactions with VOCs, and indirectly by forming other oxidants (OH) upon photolysis. Although condensable organics might not be involved in the actual nucleation, they may be important in speeding up the growth of newly formed molecular clusters so that the clusters survive to detectable sizes before being scavenged by coagulation with larger particles (Kerminen et al., 2004). From our results we found that O₃ concentrations were higher on nucleation event days for new data sets than for old data (see Fig. 5c).

Industrial emissions of VOCs are expected to have decreased while traffic-derived emissions have slowly increased with time. A global estimate yielded that the SOA (secondary organic aerosol) production rate is currently rising (Heald et al., 2008). Note, however, that with decreased nucleation, the condensable vapour will be divided among fewer particles, and average growth rates could increase even if the condensable vapour levels stay constant. In this case even if condensable vapours from VOC oxidation have remained constant, the average growth rates might have increased.

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.1.4 Statistical significance of the differences

In order to test for statistical significance of the differences between the two measurement periods, statistical analyses were carried out with R-software (R Development Core Team, 2008, see <http://www.R-project.org>) and the differences were tested with two sample *t*-tests. Since the observations are mostly not normally distributed, which is the conservative assumption for *t*-test to be valid, the results were confirmed with robust Wilcoxon rank sum tests. Since the 1996–1997 data cover only a period of 1.5 years (with two summers and one winter), we do not compare the complete datasets with each other but instead present seasonal comparisons.

Table (3) shows the mean, median, standard deviation and *p*-values of the *t*-tests and Wilcoxon rank sum tests the means of the variables for the seasonal data. Note that the data are from strong nucleation event days. Daily observations are from hours 6 a.m.–6 p.m. The difference in means is statistically significant if *p*-value<0.05. Both tests indicate statistical significance for the differences of *J*₃ in spring, summer and autumn. Due to the scarcity of data and large standard deviations, the Wilcoxon test does not indicate the winter means of *J*₃ to be statistically different.

According to the *t*-test, the differences for SO₂ and the proxy are significant for all seasons (except for the autumn proxy), while the Wilcoxon test shows statistical significance for spring and summer only. As with nucleation rate, the small number of winter observations explains the Wilcoxon test result. In autumn, the Wilcoxon test does show significant difference for SO₂ but (as with the *t*-test) not for the proxy. This is caused by solar radiation, which was significantly higher in the 2003–2006 data, negating the effect of lowered SO₂.

The condensation sink differences are statistically significant for all seasons, while the solar radiation differences are significant only in autumn. GR was statistically significantly higher in 2003–2006, in spring and summer.

Changes in the productionrate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Conditions and parameters of new particle formation

3.2.1 Separation of nucleation event and non-event days

The fact that the overall nucleation event frequency has decreased in line with the sulphuric acid proxy does not prove a causal relationship. We therefore examined the individual variables contributing to the H_2SO_4 proxy more closely with respect to their behaviour on nucleation event and non-event days. Figure 6 shows the production term ($[\text{SO}_2] \times \text{SR}$) of the H_2SO_4 proxy as a function of the condensational sink term (CS). Each point represents one day of measurements (in the case of formation events, at time when the maximum concentration of new particles formed by nucleation were reached; in case of non-events at noon). As can be seen, the data points from particle formation events and non-events tend towards different edges of the data cloud. The line that separates the two sub-sets most effectively is indicated in Fig. 6. The results illustrate that new particle formation at Melpitz becomes more probable when the ratio between the production term of the H_2SO_4 proxy and the CS increases. In contrast, the lower portion of the figure is dominated by non-nucleation days associated with comparatively low solar radiation, low $[\text{SO}_2]$, or high CS, which all contribute to a low steady-state concentration of H_2SO_4 . In conclusion, such a scatter plot of the sulphuric acid production and sink term appears to be an efficient illustration to explain a large part of the observed particle formation days, although the microphysical and meteorological understanding of the particle formation process is still missing. It is worth to note that a one-year study in the urban atmosphere of Pittsburgh, Pennsylvania came to similar conclusions (Stanier et al., 2004).

3.2.2 Sulphuric acid proxy vs. nucleation rate

Figure 7 shows two examples of typical nucleation event days in Melpitz station for the old data period and for the new data period respectively. Estimated 3 nm particle formation rate vs. the sulphuric acid proxy values are shown in the upper panels while

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the lower panels show the number concentration of 3–6 nm particles vs. the proxy on two event days, one from each period. The sulphuric acid proxy was time delayed. This time delay between the rise in sulphuric acid proxy and particle number concentration N3–6 was interpreted as the time it takes for the clusters to grow from the nucleated size of 1 nm to the detectable size of 3 nm in diameter. Based on this assumption we used the growth rate (GR) from 1 nm to 3 nm for each nucleation day and therefore we estimated the delay time as 2 nm divided by GR. Figure 7 closely resembles similar plots e.g. in Sihto et al. (2006) with the difference that they show the daily behaviour of measured H_2SO_4 concentration instead of the H_2SO_4 proxy.

A plot of the logarithm of the experimentally derived particle formation rate J_3 vs. the logarithm of the sulphuric acid proxy reveals a rather scattered plot, resulting in weak correlation (see Fig. 8). Several studies have analyzed the slope of $\log(\text{H}_2\text{SO}_4)$ vs. $\log(J_3)$ because this could reveal the number of sulfuric acid molecules required for a critical, thermodynamically stable cluster as well as give hints on the acting nucleation mechanism. These studies have observed slopes between 1 and 2 (Eisele et al., 1997; Weber et al., 1999; Kulmala et al., 2006; Sihto et al., 2006; Kuang et al., 2008).

As seen from Fig. 8 the optimal fitted line shown has a slope of about one indicating reasonable consistency with earlier studies that investigated the relationship between J_3 and H_2SO_4 . This result, together with Fig. 7, shows that our proxy variable behaves at least qualitatively similarly as H_2SO_4 which increases our confidence in interpreting the reduction of nucleation event frequency and nucleation rate between 1996–1997 and 2003–2006 as being due to reductions in sulfur dioxide emissions.

3.3 Implications for the production of CCN

After nucleating at diameters of about 1 nm in the atmosphere, the newly formed particles may grow by condensation and coagulation, and eventually reach particle sizes where they may act as cloud condensation nuclei (CCN). This growth may take several hours to days, and since many aerosol dynamical as well as meteorological effects interact during such a time span, it has been difficult to determine CCN production rates

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



on the basis of experimental observations. Here, we investigate the significance of the nucleation events as a source of CCN at Melpitz site, and whether the CCN production might have changed along with SO_2 concentrations. In the literature, CCN are defined either as particles activating to cloud drops at a given supersaturation, or alternatively (usually if CCN instruments were not available in the study) as particles larger than a given size. Here we examine three different size ranges: 50–750 nm, 100–750 nm, and 200–750 nm. The upper limit is set by the TDMPs instrument.

We examine three different CCN estimates. The first one is an estimate of CCN production by nucleation and subsequent growth. As explained in detail above, we follow the growing mode and calculate the CCN production from the increase in the number concentration into the given size range during the growth, and regard the estimate a conservative one. The second estimate concerns total production (primary plus secondary) of CCN in the given size range, and is obtained from assuming a steady-state between particle production and removal that maintains the average concentration in the given size range, and a 4-day particle lifetime. The third estimate gives the numbers of primary CCN in the given size ranges, and is obtained from emission inventories for $\text{PM}_{2.5}$ plus assumed size distributions.

Note that all of the CCN estimates here contain more or less large uncertainties. The nucleation CCN estimate is interfered by air mass inhomogenities and by influences from other than nucleated particles that are difficult to tell apart, and by the need to terminate the calculation in the morning following the nucleation event. The total CCN estimate relies on a crude SS-assumption and on a 4-day particle lifetime. The primary CCN estimate relies on uncertain $\text{PM}_{2.5}$ numbers and on assumed size distributions and boundary layer height. We would like to stress here that we are not so much interested in the absolute numbers given by the estimates than we are on the relative differences between the two periods examined. Assuming that the error sources have not changed between the periods, the estimates should give us reasonable indications of trends of the different CCN sources. Note also, that the three different CCN estimates do not “close” in the sense that the total estimate should be a sum of the nucleation

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and primary estimates, even if all estimates were error free. This is because we do not have an estimate for CCN produced by cloud processing (which would include most of the sulphate CCN).

5 The estimates for nucleation production of CCN in size ranges 50–750 nm, 100–750 nm, and 200–750 nm are presented in Table 4 as Annual Yield/cc (i.e. total number of particles per cubic centimetre produced by nucleation and growth to the respective size range within one year). For all size ranges the concentration increase per particle formation event was on the same order as the average concentration. As would be expected from the decrease of nucleation frequency and average nucleation rate between
10 1996–1997 and 2003–2006, the CCN production from nucleation has decreased in the 50–750 nm size range, but not very much ($\sim 17\%$). Surprisingly, however, the production has clearly increased in the 100–750 nm and 200–750 nm size ranges, by $\sim 47\%$ and $\sim 103\%$, respectively.

The total CCN source strengths in the different size ranges are also given in Table
15 4 (SS-production/cc/year). As with nucleation, the total CCN source has decreased in the smallest size range and increased in the two largest size ranges, but the relative changes are quite modest, all within 10%.

Table 5 shows our emission model results based on estimates of primary particle production in the three size ranges for years 1996, 1997, 2003, 2004 and 2005. All values
20 have decreased from 1996–1997 to 2003–2006, with roughly 35% average reduction in all three size ranges between the two periods. We also repeated the calculation using the size distributions applied by Laaksonen et al. (2005), and obtained a similar percentage reduction although the absolute numbers (not shown) were up to an order of magnitude higher.

25 To summarize these results, our estimates indicate that in size ranges above 100 nm, nucleation source of CCN has increased substantially, total source has remained the same or increased slightly, and primary source has decreased clearly. In addition, it is very likely that the source from cloud processing has decreased, at least for sulphate particles. It would therefore seem that the increase of the nucleation source has

**Changes in the
production rate of
secondary aerosol
particles**

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

more or less compensated for the decrease in primary and (cloud processed) sulphate sources.

The puzzling feature is of course that nucleation event frequency and average nucleation rate have dropped at the same time as nucleation production of CCN appears to have increased. One possible explanation is the observed increase in particle growth rates: the survival probability of freshly nucleated particles to sizes above 100 nm may have become larger, making it possible for a larger fraction of the new particles to reach CCN sizes. On the other hand, it is also possible that the same substances that cause the growth of the nucleated particles have made primary particles smaller than 100 nm growing above the 100 nm limit more efficiently in 2003–2006 compared with 1996–1997. It is also possible that primary sources of sub-100 nm particles have increased: after all, that would hardly be seen in the PM_{2.5} emission inventories on which we based our primary CCN calculations. To be able to further examine the reasons for the increases/decreases in production of different CCN types, we will use aerosol dynamics and regional scale modelling, but that is out of the scope of the present paper and will be left for the future.

4 Conclusions

We analysed two different datasets of experimental aerosol number size distributions at the research station Melpitz, Germany, in order to evaluate the possible influence of decreasing SO₂ concentration on secondary new particle formation and on the production of the cloud condensation nuclei (CCN) between 1996/97 and 2003–2006. During the 1990s the ambient levels of SO₂ in East Germany decreased by a factor of ten as a result of socio-economic changes, leveling off after about the year 2000. Our analysis showed a significant, and concurrent drop in the frequency of new particle formation events between the two observation periods (–45%). Along with this, a decrease in the particle formation rate (–68%) was observed. The trends were statistically significant, therefore suggesting a connection between the decreasing availability of anthropogenic

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



SO₂ and the diminishing production of new particle number. A contrasting finding, however, was the increase in the growth rates of nucleated particles (+22%), suggesting that particle nucleation and subsequent growth into larger sizes are delineated with respect to their precursor species. The delineation between particle formation rates and particle growth can be understood in terms of the different source types (SO₂: anthropogenic; VOCs: biogenic and anthropogenic), and was detected in Central Europe on the basis of a multi-annual experiment before (Birmili et al., 2003).

We also studied the effect of parameters believed to influence atmospheric nucleation such as solar radiation, CS and SO₂ concentrations. The results show that the change of SO₂ dominates over the changes of solar radiation and CS. Since sulphuric acid was not measured, we calculated a “proxy” sulphuric acid concentration making use of the fact that H₂SO₄ is formed in the reaction between SO₂ and OH-radicals, and the concentration of the latter can be correlated with intensity of solar radiation and that the CS represents H₂SO₄ loss term. The sulphuric acid proxy decreased between 1996–1997 and 2003–2006, thus supporting the conclusion that the diminishing intensity of NPF is connected to decreasing ambient levels of SO₂. The proxy correlates with measured 3 nm particle formation rates, and indeed the slope between the logarithms of these two quantities is close to unity, in agreement with that seen in earlier studies of measured H₂SO₄ values and atmospheric nucleation rates. Taken together, we have strong indication that reduction of European SO₂ pollution has caused a decrease in the production of new particles formed in nucleation and growth events.

We also examined particle concentrations in the 100–750 nm and 200–750 nm size ranges during the hours following nucleation events, when particle growth was taking place. Our analysis revealed rather counterintuitively that particle production in these size ranges due to nucleation and growth has in fact increased, although nucleation event frequencies and rates have decreased. One possible reason for this finding may have to do with the fact that particle growth rates have increased, increasing the probability that nucleated particles grow to large sizes. However, we cannot rule out the possibility that primary particle sources have increased in the 100 nm size range, and

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

interfered with our estimates. Further studies are needed to elucidate this question.

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Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Changes in the
production rate of
secondary aerosol
particles**

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Lihavainen, H., Nilsson, D., Facchini, M. C., Cavalli, F., Fuzzi, S., Hoffmann, T., Arnold, F., Hanke, M., Sellegri, K., Umann, B., Junkermann, W., Coe, H., Allan, J. D., Alfarra, M. R., Worsnop, D. R., Riekkola, M. -L., Hyötyläinen, T., and Viisanen, Y.: The role of VOC oxidation products in continental new particle formation, *Atmos. Chem. Phys.*, 8, 2657–2665, 2008, <http://www.atmos-chem-phys.net/8/2657/2008/>.

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Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Aerosols, climate, and the hydrological cycle, *Science*, 294, 2119–2124, 2001.
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Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Summary of measured gas and meteorological parameters, instruments, measuring ranges and detection limits at the Melpitz measurement station.

Parameter	Instrument	Measuring ranges	Detection limit
SO ₂	Monitor – APSA 360 UV-fluorescence, Horiba Europe	0–0.05/0.1/0.2/0.5 ppm	0.5 ppb±1%
NO ₂ /NO	Monitor – APNA 360 chemiluminescence Horiba Europe	0–0.1/0.2/0.5/1 ppm	0.5 ppb±1%
O ₃	Monitor – APOA 350E, UV-absorption Horiba Europe	0–0.1/0.2/0.5/1 ppm	0.5 ppb±1%
Temperature	Pt 100/DIN 43760	–40 to +40 °C	±0.1 K at 0 °C
Relative humidity	Humidity sensor	0–100%	±3% (20–95%)
wind speed	Cup anemometer	0–40 m/s	±0.3 m/s
Wind direction	Wind vane type RITA	0–360 °	±2 °
Global radiation	Kipp&Zonen CM6	2000 W/m ² (305–2800 nm)	

**Changes in the
production rate of
secondary aerosol
particles**

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Table 2. Particle emission parameters used for estimating the CCN production from primary mass emissions. D_{p1} and D_{p2} refer to the geometric mean diameters of the two particle modes.

Emission source	d_{p1} (nm)	d_{p2} (nm)	M (%)	EMEP sector(s)
Traffic*	70	430	5	7
Energy production**	90	430	3	1
Manufacture***	100	430	1	2–8
Other ****	30	850	0.1	8–10

* Based on diesel exhaust data Morawska et al. (1998)

** Ohlström et al. (2000)

*** Extrapolated from Figs. 3 and 12 in Ehrlich et al. (2007)

**** Other mobile emissions and agricultural emissions

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Table 3. Trends in solar radiation (SR) (in W m^{-2}), the condensation sink parameter (CS) (in s^{-1}), sulfur dioxide (SO_2) mixing ratio (in g m^{-3}), sulphuric acid proxy, and the particle formation rate (J_3) (in $\text{cm}^{-3}\text{s}^{-1}$) at Melpitz. The results show seasonally separated data for strong nucleation days. The observations cover 06:00–18:00 LT. Mean, median, standard deviation (SD) and p -values of the t -tests and Wilcoxon rank sum tests for the seasonal growth rate (GR) (in nm h^{-1}) values were calculated from monthly mean values.

Season	Variable	Mean		Median		SD		p -values		Higher in
		96–97	03–06	96–97	03–06	96–97	03–06	t -test	Wilcoxon	
Winter	SR	154	124	91	94	156	140	0.363	0.474	No difference
	CS	0.009	0.012	0.010	0.011	0.005	0.004	0.008	0.049	2003–2006
	SO_2	23.6	13.6	22.4	5.6	20.7	12.9	0.02	0.18	1996–1997/No difference*
	Proxy	2.59E+05	1.23E+05	1.10E+05	3.89E+04	3.51E+05	1.69E+05	0.047	0.156	1996–1997/No difference*
	J_3	4.9	0.7	1.2	0.4	6.4	0.9	0.073	0.247	No difference
Spring	GR	4.1	5.6	3.9	4.6	1.6	2.3	0.216	0.156	No difference
	SR	439	444	460	476	227	231	0.764	0.772	1996–1997
	CS	0.012	0.009	0.010	0.008	0.007	0.005	<0.0001	<0.0001	1996–1997
	SO_2	15.7	6.1	8.7	5.2	18.1	3.1	<0.0001	<0.0001	No difference
	Proxy	7.07E+05	3.88E+05	4.07E+05	3.19E+05	7.48E+05	3.01E+05	<0.0001	<0.0001	1996–1997
Summer	J_3	10.2	1.5	3.5	1.0	12.9	2.0	<0.0001	<0.0001	1996–1997
	GR	5.0	6.1	4.2	5.2	2.6	2.3	0.020	0.003	2003–2006
	SR	487	464	499	456	225	221	0.069	0.075	1996–1997
	CS	0.011	0.009	0.010	0.008	0.006	0.006	<0.0001	<0.0001	1996–1997
	SO_2	16.8	3.8	10.3	3.4	18.5	2.7	<0.0001	<0.0001	No difference
Autumn	Proxy	6.88E+05	2.47E+05	4.96E+05	1.85E+05	6.65E+05	2.52E+05	<0.0001	<0.0001	1996–1997
	J_3	7.4	1.8	2.7	1.0	9.7	2.2	<0.0001	<0.0001	1996–1997
	GR	5.9	7.0	5.1	6.4	3.2	2.8	0.025	0.002	2003–2006
	SR	258	326	253	331	204	203	0.017	0.013	1996–1997
	CS	0.009	0.011	0.008	0.010	0.003	0.008	<0.0001	0.054	No difference
	SO_2	13.8	4.7	6.9	4.1	16.8	3.6	<0.0001	<0.0001	2003–2006
	proxy	3.73E+05	2.07E+05	1.29E+05	1.50E+05	5.73E+05	2.17E+05	0.063	0.565	2003–2006
	J_3	6.5	2.0	3.0	1.0	7.9	2.8	0.033	0.017	1996–1997
	GR	5.6	6.4	5.0	6.0	2.9	2.3	0.474	0.334	No difference

* numbers of observations were less than 50 for each time periods and this may cause bias to results.

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Table 4. The annual yield of particles, the average yield per one nucleation event, the average particle concentrations and the hypothetical steady-state particle production rate at Melpitz during 1996–1997 and 2003–2006. To compare consistent annual mean values, we strictly selected a one year period (July 1996–June 1997) from the older dataset for our calculations.

Size range (nm)	1996–1997			2003–2006		
	50–750	100–750	200–750	50–750	100–750	200–750
Annual yield/ cc	2.29E+05	6.14E+04	1.56E+04	1.90E+05	9.00E+04	3.17E+04
Average yield/event	4.02E+03	1.08E+03	2.74E+02	3.61E+03	1.71E+03	6.03E+02
Average concentration/cc	2.46E+03	1.20E+03	3.96E+02	2.43E+03	1.27E+03	4.38E+02
SS-Production/cc/year	2.25E+05	1.09E+05	3.61E+04	2.22E+05	1.16E+05	4.00E+04

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

Table 5. Estimates of CCN number emissions shown in volume emission equivalent (cc yr^{-1}) in fixed 1000 m boundary layer. CCN in size ranges 50–750 nm; 100–750 nm and 200–750 nm are shown using sector-specified emission rates. The results are based on $\text{PM}_{2.5}$ inventories from EMEP. Years 1996 and 1997 are extrapolated from year 2000 emissions using German official $\text{PM}_{2.5}$ emission trends.

	50–750 nm	100–750 nm	200–750 nm
1996*	1.95E+04	9.18E+03	4.05E+03
1997*	1.94E+04	9.09E+03	4.01E+03
2003	1.41E+04	6.75E+03	3.05E+03
2004	1.38E+04	6.49E+03	2.86E+03
2005	1.01E+04	4.55E+03	1.83E+03

* Estimated from national $\text{PM}_{2.5}$ emission levels

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

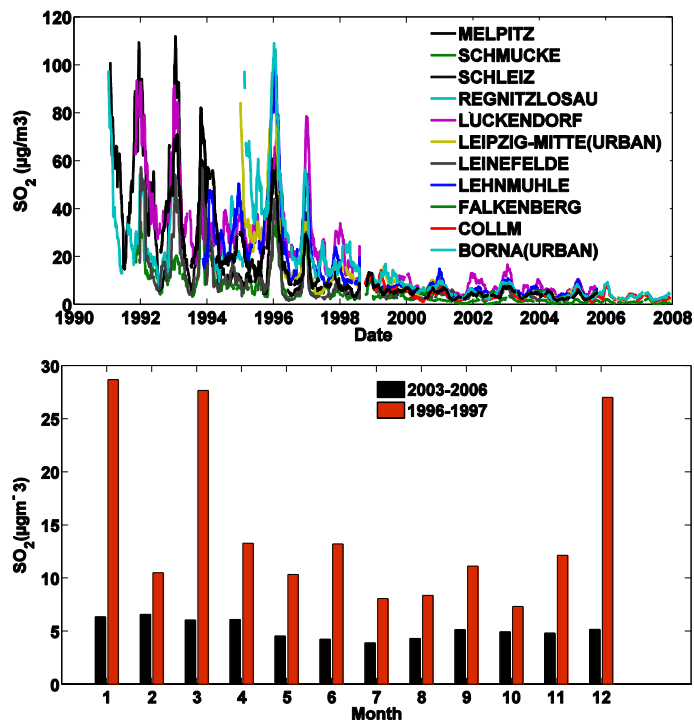


Fig. 1. (a) Measured SO₂ concentrations at Melpitz (black solid line) and some regional stations in the Leipzig area. The series are 60 day floating averages of daily average values between 10:00 and 14:00 h. The winter peaks in 1995/1996 and in 1996/1997 are clearly regional within a radius of 200 km, since they occur at all sites due to similar meteorological conditions. There is no sign that the Melpitz values are not representative for the regional SO₂ background. Monthly average SO₂ concentrations (μgm⁻³) for Melpitz in years 2003–2006 (black) and years 1996–1997 (red).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

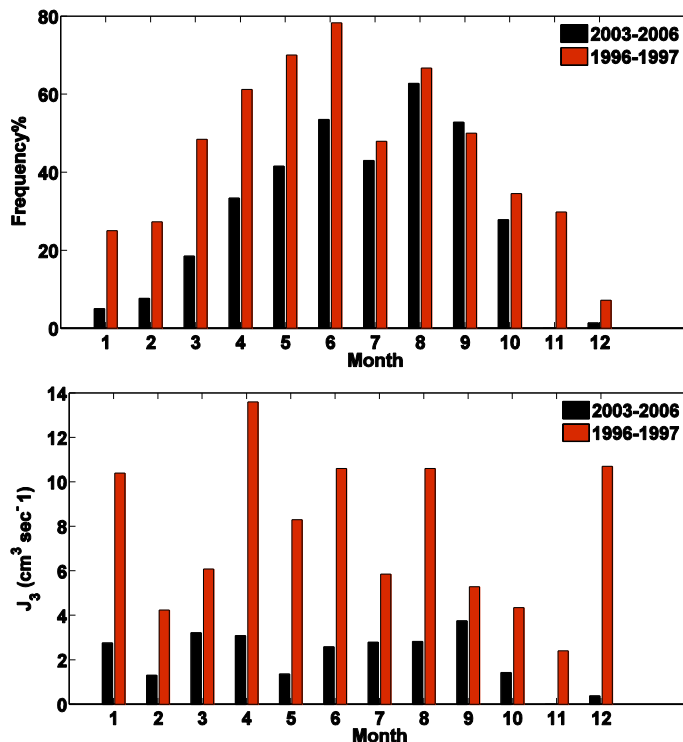


Fig. 2. Monthly average (a) frequency of new particle formation events and (b) the particle formation rate of 3 nm-particles (J_3) in $\text{cm}^3 \text{s}^{-1}$ for the particle formation events in Melpitz in years 2003–2006 (black) and years 1996–1997 (red). In 2003–2006, no nucleation was observed in November, and only a few events in December months.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

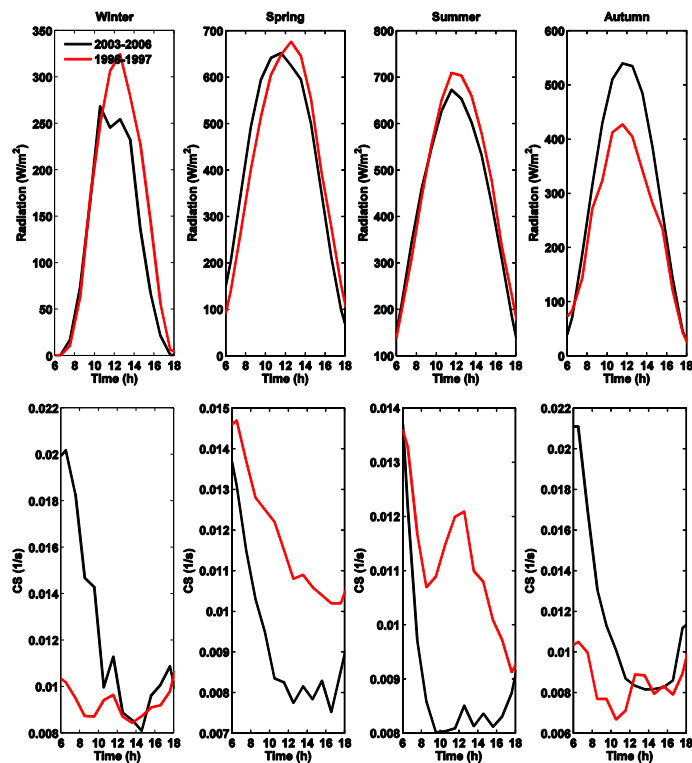


Fig. 3. (a) Global Solar Radiation “SR” (W/m^2) and (b) Condensation Sink “CS” ($1/\text{s}$) in different seasons for Melpitz 2003–2006 (black) and 1996–1997 (red).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

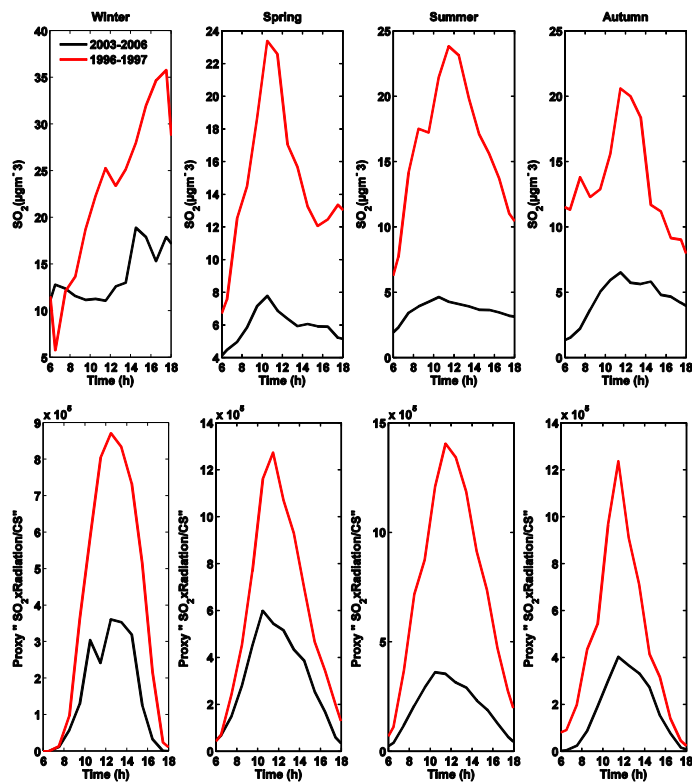


Fig. 4. (a) SO₂ concentration (μg m⁻³) and (b) sulfuric acid proxy (product of SO₂ concentration and global radiation divided by condensation sink) in different seasons for Melpitz 2003–2006 (black) and 1996–1997 (red).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

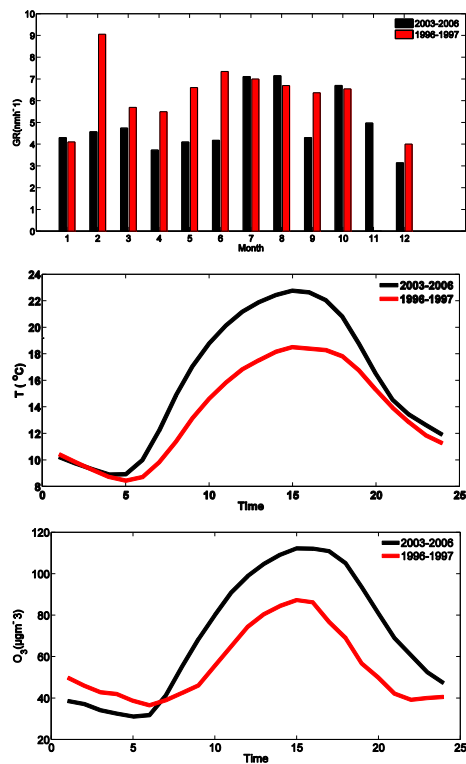


Fig. 5. (a) Growth Rate GR (nm h^{-1}) during particle formation bursts (b) Temperature T ($^{\circ}\text{C}$) and (c) O_3 concentration ($\mu\text{g m}^{-3}$) at Melpitz in 2003–2006 (black) and 1996–1997 (red).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

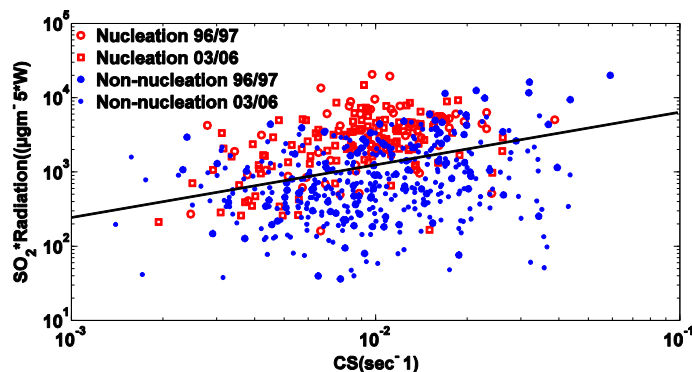


Fig. 6. The product of $[\text{SO}_2]$ and solar radiation vs. condensation sink (CS) for particle formation events (red) and non-nucleation days (blue). In case of formation events, the parameters were calculated at time when the maximum concentration of new particles formed by nucleation were reached, in case of non-events at noon (12:00 LT). The separation line determined by discriminant analysis is given by $\log_{10}([\text{SO}_2] \cdot [\text{Radiation}]) = 4.52 + 0.709 \log_{10}(\text{CS})$.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

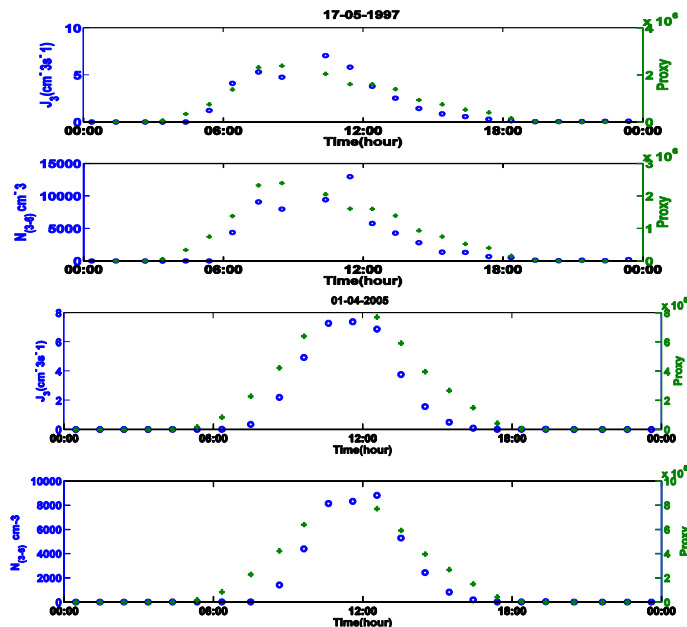


Fig. 7. Upper panels: The hourly averaged 3 nm particle formation rates (blue) versus the sulphuric acid proxy (green). Lower panel: The number concentration of 3–6 nm particles (blue) and the sulphuric acid proxy (green) on typical nucleation event days (17 May 1997 and 1 April 2005) in Melpitz for old data period and for new data period respectively. The proxy values have been shifted to the right in order to account for the time delay it takes for freshly nucleated particles to grow from 1 to 3 nm.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Changes in the production rate of secondary aerosol particles

A. Hamed et al.

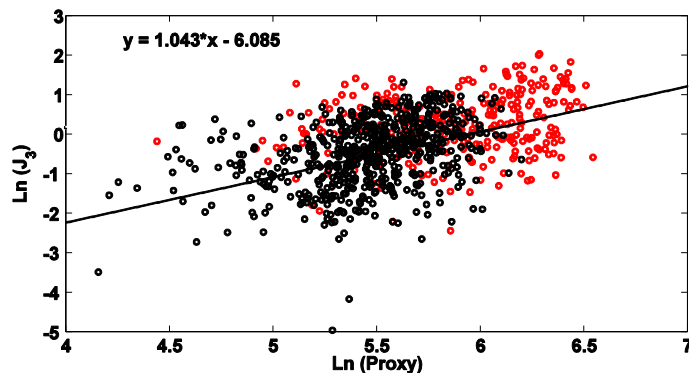


Fig. 8. The logarithm of 3 nm nucleation rate (hourly averages from strong nucleation event days between 6 a.m.–6 p.m.) versus logarithm of the sulphuric acid proxy. Melpitz 1996–1997 nucleation events (red) and (black) for Melpitz 2003–2006.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)