Atmos. Chem. Phys., 13, 5523–5532, 2013
www.atmos-chem-phys.net/13/5523/2013/
doi:10.5194/acp-13-5523-2013

Atmospheric Chemistry and Physics Open Access

Multiple daytime nucleation events in semi-clean savannah and industrial environments in South Africa: analysis based on observations

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Received: 19 June 2012 – Published in Atmos. Chem. Phys. Discuss.: 2 October 2012
Revised: 18 April 2013 – Accepted: 29 April 2013 – Published: 6 June 2013

Abstract. Recent studies have shown very high frequencies of atmospheric new particle formation in different environments in South Africa. Our aim here was to investigate the causes for two or three consecutive daytime nucleation events, followed by subsequent particle growth during the same day. We analysed 108 and 31 such days observed in a polluted industrial and moderately polluted rural environments, respectively, in South Africa. The analysis was based on two years of measurements at each site. After rejecting the days having notable changes in the air mass origin or local wind direction, i.e. two major reasons for observed multiple nucleation events, we were able to investigate other factors causing this phenomenon. Clouds were present during, or in between most of the analysed multiple particle formation events. Therefore, some of these events may have been single events, interrupted somehow by the presence of clouds. From further analysis, we propose that the first nucleation and growth event of the day was often associated with the mixing of a residual air layer rich in SO_2 (oxidized to sulphuric acid) into the shallow surface-coupled layer. The second nucleation and growth event of the day usually started before midday and was sometimes associated with renewed SO_2 emissions from industrial origin. However, it was also evident that vapours other than sulphuric acid were required for the particle growth during both events. This was especially the case when two simultaneously growing particle modes were observed. Based on our analysis, we conclude that the relative contributions of estimated H_2SO_4 and other vapours on the first and second nucleation and growth events of the day varied from day to day, depending on anthropogenic and natural emissions, as well as atmospheric conditions.

1 Introduction

Atmospheric aerosol particles have drawn considerable attention due to their health and climatic impacts (ACIA, 2005; IPCC, 2007). Formation of new aerosol particles via nucleation and their subsequent growth to larger sizes have been observed in a vast variety of environments, ranging from clean arctic air to heavily polluted megacities (Kulmala et al., 2004; Hirsikko et al., 2011). Atmospheric aerosol particle formation contributes to cloud condensation nuclei concentrations in the global atmosphere (e.g. Merikanto et al., 2009; Pierce and Adams, 2009) and therefore influences the indirect radiative effects of aerosols (Kazil et al., 2010; Makkonen et al., 2012).

Although scientific understanding on atmospheric aerosol particle formation has increased substantially during the last few years (Kerminen et al., 2010), significant uncertainties related to the factors driving or controlling the spatial and temporal variability of this process remain. The vast majority of nucleation events have been observed to take place during daytime (Kulmala and Kerminen, 2008), suggesting the central role of photochemical reactions and possible assistance by turbulent mixing in the atmosphere (Janssen et al., 2012). Systematic investigation of this topic has, however, been hampered by (i) the possibility of having more than one active nucleation mechanism in the atmosphere, (ii) the apparent and nonlinear participation of several different vapours in the nucleation process (Berndt et al., 2010; Paasonen et al., 2010; Zhang, 2010; Metzger et al., 2010; Riccobono et al., 2012; Bzdek et al., 2012), and (iii) the coupling of both nucleation and growth with meteorological conditions and the presence of pre-existing larger particles (Boulon et al., 2011; Kuang et al., 2010; Wu et al., 2011).

In this paper, we investigate atmospheric nucleation by analysing cases with multiple nucleation events during sunlight hours on the same day. We base our analysis on in situ observations combined with ancillary modelled information on the mixing layer height and H_2SO_4 concentration. While the presence of multi-event days have been reported before (Suni et al., 2008; Svenningsson et al., 2008; Manninen et al., 2010; Hirsikko et al., 2012), this phenomenon has not been systematically investigated. In addition, particle formation in temporally separated events can grow simultaneously, as will be shown and analysed in this paper. We base our analysis on continuous measurements made at a rural savannah site (Laakso et al., 2008; Vakkari et al., 2011), and at a polluted site surrounded by formal and informal settlements, as well as mining and metallurgical industries in South Africa (Hirsikko et al., 2012). From these analyses we suggest a possible mechanistic explanation for our observations.

2 Measurements and methods

Aerosol particle size distributions together with supplementary meteorological parameters and trace gas concentrations were monitored at Botsalano (latitude: 25.54° S, longitude: 25.75° E, 1400 m a.s.l.) and at Marikana in South Africa (latitude: 25° 41′ 54.51″ S, longitude: 27° 28′ 50.05″ E, 1170 m a.s.l.) during July 2006–February 2008 and February 2008–May 2010, respectively (Laakso et al., 2008; Vakkari et al., 2011; Hirsikko et al., 2012; Venter et al., 2012). Botsalano is a background site in a semi-clean savannah environment influenced by industrial and urban emissions. The measurement site at Marikana was in the middle of the relatively densely populated and heavily industrialized Bushveld Igneous Complex, from where the majority of the world's platinum group metals and chromium are produced.

The measurement instruments, data processing and the data quality assurance have been discussed by Hirsikko et al. (2012), Venter et al. (2012), Vakkari et al. (2011) and Laakso et al. (2008), therefore we only give a brief introduction here. Aerosol particle size distributions were measured with a differential mobility particle sizer (DMPS, Winklmayer et al., 1991; Mertes, 1995; Jokinen and Mäkelä, 1997) and charged particle size distributions with an air ion spectrometer (AIS, Mirme et al., 2007) in the diameter ranges 12–840 nm and 0.8–42 nm, respectively. Various instruments were deployed for monitoring meteorological parameters (e.g. wind speed and direction, global radiation) and trace gases (e.g. sulphur dioxide).

The classification of particle formation events was based on the classical method to identify growing modes of freshly nucleated particles (Dal Maso et al., 2005; Hirsikko et al., 2007). Our focus was to investigate the particle formation and initial growth, so the analysis was based primarily on ion size distributions. DMPS data were used mainly as an ancillary tool for following the further particle growth.

The condensation sink (CS), which inhibits nucleation and growth of freshly nucleated particles, was calculated according the formula presented by Dal Maso et al. (2005) and references therein. Based on the measured sulphur dioxide (SO_2) concentrations, global radiation and values of CS, we calculated a proxy for the temporal evolution of the sulphuric acid concentration according to the procedure derived by Petäjä et al. (2009, Eq. 4 therein). However, the absolute proxy concentrations have to be considered as indicative concentrations only, since the method has not been tested against measured sulphuric acid data from environments comparable to Botsalano or Marikana.

Growth rates (GR) of newly formed particles were estimated from AIS spectra with the maximum concentration method, in which the timing of maximum concentration in each size fraction is followed (Hirsikko et al., 2005). The slope of the linear fit to time-size pares is the desired growth rate. The timing of growth in our data analysis was defined as $t_{GR} = (t_3 + t_{10})/2$, i.e. the average time of the first and last data points when particles are growing from 3 nm to 10 nm. This GR analysis method fails if the growing mode has a temporally discontinuous shape, which reduces the number of days when GR is obtainable. The H_2SO_4 proxy concentration during the growth was calculated by averaging data over 40 min centred at t_{GR}. The contribution of H_2SO_4 to the particle growth was calculated by assuming that a vapour concentration of 1.5×10^7 molecules cm^{-3} is required for 3–10 nm particles to grow at the rate of 1 nm h^{-1} (Nieminen et al., 2010).

The stability of the nocturnal surface layer was investigated via a potential temperature gradient $\partial\theta/\partial z$, where θ is the potential temperature and z is the height from ground. The ambient temperature was measured at 7 m height and we assumed an adiabatic lapse rate for cooling. Positive values of $\partial\theta/\partial z$ indicate a stable, stratified boundary layer, while

negative values indicate an unstable, vertically mixed boundary layer.

The air mass histories for the nucleation event periods were calculated by using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, version 4.8) model of the Air Resources Laboratory at the National Oceanic and Atmospheric Administration (Draxler and Hess, 2004; Air Resources Laboratory, 2011). Estimated values of the boundary layer height (i.e. mixing layer depth) were obtained from the MARS database of the European Centre for Medium-Range Weather Forecasts (ECMWF) (Beljaar et al., 2001; www.ecmwf.int/research/ifsdocs/CY37r2/index.html). The ECMWF runs their Ensemble Prediction System model twice a day, i.e. at midday and midnight (UTC). The forecasts of the mixing layer show expected temporal evolution. The accuracy of these forecasts in the case of shallow nocturnal mixing layer is unknown at our measurement sites (Korhonen et al., 2013). The temporal resolution of the data was three hours. The surroundings of the station in the $1^\circ \times 1^\circ$ square were represented by 0.2° grids. In addition to temporal evolution of global radiation intensity, cloudiness over the measurement area was analysed using geostationary satellite images from MSG/SEVIRI, obtained at 30 min time resolution from Cloud-Aerosol-Water-Radiation Interactions (ICARE) online database (http://www.icare.univ-lille1.fr).

3 Results

3.1 Multiple nucleation and growth events at Marikana

From the 559 days on which new particle formation took place (Hirsikko et al., 2012), 108 days with two or three nucleation and growth events were selected. During some of these days, we were able to follow the growth of nucleated particles up to several tens of nanometers during both events of the day, which suggests that on such days this phenomenon was able to affect cloud condensation nuclei production (Kerminen et al., 2012).

From the 108 multiple event days, we rejected 16 days from the analysis because of too large gaps in the ancillary data. Considering the accuracy of modelled trajectories (Stohl, 1998; Riddle et al., 2006), we selected 23 days for which the origin and path of air masses were similar for the two successive nucleation events and no major changes (60° or more) in the local wind direction occurred between the events. The low fraction of these days suggests that changing air masses may have been the main reason for the observed multiple daytime particle formation events. Consequently, it supports previous observations that the regional area around Marikana possesses a high capability for producing nucleating and condensing vapours of both natural and anthropogenic origin (Hirsikko et al., 2012).

The abovementioned selections ensured the possibility to investigate temporal changes in various quantities specific for air masses of a certain origin and transport path. Although the selection criteria seem harsh, the remaining days represent the most optimal situations, from which mechanistic information regarding multiple events can be obtained. On the subset of 23 days, concentrations of SO_2 and sulphuric acid and the value of CS varied significantly between two successive nucleation and growth events (Figs. 1–2, Figs. S1, S3, S5, S7). The first event on each day was observed after the sunrise and it was always associated with a growing mixing layer (except on one day, when nucleation events were observed in the afternoon, after a rainy morning), increasing concentrations of SO_2 and H_2SO_4 (proxy), and sometimes also with increasing values of CS. After a night with a stably stratified boundary layer (Figs. S1, S3, S5), the peak values of the CS and SO_2 concentration in the morning are likely to originate from, and thus indicate, downward mixing of a nighttime residual layer rich in industrial emissions from stacks with the heights of 50 to 130 m, as suggested by previous observations (Hirsikko et al., 2012; Venter et al., 2012). The nocturnal boundary layer was stable during two thirds of the analysed days (see exception in Fig. S7).

The second nucleation and growth event of the day was sometimes associated with a decreasing value of CS and/or renewed higher sulphuric acid proxy concentration (Fig. 2, Figs. S.1 and S3). However, many of these cases occurred with decreasing or even smaller SO_2 and H_2SO_4 concentrations compared with the first event of the day (Figs. 1 and 2). The air mass origin varied substantially between the different days (Fig. 3, Figs. S2, S4, S6, S8). However, all trajectories were indicative of the circulation of air masses over the heavily industrialised area.

The analysis of the particle growth rate in the 3–10 nm size interval and growth due to H_2SO_4 condensation indicates clearly that vapours other than H_2SO_4 are required to maintain the observed growth (Fig. 4). From Fig. 4 it is apparent that, on three out of four analysed days from Marikana, H_2SO_4 had a larger contribution to the growth of the first particle formation event of the day. In some cases, particles formed in the first particle formation event of the day continued to grow during the second new particle formation event (Fig. 1, S1, S5, S7), increasing the required amount of nucleating and condensing vapours during the second event. Consequently, it is apparent that during simultaneously growing particle modes, especially when the H_2SO_4 concentration and the contribution to growth decreases (see example on 21 November 2009 in Figs. 1 and 4), additional vapours were evidently required to maintain particle growth of the first event of the day and to initiate another new event of particle formation and growth.

Clouds reduce photochemical reaction rates. Therefore, the effect of clouds was investigated by further selecting the days when clouds were not observed around the end of the first nucleation event of the day. We found that clouds were present during and between the successive events on 20 of the days discussed above. As can be seen from our example

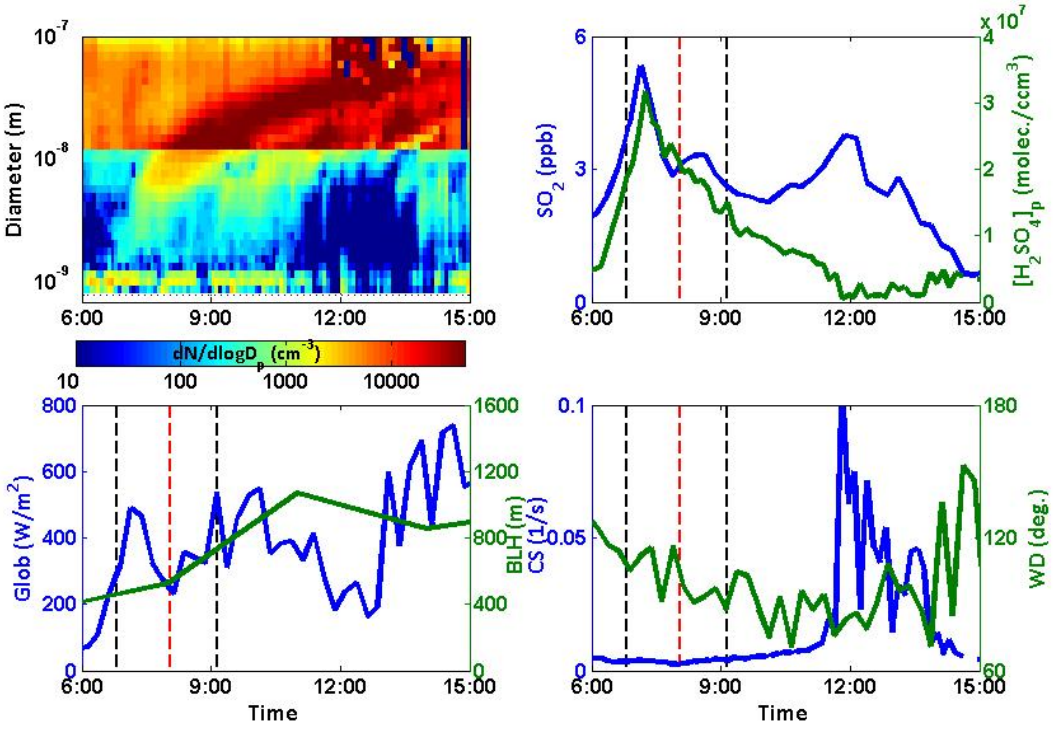

Fig. 1. Example of two consecutive nucleation and growth events (top left panel) at Marikana on 21 November 2009. The concentration of SO_2 and H_2SO_4-proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates the start of the second event. Data for $\partial\theta/\partial z$ was unavailable for this day.

cases (Fig. 1 and Figs. S1, S3, S5, S7), the H_2SO_4 concentration followed the temporal evolution of the SO_2 concentration and the particle number concentration of the first growing mode continued to increase despite the presence of clouds. We conclude that the presence and dissipation of clouds probably affected aerosol dynamics, but there are likely other reasons for ending and starting the new particle formation.

During the three cloud-free days, the first nucleation and growth event of the day took place simultaneously with the increasing SO_2 and H_2SO_4 concentrations when the surface-coupled boundary layer was already mixed up to several hundreds of meters. The first event stopped when the H_2SO_4 concentration was still increasing on two of the three days. As an example, on 28 March 2008, the sulphuric acid concentration was decreasing when the second new nucleation and growth event of the day started (compare with Fig. 1), which suggests that some other vapours were required to enhance and sustain the nucleation and growth. Similar observations were made on 24 September 2008. However, on 23 November 2008, the second nucleation and growth event of the day was observed when a new increase in sulphuric acid concentration occurred, even though the peak H_2SO_4 concentration remained lower compared with the first event.

The third nucleation and growth event of the day, if observed, took place late in the afternoon and was always associated with air masses different from those arriving at the site during the morning. These episodes occurred during daylight and freshly formed particles did not always form a well-defined growing mode.

The above discussion leads to the question of whether the first nucleation event began in the surface-coupled or decoupled boundary layer (e.g. Stratmann et al., 2003; Laakso et al., 2007; Siebert et al., 2007). Thus, it is possible that our observations are not fully representative of conditions leading to the first nucleation event but rather sustaining the particle growth. The qualitative observations of the increasing and decreasing concentrations of SO_2 and subsequently produced H_2SO_4, together with scatter plots of medians of these parameters Fig. 2 and Fig. 4, lead us to conclude that sulphuric acid was sometimes more important for particle growth during the first event of the day, while on other days H_2SO_4 had a larger contribution during the second event of the day. However, some other vapours were needed to sustain the particle growth of the first particle formation event of the day and initiate and sustain the second event of the day. Temporal behaviour of emission rates of biogenic organic vapours (e.g. Harley et al, 2003; Greenberg et al., 2003) suggests that their oxidation products are likely to participate in the particle

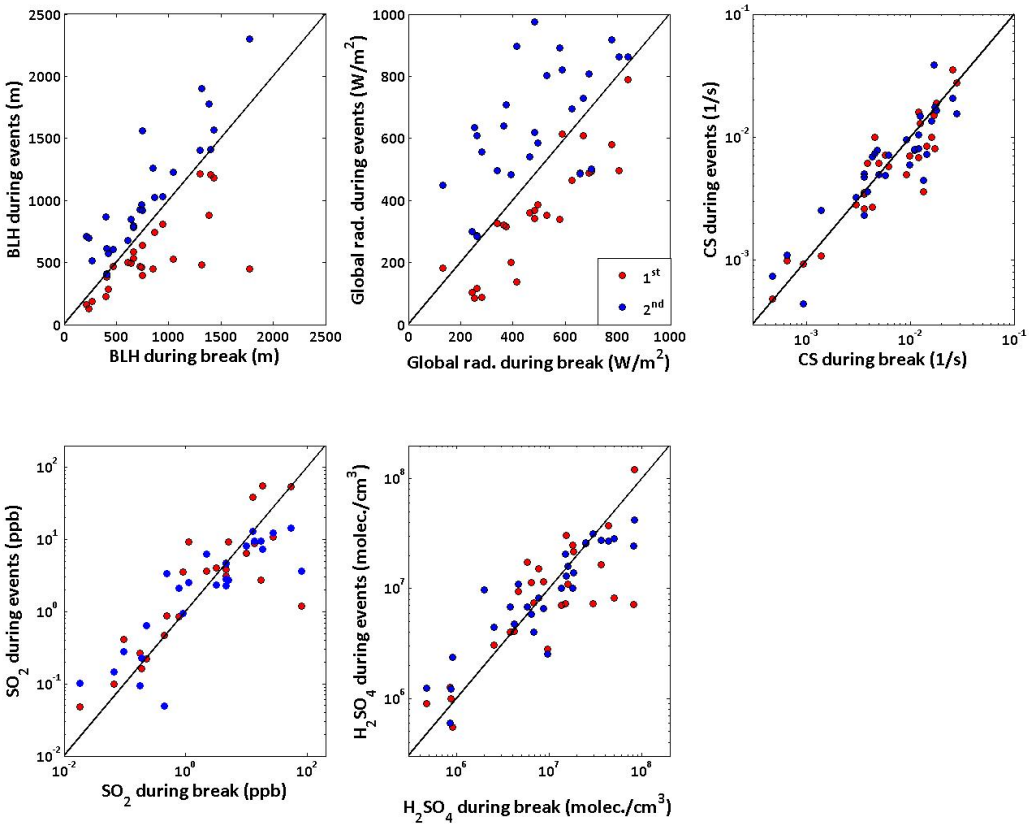

Fig. 2. Median values for the mixing layer height (BLH), global radiation, SO_2 and H_2SO_4 proxy concentrations and CS during the first (red markers) and the second (blue markers) nucleation and growth event of the day versus the corresponding parameters during the break between the events. Days from Marikana and Botsalano, when air masses' origin of successive growing modes had the same origin, were included here.

formation and growth. This was the case, especially when two simultaneously growing modes were observed. A decreasing value of CS between nucleation events results from the increasing mixing volume of the boundary layer.

3.2 Multiple nucleation and growth events at Botsalano

Compared with Marikana, the frequency of atmospheric new particle formation was somewhat lower in Botsalano. New particle formation was observed on 349 days, and multiple particle formation and growth events were detected on 31 days. However, on 21 of these days at least one of the two events did not show all the features typical of a proper nucleation and growth event (Dal Maso et al., 2005). Therefore, we analysed eight days that fulfilled the requirements of non-changing origin and path of air masses, as discussed in Sect. 3.1. For these days, the air masses arrived mainly from the south and southwest (Fig. 5, Figs. S9–16), which has previously been associated with moderate formation and growth rates, as well as limited influences from anthropogenic sources (Vakkari et al., 2011). Information about the nocturnal atmospheric stability (i.e. potential temperature gradient) was available only for 6 November 2007, since the temperature gradient measurements were started on 15 October 2007.

During the first nucleation event of the day, the particle growth from nano-sizes began immediately after the sunrise when also an increase in the H_2SO_4 concentration was evident (Fig. 6, Figs. S9, S11, S13, S15). However, at this site the growing mode was not observable after 5–12 nm on many of the analysed days (see an exception in Fig. 6). After the analysis of air mass back-trajectories, local wind direction, temporal evolution of particle size distributions and H_2SO_4 proxy concentration, we conclude that the decay of the first event at small sizes was due to the lack of condensing vapours (evidently also other than H_2SO_4) and simultaneous coagulation with larger particles, rather than due to a change in measured air mass (Fig. S9–S12). However, the first growing mode of the day suddenly disappeared in two of the cases (Figs. S13 and S15). This feature could be due to an air mass change, even though this was not supported by any of the studied quantities.

During the second nucleation event of the day, the particle growth was also observed from the small ion sizes when the boundary layer was already growing, and the growth

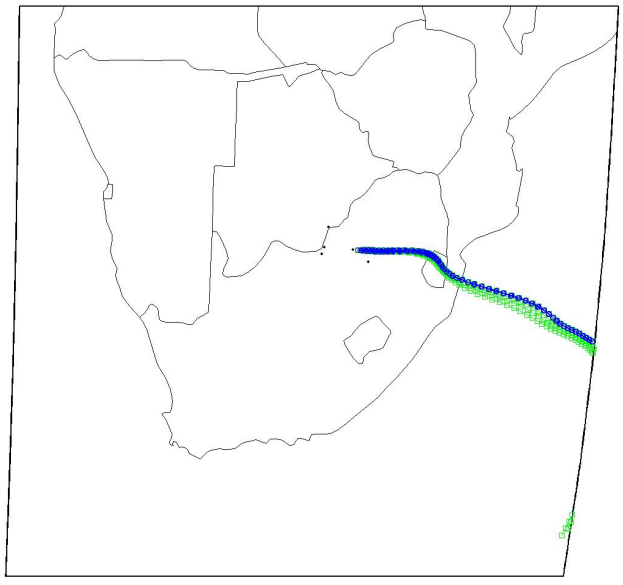

Fig. 3. 96 h air mass back-trajectories during the first (green) and second (blue) nucleation and growth event of the day on 21 November 2009.

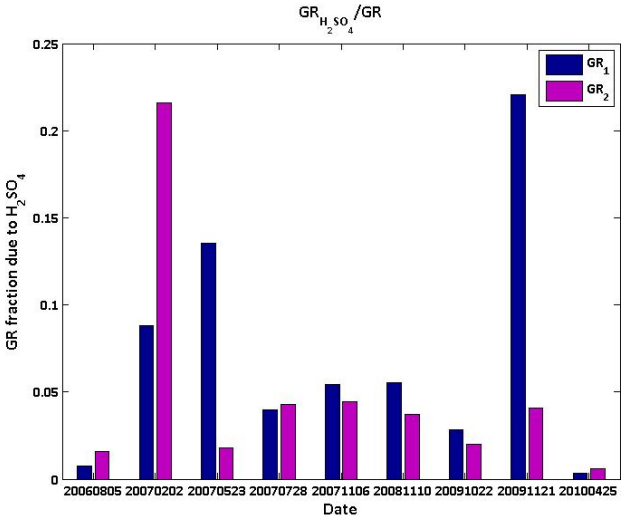

Fig. 4. Growth during the first (GR_1) and second (GR_2) nucleation and growth event of the day due to H_2SO_4 condensation only. The GR was estimated for the ion population in size range 3–10 nm. The H_2SO_4 concentration was averaged over 40 min centred at about the timing of the growth rate. Shown results are from Botsalano during 5 August 2006–6 November 2007 and from Marikana during 10 November 2008–25 April 2010.

could be followed up to sizes >20 nm (Fig. 6, Figs. S9, S11, S13, S15). This second event was typically associated with a renewed and higher concentration peak of H_2SO_4 (Fig. 6, Figs. S9, S11, S15). However, sometimes the second event was observed when the H_2SO_4 concentration was decreasing strongly (Fig. S13), which suggests contribution from

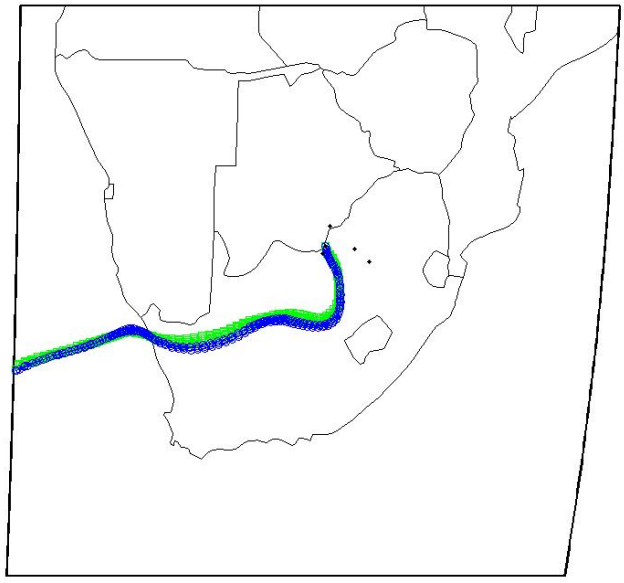

Fig. 5. 96 h air mass back-trajectories during the first (green) and second (blue) nucleation and growth event of the day on 6 November 2007.

vapours other than H_2SO_4 to either nucleation or initial particle growth. The observations further indicate that clouds probably had affected the photochemistry responsible for the observed particle formation on three of the multiple event days.

The growth rate analysis based on five days showed that sulphuric acid probably had a larger contribution to the particle growth during the first event of the day on 23 May and 6 November 2007, when also the H_2SO_4 concentration was higher than during the second event of the day (Fig. 4). The example in Fig. 6 shows two simultaneously growing particle modes on 6 November 2007. By keeping in mind that the effect of H_2SO_4 on GR was estimated from the maximum contribution by H_2SO_4 and that there were two simultaneously growing particle populations, it is apparent that condensing vapours other than H_2SO_4 were required.

In view of the above, it is clear that sulphuric acid was not alone able to control the existence of multiple new particle formation events. Furthermore, we conclude that there were days when the contribution of sulphuric acid seemed to be more important during the first event of the day, while on other days quite the opposite was observed.

4 Summary and conclusions

We analysed 139 days having two or three consecutive nucleation and growth events during one day. The observations were made in a residential and industrial environment (Marikana), and at a rural savannah site (Botsalano) in South Africa during four years (Vakkari et al., 2011; Hirsikko et

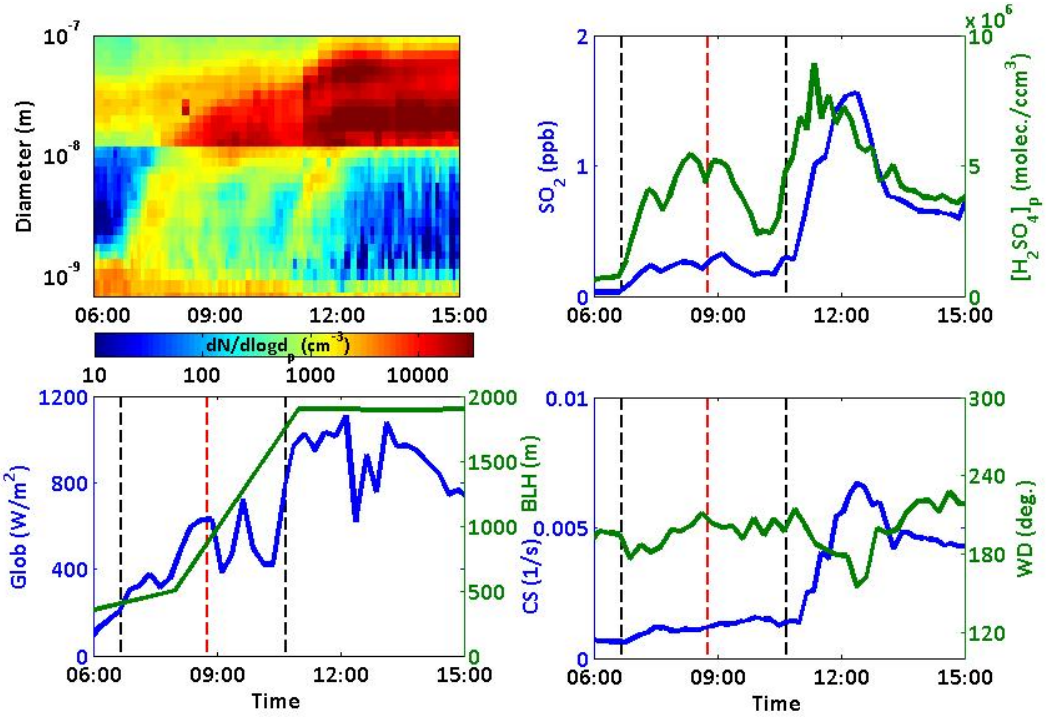

Fig. 6. Example of two consecutive nucleation and growth events (top left panel) at Botsalano on 6 November 2007. The concentration of SO_2 and H_2SO_4-proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates the start of the second event. Nocturnal $\partial\theta/\partial z > 0$.

al., 2012). In Marikana, the great majority of the analysed days were associated with changing air masses, making it impossible to track down whether the existence of multiple events during those days were due to an air mass change or some other factor. We analysed 31 event days in more detail, of which 8 were from Botsalano, when no clear change in air masses was detected. The major fraction of analysed days (20 at Marikana and 3 at Botsalano) was affected by the presence of clouds, yet clouds were clearly not the only factor affecting the occurrence of multiple nucleation and growth events during the same day.

The first nucleation event of the day occurred typically after the sunrise when the boundary layer was growing and mixed with a residual layer(s) having high concentrations of SO_2 (oxidizing to H_2SO_4), and sometimes a higher loading of aerosol particles. After the dilution and enhanced consumption of condensable vapours, the formation of new particles stopped. The fast growth of nucleated particles was observed to continue at Marikana but often to be suppressed at Botsalano. The second nucleation and growth event of the day took place before midday. Sulphuric acid, while probably being a major player in initiating the observed new particle formation events, could explain only a small fraction of the subsequent particle growth. The role of vapours other than H_2SO_4 was emphasized during the second new particle formation events, especially when two particle modes were growing simultaneously. Other studies (e.g. Paasonen et al., 2010; Riipinen et al., 2011) have shown that low-volatility organic vapours formed in the atmosphere from biogenic volatile precursors can have substantial effects on both nucleation and growth of nucleated aerosols. In South Africa, such vapours are likely to be present due to active emissions from the local biosphere (Laakso et al., 2008).

We had limited observation capabilities for determining the chemical composition of aerosol particles or gas phase at our measurement sites. Adding devises capable of measuring at least the aerosol chemical composition, H_2SO_4 and organic species concentrations would be beneficial. Online-observations of aerosol chemical composition were later carried out at Welgegund, approximately 100 km south of Marikana, where the measurement trailer was permanently located in May 2010 (Tiitta et al., 2013). As a future perspective, we also suggest that boundary layer dynamics and structure should be measured as such information might provide additional mechanistic insight.

As was demonstrated in the Sect. 3, multiple particle formation events do not always have climatic relevance in terms of cloud condensation nuclei production at Botsalano, since most of the first events of the day were suppressed at small size (<12 nm). At Marikana the growth of at least one of the successive particle formation events could be followed to sizes >20 nm (e.g. Fig. 1, S3, S5). We cannot exclude the

possibility that some of the analysed multiple events were actually not separate phenomena, but rather a single event interfered by clouds or some other mechanism discussed above. We consider the presented explanations for the formation of multiple nucleation events, when air mass was not changing, to be specific for the region. This is due to the fact that these events are likely depended on the emissions of both anthropogenic and natural emissions, atmospheric conditions such as its oxidation capability, boundary layer dynamics, the ambient temperature and relative humidity.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/13/5523/2013/acp-13-5523-2013-supplement.pdf.

Acknowledgements. The support from Tshepo Lenake, Rustenburg Municipality, the Finnish Academy (project numbers: 117505 and 132640) and the North-West University are kindly acknowledged. The authors would like to acknowledge referees for reviewing and helping to improve the manuscript.

Edited by: U. Baltensperger

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