Reply for referee Dr. Pierce,

Authors: We would like to thank Dr. Pierce for his valuable comments to improve our manuscript. In the following, we reply in detail and describe how the manuscript is revised. Please find copy of the revised manuscript and new supplement material at the end of this this response document.

Our aim was to investigate reasons behind the observations of two or more nucleation and subsequent growth events in one day during daylight hours measured in South-Africa. Our analysis had to be based on available in-situ data. In addition, we have used satellite data for cloud cover analysis and modeled data for air mass back-trajectories and mixing layer depth. Error sources and data processing/cleaning of our data have been discussed in detail by Hirsikko et al. (2012) and Laakso et al. (2008). The modeled data possess also uncertainties. Thus, we have to bear in mind that estimates of mixing layer depth evolution or air mass back-trajectories are not absolute and can only be considered indicative.

Addition of some measurement devises (e.g. radio sounding of gases and particle concentration, vertical air motion, profiles of horizontal wind, chemical analysis of particulate and gas phases) would evidently have provided strong support for analysis presented here. Unfortunately, such data was not available. However, in future, our aim is to carry out campaign based measurements with a Doppler lidar in order to characterize and investigate the real wind field and turbulent nature of boundary layer around measurement site. Preliminary analysis of recent Vaisala ceilometer observations have shown strong stratification of boundary layer, where layers of increased aerosol content can be distinguished.

Referee: The authors claim that organics are likely a primary driver for the 2nd nucleation events since none of the measured factors seem to clearly indicate their importance in initiating these 2nd nucleation events. Organics have indeed been found to be important in nucleation and the early growth of freshly nucleated particles, but its not obvious from what is presented that organics are playing a stronger role in the 2nd events compared to the 1st events. Given the data and instruments presented in this paper, I think it should be relatively straightforward to determine if concentrations of condensable low volatility organics are higher during the 2nd event than the 1st.

(1) The authors could determine the maximum growth rate possible from H2SO4 alone and compare this to the growth rates during the 1st and 2nd events. If the excess growth rate (above the maximum H2SO4 growth rate) for the 2nd events are clearly higher than the 1^{st} events, then this is clear evidence for the increased importance of organics during the 2nd event.

(2) The authors could calculate the maximum possible increase in the total aerosol volume with time due to H2SO4 alone and compare this to the actual change in total aerosol volume (integrated over the DMPS size distribution and corrected by the change in BL height). As with the growth rates, you can see if the excess dV/dt is higher during the 2nd events than the 1st event. Due to the need for correcting for BL-height changes, using growth rates might be more straightforward than dV/dt. If the above evidence for the role of organics in the 2nd nucleation events can be shown, the paper will be significantly stronger and will not need to rely on speculation on the drivers for the 2nd nucleation events.

Authors: We agree with this comment. Furthermore, we cannot directly show which fraction of growth or particle mass is due to organic compounds, since there are other vapours contributing on particle growth as well. However, temporal evolution of biogenic organic emission rate suggests that availability of variety of organic vapors would be larger during second event of the day. We have done following analysis and text revision based on proposed analysis.

(1) We have prepared Fig. 4 (see full revised manuscript at the end of this response) and made following text editions.

Abstract

'' As a result of our analysis, we propose that the first nucleation and growth event of the day was often associated with mixing of a residual layer rich with SO_2, oxidized to sulphuric acid, into the shallow surface coupled layer. However, it was evident that also other vapours were required to maintain particle growth. The second event of the day started usually before midday and was sometimes associated with SO_2 emissions from the industrial origin. However, our analysis indicates that also vapours other than sulphuric acid, most likely oxidation products of biogenic organic vapours, were needed to initiate and sustain the second event of the day. This was especially the case when two simultaneously growing modes were observed. Based on our analysis we conclude that relative contribution of H_2SO_4 and other vapours on the first and second particle formation events of the day varies from day to day, and is also dependent on other atmospheric and dynamical conditions.''

Methods: We included description how we calculated particle growth rate. In addition, we have included description how we estimated contribution of H_2SO_4 to particle growth.

Sect. 3.1.

'' The analysis of the particle growth rate in 3-10 nm size interval and growth due to H_2SO_4 condensation indicate 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 larger contribution to the growth of 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 H_2SO_4 concentration and contribution to growth decreases (see example on 21st November 2009 in Figs. 1 and 4), additional vapours are evidently required to maintain particle growth of the first event of the day and to initiate another new particle formation event.''

'' The above discussion leads to the question of whether the first nucleation event began in the boundary layer coupled with or was decoupled from the surface (e.g. Stratmann et al., 2003; Laakso et al., 2007; Siebert et al., 2007). 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. 3) and Fig. 4 lead us to conclude that sulphuric acid was sometimes more important during the first event of the day, while on other days H_2SO_4 had 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 suggest that their oxidation products are likely to participate in the particle formation and growth. This was especially the case when two simultaneously growing modes were observed.‘’

Sect. 3.2

‘’ 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 second event of the day (Fig. 4). The example in Fig. 6 shows two simultaneously growing particle modes on 6 November 2007, while from Fig. 4. we can see that due to faster growth H_2SO_4 had smaller contribution during the second event of the day. 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 addition of other vapours is 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. 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 some other days quite opposite was observed.‘’

(2) We agree that this kind of analysis would provide valuable information. However, for Botsalano site this type of analysis is not relevant because of suppression of the first event. Therefore, we propose following text edition

Sect. 3.1

‘’ 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 suggest that on such days this phenomenon was able to affect cloud condensation nuclei production (Kerminen et al., 2012).‘’

Sect. 3.2.

‘’ During the first 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, S14, 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 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 day suddenly disappeared in two of the cases (Figs. S13 and S15). This feature could be due to an air mass change, even though not supported by any of the studied quantities.‘’

Conclusions

‘’ 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 either one of the successive particle formation events could be followed to > 20 nm (e.g. Fig. 1, S3, S5).‘’

Referee: Its not clear where the "implications of the driving factors" (as mentioned in the title) are in the discussion. What are the implications of the driving factors (e.g. Would you expect multiple nucleation to be present in other locations based on locations where the timing of the driving factors might be similar? Might CCN production be different in these locations than in locations where only 1 nucleation event occurs?).

Authors: Based on referee comments we have slightly changed focus of the manuscript.

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

Thus, we do not draw as strong conclusions about driving factors, but rather describe how measured, modelled or calculated quantities vary between days. As we have written in conclusions, we consider that results are specific for the environment, which can be seen in differences between particle formation events in Marikana and Botsalano. In the latter, the first event suppresses around 5-12 nm, but particles of the second event grow to climatically relevant sizes. Whereas in Marikana, there is no clear pattern which one of the events produce large enough particles.

Referee: P26034 L11: Why are SO2 concentrations in surface layer just before sunrise so much lower than SO2 concentrations in the residual layer. Presumably the two layers had similar concentrations when they became decoupled overnight. Is this because of fast dry deposition of SO2 in the surface layer overnight, or does the presence of a nocturnal jet cause different wind directions in the surface layer and the residual layers (and thus a different air-mass history). Would you expect low-volatility organic precursors to be in higher concentrations in the surface or residual layers?

Authors: The nocturnal atmosphere over Southern Africa is often stable stratified, which can be identified by investigating potential temperature gradient. Stack height in Marikana area is 50-130 m. Therefore, emissions (i.e. SO2) from large industrial area tend to be trapped within surface decoupled boundary layer during night-time and become mixed into the surface coupled layer after increasing mixing layer depth. This pattern is pronounced at Marikana (Hirsikko et al., 2011; Venter et al., 2012).

Methods: We included description how potential temperature is obtained and what it means.

Sect. 3.1
'' 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 downward mixing of a night-time residual layer rich in industrial emissions from the stacks with the heights of 50 to 130 m, as suggested by previous observations (Hirsikko et al., 2012; Venter et al., 2012). Nocturnal boundary layer was stable during two thirds of the analysed days (see exception in Fig. S7).''

Sect. 3.2.
'' Information about the nocturnal atmospheric stability (i.e. potential temperature gradient) was available only for 6 November 2007 due to starting temperature measurements on 15 October 2007. ''

Referee: P26035 L21: The decrease in CS between nucleation events is not obvious in Figures 1 and 2.

Authors: Decrease in CS is observed only on few days as can be seen from examples in supplements and revised Fig. 3 (notice: Fig. 2 in revised manuscript).

Referee: Figure 3, P26036 L5-6 and L16-19, and P26037 L2-3: Growth of the first nucleation mode isn't suppressed, it just disappears entirely! Within the span of about 20 minutes (maybe less), the nucleation-mode dN/dlogDp changes from several 1000 cm-3 to around 100 cm-3 (more than a 10x decrease). This could not have been caused by the BL lifting (not a 10x loss at least) or by coagulational losses (the condensation sink timescale is about 1 hour according to Figure 3, so the coagulation sink timescale for _10 nm particles will be something on the order of 10 hours or more). The only reason for this fast decrease in the nucleation-mode concentration that I can think of is a switch to an airmass where the first nucleation event was not occurring. This may be a clue to the reason for the 2nd events in Botsalano. It is probably incorrect to say that the growth of the 1st nucleation event is "suppressed".

Authors: We disagree that all multiple events would have been affected by air mass change (see also supplement material). However, we agree that in the given example (former Fig. 3) the first event may have stopped due to air mass change although none of the parameters available support that. We have moved Fig. 3 to supplements and included new example with figure of air mass history and the following text revision:

Sect. 3.2

''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 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 day suddenly disappeared in two of the cases (Figs. S13 and S15). This feature could be due to an air mass change, even though not supported by any of the studied quantities.''

Referee: Figure 3: The H2SO4 concentration goes to 0 shortly after the 2nd nucleation event starts. How does this happen if SO2 and Glob are non-zero, CS does not go to infinity, and you are using the Peteja method for estimating [H2SO4]?

Authors: We have used the H_2SO_4 proxy method (Eq. 4) introduced by Petäjä et al. (2009)

$$P = \frac{[SO2] \cdot Glob}{CS},$$

where values of global radiation (Glob), sulphuric dioxide concentration (SO_2) and calculated condensation sink (CS) should be zero or larger. However, due to instrumental malfunction any of these variables may have negative, clearly erroneous, values. When going through our calculations for the ACPD version of manuscript, we noticed that H_2SO_4 proxy calculations were made with uncleaned CS (i.e. DMPS size distributions) data. After recalculation of CS and H_2SO_4, we observe

similar temporal evolution between SO_2 and $H2SO_4$, as one could expect. We have revised the Fig. 3 with recalculated CS and H_2SO_4 proxy and moved it to supplements.

Referee: P26036 L14-16: Figure 3 shows neither an increasing H2SO4 concentration (it decreases to 0 as stated in the previous point) nor a decreasing CS for the 2nd nucleation event. Though I suppose this is what you are saying in the last sentence of this paragraph.

Authors: After revising the Fig. 3 (Fig. S15), increasing trend of H_2SO_4 concentration is observed around the start of second nucleation event. The correction in H_2SO_4 calculation allows us to rewrite the sentences on p. 26036, l. 16-19: 'The second event was typically associated with at renewed and higher concentration peak of H_2SO_4 (Fig. 5, Figs. S9, S11, S15). However, there were also cases in which the H_2SO_4 concentration was decreasing strongly when the second a new particle formation event was observed, which suggests strong contribution from other vapours, preferably of biogenic origin (Fig. S13).''

Referee: P26037 L1: "back-ground" should be "background".

Authors: Typo corrected.

References

Hirsikko, A., Vakkari, V., Tiitta, P., Manninen, H.E., Gagné, S., Laakso, H., Kulmala, M., Mirme, A., Mirme, S., Mabaso, D., Beukes, J.P. and Laakso, L.: Characterisation of sub-micron particle number concentrations and formation events in the western Bushveld Igeneous Complex, South Africa, Atmos. Chem. Phys., 12, 3951-3967, doi:10.5194/acpd-12-3951-2012, 2012.

Laakso, L., Laakso, H., Aalto, P.P., Keronen, P., Nieminen, T., Pohja, T., Siivola, E., Kulmala, M., Kgabi, N., Molefe, M., Mabaso, D. Phalatse, D., Piennaar, K., and Kerminen, V.-M.: Basic characteristics of atmospheric particles, trace gases and meteorology in a relatively clean Southern African Savannah environment, Atmos. Chem. Phys., 8, 4823–4839, doi:10.5194/acp-8-4823-2008, 2008.

Petäjä, T., Mauldin III, R.L.., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M.: Sulphuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys., 9, 7435-7448, doi: 10.5194/acp-9-7435-2009, 2009.

COPY OF MANUSCRIPT

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

A. Hirsikko[1,*], V. Vakkari[2], P. Tiitta[3], J. Hatakka[1], V.-M. Kerminen[2], A.-M. Sundström[2], J.P. Beukes[4], H.E. Manninen[2], M. Kulmala[2] and L. Laakso[1,4]

[1]Finnish Meteorological Institute, Research and Development, P.O. Box 503, 00101, Finland
[2]Department of Physics, University of Helsinki, P.O. Box 64, 00014 University of Helsinki, Finland
[3]Fine Particle and Aerosol Technology Laboratory, Department of Environmental Science, University of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland
[4]School of Physical and Chemical Sciences, North-West University, Potchefstroom, South Africa

[*]Currently at: Forschungszentrum Jülich GmbH, Institut für Energie-und Klimaforschung: Troposphäre (IEK-8), Jülich, Germany.

Recent studies have shown very high nucleation day frequencies in different environments in South Africa. Our aim here was to investigate the reasons behind two or three consecutive daytime nucleation events followed by subsequent particle growth. We analysed 108 and 31 days, respectively, observed in a polluted industrial and moderately-polluted rural environment in South Africa based on two years of measurements at each site. After rejecting days having notably changing air mass origin or local wind direction, which was major reason for observations of multiple nucleation events, we were able to investigate other factors causing this phenomenon. As a result of our analysis, we propose that the first nucleation and growth event of the day was often associated with mixing of a residual layer rich with SO_2, oxidized to sulphuric acid, into the shallow surface coupled layer. However, it was evident that also other vapours were required to maintain particle growth. The second event of the day started usually before midday and was sometimes associated with SO_2 emissions from the industrial origin. However, our analysis indicates that also vapours other than sulphuric acid, most likely oxidation products of biogenic organic vapours, were needed to initiate and sustain the second event of the day. This was especially the case when two simultaneously growing modes were observed. Based on our analysis we conclude that relative contribution of H_2SO_4 and other vapours on the first and second particle formation events of the day varies from day to day, and is also dependent on other atmospheric and dynamical 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 formation contributes to cloud condensation nuclei concentrations in the global atmosphere (e.g. Merikanto et al., 2009; Pierce and Adams, 2009) and therefore influence the indirect radiative effects of aerosols (Kazil et al., 2010; Makkonen et al., 2012).

Although scientific understanding on atmospheric aerosol 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; 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 of 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. 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 in a rural savannah site (Laakso et al., 2008; Vakkari et al., 2011), and in a polluted site surrounded by formal and informal settlements, and mining and metallurgical industries in South Africa (Hirsikko et al., 2012). From these analyses we suggest possible mechanistic explanation for our observations.

2. Measurements and Methods

Aerosol particle size distributions together with supplementary meteorological parameters and trace gases were monitored at Botsalano (latitude: 25.54° S longitude: 25.75° E, 1400 m ASL) and at Marikana in South Africa (latitude: 25°41'54.51"S, longitude: 27°28'50.05"E, 1170 m ASL) 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 (Winklmayer et al., 1991; Mertes, 1995; Jokinen and Mäkelä, 1997) and charged particle size distributions with an Air Ion Spectrometer (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).

Particle formation event classification 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 particle formation and initial growth, so the analysis was based primarily on ion size distributions. DMPS data were used mainly as ancillary data to follow the further 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, 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), and slope of linear fit to time-size points is the desired growth rate. The timing of growth in our data analysis is defined as $t_{GR}=(t_3+t_{10})/2$, i.e. the average of times of 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 number of days when GR is obtainable. The H_2SO_4 proxy concentration during the growth was calculated by averaging data over 40 minutes centred at t_{GR}. The contribution of H_2SO_4 to the particle growth was calculated by assuming that a vapour concentration of $1.5 \cdot 10^7$ molecules/cm^3 is required for 3-10 nm particles to grow at the rate of 1 nm/h (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 potential temperature and z is the height from ground. The temperature was measured at the 7-m height and we assumed 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 history for the nucleation event periods were calculated by using the model Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, version 4.8) of the Air Resources Laboratory at the National Oceanic and Atmospheric Administration (Draxler and Hess, 2004; Air Resources Laboratory, 2011). The estimate of the boundary layer height (i.e. mixing layer depth) was 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, especially in the case of shallow mixing layer, is unknown at our measurement sites. The temporal resolution of the data was three hours. The surroundings of the station in the 1°×1° 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 minutes 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 suggest 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 days suggests that changing air masses may have been the primary reason for the observed multiple daytime particle formation events. Consequently, it supports previous observations that 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 afore-mentioned decisions 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 could 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 (Fig. 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 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 downward mixing of a night-time residual layer rich in industrial emissions from the stacks with the heights of 50 to 130 m, as suggested by previous observations (Hirsikko et al., 2012; Venter et al., 2012). 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 air mass circulation over the heavily industrialised area.

The analysis of the particle growth rate in 3-10 nm size interval and growth due to H_2SO_4 condensation indicate 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 larger contribution to the growth of 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 H_2SO_4 concentration and contribution to growth decreases (see example on 21st November 2009 in Figs. 1 and 4), additional vapours are evidently required to maintain particle growth of the first event of the day and to initiate another new particle formation event.

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 21 of above discussed days. As can be seen from our example 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 or dissipation of clouds cannot be solely responsible for either ending or starting of 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 boundary layer coupled with or was decoupled from the surface (e.g. Stratmann et al., 2003; Laakso et al., 2007; Siebert et al., 2007). 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. 3) and Fig. 4 lead us to conclude that sulphuric acid was sometimes more important during the first event of the day, while on other days H_2SO_4 had 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 suggest that their oxidation products are likely to participate in the particle formation and growth. This was especially the case 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

Particle formation day frequency was smaller in semi-rural Botsalano compared to Marikana. New particle formation was observed on 349 days, from which 31 multiple particle formation and growth event days were detected. However, on 21 of these days either one of the two events did not show all the features typical for a proper nucleation and growth event (Dal Maso et al., 2005). Therefore, we analysed eight days that fulfilled requirements of non-changing origin and path of air masses, as discussed in the Sect. 3.1. For these days, the air masses arrived mainly from the south and south-west (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 due to starting temperature measurements on 15 October 2007.

During the first 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, S14, 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 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 day suddenly disappeared in two of the cases (Figs. S13 and S15). This feature could be due to an air mass change, even though 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 could be followed up to sizes >20 nm (Fig. 5, Figs. S9, S11, S13, S14, S15). The second event was typically associated with at renewed and higher concentration peak of H_2SO_4 (Fig. 5, Figs. S9, S11, S15). However, there were also cases in which the H_2SO_4 concentration was decreasing strongly when the second a new particle formation event was observed, which suggests strong contribution from other vapours, preferably of biogenic origin (Fig. S13). The observations indicate that clouds had probably affected the photochemistry behind observed particle formation on three 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 second event of the day (Fig. 4). The example in Fig. 6 shows two simultaneously growing particle modes on 6 November 2007, while from Fig. 4. we can see that due to faster growth H_2SO_4 had smaller contribution during the second event of the day. 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 addition of other vapours is 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. 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 some other days quite 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 in a rural savannah site (Botsalano) in South Africa during four years (Vakkari et al., 2011; Hirsikko et 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 chance or some other factor.

We analysed 31 event days in more detail, of which 8 were from Botsalano, when no clear change in air mass was detected. 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 (quickly oxidizing to H_2SO_4), and sometimes increased number of background 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-volatile 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 the particle or gas phase at our measurement sites. Adding such devises at least for particle phase chemical composition, H_2SO_4 and organic species concentration in the measurement equipment would be preferable. As a future it is suggested that boundary layer dynamics and structure measurements could offer information to gain 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 either one of the successive particle formation events could be followed to > 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. Even though, we suggest the presented conclusions to be valid. We consider that presented results of reasons behind multiple nucleation events, when air mass was non-changing, are specific for the region because they depend on the emissions of anthropological and natural vapours, other atmospheric (e.g. RH, oxidation capability) and dynamical conditions.

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References

ACIA: Arctic climate impact assessment, Cambridge University Press, New York, USA, 2005.

Air Resources Laboratory: Gridded Meteorological Data Archives, available at: http://www.arl.noaa.gov/archives.php, 2011.

Beljaar, A., Jacob, C., and Morcrette, J.J.: New physics parameters in the MARS archive, ECMWF Newsletter, 90, 17-21, 2001.

Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Grüner, A., Spindler, G., Mauldin III, R.L., Curtius, J., Kulmala, M. and Heintzenberg, J.: Laboratory study on new particle formation from the reaction OH + SO2: influence of experimental conditions, H2O vapour, NH3 and the amine tert-butylamine on the overall process, Atmos. Chem. Phys., 10, 7101-7116, 2010.

Boulon, J., Sellegri, K., Hervo, M., Picard, D., Pichon, J.-M., Fréville, P., and Laj, P.: Investigation of nucleation events vertical extent: a long term study at two different altitude sites, Atmos. Chem. Phys., 11, 5625-5639, doi:10.5194/acp-11-5625-2011, 2011.

Bzdek, B.R., Zordan, C.A., Pennington, M.R., Luther III, G.W. and Johnston, M.V.: Quantitative Assessment of the Sulfuric Acid Contribution to New Particle Growth, Environ. Sci. Technol., 46, 4365-4373, 2012.

Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P.P., and Lehtinen, K.E.J.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, Boreal Environ. Res., 10, 323–336, 2005.

Draxler, R. R., and Hess, G. D.: Description of the HYSPLIT 4 Modelling System, NOAA Technical Memorandum ERL ARL–224, 2004.

Hirsikko, A., Laakso, L., Hõrrak, U., Aalto, P.P., Kerminen, V.-M. and Kulmala, M.: Annual and size dependent variation of growth rates and ion concentrations in boreal forest, Boreal Environ. Res., 10, 357-369, 2005.

Hirsikko, A., Bergmann, T., Laakso, L., Dal Maso, M., Riipinen, I., Hõrrak, U. and Kulmala, M.: Identification and classification of the formation of intermediate ions measured in boreal forest, Atmos. Chem. Phys., 7, 201-210, 2007.

Hirsikko, A., Nieminen, T., Gagné, S., Lehtipalo, K., Manninen, H.E., Ehn, M., Hõrrak, U., Kerminen, V.-M., Laakso, L., McMurry, P.H., Mirme, A., Mirme, S., Petäjä, T., Tammet, H., Vakkari, V., Vana, M., and Kulmala, M.:, Atmospheric ions and nucleation: a review of observations, Atmos. Chem. Phys., 11, 767-798, doi:10.5194/acp-11-767-2011, 2011.

Hirsikko, A., Vakkari, V., Tiitta, P., Manninen, H.E., Gagné, S., Laakso, H., Kulmala, M., Mirme, A., Mirme, S., Mabaso, D., Beukes, J.P. and Laakso, L.: Characterisation of sub-micron particle number concentrations and formation events in the western Bushveld Igeneous Complex, South Africa, Atmos. Chem. Phys., 12, 3951-3967, doi:10.5194/acpd-12-3951-2012, 2012.

IPCC, Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007.

Janssen, R.H.H., Vilà-Guerau de Arellano, J., Ganzeveld, L.N., Kabat, P., Jimenez, J.L., Farmer, D.K., van Heerwaarden, C.C., and Mammarella, I.: Combined effects of surface conditions, boundary layer dynamics and chemistry on diurnal SOA-evolution, Atmos. Chem. Phys. Discuss., 12, 9331-9375, doi:10.5194/acpd-12-9331-2012, 2012.

Jokinen, V., and Mäkelä, J. M.: Closed loop arrangement with critical orifice for DMA sheath/excess flow system, J. Aerosol Sci., 28, 643–648, 1997.

Kazil, J., Stier, P., Zhang, K., Quaas, J., Kinne, S., O'Donnell, D., Rasts, S., Esch, M., Ferrechat, S., Lohmann, U., and Feichter, J.: Aerosol nucleation and its role for clouds and Earth's radiative forcing in the aerosol-climate model ECHAM5-HAM, Atmos. Chem. Phys., 10, 10733–10752, doi:10.5194/acp-10-10733-2010, 2010.

Kerminen, V.-M., Petäjä, T., Manninen, H.E., Paasonen, P., Nieminen, T., Sipilä, M., Junninen, H., Ehn, M., Gagné, S., Laakso, L., Riipinen, I., Vehkamäki, H., Kurten, T., Ortega, I.K., Dal Maso, M., Brus, D., Hyvärinen, A., Lihavainen, H., Leppä, J., Lehtinen, K.E.J., Mirme, A., Mirme, S., Hõrrak, U., Berndt, T., Stratmann, F., Birmili, W., Wiedensohler, A., Metzger, A., Dommen, J., Baltensberger, U., Kiendler-Scharr, A., Mentel, T.F., Wildt, J., Winkler, P.M., Wagner, P.E., Petzold, A., Minikin, A., Plass-Dülmer, C., Pöschl, U., Laaksonen, A., and Kulmala, M.: Atmospheric nucleation: highlights of the EUCAARI project and future directions, Atmos. Chem. Phys., 10, 10829-10848, doi:10.5194/acp-10-10829-2010, 2010.

Kerminen, V.-M., Paramonov, M., Anttila, T., Riipinen, I., Fountoukis, C., Korhonen, H., Asmi, E., Laakso, L., Lihavainen, H., Swietlicki, E., Svenningsson, B., Asmi, A., Pandis, S.N., Kulmala, M. and Petäjä, T.: Cloud condensation nuclei production associated with atmospheric nucleation: a synthesis based on existing literature and new results, Atmos. Chem. Phys., 12, 12037-12059, 2012.

Kuang, C., Riipinen, I., Sihto, S.-L., Kulmala, M., McCormick, A.V., and McMurry, P.H.: An improved criterion for new particle formation in diverse atmospheric environments, Atmos. Chem. Phys. 10, 8469-8480, doi:10.5194/acp-10-8469-2010, 2010.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, doi: 10.1016/j.jaerosci.2003.10.003, 2004.

Kulmala, M., and Kerminen, V.-M.: On the formation and growth of atmospheric nanoparticles, Atmos. Res., 90, 132-150, doi: 10.1016/j.atmosres.2008.01.005, 2008.

Laakso, L., Grönholm, T., Kulmala, L., Haapanala, S., Hirsikko, A., Lovejoy, E.R., Kazil, J., Kurtén, T., Boy, M., Nilsson, E.D., Sogachev, A., Riipinen, I., Stratmann, F., and Kulmala, M.:

575 Hot-air balloon measurements of vertical variation of boundary layer new particle formation, Boreal
576 Env. Res. 12, 279–294, 2007.

577 Laakso, L., Laakso, H., Aalto, P.P., Keronen, P., Nieminen, T., Pohja, T., Siivola, E., Kulmala, M.,
578 Kgabi, N., Molefe, M., Mabaso, D. Phalatse, D., Piennaar, K., and Kerminen, V.-M.: Basic
579 characteristics of atmospheric particles, trace gases and meteorology in a relatively clean Southern
580 African Savannah environment, Atmos. Chem. Phys., 8, 4823–4839, doi:10.5194/acp-8-4823-2008,
581 2008.

582 Manninen, H.E., Nieminen, T., Asmi, E., Gagné, S. Häkkinen, S., Lehtipalo,K., Aalto, P., Vana,
583 M., Mirme, A., Mirme, S., Hõrrak, U., Plass-Dülmer, C. Stange, G., Kiss, G., Hoffer, A., Törõ, N.,
584 Moerman, M., Henzig, B., de Leeuw, G., Brinkenberg, M., Kouvarakis, G.N.,Bougiatioti, A.,
585 Mihalopoulus, N., O'Dowd, C., Ceburnis, D., Arneth, A., Svenningsson, B., Swietlicki, E., Tarozzi,
586 L., Decesari, S., Facchini, M.C., Birmili, W., Sonntag, A., Wiedensohler, A., Boulon, J., Sellegri,
587 K., Laj, P., Gysel, M., Bukowiecki, N., Weingartner, E., Wehrle, G., Laaksonen, A. Hamed, A.,
588 Joutsensaari, J., Petäjä, T., Kerminen, V.-M, and Kulmala, M.: EUCAARI ion spectrometer
589 measurements at 12 European sites —analysis of new particle formation events, Atmos. Chem.
590 Phys., 10, 7907-7927, doi:10.5194/acp-10-7907-2010, 2010.

591 Makkonen, R., Asmi, A., Kerminen, V.-M., Boy, M., Arneth, A., Hari, P., and Kulmala, M.: Air
592 pollution control and decreasing new particle formation lead to strong climate warming, Atmos.
593 Chem. Phys., 12, 1515-1524, doi:10.5194/acp-12-1515-2012, 2012.

594 Merikanto, J., Spracklen, D.V., Mann, G.W., Pickering, S.J., and Carslaw, K.S.: Impact of
595 nucleation on global CCN, Atmos. Chem. Phys., 9, 8601–8616, doi:10.5194/acp-9-8601-2009,
596 2009.

597 Mertes, S., Schröder, F., and Wiedensohler, A.: The particle detection efficiency curve of the TSI-
598 3010 CPC as a function of temperature difference between saturator and condenser, Aerosol Sci.
599 Technol., 23, 257–261, doi: 10.1080/02786829508965310, 1995.

600 Mirme A., Tamm, E., Mordas, G., Vana, M., Uin, J., Mirme, S., Bernotas, T., Laakso, L., Hirsikko,
601 A., and Kulmala, M.: A wide-range multi-channel Air Ion Spectrometer, Boreal Environ. Res., 12,
602 247–264, 2007.

603 Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10 nm particle growth by vapor
604 condensation – effects of vapor molecule size and particle thermal speed, Atmos. Chem. Phys., 10,
605 9773-9779, doi:10.5194/acp-10-9773-2010, 2010.

606 Paasonen, P., Nieminen, T., Asmi, E., Manninen, H.E., Petäjä, T., Plass-Dülmer, C., Flentje, H.,
607 Birmili, W., Wiedensohler, A., Hõrrak, U., Metzger, A., Hamed, A. Laaksonen, A., Facchini, M.C.,
608 Kerminen, V.-M., andKulmala, M.: On the roles of sulphuric acid and low-volatility organic
609 vapours in the initial steps of atmospheric new particle formation, Atmos. Chem. Phys., 10, 11223-
610 11242, doi: 10.5194/acp—10-11223-2010, 2010.

611 Petäjä, T., Mauldin III, R.L.., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M.,
612 Adamov, A., Kotiaho, T., and Kulmala, M.: Sulphuric acid and OH concentrations in a boreal forest
613 site, Atmos. Chem. Phys., 9, 7435-7448, doi: 10.5194/acp-9-7435-2009, 2009.

614 Pierce, J. R., and Adams, P.J.: Uncertainty in global CCN concentrations from uncertain nucleation
615 and primary emission rates, Atmos. Chem. Phys., 9, 1339–1356, doi:10.5194/acp-9-1339-2009,
616 2009.

617 Riccobono, F., Rondo, L., Sipilä, M., Barmet, P., Curtius, J., Dommen, J., Ehn, M., Ehrhart, S.,
618 Kulmala, M., Kürten, A., Mikkilä, J., Paasonen, P., Petäjä, T., Weingartner, E. and Baltensperger,
619 U.: Contribution of sulfuric acid and oxidized organic compounds to particle formation and growth,
620 Atmos. Chem. Phys., 12, 9427-9439, 2012.

621 Riddle, E.E., Voss, P.B., Stohl, A., Holcomb, D., Maczka, D., Washburn, K., and Talbot, R.W.:
622 Trajectory model validation using newly developed altitude-controlled balloons during the
623 International Consortium for Atmospheric Research on Transport and Transformations 2004
624 campaign, J. Geophys. Res., 111, D23S57, doi:10.1029/2006JD007456, 2006.

625 Riipinen, I., Pierce, J.R., Yli-Juuti, T., Nieminen, T., Häkkinen, S., Ehn, M., Junninen, H.,
626 Lehtipalo, K., Petäjä, T., Slowik, J., Chang, R., Shantz, N.C., Abbatt, J., Leaitch, W.R., Kerminen,
627 V.-M., Worsnop, D.R., Pandis, S.N., Donahue, N.M., and Kulmala, M.: Organic condensation: a
628 vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, Atmos.
629 Chem. Phys., 11, 3865-3878, doi:10.5194/acp-11-3865-2011, 2011.

630 Siebert, H., B. Wehner, B., Hellmuth, O., Stratmann, F., Boy, M., and Kulmala, M.: New-particle
631 formation in connection with a nocturnal low-level jet: Observations and modeling results,
632 Geophys. Res. Lett., 34, L16822, doi:10.1029/2007/GL029891, 2007.

633 Stohl, A.: Computation, accuracy and application of trajectories – a review and bibliography,
634 Atmos. Environ., 32, 947–966, doi: 10.1016/S1352-2310(97)00457-3, 1998.

635 Stratmann, F., Siebert, H., Spindler, G.,Wehner, B., Althausen, D., Heinzenberg, J., Hellmuth, O.,
636 Rinke, R., Schmiedler, U., Seidel, C., Tuch, T., Uhrner, U., Wiedensohler, A., Wandinger, U.,
637 Wendisch, M., Schell, D., and Stohl, A.: New-particle formation events in a continental boundary
638 layer: first results from the SATURN experiment, Atmos. Chem. Phys. 3, 1445-1459, doi:
639 10.5194/acp-3-1445-2003, 2003.

640 Suni, T., Kulmala, M., Hirsikko, A., Bergman, T., Laakso, L,. Aalto, P.P., Leuning, R., Cleugh, H.,
641 Zegelin, S., Hughes, D., van Gorsel, E., Kitchen, M., Vana, M., Hõrrak, U., Mirme, S., Mirme, A.,
642 Sevanto, S., Twining, J., and Tadros, C.: Formation and characteristics of ions and charged aerosol
643 particles in a native Australian Eucalypt forest, Atmos. Chem. Phys., 8, 129-139, doi:10.5194/acp-
644 8-129-2008, 2008.

645 Svenningsson B., Arneth, A., Hayward, S., Holst, T., Massling, A., Swietlicki, E., Hirsikko, A.,
646 Junninen, H., Riipinen, I., Vana, M., Dal Maso, M., Hussein, T., and Kulmala, M.: Aerosol particle
647 formation events and analysis of high growth rates observed above a subarctic wetland-forest
648 mosaic, Tellus, 60B, 353-364, doi: 10.1111/j.1600-0889.2008.00351.x, 2008.

649 Vakkari, V., Laakso, H., Kulmala, M., Laaksonen, A., Mabaso, D., Molefe, M., Knabi, N., and
650 Laakso, L.: New particle formation events in semi-clean South African savannah, Atmos. Chem.
651 Phys., 11, 767-798, doi:10.5194/acp-11-767-2011, 2011.

652 Venter, A.D., Vakkari, V., Beukes, J.P., van Zyl, P.G., Laakso, H., Mabaso, D., Tiitta, P., Josipovic,
653 M., Kulmala, M., Pienaar, J.J., and Laakso, L.: An air quality assessment in the industrialized
654 western Bushveld Igneous Complex, South Africa, accepted to the S. Afr. J. Sci., 2012.

655 Winklmayr, W., Reischl, G., Lindner, A., and Berner, A: A new electromobility spectrometer for
656 the measurement of aerosol size distributions in the size range from 1 to 1000 nm, J. Aerosol Sci.,
657 22, 289–296, doi: 10.1016/S0021-8502(05)80007-2, 1991.

658 Wu Z.J., Hu, M., Yue, D.L., Wehner, B., and Wiedensohler, A.: Evolution of particle number size
659 distribution in an urban atmosphere during episodes of heavy pollution and new particle formation,
660 Sci. China Earth Sci., 54, 1772–1778, doi: 10.1007/s11430-011-4227-9, 2011.

661 Zhang, R.: Getting to the critical nucleus of aerosol formation, Science, 328, 1366-1367, doi:
662 10.1126/science.1189732, 2010.
663

Figure 1. Example of two consecutive negative ion nucleation events (top left panel) at Marikana on 21 November 2009. 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 start of the second event. Data for $\partial\theta/\partial z$ was unavailable for this day.

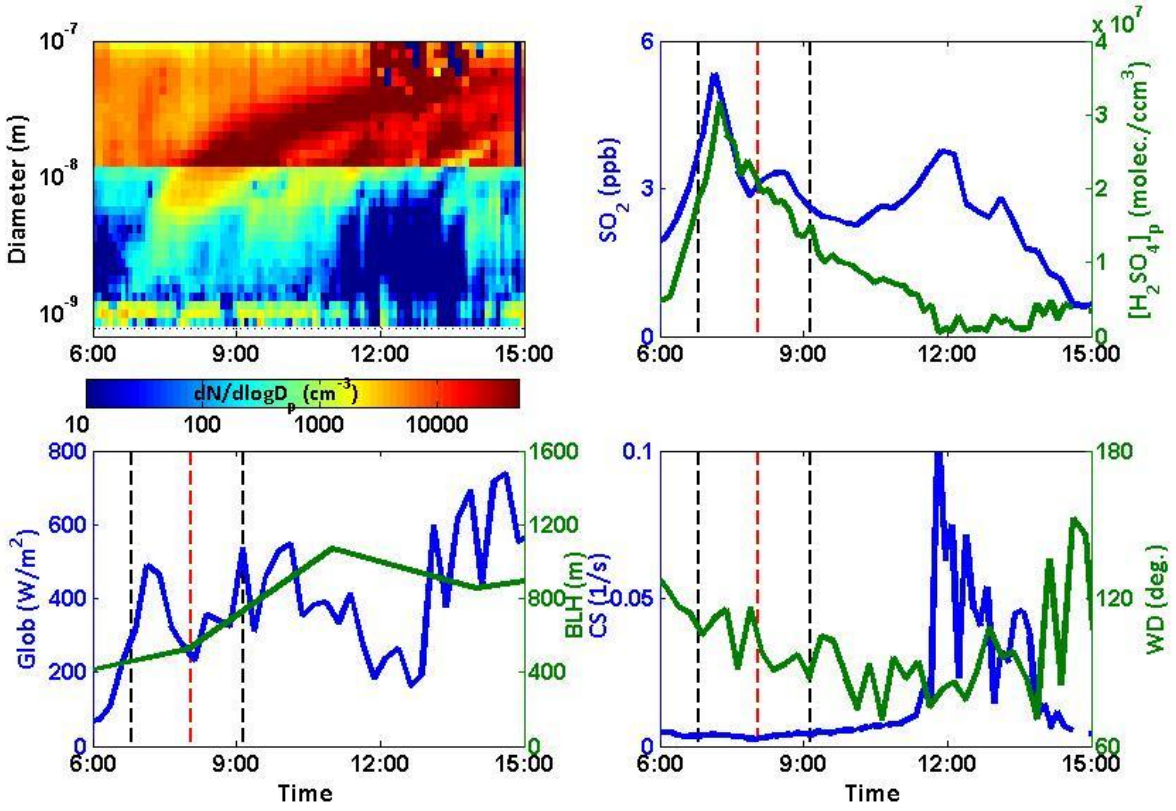


Figure 2. Median values for mixing layer depth (BLH), global radiation, SO_2 and H_2SO_4 proxy concentrations and CS during the first (red markers) and the second (blue markers) particle formation event versus the corresponding parameters during the break between the events. Days having same airmass origin during successive growing modes from Botsalano and Marikana were included here.

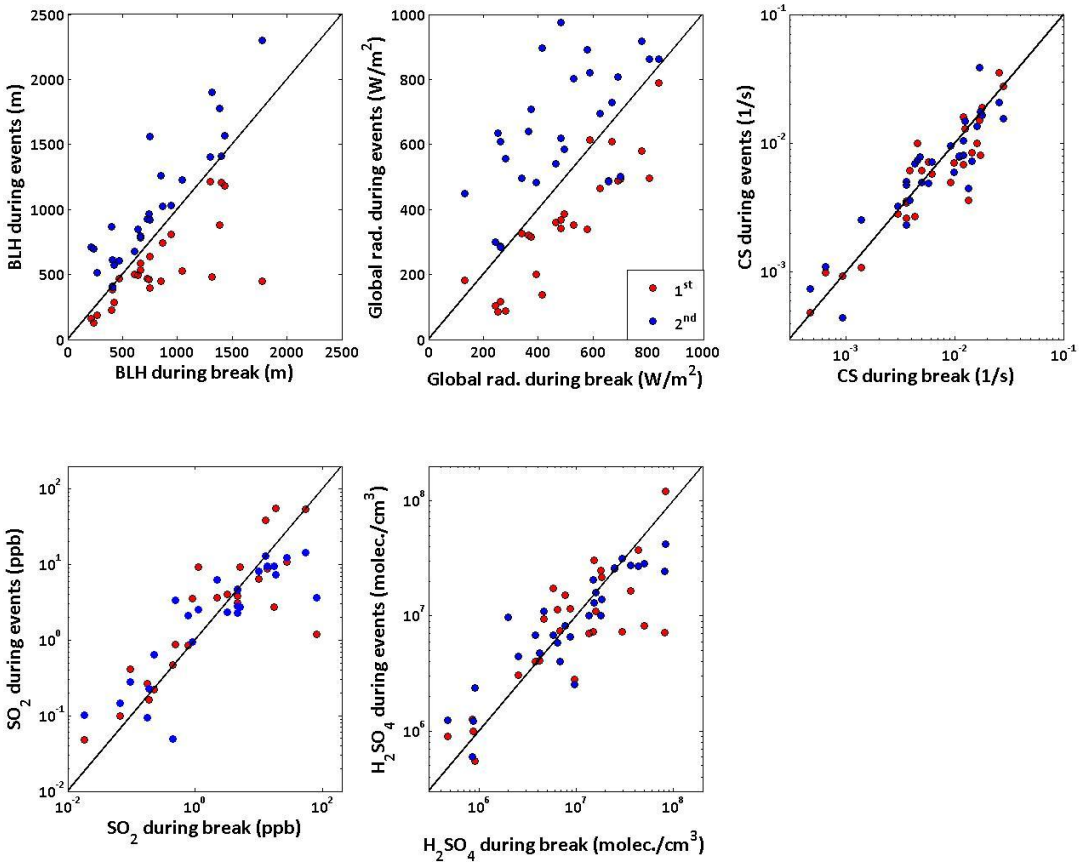


Figure 3. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 21 November 2009.

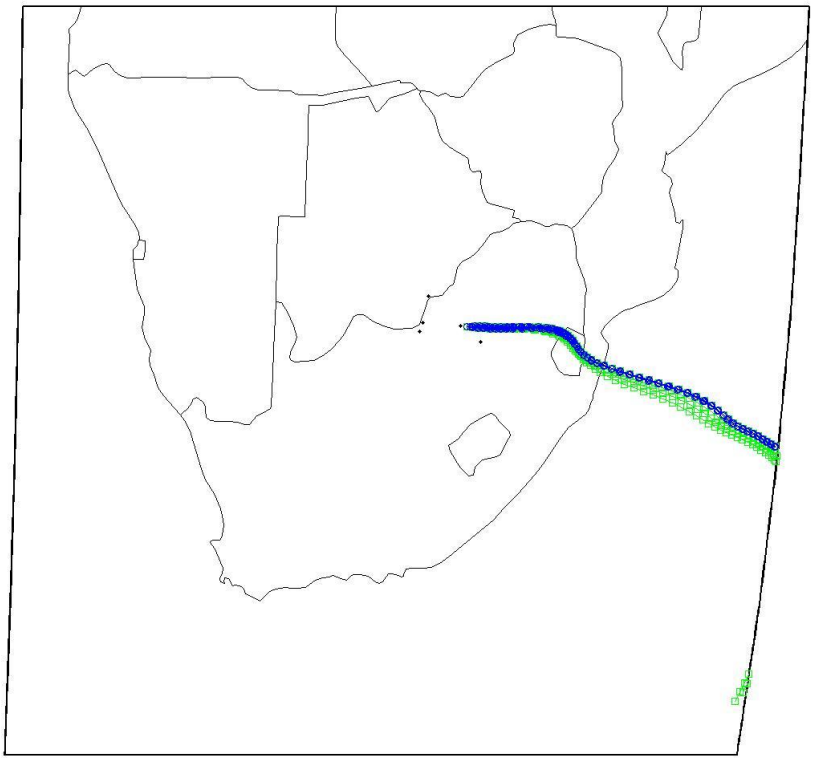


Figure 4. Growth of the first (GR_1) and second (GR_2) event of the day due to H2SO4 only. The GR was estimated for ion population in size range 3-10 nm. H_2SO_4 concentration is average over 40 min centred round timing of the growth rate. Shown results are from Botsalano during 5.8.2006-6.11.2007 and from Marikana during 10.11.2008-25.4.2010.

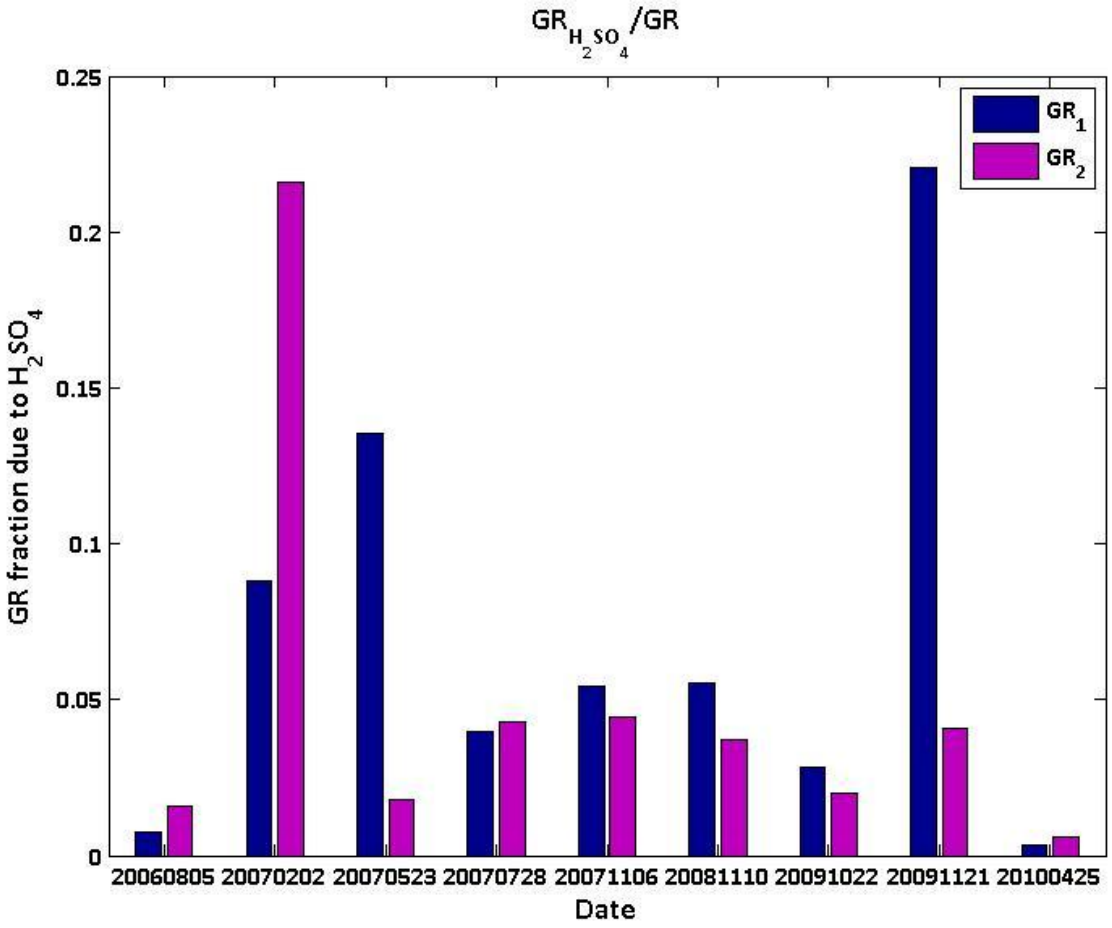


Figure 5. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 6 November 2007.

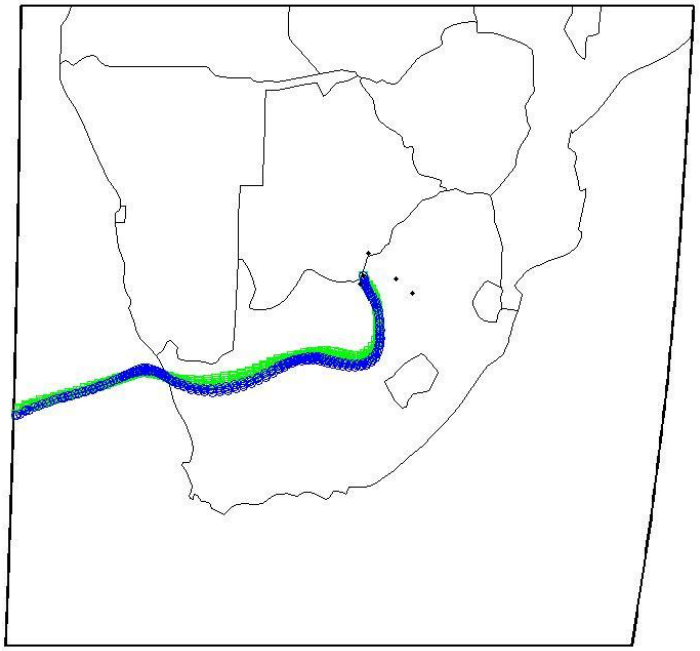
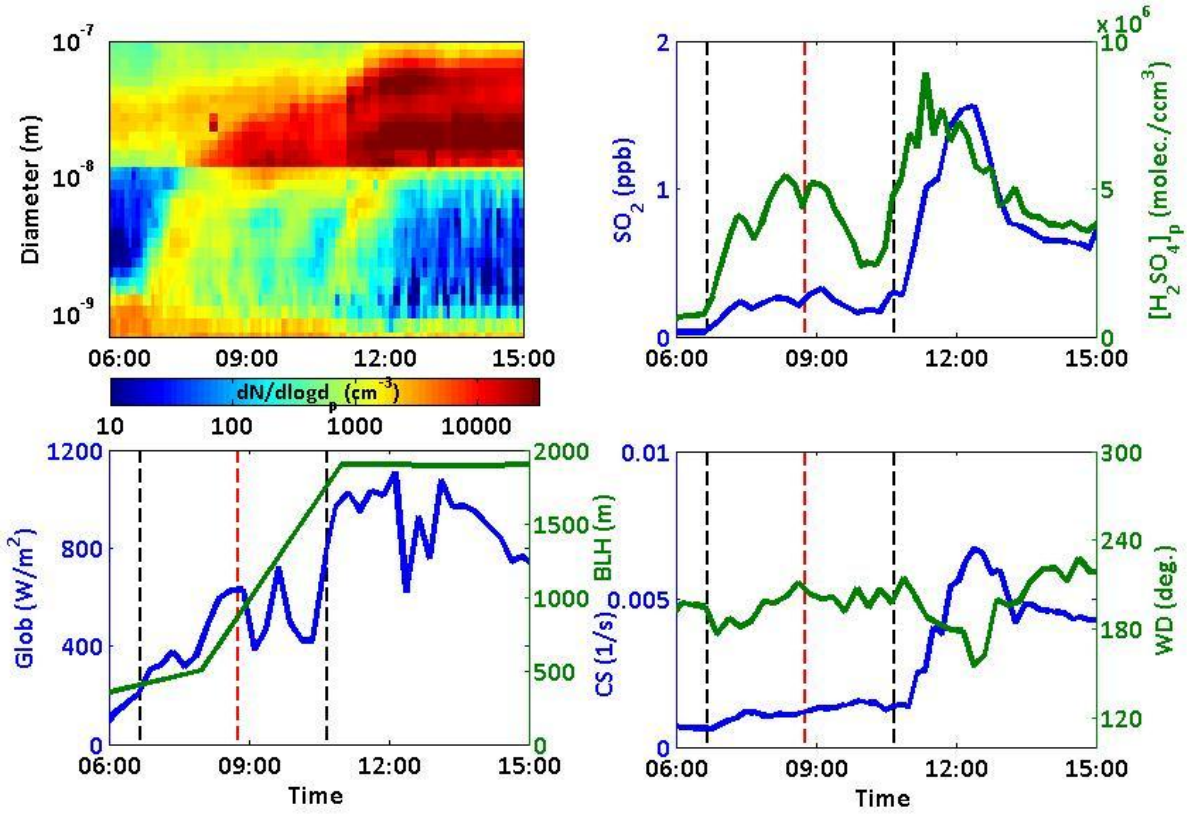


Figure 6. Example of two consecutive negative ion growth events (top left panel) at Botsalano on 6 November 2007. Concentration of SO_2 and H_2SO_4-proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height and global radiation (bottom left panel) are also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



COPY OF SUPPLEMENT

SUPPLEMENT

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

A. Hirsikko[1,*], V. Vakkari[2], P. Tiitta[3], J. Hatakka[1], V.-M. Kerminen[2], A.-M. Sundström[2], J.P. Beukes[4], H.E. Manninen[2], M. Kulmala[2] and L. Laakso[1,4]

[1]Finnish Meteorological Institute, Research and Development, P.O. Box 503, 00101, Finland
[2]Department of Physics, University of Helsinki, P.O. Box 64, 00014 University of Helsinki, Finland
[3]Fine Particle and Aerosol Technology Laboratory, Department of Environmental Science, University of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland
[4]School of Physical and Chemical Sciences, North-West University, Potchefstroom, South Africa

[*]Currently at: Forschungszentrum Jülich GmbH, Institut für Energie-und Klimaforschung: Troposphäre (IEK-8), Jülich, Germany.

This supplement contains example figures of the multiple nucleation events together with ancillary data and air mass back-trajectory figures.

Figure S1. Two consecutive ion growth events (top left panel) at Marikana on 10 November 2008. 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 (BLH) 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 start of the second event. During night $\partial\theta/\partial z > 0$.

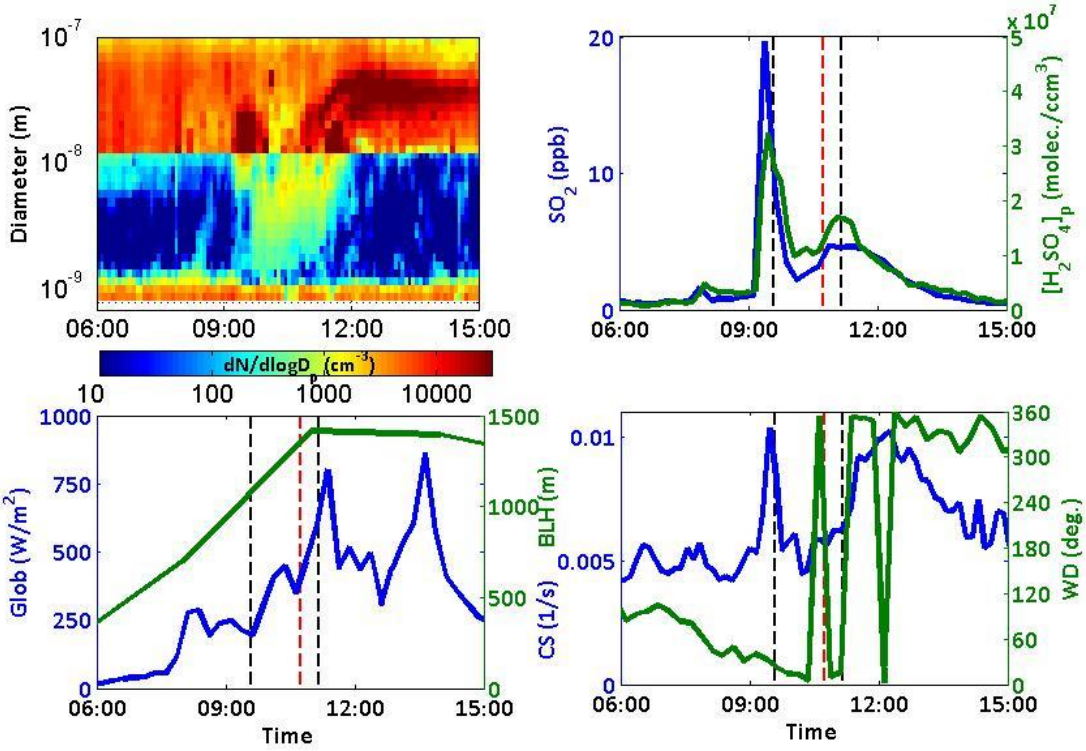


Figure S2. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 10 November 2008.

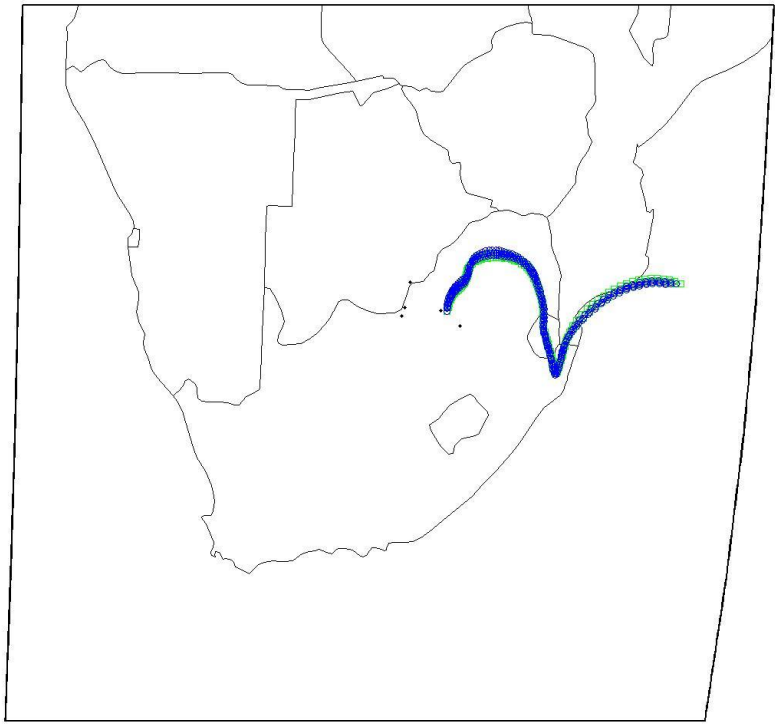


Figure S3. Two consecutive ion growth events (top left panel) at Marikana on 10 December 2008. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. During night $\partial\theta/\partial z > 0$.

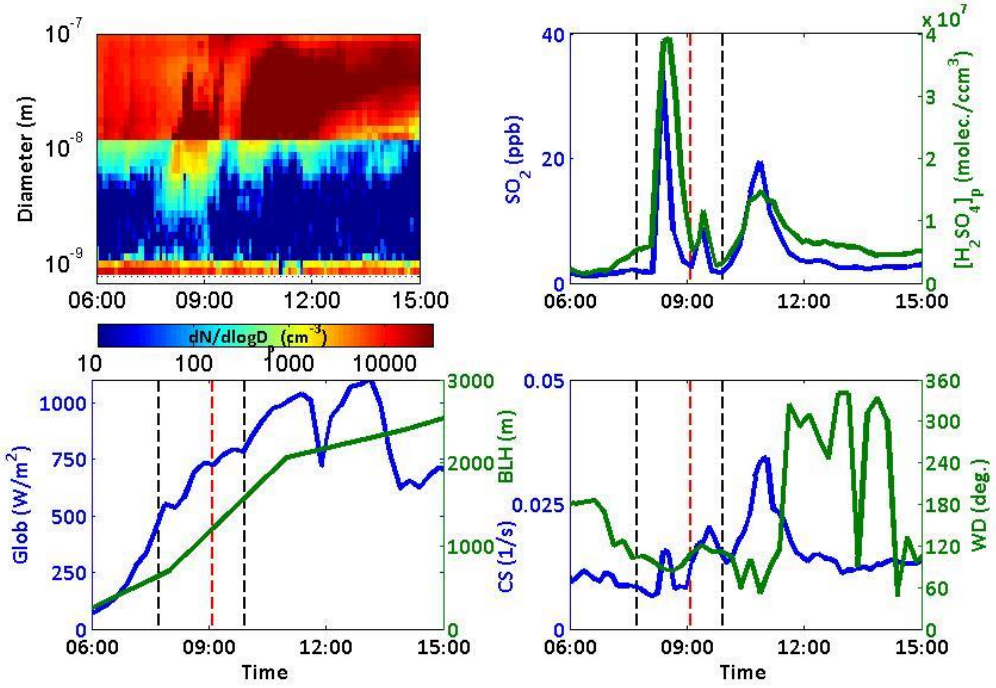


Figure S4. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 10 December 2008.

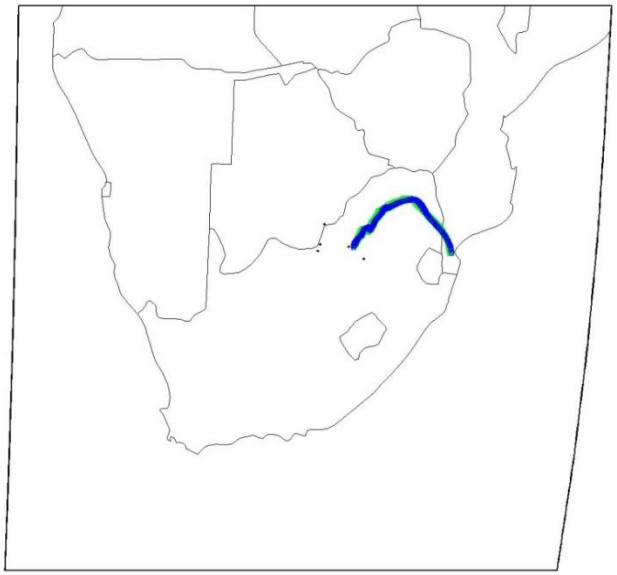


Figure S5. Two consecutive ion growth events (top left panel) at Marikana on 24 September 2009. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. During night $\partial\theta/\partial z > 0$.

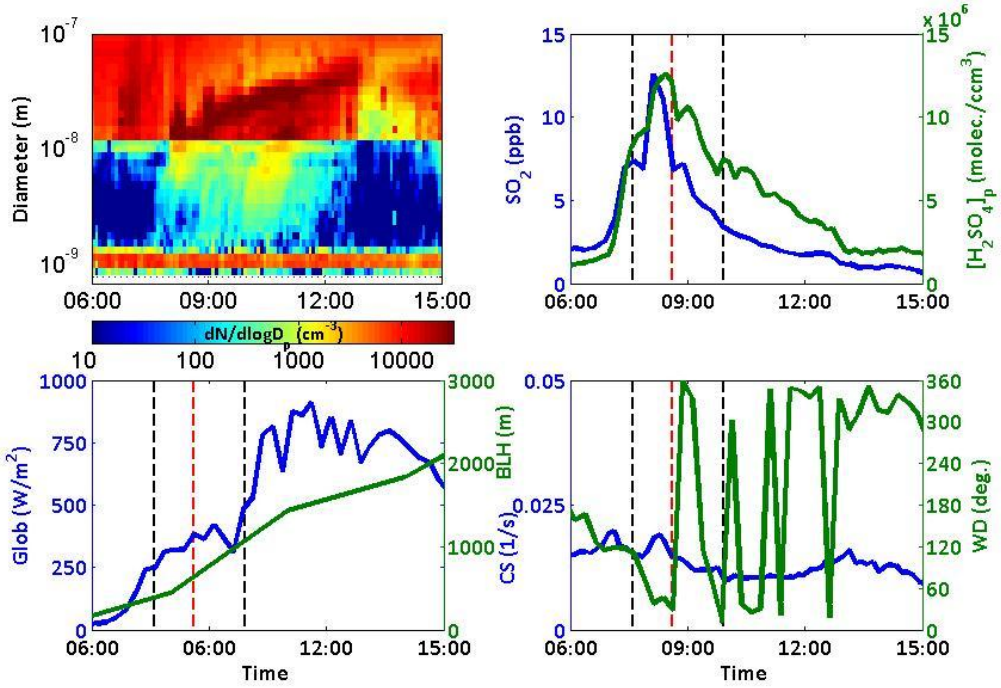


Figure S6. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 24 September 2009.

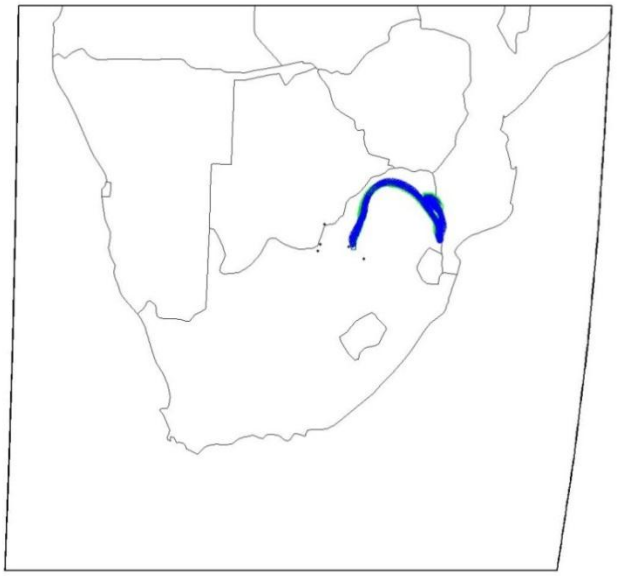


Figure S7. Two consecutive ion growth events (top left panel) at Marikana on 17 November 2009. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. During night $\partial\theta/\partial z < 0$.

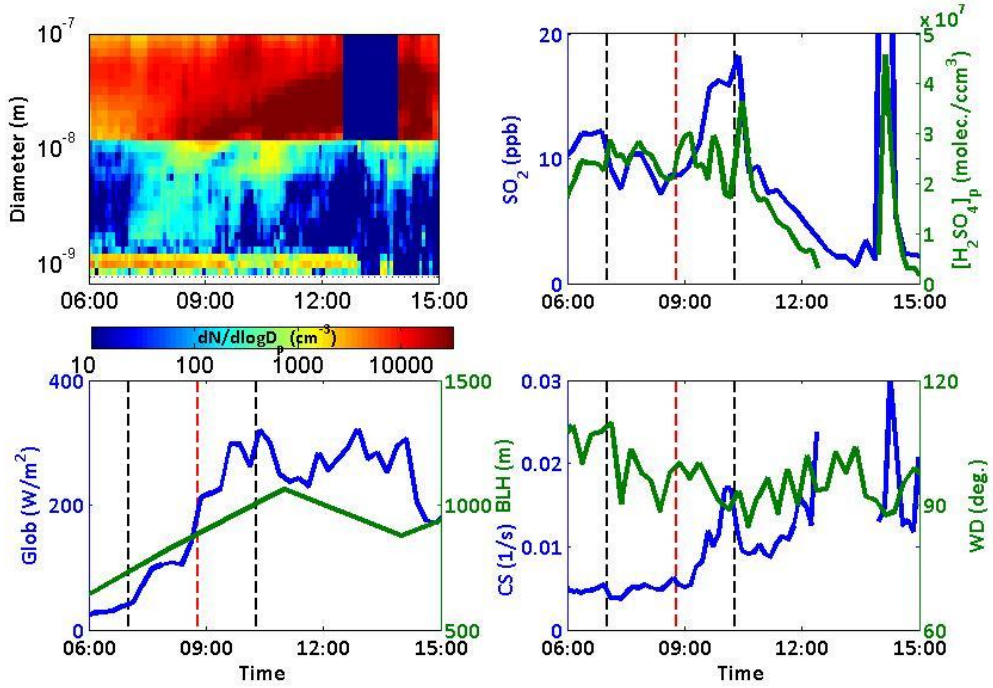


Figure S8. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 17 November 2009.

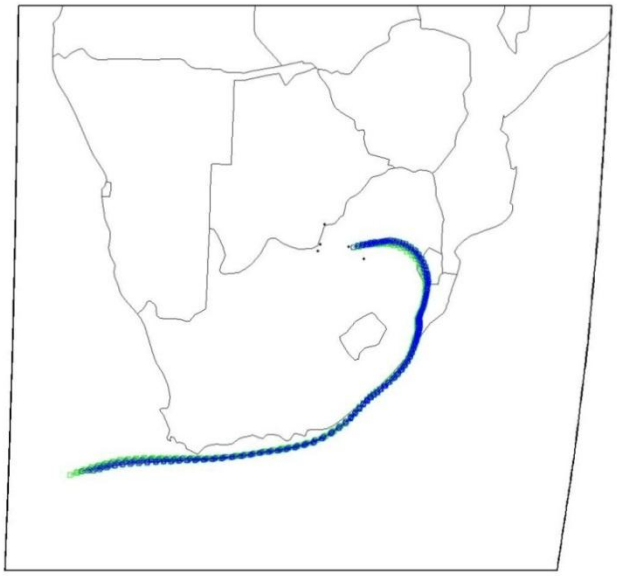


Figure S9. Two consecutive ion growth events (top left panel) at Botsalano on 5 August 2006. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. Value for $\partial\theta/\partial z$ was not available.

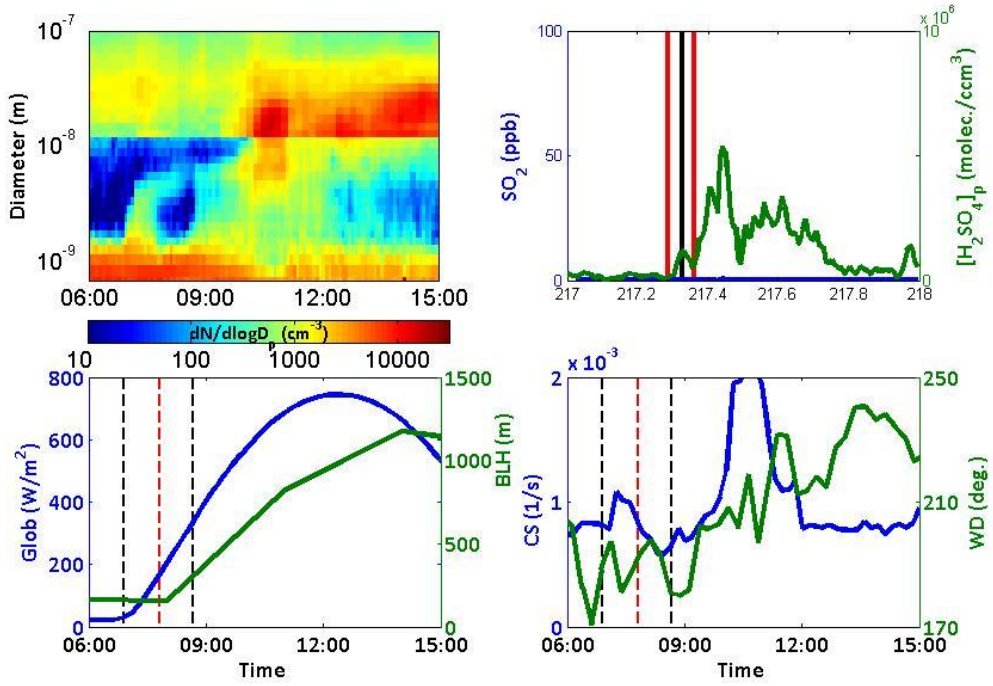


Figure S10. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 5 August 2006.

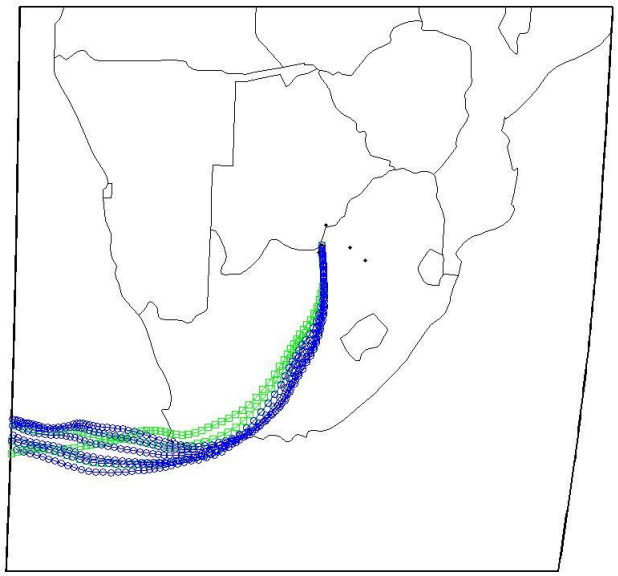


Figure S11. Two consecutive ion growth events (top left panel) at Botsalano on 18 August 2006. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. Value for $\partial\theta/\partial z$ was not available.

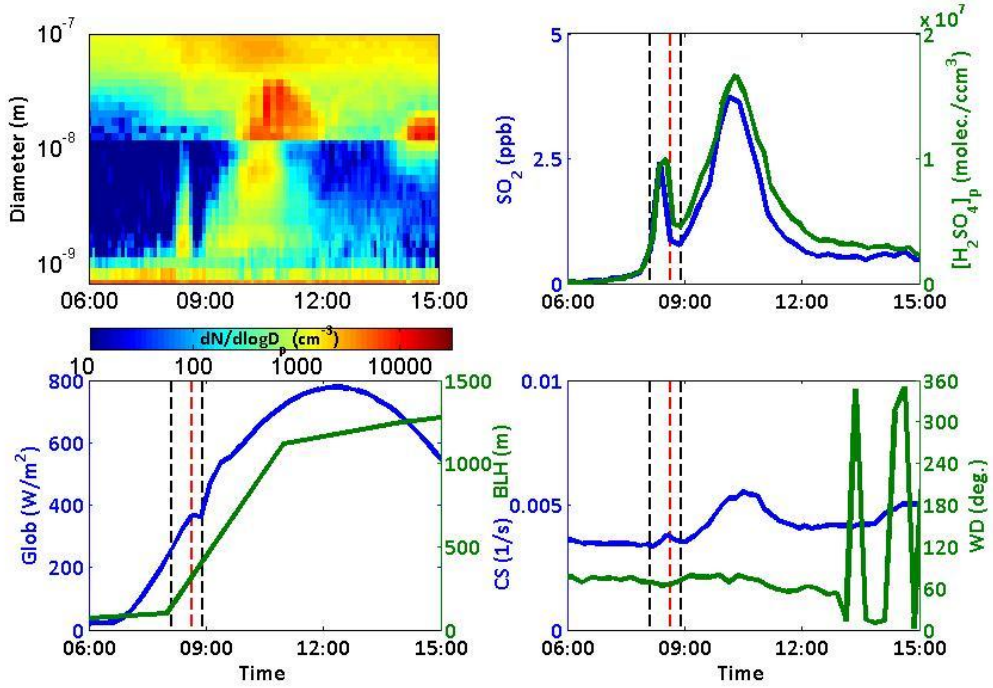


Figure S12. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 28 July 2007.

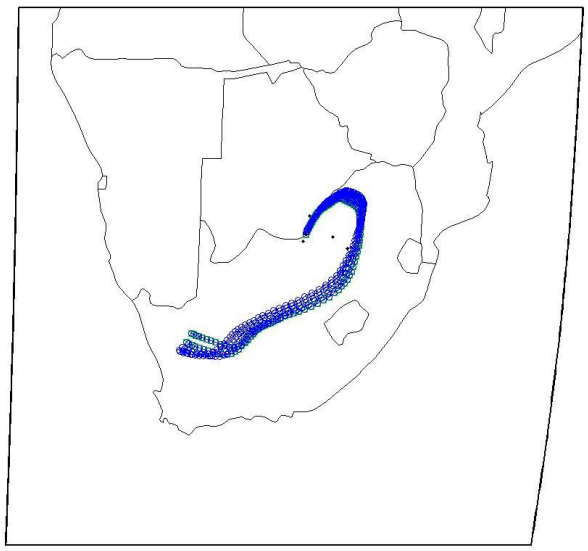


Figure S13. Two consecutive ion growth events (top left panel) at Botsalano on 23 May 2007. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. Value for $\partial\theta/\partial z$ was not available.

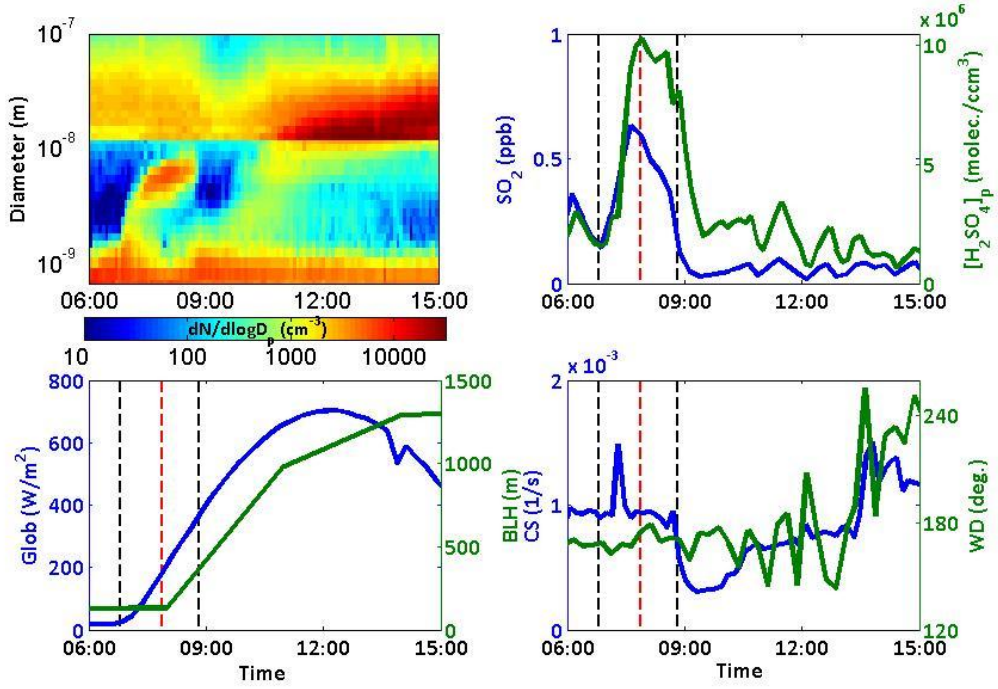


Figure S14. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 23 May 2007.

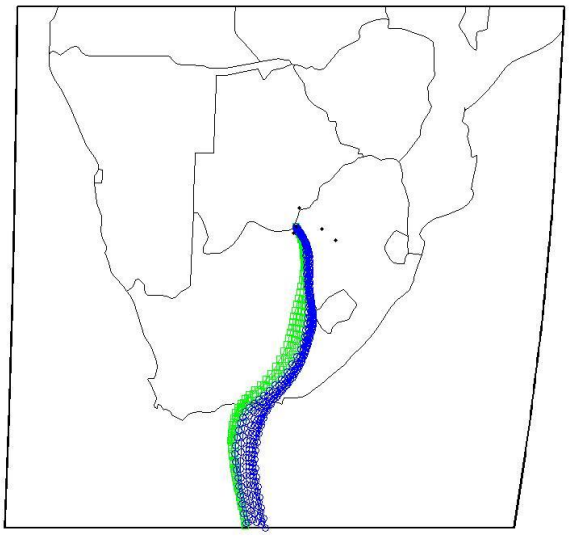


Figure S15. Two consecutive ion growth events (top left panel) at Botsalano on 28 July 2007. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The first black and red lines indicate the start and end of the first nucleation event, while the second vertical black line indicates start of the second event. During night $\partial\theta/\partial z > 0$.

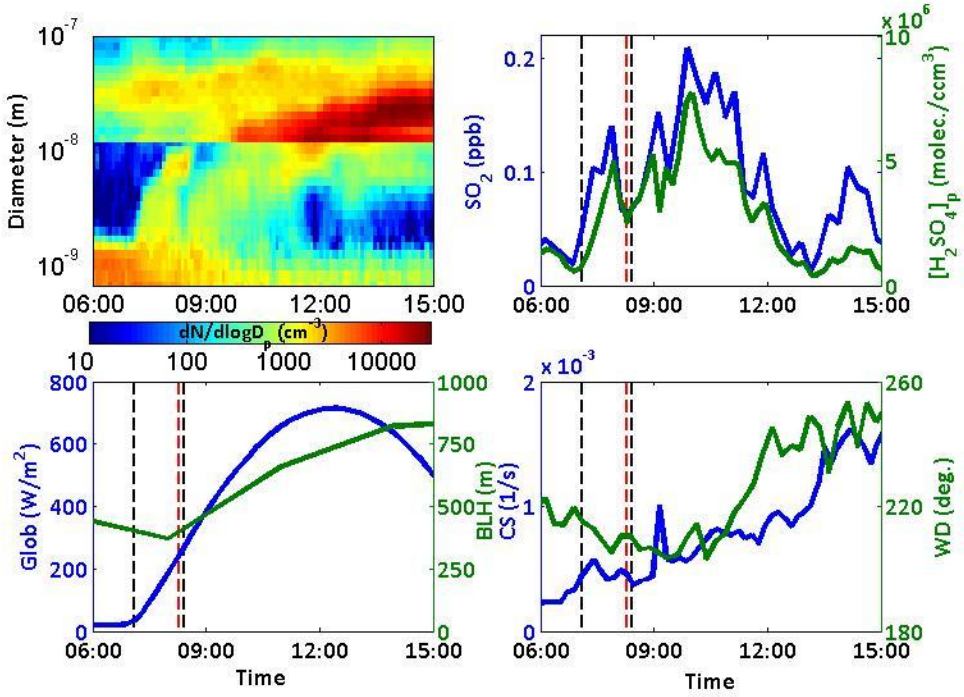


Figure S16. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 28 July 2007.