Reply for referee 2

Authors:
We would like to thank the referee 2 for reviewing our manuscript. In the following we answer to comments and questions presented by the referee, and discuss about implemented major changes in the manuscript. Together with modifications based on referee 1 comments we propose our manuscript to be publishable, since conclusions are based on more solid background. Please find revised manuscript and supplement material at the end of this document.

Referee:
The first author has done an excellent job in writing a clear and concise manuscript and in developing the argument for the presented hypotheses. This is a difficult assignment given the very significant limitations of the observational data set, which provides a only a very weak support for these hypotheses (although the hypotheses may be correct). The weaknesses of the data arise from the absence of altitude-resolved SO2 measurements, gas phase H2SO4 measurements, and measurements of nucleating compounds other than H2SO4, from the presence of clouds in the majority of the analyzed cases, from the very small fraction of events that support the hypotheses, and from features in the data which are in conflict with the hypotheses. These points are discussed in more detail below. To the authors' credit, they thoroughly disclose and discuss the data.

Overall, the manuscript develops plausible hypotheses from observations and from circumstantial evidence, but the data offer only a very weak support for their validity, and it would be up to future studies to place these hypotheses on solid footing. This approach to publishing results can be seen in a negative and in a positive light: On the one hand, the authors can claim precedence if their hypotheses are proved correct by future, more thorough research, without having to do the research themselves, while they take little risk if their hypotheses are not proved correct, or are even disproved. This approach has become more acceptable in an environment in which the number of publications and citations are an indicator of quality. On the other hand, one could say that the authors have done their best to extract the most from the available observations, and that the conclusions are only as good as the data. Even if one favors the latter, more positive assessment, it must be clear that the conclusions of this manuscript are very weak because the data are very weak, and because of this, I do not recommend this manuscript for publication.

Authors:
We agree that information about aerosol particle chemical composition and gas phase H_2SO_4 would have provided crucial information about participation of different compounds on nucleation and growth. Unfortunately, we did not have such measurements, although the mobile measurement station in South Africa is the most comprehensive atmospheric observation station in the area. These would be the kind of observations where we are aiming in the future when appropriate funding is secured. In general, instruments for measuring gas phase H_2SO_4 has become more popular. However, majority of measurement stations still lack for such observations. Therefore, use of proxies is popular even though absolute concentration may not be validated by direct observations at particular site.

Due to high costs, observations of vertical distributions of SO_2 are rare even in more comprehensive facilities. As an example, we have only couple of airborne (balloon or air plane) measurement

campaigns per year in Finland. Thus we believe that such requirement for a young research infrastructure would be unreasonable, although such data would provide more solid background for conclusions of SO_2 rich nighttime residual layer suggested also by observations by Hirsikko et al. (2012) and Venter et al. (2012). Despite the limited chemical compound information, we propose that this manuscript would be publishable after proposed revision and supplement material.

Referee:
Marikana station
The authors analyze and discuss the role of clouds for the observations: "We found that presence of clouds between the successive events may have been one reason to stop nucleation on 21 of above discussed days."

The number of total days which met the (evidently stringent) criteria for analyzability was 24 at the Marikana station, which left three days without clouds. These are discussed as follows: "The first event stopped when H2SO4 concentration was still increasing on two of the three days. As an example, on 28 March 2008, 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 H2SO4 concentration remained lower compared with the first event."

In the conclusions, the authors write
"It is possible 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."

I agree with the authors that one possible explanation for the second nucleation event could be a nucleating compound other than H2SO4. However, for the Marikana station, there are only 2 (!) days where the presence of clouds or increased H2SO4 during the second nucleation event are not equally valid hypotheses.

These two days represent an extremely small sample of positive outcomes to support the following conclusion of the manuscript:

"The observations indicated that while sulphuric acid was the most probable candidate for initiating the first event, other vapours were probably needed for promoting the start of the second event."
The fact that this conclusion is weak is highlighted by the use of the words "probable and "probably".

Authors: We do not agree with this comment, since clouds were not solely responsible for starting or ending nucleation event. We have revised description of cloud effect in the following way.

Sect. 3.1
‘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. ‘’

Referee:
Botsalano station

At the Botsalano station, multiple particle formation events occurred on 31 days, but only on eight of these days the particles showed growth behavior that is typical for a nucleation event. The authors write: "The observations indicate that clouds had probably affected observed particle formation on three days."
later,
"The second nucleation and growth event of the day was typically associated with an increasing H2SO4 concentration and sometimes also with a decreasing value of CS."

From the eight days with proper nucleation events, clouds may have affected nucleation on three days, and increasing H2SO4 was typically observed during the second nucleation event. Hence the hypothesis and conclusion that "... other vapours were probably needed for promoting the start of the second event" is not supported by the data with the exception of very few days.

Authors:
We agree that it seems contradictory. Therefore, we have modified Section 3.2 in the following way

‘’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. ‘’

Referee: Boundary layer height
Figure 3 shows that the boundary layer height is decreasing during the start of the first nucleation event. This is at odds with the conclusion
"As a result of our analysis, we propose that the first nucleation and growth event of the day was driven by mixing of a residual layer rich with SO2, oxidized to sulphuric acid, into the surface coupled boundary layer."

Although the hypothesis that mixing of air rich in SO2 into the boundary layer initiates nucleation in the morning may be correct, the data do not seem to provide unambiguous support for this.

Authors:

We have used mixing layer temporal evolution modeled by ECWWF. It is plausible that shallow nocturnal mixing layer height and its temporal evolution are difficult to get right by any model, even though measured and modeled day-time mixing layer height and evolution have been seen to agree reasonably well. Therefore, we should not pay too much attention on modeled nocturnal mixing layer evolution, but rather focus on day-time information. Night-time atmospheric stability can be investigated via potential temperature gradient. We have revised manuscript accordingly:

Sect. 2. Measurements and Methods: We have included description of derivation and measurements related to potential temperature gradient. In addition, we included short notice about reliability of modeled mixing layer height.

Sect. 3.1.

‘’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).’’

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.’’

‘’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).’’

In addition to these modifications, information about potential temperature was included in the figure captions.

Referee:

SO2 levels

Observed SO2 mixing ratios between 0.1 and 5 ppt are shown in Figure 1 and 3. In Figure 2, it is shown that the SO2 mixing ratio is < 10 ppt for the majority of the first nucleation events during a day. SO2 levels < 10 ppt are very low, more common in the clean marine boundary layer, but inconsistent with the polluted industrial and moderately-polluted rural environments described in this paper. Also, SO2 < 10 ppt is usually too low to produce significant nucleation in the boundary layer. Hence the SO2 units are probably ppb rather than ppt. However, if the units are indeed ppt, then one of the hypotheses of the paper, "... we propose that the first nucleation and growth event of the day was driven by mixing of a residual layer rich with SO2, oxidized to sulphuric acid, into the surface coupled boundary layer" cannot be upheld. Rich in SO2 means hundreds of ppt or more. In

addition, SO2 in the ppt range would be inconsistent with the polluted industrial and moderately-polluted rural environments described in the paper: again, polluted means hundreds of ppt of SO2 or more.

Authors: Thank you for pointing out an obvious misspelling, which we apologise. The SO_2 mixing ratio is in order of ppb (Vakkari et al., 2011; Hirsikko et al, 2012; Venter et al., 2012), and it is changed in the manuscript and is implemented in supplement material.

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

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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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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.

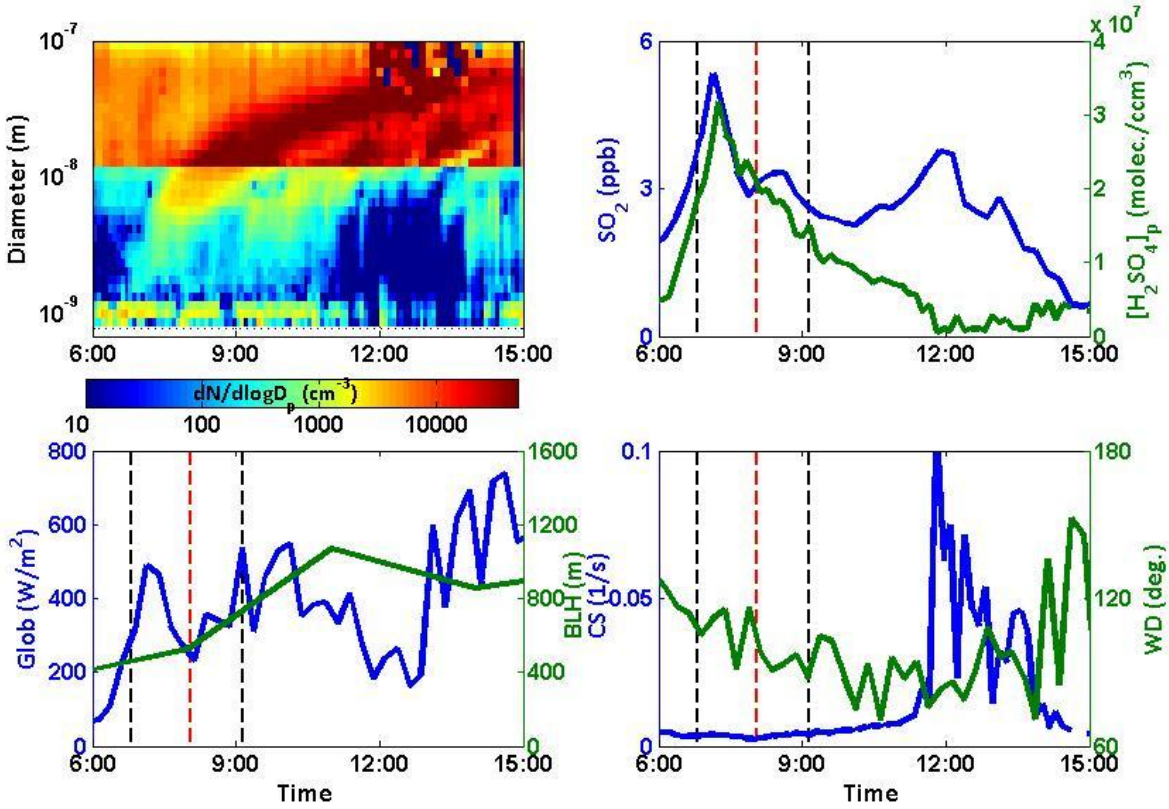


Figure 2. Median values for mixing layer depth (BLH), global radiation, SO_2 and H_2SO_4 proxy concentrations and CS during the first (red markers) and the second (blue markers) particle formation event versus the corresponding parameters during the break between the events. Days having same airmass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

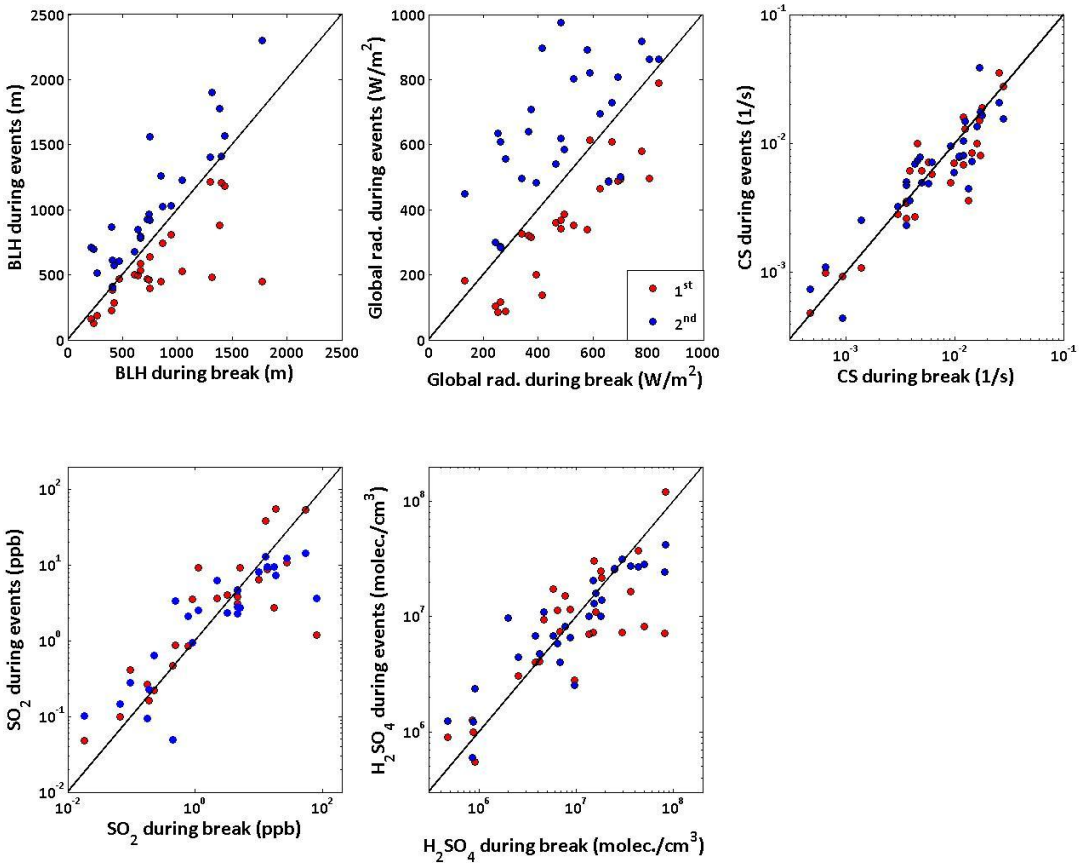


Figure 3. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 21 November 2009.

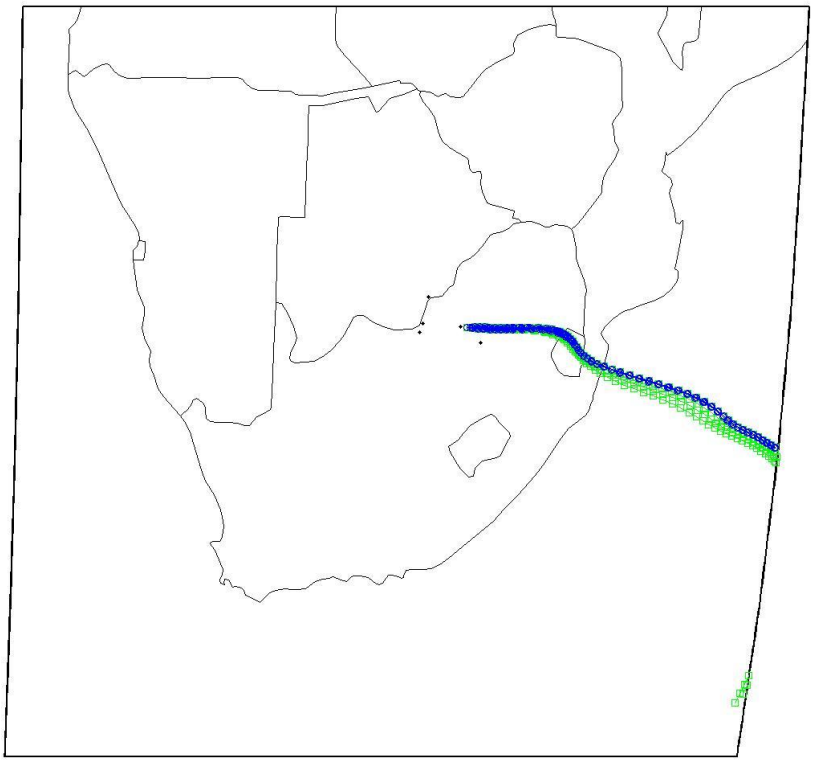


Figure 4. Growth of the first (GR_1) and second (GR_2) event of the day due to H2SO4 only. The GR was estimated for ion population in size range 3-10 nm. H_2SO_4 concentration is average over 40 min centred round timing of the growth rate. Shown results are from Botsalano during 5.8.2006-6.11.2007 and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

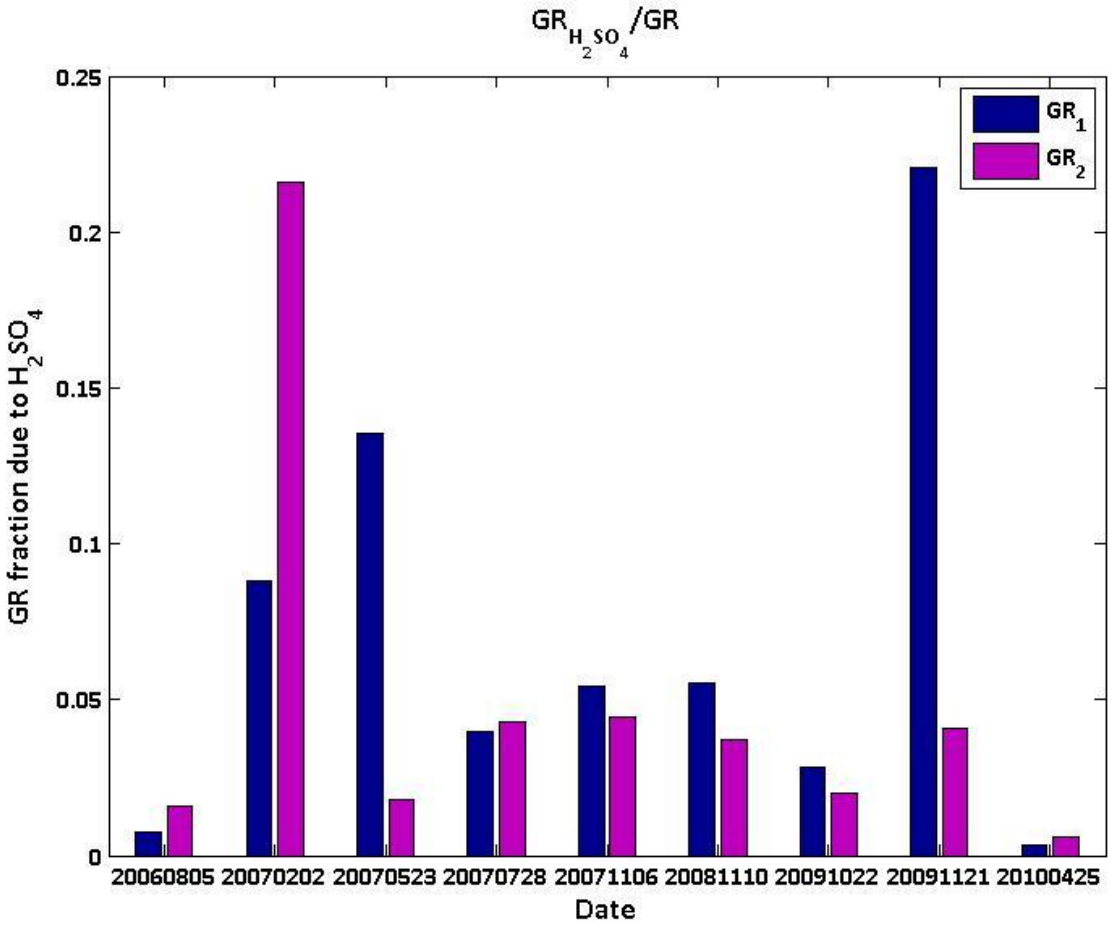


Figure 5. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 6 November 2007.

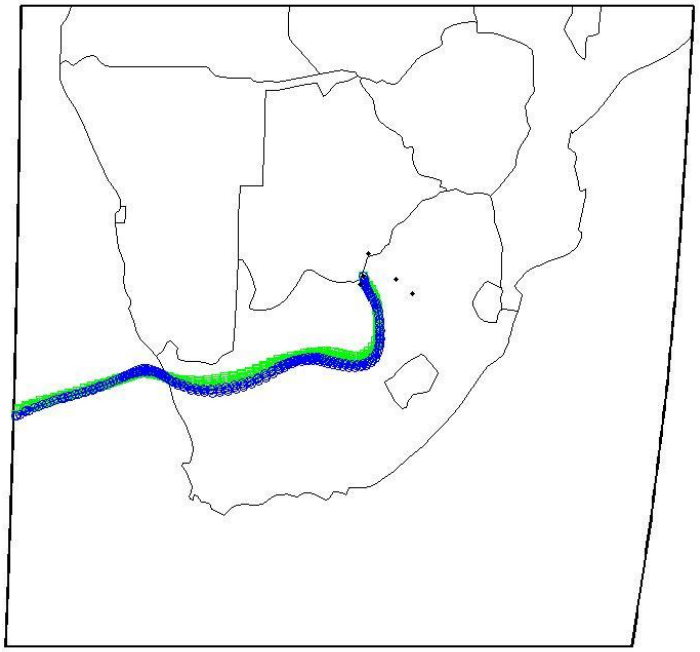
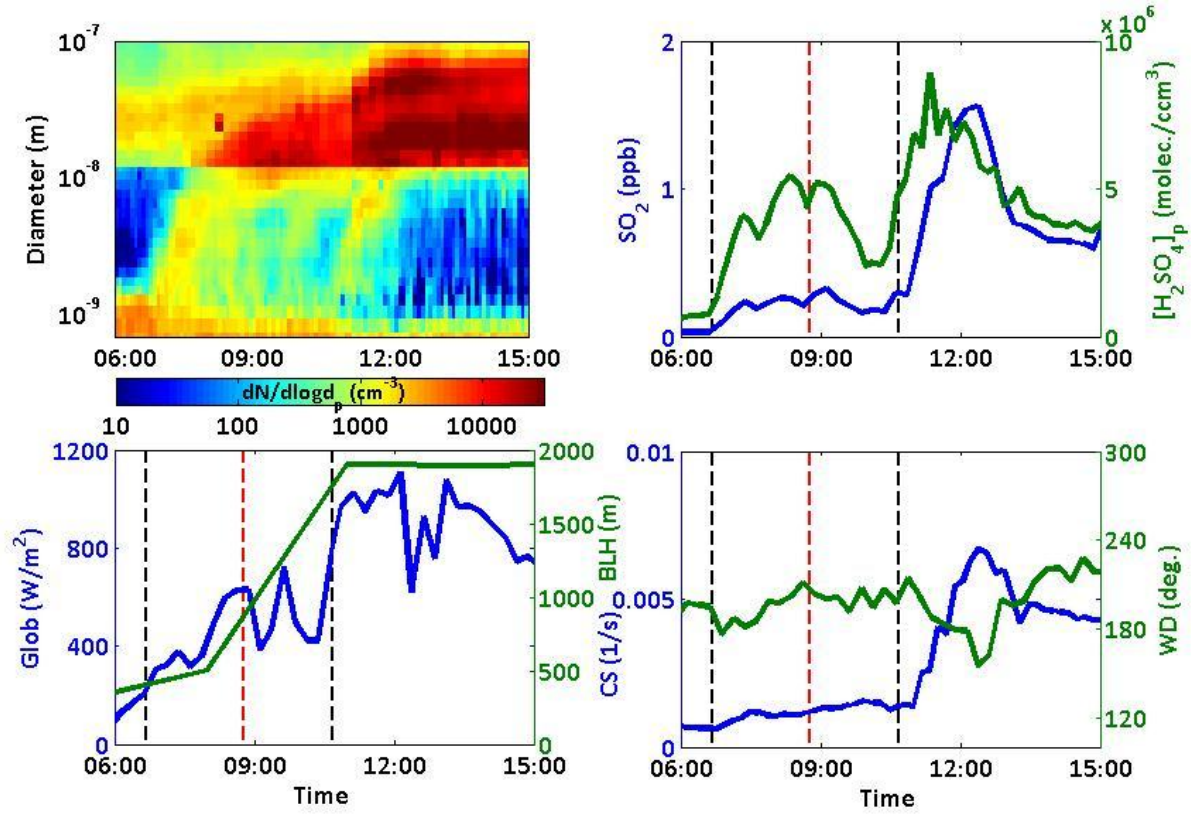


Figure 6. Example of two consecutive negative ion growth events (top left panel) at Botsalano on 6 November 2007. Concentration of SO_2 and H_2SO_4-proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height and global radiation (bottom left panel) are also 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 THE SUPPLEMENT

SUPPLEMENT

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

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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 $\partial\theta/\partial z > 0$.

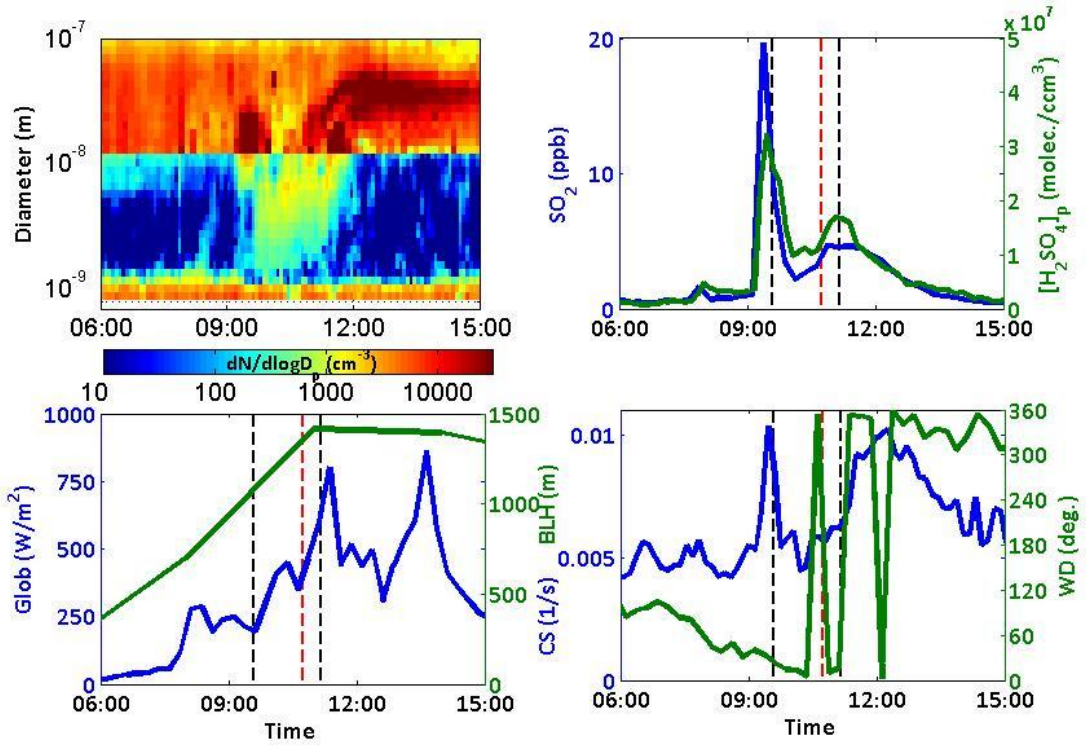

Figure S2. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 10 November 2008.

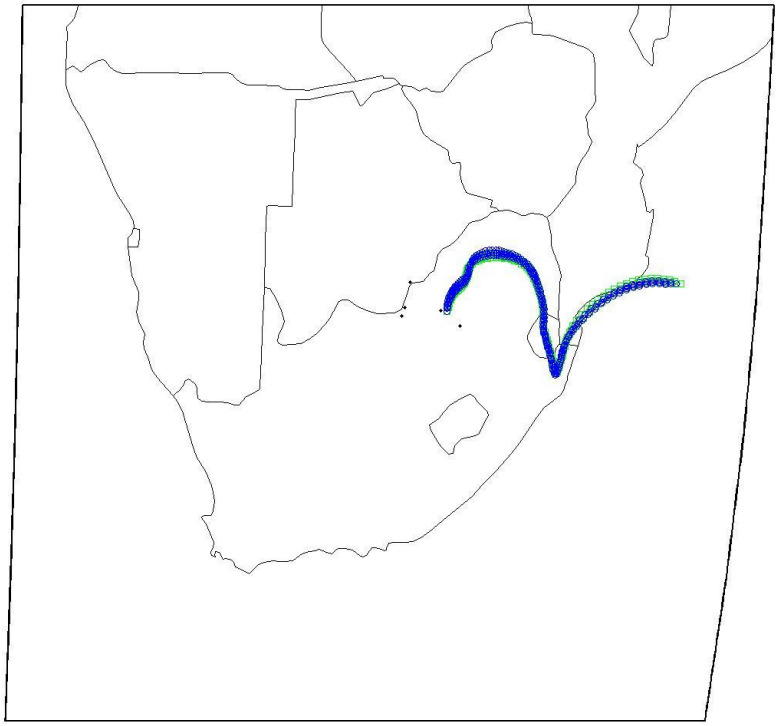

Figure S3. Two consecutive ion growth events (top left panel) at Marikana on 10 December 2008. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. 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 $\partial\theta/\partial z > 0$.

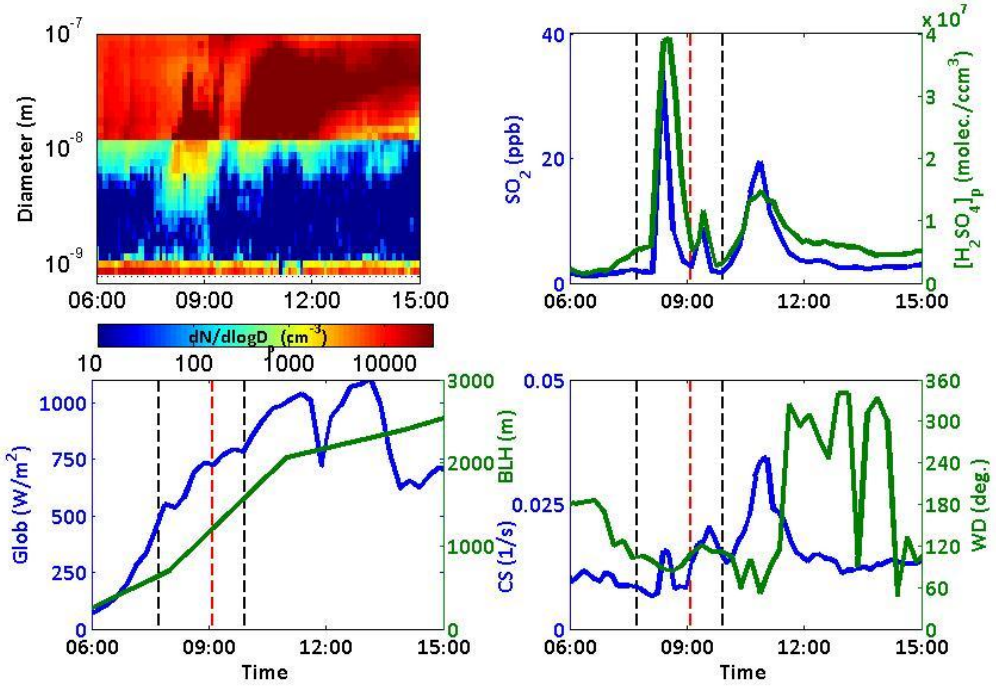

Figure S4. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 10 December 2008.

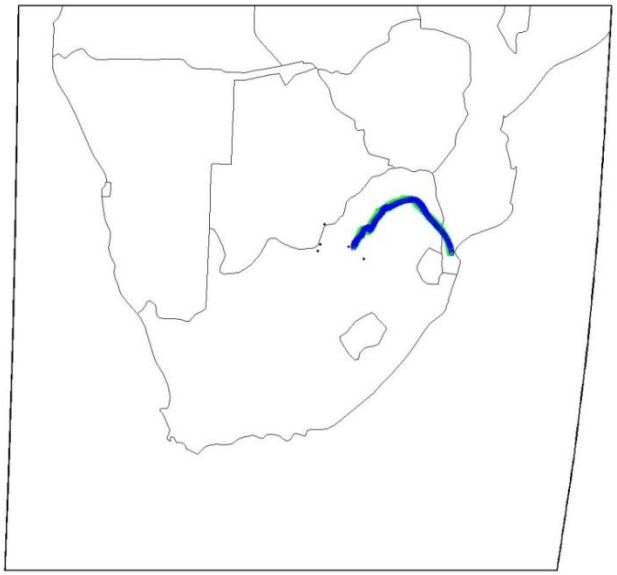

Figure S5. Two consecutive ion growth events (top left panel) at Marikana on 24 September 2009. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. 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 $\partial\theta/\partial z > 0$.

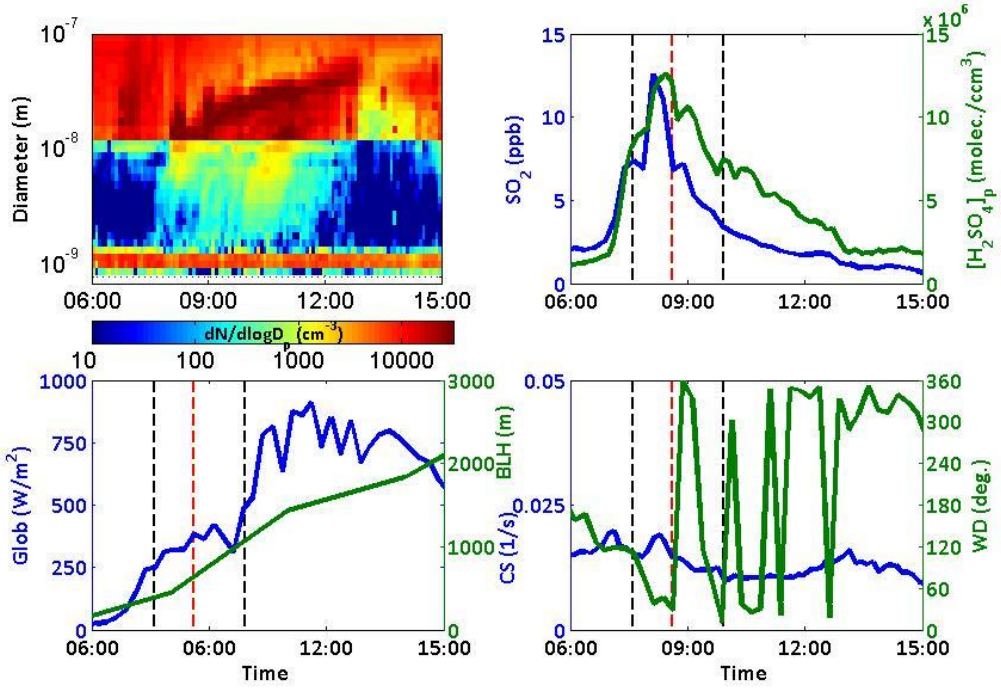

Figure S6. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 24 September 2009.

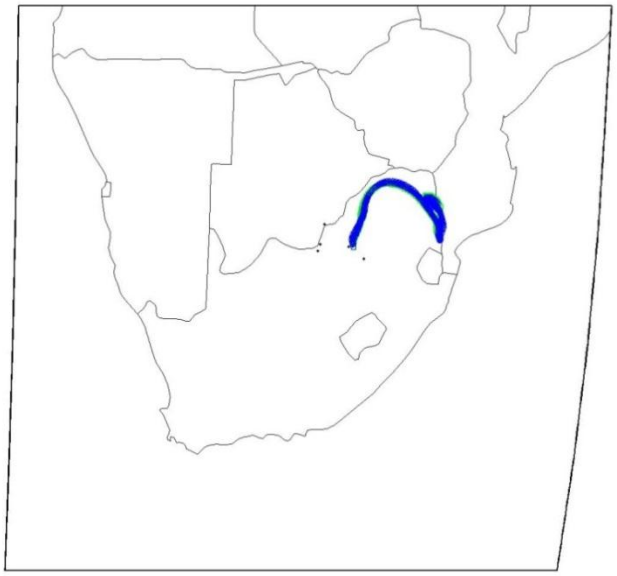

Figure S7. Two consecutive ion growth events (top left panel) at Marikana on 17 November 2009. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. 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 $\partial\theta/\partial z < 0$.

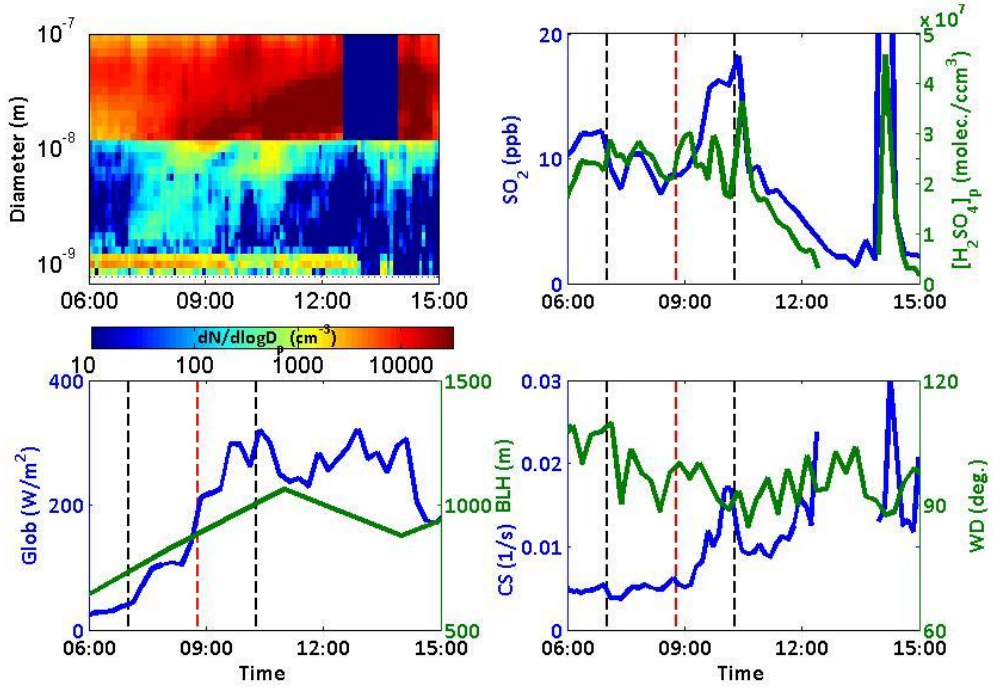

Figure S8. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 17 November 2009.

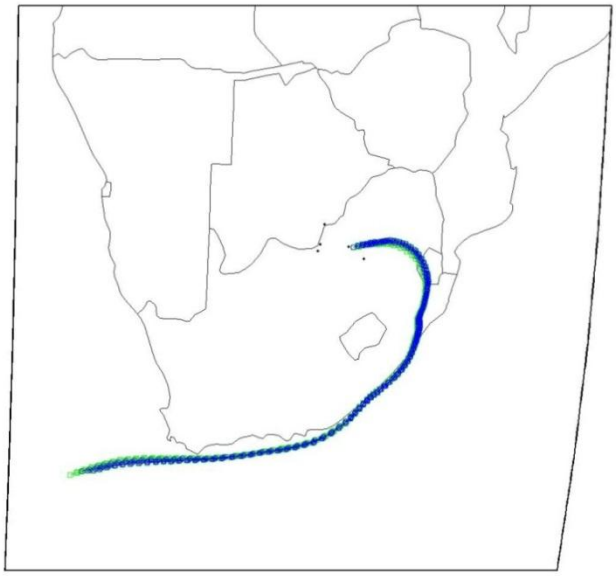

Figure S9. Two consecutive ion growth events (top left panel) at Botsalano on 5 August 2006. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The 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.

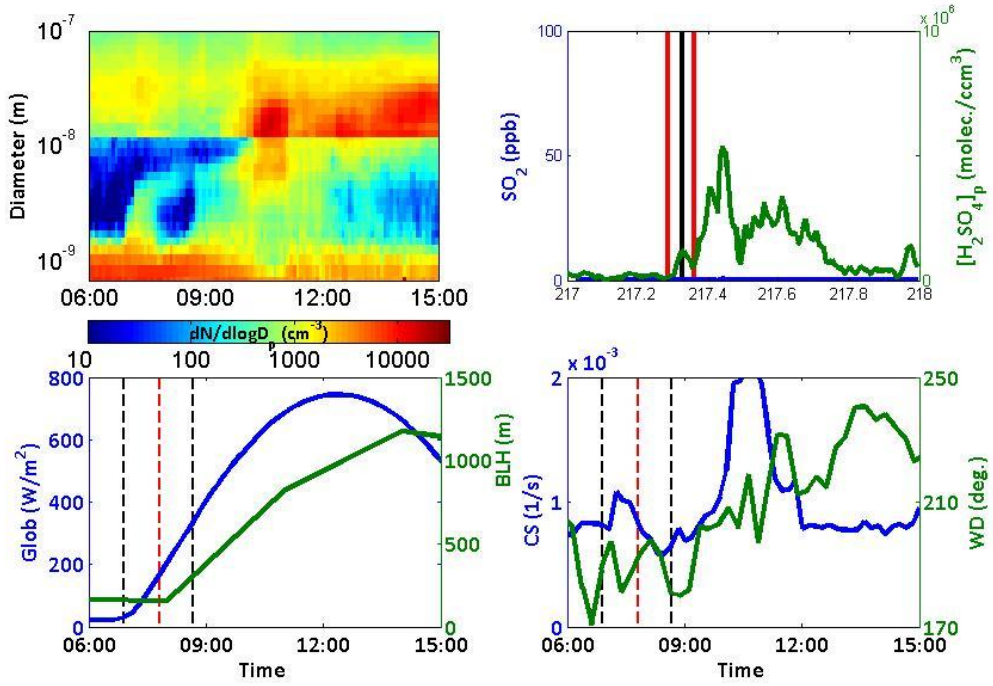

Figure S10. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 5 August 2006.

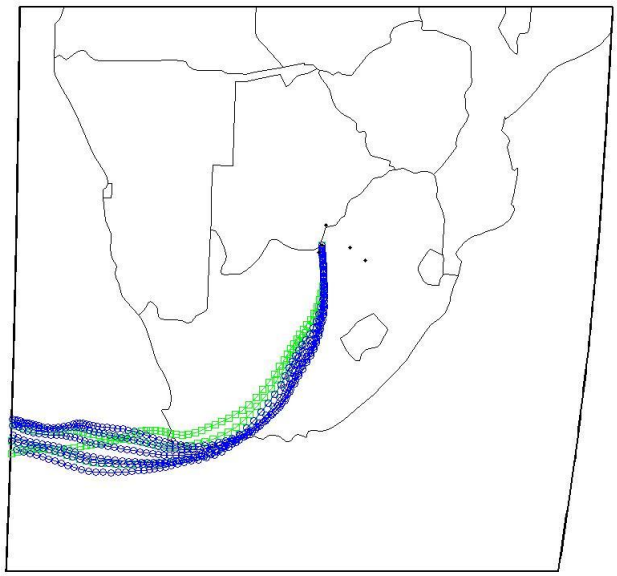

Figure S11. Two consecutive ion growth events (top left panel) at Botsalano on 18 August 2006. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. 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.

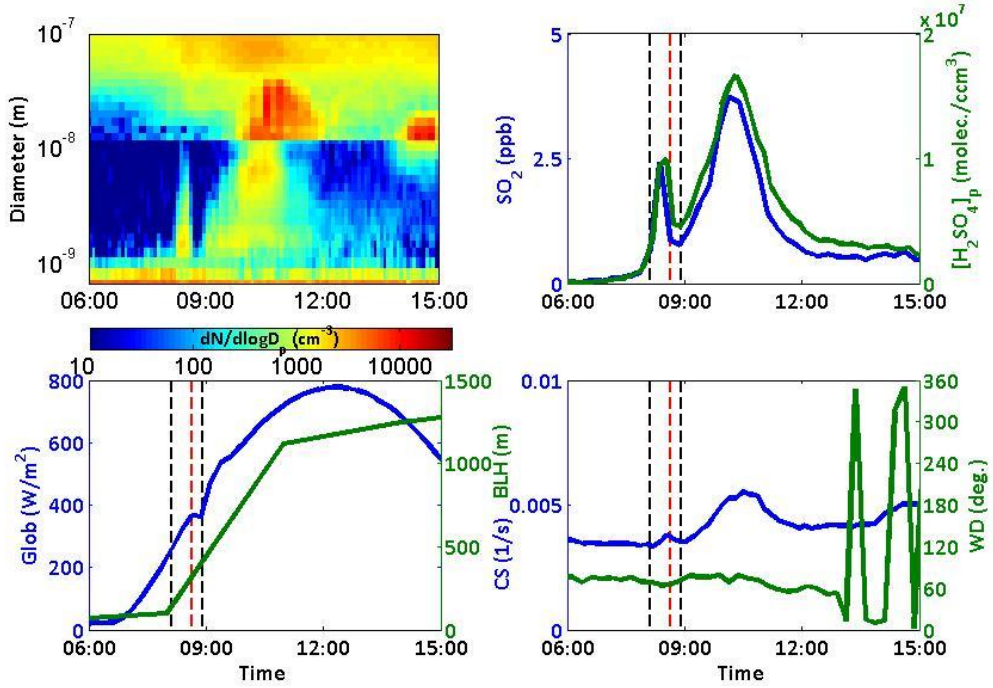

Figure S12. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 28 July 2007.

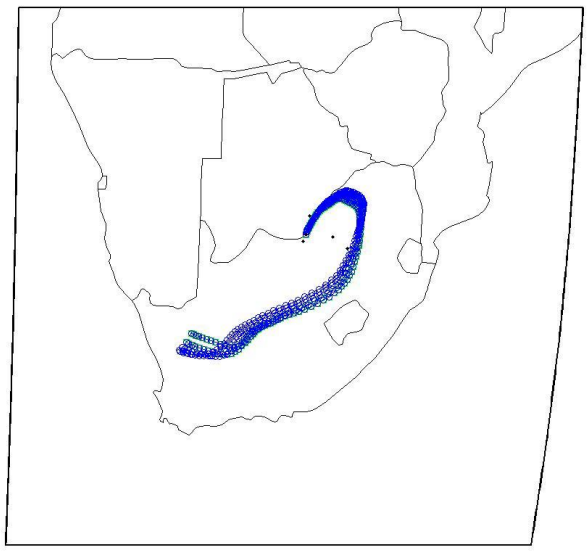

Figure S13. Two consecutive ion growth events (top left panel) at Botsalano on 23 May 2007. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The 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.

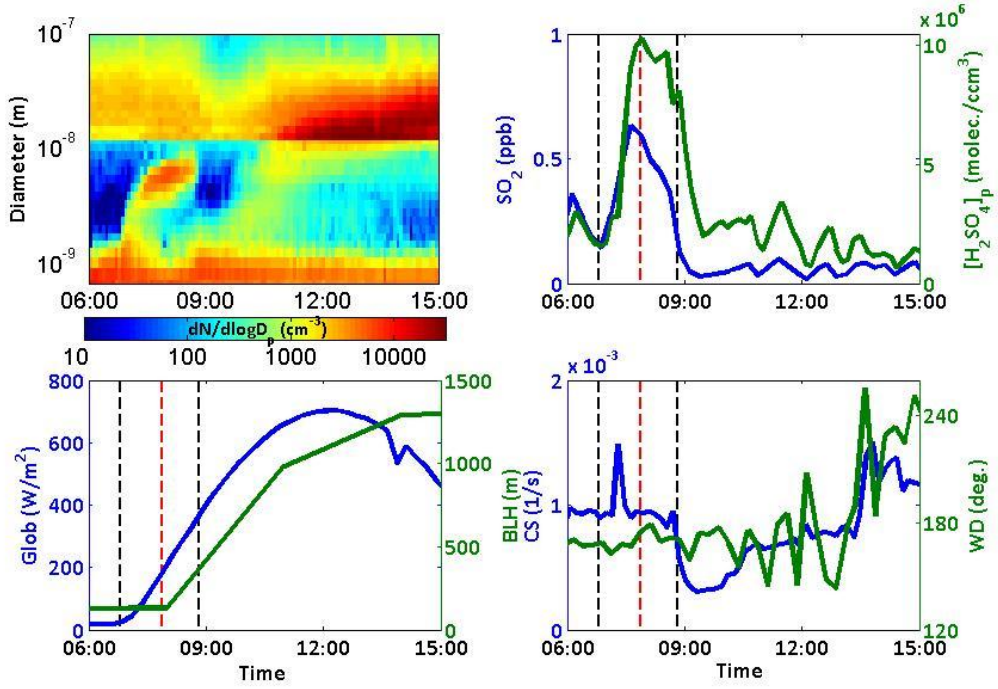

Figure S14. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 23 May 2007.

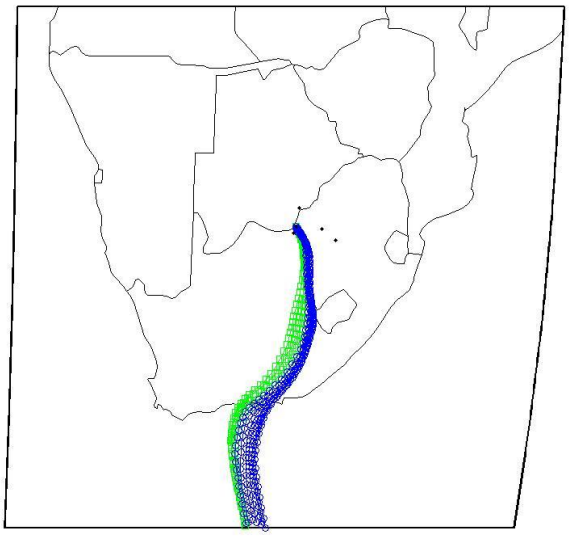

Figure S15. Two consecutive ion growth events (top left panel) at Botsalano on 28 July 2007. Concentration of SO_2 and H_2SO_4 proxy (top right panel), values of CS and wind direction (bottom right panel), and boundary layer height (BLH) and global radiation (bottom left panel) are also presented. The 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 $\partial\theta/\partial z > 0$.

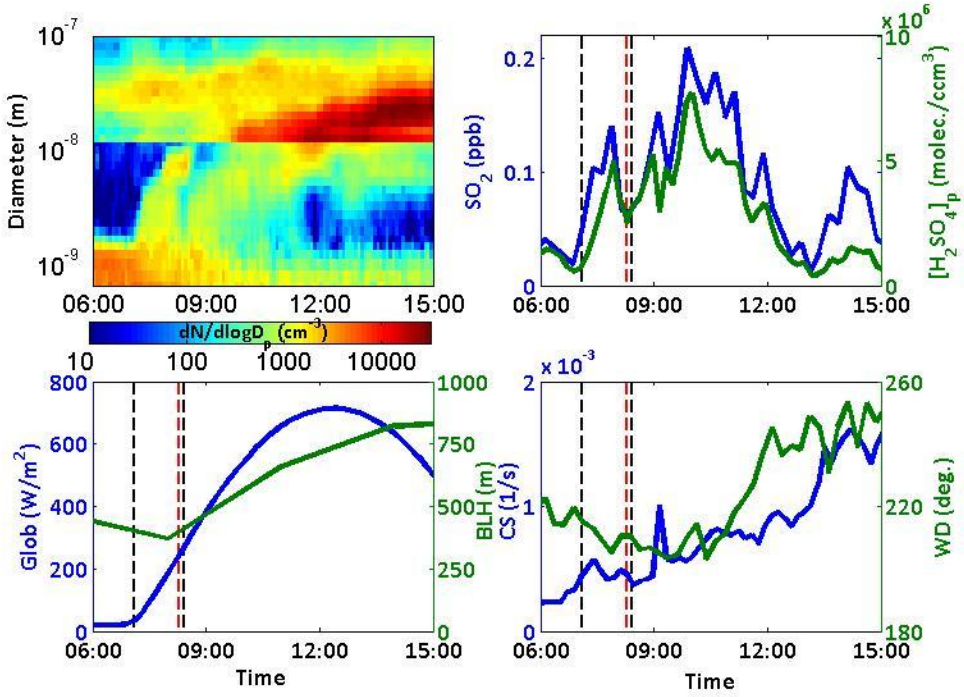

Figure S16. 96-hour air mass back-trajectories during the first (green) and second (blue) particle formation events on 28 July 2007.