Reply for the referee no 1

We would like to thank the referee for reviewing our manuscript. We have revised the manuscript according to the comments, for which we will reply in the following.

Referee: 1. There should be a summary of the gas and PM results in the paper. While page 1898, line 14 gives the citation to Venter et al. (2012) which apparently summarizes the gas phase data, it would be interesting to know the SO2 concentrations, NOx concentrations, and particulate levels in general (such as during nucleation event periods, on average, 5th and 95th percentiles – basic characterization information). This could be in a short table, or in the text. This is especially important since the gaseous data is at the submitted stage right now, and is in a less common journal (the S. Afr. J. Sci.). But even if the gas data was already published in a common and open access journal, I think there should still be summary in the current nucleation-focused work.

Authors: South African Journal of Science (http://www.sajs.co.za/) is an open-access journal with ISI citation index and thus the requested material will be freely available. However, we also included new table and following text at the beginning of the Results section:

A summary of daytime (08:00-14:00) gaseous and particulate pollutant concentrations at Marikana during the measurement period is shown in Table 1. As reported by Venter et al. (2012), the measured concentrations of SO_2, NO_x, CO and BC were relatively high but generally within the limits of European and South African air quality standards. The concentrations of O_3 and PM_{10} were observed to exceed regulations frequently.

Table 1. Median, 95th and 5th percentiles of global radiation, trace gas and estimated sulphuric acid concentrations, particle mass (in prevailing conditions) and black carbon mass concentrations during 08:00-14:00 local time on particle formation and undefined days, which classification was based on the DMPS data. Only median value is presented on non-event day.

	Event: **median** **95%** **5%**	**Undefined:** **median** **95%** **5%**	**Non-event:** **median**
CS (10^{-2} s^{-1})	0.89 2.17 0.23	0.74 1.8 0.11	0.89
$[H_2SO_4]_p$ **(10^6 molec. cm^{-3})**	6.2 31.2 0.8	3.2 16.4 0.5	3.1
SO_2 (ppb)	2.4 18.1 0.2	1.4 9.3 0.1	2.3
O_3 (ppb)	22.4 60.1 2.3	22.7 54.0 3.3	25.1
NO_x (ppb)	8.0 38.1 1.8	6.5 28.2 1.6	9.2
CO (ppb)	189 472 101	181 434 98	182
GLOB (W m^{-2})	489 971 137	421 907 126	156
PM_{10} (µg m^{-3})	26.6 74.62 7.6	26.8 69.6 8.1	32.4
BC (µg m^{-3})	1.2 4.1 0.3	1.0 3.2 0.3	NaN

Referee: 2. This information on general gas and particle level pollution (see #1) should be in the abstract.

Authors: We revised the abstract based on this comment and suggestions by referee no 2.

South Africa holds significant mineral resources, with a substantial fraction of these reserves occurring and being processed in a large geological structure termed the Bushveld Igneous Complex (BIC). The area is also highly populated by informal, semi-formal and formal residential developments. However, knowledge of air quality and research related to the atmosphere is still very limited in the area. In order to investigate the characteristics and processes affecting sub-micron particle number concentrations and formation events, air ion and aerosol particle size distribution and number concentration, together with meteorological parameters, trace gases and particulate matter (PM) were measured for over two years at Marikana in the heart of the western BIC. The observations showed that trace gas (i.e. SO_2, NO_x, CO) and black carbon concentrations were relatively high, but in general within the limits of local air quality standards. The area was characterised by very high condensation sink due to background aerosol particles, PM_{10} and O_3 concentration. The results indicated that high amounts of Aitken and accumulation mode particles originated from domestic burning for heating and cooking in the morning and evening, while during daytime SO_2-based nucleation followed by the growth by condensation of vapours from industrial, residential and natural sources was the most probable source for large number concentrations of nucleation and Aitken mode particles. Nucleation event day frequency was extremely high, i.e. 86 % of the analysed days, which to the knowledge of the authors is the highest frequency ever reported. The air mass back trajectory and wind direction analyses showed that the secondary particle formation was influenced both by local and regional pollution and vapour sources. Therefore, our observation of the annual cycle and magnitude of the particle formation and growth rates during nucleation events were similar to results previously published for a semi-clean savannah site in South Africa.

Referee: 3. As it relates to nucleation, the use of direction analysis (does nucleation occur preferentially from certain wind directions) would perhaps add more richness to the data analysis.

Authors: We included the following text at the end of Sect 4.3.3:

In addition to source and sink rates of nucleating and condensing vapours, particle formation is also affected by turbulent mixing of the boundary layer, as well as air mass origin and path. We, therefore, calculated 96-hour air mass back trajectories in one hour resolution with a model (Hybrid Single-particle Lagrangian Integrated Trajectory-HYSPLIT version 4.8) by the National Oceanic and Atmospheric Administration (Draxler and Hess, 2004; Air Resources Laboratory, 2011).

The discussion in sections 5.2 and 5.3 was also revised:

Sect. 5.2: *Air mass back trajectory analysis showed that despite the origin of the air masses, every trajectory circulated over the industrialised area of the western BIC and large cities nearby. The possible accumulation of trace gases from regional sources (Venter et al, 2012) may result in the*

observed high particle formation day frequency. Particle formation is also controlled by solar radiation. As is shown in Table 1, the non-event days were likely influenced by presence of optically thick clouds.

Sect. 5.3: *Particle formation and growth rates (J_{12} and GR_{12-30}) were higher from spring to autumn (Fig. 10, also compare to Fig. 5). Thus, ambient conditions were less favourable for 12-30 nm particle formation and subsequent growth in winter (Table 1 and 4). Magnitudes of formation and growth rates could not be explained by the estimated sulphuric acid concentration which indicates a substantial contribution from other vapours in these processes. We suggest that vapours of organic origin are probable candidates. The local wind direction did not seem to enhance formation or growth rates. This was expected, since the above discussed analysis indicated that particle formation and growth is probably affected by accumulation of trace gas species (e.g. SO_2 and organics) from regional sources.*

Referee: 4. Page 1903, line 15. Include how much data (for <3 nm, or >3 nm) is left over after the data cleaning.

Authors: We agree that this is very important information, which we had forgotten to highlight. We have modified text as follows:

Based on the above-mentioned results, it was decided to use the AIS data as follows: 1) sub-3 nm ion data was used only if the flow rate was at the desired level (60 lpm ± 5%), 2) data of ions larger than 3 nm in diameter were used if the flow rate had decreased by at most 20%, and 3) all the data affected by high electrometer noise (due to the accumulation of dirt on the electrometers) were excluded. After selecting the data based on the flow rate we were able to analyse 14 % and 78 % of the data of sub-3 nm and larger than 3 nm ions, respectively. The data cleaning removed large fractions of data for ions larger than 10 nm in diameter during the wet period (see Sect. 5.3).

Referee: 5. Section 4.2 on the procedures taken to correct data for high altitude are not clear. They are likely clear to those who are experts in data inversion for AIS and DMPS, but to others a better explanation of the correction is needed. Is the high altitude data being adjusted for comparability to sea level instrumentation, or is it the other way around?

Authors: We have presented a brief summary and appreciate references of the mobility to diameter conversion in a paper by Hirsikko et al. (2011). It is true that the deployment of two different temperature and pressure schemes is confusing, even though we had used the same mobility to diameter conversion algorithm (Millikan, 1923) for both particle datasets. We wanted to follow the example of previous papers (e.g. Manninen et al., 2010; Vakkari et al., 2011; Hirsikko et al., 2011 and references therein), where the ion mobility is converted to diameter by utilizing average summer temperature (ca. 23 °C) at sea level (1 atm) while diameters based on DMPS measurements are calculated at instant temperature and pressure inside the Differential Mobility Analyser. This leads only ca. 6 % difference when we compare the derived diameters. The text in the manuscript was revised as follows:

Our measurements were performed at a relatively high altitude (1170 m ASL), where annual average temperature and pressure were 19 ºC and 886 hPa, respectively. The mobility of an ion depends on both ambient pressure and temperature. Thus at higher altitudes the ions may become

more mobile compared to sea level. In this work we decided to use the Millikan diameter conversion (Millikan, 1923) for both the ion and particle datasets. Following the convention in previous publications (e.g. Manninen et al., 2010; Vakkari et al., 2011; Hirsikko et al., 2011 and references therein), the ion diameters were adjusted to average summer temperature (23 ºC) at sea level (1000 hPa), while the diameters of the DMPS data were calculated by using instant temperature and pressure inside the DMA. This led to a ca. 6 % underestimation of the ion diameters compared to diameters of DMPS size distribution data. This small discrepancy in derived diameters due to different temperature and pressure scheme is small compared to other sources of uncertainty.

Referee: 6. In section 4.3.3 the notation H2SO4 – proxy seems like it should be more compact, and not subject to the confusion that it might be H2SO4 minus proxy (which is what I first thought it was).

Authors: We changed the notation H2SO4-proxy to $[H2SO4]_p$ throughout the manuscript.

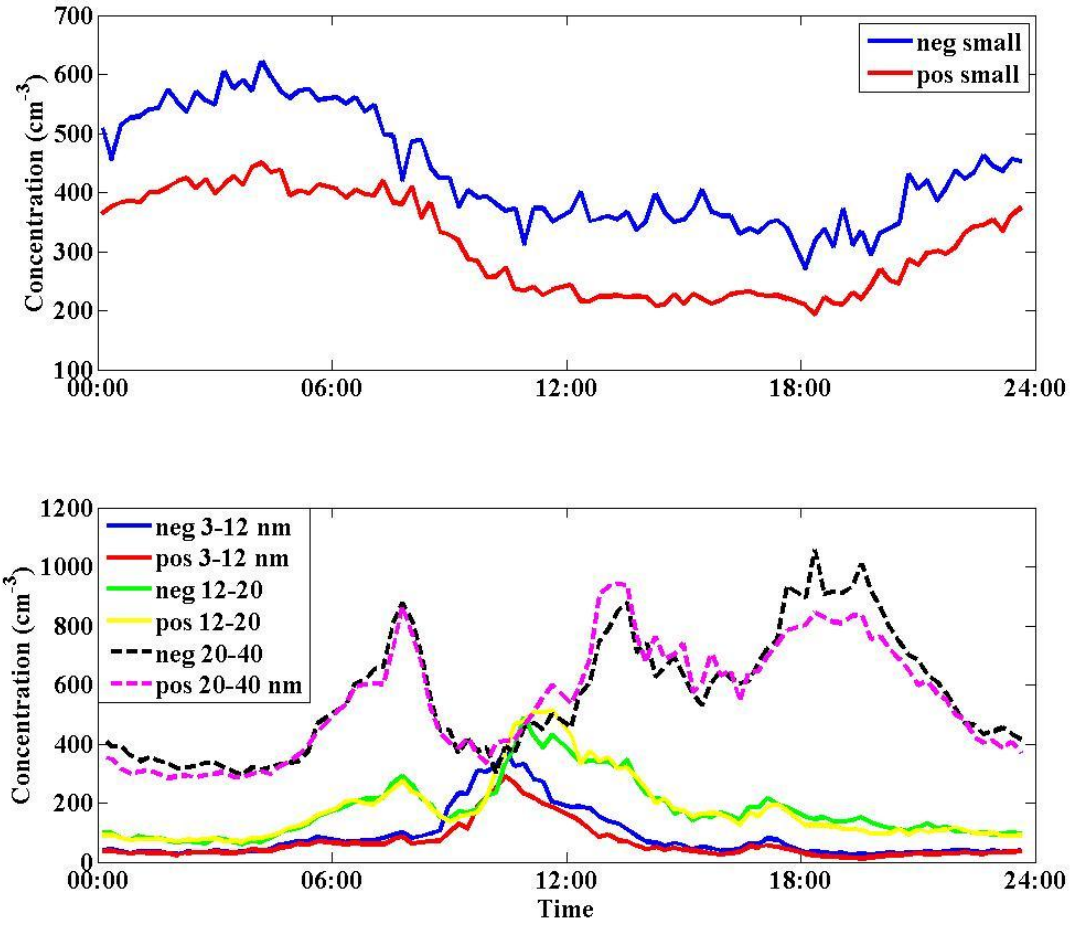
Referee: 7. A quantitative table of values for ion counts, particle counts, CS, etc. seems appropriate for the paper.

Authors: We think that particle number concentrations are already presented comprehensively by figures in the manuscript. In addition, as discussed in our answer to comment 1, we have included a new table (Table 1) together with explanations in the manuscript, which shows trace gas concentrations, CS, global radiation, particle mass (PM10) and black carbon during the most intensive nucleation period (from 8 AM to 2 PM) on particle formation, undefined and non-event days.

We have included a new figure, which presents ion concentrations during the periods when the flow rate inside the AIS was appropriate:

We also calculated small and nucleation mode ion concentrations during the period when the AIS flow rate was at the desired level (Fig. 6). The small ion concentrations were observed to follow the evolution of the mixing layer height, while as was expected, nucleation and Aitken mode ion concentration showed similar diurnal cycle as was shown in Fig. 5. The concentrations of ions larger than 3 nm in diameter reflected the number concentration measured with the DMPS. The median small ion concentrations were 320 cm^{-3} and 450 cm^{-3} for positive and negative small ions respectively, which are typical for polluted environments (Hirsikko et al., 2011).

Figure 6. Median diurnal concentrations: small ion concentrations are shown in the upper panel and concentrations of nucleation mode and 20-40 nm ions are presented in the lower panel.



Referee: 9. page 1909, line 7. More explanation or citations needed on how the authors are separating regional and local events.

Authors: We agree that our explanation requires some clarification. We made following changes in the text:

The nucleation events were observed on 86 % (DMPS), 84 % (negative ions) and 78 % (positive ions) of the analysed days at Marikana (Table 3, Fig. 9). With the ion spectrometer we were able to follow the growth of freshly nucleated ions, which allowed us to identify local charged particle formation events. The growing ion mode, however, was often visible from 3-7 nm upwards, which is an indication of a small contribution of ions to particle formation, or particle formation in residual layer or regional scale. If these observations were due to dominance of electrically neutral pathways in nucleation, then this would be in agreement with the theory and earlier observations that ion-mediated particle formation requires an environment of low nucleation rates, low temperature and aerosol content, but preferably having high concentrations of small ions and being rich with sulphuric acid (e.g. Laakso et al., 2002; Curtius et al., 2006; Iida 2006; Yu, 2010). Despite the relatively high estimate of sulphuric acid concentration, none of these requirements were met at Marikana. It is also possible that the nucleation already began in a residual layer before mixing into the boundary layer or some horizontal distance before the measurement site. Therefore, we suggest that regional new particle formation was significant at Marikana, despite the strong local pollution sources. This is understandable, as the typical transport time above the western BIC area is short (1-2 hours maximum).

In addition, we have revised our manuscript based on the comments of misspelling.

References

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

Curtius, J., Lovejoy, E. R., and Froyd, K. D.: Atmospheric ion induced aerosol nucleation, Space Sci. Rev., 125, 159–167, 2006.

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

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, 2011.

Iida, K., Stolzenburg, M., McMurry, P., Dunn, M. J., Smith, J. N., Eisele, F., and Keady, P.: Contribution of ion-induced nucleation to new particle formation: Methodology and its application to atmospheric observations in Boulder, Colorado, J. Geophys. Res., 111, D23201, doi:10.1029/2006JD007167, 2006.

Laakso, L., Mäkelä, J. M., Pirjola, L., and Kulmala, M.: Model studies on ion-induced nucleation in the atmosphere, J. Geophys. Res., 107(D20), 4427, doi:10.1029/2002JD002140, 2002.

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

Millikan, R.A.: The general law of fall of a small spherical body through a gas, and its bearing upon the nature of molecular reflection from surfaces, Phys. Rev., 22, 1-23, 1923.

Vakkari, V., Laakso, H., Kulmala, M., Laaksonen, A., Mabaso, D., Molefe, M., Kgabi, N., and Laakso, L.: New particle formation events in semi-clean South African savannah, Atmos. Chem. Phys., 11, 3333-3346, 2011.

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

Yu, F., Luo, G., Bates, T. S., Andersson, B., Clarke, A., Kapustin, V., Yantosca, R. M., Wang, Y., and Wu, S.: Spatial distributions of particle number concentrations in the global troposphere: Simulations, observations, and implications for nucleation mechanism, J. Geophys. Res., 115, D17205, doi:10.1029/2009JD013473, 2010.