Reply for the referee no 2

We would like thank referee for comments and suggestions to improve our manuscript. We have implemented the following corrections and changes.

Referee: 1. I think it makes sense to give some background to the project in the abstract, but in the current version half the abstract is spent on providing background information and describing the site. I recommend a larger fraction of results and conclusions in the abstract.

Authors: We revised the abstract based on this comment and suggestions by referee no 1

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: 2. It is interesting that the number of days with new particle formation events is higher here than in previous studies focusing on new particle formation. Could the authors add some discussion on what the reason for this might be? For instance, is the concentration of H2SO4 higher (or is the CS lower) in this study compared to other similar studies? Also, is there a clear difference between event days and non-event days (e.g. in terms of gas-phase concentrations or meteorological conditions) that may explain why new particle formation occur or does not occur on a certain day?

Authors: Based on this comment and comment 1 by referee 1, we included a new table to manuscript

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

The fourth paragraph in Sect 5.2 was modified as follows:

Typically, particle formation events at Marikana began earlier in the morning during the wet period than during the dry period, due to the earlier sunrise (Fig. 5). Although the difference of nucleation event day frequency between the various months was small, we may conclude that the DMPS nucleation event day frequency was slightly higher in summer and early autumn (wetter period) than in winter and spring (dryer period). In summer, the air was cleaner, but the estimated sulphuric acid concentration showed lower monthly median values (Fig. 7). In contrast, based on the ion spectrometer the nucleation event day frequency was slightly higher during late autumn and winter having a similar annual cycle as $[H_2SO_4]_p$ (Fig. 7). Nevertheless, as shown in Table 1, concentrations of SO_2, $[H_2SO_4]_p$ and CS were typical for urban environments, but also higher during nucleation and growth events compared to undefined and non-event days, or to values observed in rural environments (e.g. Hirsikko et al., 2007b; Petäjä et al., 2009; Asmi et al., 2011; Wu et al., 2011; Mikkonen et al., 2011).

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.

The first paragraph in Sect. 5.3 is also revised

Particle formation and growth rates (J_{12} and $GR_{12\text{-}30}$) 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.

High formation rates were observed to occur simultaneously with fast growth rates (Fig. 11). Both formation and growth rates were observed to correlate with concentrations of Aitken mode particles during nucleation events, but not with the accumulation mode particle concentrations. When comparing our results of J_{12} and $GR_{12\text{-}30}$ (Fig. 10) to observations by Vakkari et al. (2011) in the semi-clean South African savannah, we notice that both the magnitude and temporal variation of these parameters were similar.

Referee: 3. Can the estimated H2SO4 concentrations explain the observed growth rates?

Authors: The following sentences were included:

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.

Referee: 4. Page 1907, lines 23-25: Do the authors mean that nucleation, Aitken and accumulation mode particle concentrations were correlated with BC, CO and NOx concentrations: : :? I think it would be easier to follow the discussion in this paragraph if a figure was added showing the median diurnal cycles of BC, CO, NOx, SO2, and estimated H2SO4 similar to Fig. 5. An alternative would be to provide a table with daytime correlation coefficients for each mode with BC, CO, NOx, and SO2?

5. Page 1908, lines 1-4: This sentence could be phrased more clearly. I suppose the authors mean that the lack of correlation between the three modes with SO2 in the morning and evening suggest that the responsible source for the peaks in the morning and evening is residential combustion. However, the authors say on page 1907, lines 23-25, that concentrations of the three modes were associated with SO2 in daytime. I suppose then that the authors do not think that morning is included in "daytime", but this needs to be explained more clearly.

6. Page 1907, lines 25-27: Wouldn't you expect the concentration of nucleation mode particles to be anti-correlated to the CS, not being independent? That being said, I know this is not always the case.

Authors: In the following we will present changes due to comments no 4-6: We agree that figure showing median diurnal cycles of BC, CO, NOx, SO_2, H_2SO_4 would add value to our paper. However, such figures will be presented by Venter et al., 2012. We have included a new figure showing the variation of particle concentrations as a function SO2 and a table presenting correlation coefficients between trace parameters and particle concentrations:

Figure 8. Concentrations of nucleation ($dN_{12\text{-}20\ nm}$), Aitken ($dN_{20\text{-}50\ nm}$ and $dN_{50\text{-}100\ nm}$) and accumulation ($dN_{100\text{-}840\ nm}$) mode particles are presented as a function of SO_2 concentration during the dry season (upper panel) and the wet season (lower panel). Red dots indicate daytime concentrations (between 06:30-17:30) and black dots represent night-time (between 18:30-05:30) concentrations.

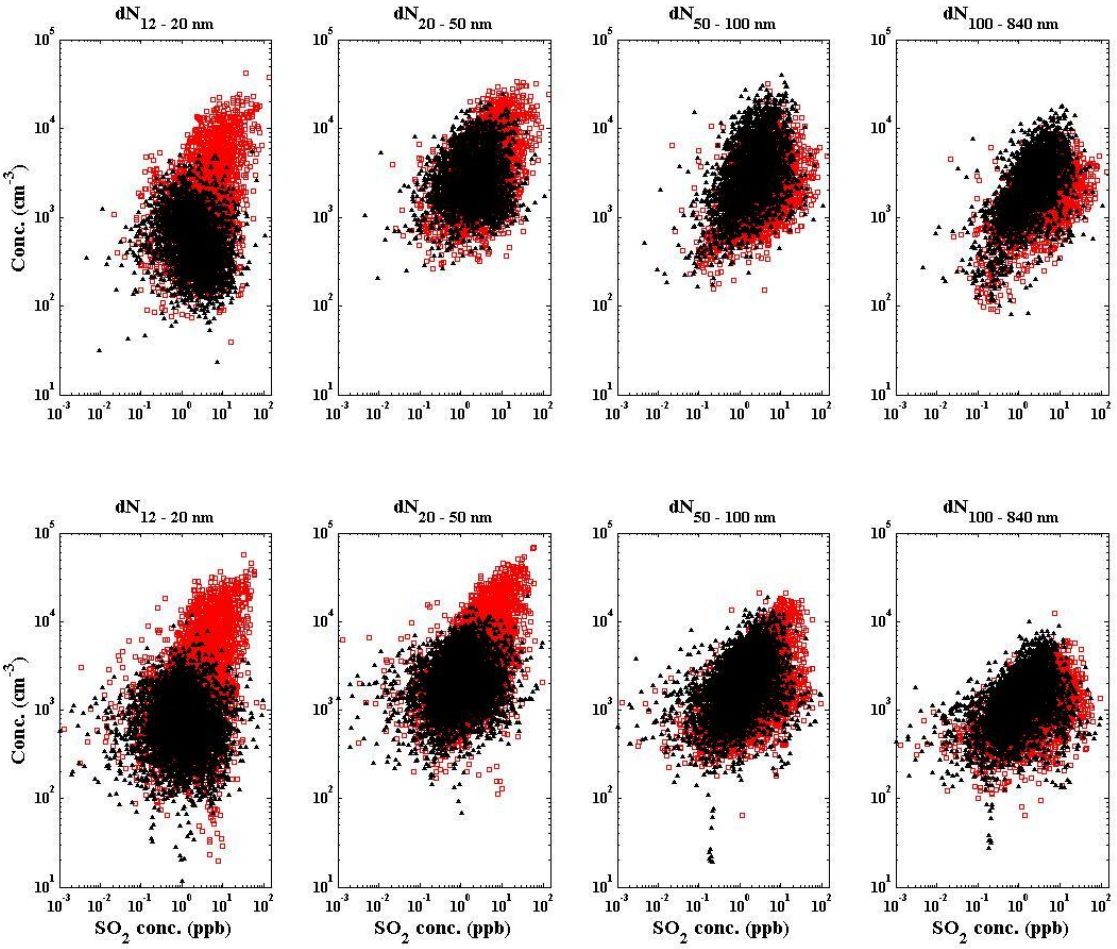

Table 2. Here Pearson correlation coefficients (r) between various trace parameters and particle concentrations are presented. Particle concentrations were calculated for four size ranges: 12-20 nm, 20-50 nm, 50-100 nm and 100-840 nm.

Dry | Wet season	**Conc.$_{12\text{-}20\ nm}$**	**Conc.$_{20\text{-}50\ nm}$**	**Conc.$_{50\text{-}100\ nm}$**	**Conc.$_{100\text{-}840\ nm}$**
SO_2: daytime	0.48 | 0.49	0.38 | 0.51	0.18 | 0.36	0.29 | 0.30
night-time	-0.05 | -0.02	0.10 | 0.09	0.21 | 0.14	0.30 | 0.12
CO: daytime	-0.13 | -0.02	0.04 | -0.03	0.44 | 0.09	0.69 | 0.41
night-time	0.14 | 0.35	0.65 | 0.51	0.76 | 0.58	0.82 | 0.67
NO_x: daytime	-0.08 | 0.00	0.07 | -0.01	0.38 | 0.09	0.47 | 0.32
night-time	0.26 | 0.47	0.53 | 0.53	0.53 | 0.46	0.55 | 0.43
BC: daytime	-0.08 | 0.02	0.08 | -0.01	0.41 | 0.09	0.68 | 0.45
night-time	0.07 | 0.35	0.57 | 0.51	0.72 | 0.58	0.84 | 0.67
CS: daytime	0.02 | 0.15	0.30 | 0.40	0.74 | 0.72	0.96 | 0.86
night-time	0.00 | 0.12	0.68 | 0.46	0.91 | 0.85	0.99 | 0.97

The text was revised as follows:

Venter et al (2012) indicated that NO_x, CO, BC and particulate mass mainly originated from local residential combustion for heating and cooking at Marikana, while SO_2 mainly originated from high stack industry emissions. Correlation coefficients between nucleation, Aitken and accumulation mode particle concentrations and trace gas, BC and CS are presented in Table 2. In addition, the relationship between particle and SO_2 concentrations are shown in Fig. 8. These observations together with the temporal variation of the particle number concentrations indicate that the morning and evening concentration peaks (Fig. 5) were due to the local residential combustion rather than due to industrial emissions. During the dry periods, which correspond to winter and the colder autumn and spring months, domestic burning is a major particle source. Residential combustion mainly takes place during the early morning and evening. Evening concentration peaks (Fig. 5) are usually more pronounced due to the need for space heating. The morning residential combustion period is usually curtailed due to warming temperatures and residents leaving for work. During the wet periods, which correspond to summer and the wetter autumn and spring months, domestic heating probably plays a smaller role as a particle source. Hence the observed Aitken and accumulation mode particles concentrations were higher in the dry periods (Fig. 4).

Referee: 7. Page 1907, lines 9-11: I think it looks as the nucleation mode midday concentration was higher during the dry season in Fig. 5.

Authors: We have revised the paragraph on page 1907, lines 6-11 as follows

Nucleation mode (12-20 nm in diameter) particle concentrations also had three concentration peaks during the day, the most important being at or before midday (Fig. 5). However, nucleation mode particle concentrations did not show as clear annual cycle as was seen with larger particles (Fig. 4).

Referee: 8. Page 1912, lines 14-15: Only the Aitken mode particles did originate from nucleation in the afternoon, not the accumulation mode particles, right?

Authors: Thank you for noticing our misspelling. We have rewritten the sentence as follows

Aitken and accumulation mode particles originated from domestic burning for heating and cooking, but in the afternoon an increased Aitken mode particle concentrations were also observed due to regional nucleation and subsequent growth from industrial, residential and biological emissions.

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

References

Asmi, E., Kivekäs, N., Kerminen, V.-M., Komppula, M., Hyvärinen, A.P., Hatakka, J., Viisanen, Y., and Lihavainen, H.: Secondary new particle formation in Northern Finland Pallas site between the years 2000 and 2010, Atmos. Chem. Phys. Discuss., 11, 25709-25750, 2011.

Hirsikko, A., Yli-Juuti, T., Nieminen, T., Vartiainen, E., laakso, L., Hussein, T., and Kulmala: Indoor and outdoor air ions and aerosol particles in the uban atmosphere of Helsinki: characteristics, sources and formation, Boreal Evn. Res., 12, 295-310, 2007b.

Mikkonen, S., Romakkaniemi, S., Smith, J.N., Korhonen, H., Petäjä, T., Plass-Duelner, C., Boy, M., McMurry, P.H., Lehtinen. K.E.J., Joutsensaari, J., Hamed, A., Mauldin III, R.L., Birmili, W., Spindler, W., Arnold, F., Kulmala, M., and Laaksonen, A.: A statistical proxy for sulpuhuric acid concentration, Atmos. Chem. Phys., 11, 11319-11334, 2011.

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, 2009.

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.

Wu, Z., Hu, M., Yue, D., Wehner, B., and Wiedensohler, A.: Evolution of particle number size distribution in an urban atmosphere during episodes of heavy pollution and new particle formation, Science China, Earth Sciences, 54(11), 1772-1778, 2011.