Referee 1: we thank Referee 1 for his comments and suggestions.

Comment 1: Sections 2.2.3 and 2.3.1: The APi-TOF (Atmospheric Pressure interface-Time Of Flight) mass spectrometer is introduced in this section; however, none of its data is shown, although it is mentioned (end of section 2.2.3) that APi-TOF data was used to derive a proxy for determining the H2SO4concentrations from other parameters like the global radiation, the condensation sink, the RH and the SO2 concentration. As the values of the sulfuric acid concentrations are crucial for the conclusion that other compounds besides sulfuric acid are required to explain the observed nucleation rates, the evaluation of the [H2SO4] deserves much more attention. Several points need to be addressed when reporting H2SO4 levels: (i) the empirical factor k was determined from data between January 30 and February 6, which is a rather short time to gain confidence in the derived factor, (ii) it is mentioned that the period between February 10 and February 29 was characterized by unusual cold temperatures, it is therefore questionable if the derived scaling factor is valid under such conditions, and, most importantly (iii) the APi-TOF cannot directly measure the sulfuric acid concentration as it measures only atmospheric ions and not the neutral H2SO4molecules. Previous studies, like the ones cited (Petäjä et al., 2009; Mikkonen et al., 2011) were however deriving scaling factors based on measurements with a chemical ionization mass spectrometer (CIMS), which can measure the neutral [H2SO4] and should therefore yield much more reliable approximations. To my knowledge the method of deriving H2SO4values from APi-TOF ion measurements has not been described anywhere in the literature before; therefore a detailed description is required in this manuscript. Furthermore, an evaluation of the deployed methods should be presented, which relies on a side-by-side measurement of an APi-TOF and a CIMS over a certain period. In summary, in order to report any [H2SO4] values and use them for the interpretation of the data the methods used to evaluate the sulfuric acid concentrations need to be presented in much greater detail and the authors need to convince the reader that their derived concentrations are accurate enough to be used at all. Detailed error estimates are required as well.

Reply 1: (i) and (ii): It is true that the empirical factor was obtained from a rather short period, but during which atmospheric conditions were very similar to the ones observed during the studied period. Especially, between 30 January and 6 February, temperatures were very low, on average -11.8°C. We clearly believe that the use of this factor gave us the opportunity to work with a proxy adapted to the site and especially to the unusual conditions observed in February 2012. The similarity of the two periods regarding atmospheric conditions is now mentioned in the text. We also strongly believe that the use of this proxy is much more reliable than the use of any other proxy that would be derived from other location/time periods. At last, using one proxy or another is only a matter of scaling factor, and the relative abundance of sulfuric acid from one to the other period would be preserved. Here we only discuss this relative change in the sulfuric acid concentration, and not the absolute values of sulfuric acid.

(iii) Referee is correct that the deriving neutral H2SO4 concentration form natural ion concentration is not trivial and not widely reported in literature. In the present study, we follow the method described by (Eisele 1989) to calculate neutral H2SO4 concentration based on naturally charged negative ion measurements, more precisely on the relative ion concentrations of NO3- and HSO4- ions. Detailed explanation can be found from (Eisele 1989), now referenced in the manuscript. In short, the theory behind is based on observations where NO3- ion is dominant during most of the time, except when sulphuric acid is present, during these periods, HSO4- is the dominant naturally charged ion. HSO4- ion is formed from a reaction between NO3- and H2SO4. It can be assumed that the NO3- ion acts as a reagent ion in CI-source and the ratio of HSO4- and NO3 – ion species could be used to estimate the neutral concentration of H2SO4. Eisele 1989 used a coefficient (derived from collision frequency, assumed ion life time and reaction rate coefficients) cc=4.1x10^6 in Eq 1.

$$[H2SO4] = cc\frac{[HSO_4{}^-] + [HNO_3HSO_4{}^-]}{[NO_3{}^-] + [(HNO_3)_1NO_3{}^-]} \qquad \text{Eq1}$$

Due to differences between instruments that Eisele was using and the one used in this study the “calibration” coefficient cannot be used directly. Instead we compared sulphuric acid concentration calculated form naturally charged ion signals to measured sulphuric acid concentration by calibrated CI-APiTOF (Jokinen, et al. 2012). The comparison was done for measurements in Hyytiälä field station (Hari and Kulmala 2005). Comparison of the two concentrations is depicted in Figure 1. From this we obtained a new calibration coefficient for our instrumentation that was 9.7e4.

The methodology is now described in the manuscript.

After adjusting the proxy, the average positive and negative bias between proxy estimations and the Api-Tof derived concentrations were 0.57×10^7 and -0.97×10^7 cm^{-3}, respectively, which is now also mentioned in the text. This deviation is significantly lower than the differences which are observed between H_2SO_4 averaged concentrations from the three sub-periods, suggesting that the proxy is accurate enough to draw global conclusions concerning the role of H_2SO_4 in the nucleation process during the studied period at the Puy de Dôme.

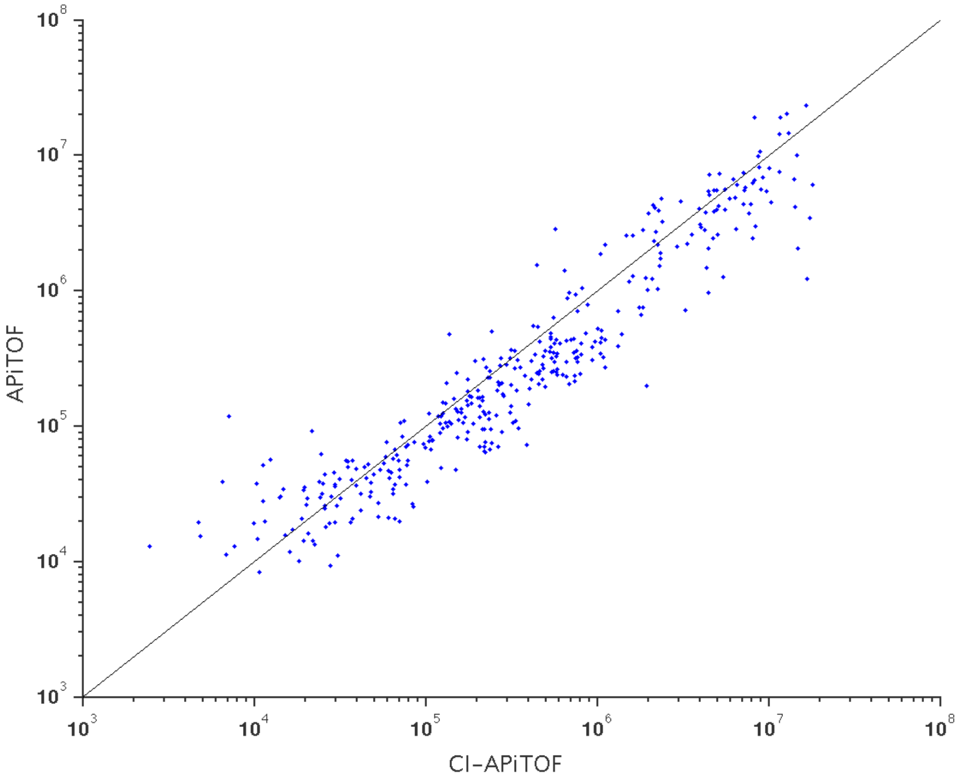

Figure 1. Sulphuric acid concentration calculated from naturally charged ions (APiTOF) and measured by CI-APiTOF.

Comment 2: Nucleation rates are known to depend strongly on temperature and also on relative humidity in some systems. However, these effects are neglected from the discussion of the observed nucleation rates. Instead, the nucleation rates are discussed mainly in terms of the sulfuric acid concentration and the degree of pollution (condensation sink and black carbon concentration) during NPF. If one compares the temperatures (T) and the relative humidities (RH) of the different sub-periods, at least qualitatively the variation of T and RH can also explain the occurrence of NPF. In my opinion the amount of data is too small to disentangle the effect of all involved parameters unambiguously. This should be explicitly stated.

Reply 2: It is true that a potential effect of temperature and RH on NPF is interesting to discuss. For that purpose, an additional section was added to the manuscript. But, as also suggested by Referee 1, we do believe that the small size of the dataset does not allow a complete multi-component analysis of the effects of the different atmospheric parameters.

The newly added section is reported below:

"3.2.4 A potential additional effect of temperature and relative humidity?

In the present study, the occurrence of nucleation and the concentration of nucleated clusters have been discussed so far in terms of sulfuric acid concentration and condensation sink only. However, temperature and relative humidity display significant variations in the course of the measurement period and were previously reported in the literature to have effect on the occurrence of nucleation and on the characteristics of the events (formation rates, cluster concentrations). In fact, low temperatures could favor nucleation, and could in particular explain, together with low CS, the occurrence of NPF in the FT and in the low stratosphere (Young et al., 2007). In contrast, the role of the RH appears to be more equivocal. Numerous observations suggest that nucleation could be favored at low RH (e.g.: Birmili et al., 2003) and both the cluster formation rates (Sihto et al., 2006) and the concentration of freshly formed particles (Jeong et al., 2004) were already reported to be anticorrelated with RH. Nonetheless, NPF events were observed in the vicinity of clouds, where RH often exceeds 90% (Clarke et al., 1998). In a more recent study based on model simulations, Hamed et al. (2011) suggest that high RH impact the amount of solar radiation, and thus the source of condensable species, rather than the sink term.

Thus, it is likely that at the Puy de Dôme, the very low temperatures measured during Period 1 (average -14.24 °C) could explain, at least partly, the occurrence of nucleation, and maybe the intensive formation of neutral clusters compared to Period 3. However, regarding previous observations from the literature, one could have expected less intense NPF events since high RH were simultaneously recorded during Period 1 (90.8%). The opposite trend is observed for the second NPF period, Period 3, which displays increased temperatures (4.96 °C) and decreased RH (51.8 %) compared to Period 1. During Period 2, RH is further decreased (29.3 %) and temperatures remain low (-1.40 °C) but, as previously mentioned, nucleation is not triggered. The previous observations suggest that atmospheric parameters, including temperature, RH, but also sources and sinks, cannot be considered separately. This might be explained by the fact that their effects combine with each other, but the amount of data used in the present study seems to be too small to analyze such combinations or to disentangle the effects of all parameters unambiguously.”

Comment 3: I am not completely convinced, that neutral nucleation dominates to the extent the authors suggest. Taking the data from Table 1, one can calculate the fraction of the ion-induced nucleation (IIN) from the ratio of the ion-induced formation rates (JIIN,1.5= J1.5++ J1.5–) and the total formation rates (J1.5tot). These fractions are rather low for the first three events (<5%) (all belonging to sub-period 1) but are 49% and 19% for the last two events (both belonging to sub-period 3). If one takes into account the low temperatures during sub-period 1 (-14 °C) and compares this to the temperature during sub-period 3 (+5 °C) another possibility, consistent with the observations, would be that theneutral nucleation pathway dominated due to the lower temperatures (and maybe higher RH). In their revision, the authors should therefore discuss such a possibility. The fact that IIN is compatible with neutral nucleation during sub-period 3 can also be concluded from the data in Table 3 where the concentration of charged nuclei is much higher than the neutral one. Since during sub-period 3 the site was influenced by free tropospheric air (in contrast to sub-period 1) it would be possible that IIN is rather important under these conditions.

Reply 3: In the new version of the manuscript Period 1 and 3 are considered separately:

"Moreover, the average formation rates of total 1.5 nm particles exceeds those of charged particles, especially during Period 1 which displays ion induced nucleation fractions (IIN) lower than 4.3% ($J_{1.5}^{tot} \approx 37\times J_{1.5}^{+}$ and $J_{1.5}^{tot} \approx 77\times J_{1.5}^{-}$), which is relatively low compared to the average values reported for altitude sites (Boulon et al., 2010; Manninen et al., 2010), and especially for the Puy de Dôme (12.5±2.0%, Boulon et al., 2011). In contrast, the IIN are higher during Period 3, with a value close to 50% on the 28th of February, suggesting that charged pathways could be promoted in the FT compared to the interface between the BL and the FT. However, besides the height of the BL itself, atmospheric parameters such as temperature and relative humidity display significant variations between the different periods, and could also explain the previous observations (Table 3 and Fig. 4). This potential effect is further discussed in Section 3.2.4."

Comment 4: page 18356, line 15: following the arguments given in comment (3) 40 times higher neutral nucleation rates are an extreme case because the fraction of IIN can also reach ~50% during observations made in this study; this statement should therefore be revised

Reply 4: As previously mentioned in Reply 3, corrections were made.

Comment 5: page 18358, line 21: remove extra dot before the word "and"

Reply 5: Removed

Comment 6: page 18359, line 5: "Milikan diameters"

Reply 6 : Correction was made.

Comment 7 : page 18359, line 12: "ensures"

Reply 7 : Correction was made.

Comment 8 : page 18359, line 17: the word "further" should be removed

Reply 8: Removed

Comment 9: page 18360, line 4: replace the word "sampling" by "activation of particles"

Reply 9: The word was replaced accordingly.

Comment 10: page 18361, line 7: maybe better to use "deriving" instead of "defining"

Reply 10: It might in fact be better.

Comment 11: page 18361, line 25: Which other trace gases besides SO2 were measured? Could these measurements give further insight into the origin of air masses?

Reply 11: Trace gases that were measured are CO, O_3 and NOx. These species provide information on the level of pollution of the air masses rather than on their origin. Time series of NO_2 concentration were added to the manuscript to distinguish between the BL and the FT. CO was added to supply the lack of BC data during period 3.

Comment 12: page 18363, line 4: there is something wrong with the unit of k, it should be $m^2W^{-1}s^{-1}$

Reply 12: Of course, correction was made.

Comment 13: page 18364, line 18: The particle concentration in the size range between 1 and 2.5 nm could also include sub-critical particles (the authors mention that the critical size is somewhere close to 1.5 nm in the introduction). If the PSM was operating in scanning mode it should also be possible to provide a number concentration for particles between 1.5 and 2.5 nm. Do the authors have evidence that a size of 1 nm is above the critical diameter?

Reply 13: It is true that the PSM was operating in a scanning mode. However concentrations in each sub-classes were very noisy, maybe due to the unusual atmospheric conditions, and did not allow further analysis of the cluster size distribution.

Comment 14: page 18364, equation (5) and page 18365, equation (6): Shouldn't the denominator in the third term on the RHS of the equations contain the width of the size bin N1-2.5, which is 1.5 nm instead of 1 nm?

Reply 14: Referee is of course right but this is only a typing error, correct equations were used for the calculations.

Comment 15: page 18366, lines 27 and 28: "ion concentrations"

Reply 15: The sentence was slightly changed but correction was made.

Comment 16: page 18367, line 16: remove the word "at"

Reply 16: Done!

Comment 17: page 18367, line 22: "maxima" instead of "maximum"

Reply 17: Changed!

Comment 18: page 18372, lines 21 to 23: I do not agree with that statement. Figure 6b clearly shows that the nanoparticle concentrations decrease when the condensation sink (CS) exceeds ~$7x10^{-3}s^{-1}$. It rather seems that there is a range where the CS has no clear effect; however, for large values it has an effect as the concentrations decrease by about one order of magnitude as CS increases from $7x10^{-3}$ to $3x10^{-2}s^{-1}$.

Reply 18: It is true that one can see that cluster concentrations, and especially neutral ones, decrease with an increasing CS for values above ~$7x10^{-3}s^{-1}$. Thus the occurrence of nucleation and the number of nucleated clusters are now discussed separately in the manuscript: “The second important result highlighted by Tables 1-3 is that the occurrence of NPF does not seem to be limited by the condensation sink. In fact, NPF is triggered during Periods 1 and 3, which display CS values significantly higher compared to Period 2. This observation contradicts the previous result by Boulon et al. (2011) at the Puy de Dôme for ionic clusters but supports the results reported at the Jungfraujoch station (Boulon et al., 2010). However, based on Fig. 6b, we observed that while cluster concentrations are not deeply impacted by the CS up to ~7×10^{-3} s^{-1}, seem to decrease with an increasing CS above this threshold value, suggesting that high CS values do not inhibit the nucleation process but could limit the number of nucleated clusters. …”

Comment 19: page 18380, line 5: “third row” instead of “second raw”

Reply 19: Changed!

Comment 20: page 18381, line 8: “in the table”?

Reply 20: Correction was done

Comment 21: page 18382, line 2: “indicated in the table”
Reply 21: Changed!

Comment 22: page 18383, line 3: “calculated” instead of “calculating”

Reply 22: Changed!

Comment 23: page 18384, line 3: “shaded” instead of “shading”

Reply 23: Changed!

Comment 24: page 18385, figure 3: It is surprising that all Js are positive throughout the whole day (from 8 to 18 UTC). In fact, J3tot is always larger than 0.4 cm^{-3} s^{-1} even in the early morning and in the late evening when there is no sunlight anymore. What is the explanation for this observation?

Reply 24: This figure was removed since it included statistics calculated from the FT and the interface between the BL and the FT all together. However, to answer the question, negative J values were found earlier in the morning and later in the evening, this is the reason why the figure only showed results between 8:00 and 18:00 (UTC). It is true that one could have expected to have negative values earlier than 18:00 (UTC) because of the lack of sunlight, but it is obviously not the case and we have no robust explanation for that.

Comment 25: page 18387, line 2: “close” instead of “closed”

Reply 25: Correction done.

Comment 26: page 18388, figure 6a: red/magenta circles seem to be missing for the high H2SO4 values; the word “no” seems to be missing in the last row of the legend

Reply 26: Magenta circles correspond to neutral cluster concentrations recorded during NPF event days, i.e. during Periods 1 and 3. During these periods, maximum H_2SO_4 values are around 2×10^8, and are represented on Fig. 6, sometimes hidden by the green and blue crosses. Correction was done in the legend.

References:

Eisele, F. L. (1988) "1st Tandem Mass-Spectrometric Measurement of Tropospheric Ions."*Journal of Geophysical Research-Atmospheres* 93 (D1) 716-724

Eisele, F. L. (1989) "Natural and Transmission-Line Produced Positive-Ions." *Journal of Geophysical Research-Atmospheres* 94 (D5) 6309-6318

Eisele, F. L. (1989) "Natural and Anthropogenic Negative-Ions in the Troposphere." *Journal of Geophysical Research-Atmospheres* 94 (D2) 2183-2196

Hari, P. and M. Kulmala (2005) "Station for measuring ecosystem-atmosphere relations (SMEAR II)." *Boreal Environment Research* 10 (5) 315-322

Jokinen, T., M. Sipilä, H. Junninen, M. Ehn, G. Lönn, J. Hakala, T. Petäjä, R. L. Mauldin, M. Kulmala and D. R. Worsnop (2012) "Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF." *Atmospheric Chemistry and Physics* 12 (9) 4117-4125

Junninen, H., M. Ehn, T. Petäjä, L. Luosujärvi, T. Kotiaho, R. Kostiainen, U. Rohner, M. Gonin, K. Fuhrer, M. Kulmala and D. R. Worsnop (2010) "A high-resolution mass spectrometer to measure atmospheric ion composition." *Atmospheric Measurement Techniques* 3 (4) 1039-1053