

We thank Referee #1 for his comments and suggestions that, we believe, have helped improving the manuscript. We have addressed the comments point by point below. In addition, the errorbars shown on Fig. 9.b were modified, as those did not correspond to the actual variability of N_{50} absolute increase in the original version of the manuscript (former Fig. 8.b).

Comment 1: Classification of plume- vs non-plume days:

As the classification is critical for the statistical study, more details and illustrations are missing to describe and validate the classification of plume- vs non-plume days. As SO_2 represents indeed a clear tracer of the volcanic plume, a time series of SO_2 mixing ratio values at Mado with highlighted volcanic events would be welcome in order to evaluate the amplitude of background variations in SO_2 mixing ratios.

As this is the root of the paper, an illustration with AIS and DMPS observations for one representative strong plume day and one weakly influenced plume day before statistical representation of Fig. 1 would be required.

Reply 1: Adding a figure to support the method we followed to detect the volcanic eruption plume at the station, and to illustrate as well NPF events occurring in such unusual conditions, is in fact a good suggestion. Hence, we have included a new figure (Fig. 1) in the revised version of the manuscript, which displays a. The timeseries of the SO_2 mixing ratio with some indication of the eruptive periods, b. AIS and DMPS observations showing an NPF event on a regular plume day and c. on a strong plume day.

Comment 2: Selection of plume-days, page 7, lines 19-27 : If I understand correctly, selected days are considered as ‘plume-days’ when at least one of the hourly averages of the SO_2 mixing ratio exceeds 1 ppb over the 5 hours of interest each day (between 6 :00 and 11 :00 LT). The volcanic plume was detected during the 5 hours of the time window of interest for only 20 of the 36 ‘plume-days’. I am wondering if the authors should not restrict their study to these ‘fully volcanically influenced days’ ? If not, they should assess the impact of mixing in their study ‘plume days’ hours without any volcanic plume. This choice may artificially tend to decrease the difference between plume- and non plume-days.

Reply 2: We agree with the fact that including days with very short plume occurrence in the statistics did not give the most accurate picture of the volcanic eruption plume signature on NPF and related variables of interest. Hence, we have revised our classification to include only the days when the volcanic plume was detected over at least 3 hours between 06:00 and 11:00 LT. These days represent 80% of the former plume days (29/36); remaining 7 days with short plume occurrence, which are now excluded from the revised classification, were found in September and October. Corresponding statistics and results have been updated throughout the manuscript, but it is worth noticing that the main conclusions of this work were not affected.

Note that plume days were not restricted to the days when the plume was observed over the five hours of interest to allow a fair compromise between the number of plume days, that we wanted to keep sufficient for the relevance of our analysis, and significant influence of the volcanic eruption plume. Effect of the more “intense” plume conditions, both in terms of SO_2 levels and time duration of the plume occurrence, is further investigated by the mean of the so-called strong plume days.

Comment 3: Start time of NPF events, page 9:

Why are the detection and evaluation of the start time made by a visual inspection?

What is the difficulty in automating the detection of a concentration increase in the 1.5-2.5 nm range? Visual inspection is subject to large uncertainty and raise questions on the accuracy and reproducibility of the obtained results. An illustrative example would be also welcome to see how strong are the AIS/DMPS signals for days only poorly-contaminated by volcanic plumes.

Reply 3: The detection of the concentration increase could undoubtedly be automated, and recent studies have by the way reported different methods to allow for an automatic monitoring and description of NPF (eg: Hussein et al., 2005; Dall’Osto et al., 2017; Dada et al., 2018). Nonetheless, to our knowledge, the visual approach for the identification and analysis of NPF has, to date, been the most commonly

used and is still popular. This is for instance illustrated by the very recent study by Hakala et al. (2019), who visually determined 4 different times to describe the progression of each NPF event. There is for sure an uncertainty which is associated to this analysis “by eye”, but we believe that such approach is less risky than automated ones with respect to more “critical” errors. In our case, such error could for instance be the detection of a concentration increase which is not connected to any clear NPF event. As previously mentioned in Reply 1, an additional figure was added (Fig. 1) in the revised version of the manuscript to illustrate the NPF process in plume conditions.

Comment 4: Particle growth rate, pages 10-11:

Comment 4.A: Page 10, lines 3-8: The authors do not highlight any impact of the volcanic plume on the particle growth rate between 12 and 19 nm. The interpretation of the authors is that it may be difficult to clearly identify the impact of volcanic plumes at the Mado Observatory as the atmospheric dynamics is complex around this site and there may be an importation of growing particles likely transported to this site. The same processes (of imported particles, including potentially biomass burning aerosols as mentioned for CS variations in Sept and Oct) could also bias the observations of J2 and J12? The authors should comment on this and propose some solutions to ‘clean’ data by removing periods with strong influences by other sources of aerosols (urban, biomass burning, etc..).

Reply 4.A: It is absolutely true that, while affecting the determination of the particle growth, complex topography and atmospheric dynamics in turn also affect the calculation of particle formation rates. This is now clearly stated in Section 3.1.3: *“However, assessing the real effect of these specific conditions on the particle formation and growth is challenging”*. Also, following a comment from Referee #2, we have included an additional discussion in Section 3.1.3 to explain the limited effect of the plume on measured growth rates: *“This observation is most likely related to the fact that not only the amount of precursor vapours (including for instance SO₂, see Fig. 1.a) was increased in the volcanic plume, but also the number concentration of the particles to grow, from both primary and secondary origin, as also reflected in the variations of the CS (Section 3.2.1) and discussed later in Section 3.3.1”*. Instead of cleaning the data and removing some periods, the best would be to be able to evaluate the contribution of the different sources to the observed NPF events, and in turn to GR and J, in the same manner we have discussed the particle size distributions in Section 3.3.1. This is however much more complex for J and GR, and such detailed analysis of the impact of different conditions (anthropogenic air masses, biomass burning...) is anyway beyond the scope of the present study. Instead, our main goal was only to evaluate the effect of the plume conditions on J and GR in comparison with non-plume days. For that purpose, we have used a statistical approach, which allows for the comparison of a number of plume and non-plume days which is assumed to be sufficient to smooth the specificities of each single event with respect to all conditions other than plume occurrence.

Comment 4.B: Clearly higher values of J2 and J12 values are not observed under volcanic influence for the month of Sept. A clear volcanic signature is not identified either for J2 values for the month of Oct (with also surprisingly very spread J2 values for strong plume days). The authors should describe these discrepancies in the text and provide some interpretations or suggestions of interpretation (impact of biomass burning activities, or others?).

By contrast, page 10, lines 9-14: why is observed in May so much increase in J2 and J12 values for plume-days compared to non-plume days? Is there a specificity of the volcanic events, or of the meteorological conditions occurring in May? Opposite case: why is not observed an obvious distinct behaviour of plume-days in Oct?

Reply 4.B: It is true that we should have commented more on the comparison between the formation rates measured in and off- plume conditions, as different trends are effectively highlighted in this study. We have thus included a paragraph in Section 3.2.1, which discusses the variability of CS, together with that of SO₂ mixing ratio, as we believe they are key parameters driving the variations of J₁₂ and J₂. This discussion also refers to the variations of the particle growth rate, in response to one of the comments from Referee #2: *“In addition, the balance between the amount of SO₂ and the magnitude of the CS most likely influenced the strength of the observed events, and explained in specific the variable trends*

highlighted earlier in the comparison of the particle formation rates calculated on plume and non-plume days (see Sect. 3.1.3, Fig. 3.b and c). Indeed, as reported previously, the largest CS increase observed between non-plume and plume NPF event days occurred in May, when SO₂ mixing ratios were also the highest (Fig. 1), with a median of 26.7 ppb [25th percentile: 1.1 ppb; 75th percentile: 120.5 ppb] calculated during nucleation hours (06:00 and 11:00 LT). We may thus hypothesize that the resulting conditions were highly favourable to NPF, and not only lead to high NPF frequency (Fig. 2), but also to stronger events, with increased particle formation rates compared to non-plume days (Fig. 3.b and c). In September and October, the median CS measured in plume conditions were comparable to that observed in May (Fig. 4.a), but SO₂ mixing ratios were in contrast lower during nucleation hours, with medians around 3.4 ppb [1.5 ppb; 5.6 ppb] and 3.8 ppb [1.9 ppb; 16.9 ppb], respectively. This most likely resulted in less favourable conditions for NPF than in May, which in turn did not enhance the particle formation rates compared to non-plume days. Higher CS observed on plume days also supported the fact that in plume conditions, as suggested in the previous section, the number of particles to grow was increased compared to non-plume days, and the concurrent strengthening of the precursor source rate was on average not sufficient to result in faster particle growth. Nonetheless, while it was possible to evidence the abovementioned trends with our statistical approach, one should keep in mind that both the occurrence and characteristics of NPF are likely to be affected at very short time scales due to the variable nature of the volcanic eruption. Deeper investigation of the effect of the volcanic eruption plume on NPF would thus require more detailed analysis of the event to event variability, which was however beyond the scope of the present work”.

Comment 4.C: More generally, the authors should discuss the advantages and also the disadvantages or limitations to have data collected at a high altitude atmospheric observatory and the potential biases that may affect the results at such a site (including complex atmospheric dynamics, fluctuating relative humidity, is it easier or not to identify imported species, a less polluted background or not, etc...).

Reply 4.C: We believe that the main specificities of a site such as the Maïdo which were relevant to the present work have been mentioned in the manuscript, including in particular the complex topography and atmospheric dynamics which affect the transport of both NPF gaseous precursors and growing/pre-existing particles, with consequent effect on NPF characteristics, particle size distribution and in turn CCN population. Deeper analysis of the advantages/disadvantages of high altitude observatories is behind the scope of the present work; it is however of high interest, and is the main focus of a review dedicated to the observation of NPF from such high altitude sites, currently in preparation.

Comment 5: Which is the impact of relative humidity on NPF? As relative humidity is measured at Maïdo, is there any correlation with NPF? Are observed higher RH values during plume-days (as the Piton de la Fournaise plume may be rich in volcanic water vapour) or not?

Reply 5: The effect of RH on NPF is not plain to understand, as contrasting observations have been reported, regarding in specific its influence on the particle formation rates (e.g. Birmili et al., 2003; Duplissy et al., 2016). We have investigated the variations of RH observed at Maïdo on event days, in and off-plume conditions, and on non-event days, together with that of temperature and radiation, which are also reported as key meteorological parameters. The results of this analysis are reported at the beginning of Section 3.2: “NPF has been previously reported to be influenced by various atmospheric parameters, including solar radiation, temperature (Dada et al., 2017), as well as RH, which effect on the process is certainly the less evident to predict and understand (e.g. Birmili et al., 2003; Duplissy et al., 2016). In the frame of the present analysis, the median diurnal variations of the abovementioned parameters reported on Fig. S1 (in the Supplementary) did not highlight any specificity for the events observed on plume days, and displayed similar behaviour in and off-plume conditions”.

A corresponding figure showing the median diurnal patterns of temperature, RH and global radiation measured in the different conditions (non-event days, event days in and off-plume) was included in the Supplementary; note that all the figures originally shown in the different Appendices were moved to the Supplementary in order not to multiply the number of Appendices.

Comment 6: Impact of condensation sink (CS) page 11:

Right of Fig. 3: in the plot of CS vs SO₂ mixing ratio for plume-days and strong-plume days, could it be added non-plume days to assess if obvious differences are observed between plume- and non-plume-days in this representation?

Left of Fig. 3: how do the authors explain the large CS observed in Sept and Oct for non-plume days?

Reply 6: It was unfortunately not possible to include non-plume days in Fig. 4.b (former Fig. 3.b) because SO₂ mixing ratios were mostly below the detection limit of the instrument outside of the eruptive periods, as indicated in Section 2.1: “*The detection limit of the instrument was about 0.5 ppb, which is above the usual SO₂ mixing ratios encountered at Maïdo outside of the eruptive periods of the Piton de la Fournaise (see Fig. A1 in Foucart et al. 2018)*”. This is now also recalled in Section 2.3: “*The relatively low SO₂ mixing ratios observed outside of the eruptive periods, mostly below the detection limit of the instrument, reflect the low pollution levels characteristic of this insular station, located at high altitude in a region rarely subject to significant influence of pollution from continental origin*”.

Detailed investigation of the origin of the large CS observed on non-event days in September and October was behind the scope of the present work, nonetheless this observation is already briefly discussed in the manuscript (Section 3.2.1): “*Indeed, comparable median CS were observed in August regardless the occurrence of NPF later during the day, higher values were in contrast obtained on event days in May, while the opposite was observed in September and October, most likely related to biomass burning activity in South Africa and Madagascar during austral spring (Clain et al., 2009; Duflot et al., 2010; Vigouroux et al., 2012).*”

Comment 7: Relationship between J₂ and [H₂SO₄], page 12:

According to Fig. 4, a correlation relationship between J₂ and [H₂SO₄] is not obvious: data points are very scattered, as illustrated by the very low value of R² of 0.21 and 0.11 for all plume and strong-plume days respectively. In this context, is it meaningful to try to fit anyway a correlation relationship and estimate k and a coefficient?

Moreover, except higher concentrations of H₂SO₄, data associated to strong-plume days do not seem to present a very different relationship between J₂ and [H₂SO₄] (Fig. 4a). The weak difference in the relationship which is retrieved seems just to result from the influence of 3 points, potentially outliers? If these points would have been represented in black, and not in yellow, it would be very difficult to distinguish any different behaviour.

Reply 7: The correlation between J₂ and [H₂SO₄] derived from data measured on all plume days is definitely moderate but still significant, as indicated by the corresponding p-value (2.35×10^{-24}). Regarding strong plume days, we found a mistake in the selection of the data points for the fitting procedure. Using the correct data finally lead to very similar fit parameters to that obtained for all plume days, which is now explicitly mentioned in the revised version of the manuscript: “*the relationship between J₂ and [H₂SO₄] did not appear to be significantly different on strong plume days compared to regular plume conditions*”. For that reason (and also for more clarity) strong plume days are not any longer highlighted on Fig. 5. Additional discussion regarding the contributions of charged and neutral nucleation pathways was also included in Section 3.2.2, based on the use of the parameterisation by Määttä et al. (2018): “*As evidenced on Fig. 5.a, the total formation rate of 2 nm-clusters was mostly explained by ion induced nucleation for [H₂SO₄] below $\sim 8 \times 10^8 \text{ cm}^{-3}$, while neutral pathways seemed to explain the observations at larger sulfuric acid concentrations*”.

Also, since the results reported in Sections 3.1 and 3.2 only revealed limited signature of strong plume conditions on NPF characteristics (and related parameters of interest), we have decided not to put any focus on these specific days in the last Section (3.3) in order to make our message as clear as possible.

Minor comments:

Comment 1: ‘Active volcanic plume’: I do not understand this term. Given lines 31-32 in the introduction, I am wondering if the authors may want to refer to a volcanic plume emitted during an

eruption compared to passive degassing emitted out of eruptive periods. If so, please refer rather to ‘volcanic eruption plume’

Reply 1: Changed throughout the manuscript.

Comment 2: Page3,lines5-8: ‘primary particles are fragment of ash while secondary particles...’ : Volcanic primary particles do not include only ash particles but also sulfate aerosols, as illustrated by near-source measurements (e.g. refer to first publications on this matter which include Allen et al., 2002 ; Mather et al., 2003, 2004, etc..).

Reply 2: We thank the reviewer for pointing out this omission. This has been addressed in the revised version of the manuscript:

- In the introduction: *“Primary sulphate aerosols of volcanic origin were also evidenced by near source measurements conducted at Masaya volcano by Allen et al. (2002), who were however not able to identify their precise mechanisms of formation. Several pathways were later suggested for the formation of H₂SO₄ at the vent, including catalytic oxidation of SO₂ inside the volcanic dome Zelenski et al. (2015), high temperature chemistry in the gas phase (Roberts et al., 2019), as well as aqueous production of H₂SO₄ from SO₂ (Tulet et al., 2017). H₂SO₄ produced by the mean of the aforementioned reactions is expected to contribute to the formation and growth of particles in the close vicinity of the volcano, which are in turn assimilated to primary volcanic aerosols”*.
- In Section 3.2.1: *“This nomenclature is consistent with earlier results from Allen et al. (2002), who reported the presence of primary sulphate aerosols at Masaya volcano”*.

Comment 3: ‘Here we report observations of NPF performed at the high-altitude observatory of Maïdo (2165 m a.s.l., La Réunion Island) between 1st January and 31st December 2015. During this period of time, 3 effusive eruptions of the Piton de la Fournaise, located 39 km away from the station, were observed and documented, resulting in 36 days of measurement in volcanic plume conditions to be compared with 250 “non -plume days”. 250 + 26 = 276 days, what happens with the missing 89 (=365-276) days?’

Reply 3: It is true that the reported numbers were somewhat confusing and needed some clarification, now available in Section 2.3: *“In the end, after filtering the data for instrument malfunctioning and / or absence of measurements (71 days in total), 29 plume days and 250 non-plume days were included in the analysis. The 15 remaining days, with late or short plume occurrence, will not be further discussed”*.

Comment 4: There are many references to a study in preparation (Sahyoun et al., in prep) which is presented as an earlier work: has this paper been submitted to a journal with open discussion where it would be accessible or has it been published since then? If yes, please update so that the reader can have access to this manuscript.

Reply 4: This paper was indeed not published when we first submitted our manuscript. We have now included the reference:

Sahyoun, M., Frenay, E., Brito, J., Duplissy, J., Gouhier, M., Colomb, A., Dupuy, R., Bourianne, T., Nowak, J. B., Yan, C., Petäjä, T., Kulmala, M., Schwarzenboeck, A., Planche, C. and Sellegri, K. : Evidence of new particle formation within Etna and Stromboli volcanic plumes and its parameterization from airborne in-situ measurements, *J. Geophys. Res.-Atmos*, <https://doi.org/10.1029/2018JD028882>, 2019.

Comment 5: Abstract is very long, if possible you should try to shorten it (possibly remove the mention to the correlation relationship between J₂ and H₂SO₄ concentration which does not seem obvious (as developed above).

Reply 5: The abstract is indeed quite long, but we believe it gives the opportunity to the readers (who are nowadays often busy!!) to quickly get the storyline and main results of this work.

Comment 6: Please reformulate these sentences for clarity:

- 1) abstract, Page 1, line 17 : ‘as those form the baseline to calculate..’
- 2) abstract, Page 1, line 30 : ‘recorded in the different conditions’: recorded in the different conditions described thereafter..
- 3) abstract, Page 1, line 26-27: ‘compared to non-plume days, during which condensable species were in contrast transported from lower altitude by the mean of convective processes’: it is difficult to understand the meaning of this sentence if we have not read the manuscript yet.
- 4) Page 2, lines 21-22 : ‘the radiative forcing... still has a large uncertainty’
- 5) Page 11, line 16 : ‘loss rate of the vapours’ ? What do you mean by ‘vapours’?

Reply 6:

- 1) This part of the sentence was removed as the information it contains is not of the highest importance for the abstract. This topic is further discussed in the introduction.
- 2) Changed to: “based on the analysis and fitting of the particle size distributions recorded in and off-plume conditions”.
- 3) For more clarity this part of the sentence was also removed from the abstract; corresponding results are discussed in details in the manuscript.
- 4) Changed to “the radiative forcing associated to these effects (usually referred to as “indirect effect”) is known with a still large uncertainty”.
- 5) Changed to “the strengthened loss rate of the condensing vapours involved in particle formation and growth”.

References:

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Hussein, T., Dal Maso, M., Petaja, T., Koponen, I. K., Paatero, P., Aalto, P. P., Hameri, K., and Kulmala, M.: Evaluation of an automatic algorithm for fitting the particle number size distributions, *Boreal Environ Res*, 10, 337-355, 2005.