Interactive comment on "Observation of aerosol size distribution and new particle formation at a mountain site in subtropical Hong Kong" by H. Guo et al.

Anonymous Referee #1

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Comment: The manuscript examines aerosol size distributions and specifically the process of secondary particle formation during a 3 months campaign in Hong Kong. The size distribution measurements are supported by rather extensive gas phase and meteorological measurements. Indeed, as the authors point out, this type of studies are rare in the region, and I find the dataset interesting and potentially important for scientific community.
However, in my opinion, the analysis and writing of the manuscript should be largely improved, if not even rewritten, before it could be accepted to publication in ACP. In its current form, the analysis is not full and the presented results are confusing and speculative.

Response: We thank the reviewer for his/her constructive comments. Our replies follow each of the major concerns and specific points raised by the reviewer below.

My major concerns are:
1) For a large part of the work the authors present linear correlations and R2 values for nucleation mode concentration and various measured parameters. The R^2 values for individual events, which are based on hourly data-points, are not sufficient to make conclusions on the particle formation mechanisms as the authors claim. Statistical significance of the correlations should be at least examined. Even then, the chosen linear correlation model is hardly justified. Many atmospheric compounds have a profound diurnal cycle making the correlation analysis difficult and the variables are not independent. Moreover, a better idea of the compounds involved in particle formation and growth could be obtained by comparing particle formation and non-formation days. Also, as the nucleation mode concentration depends on e.g. particle nucleation rate, growth rate and sink, I would recommend rather examining directly these correlations with gas phase and meteorological parameters instead of the particle number.

Response: We agree with the reviewer's comments on the method to analyze and present the data, and we changed the way we compared the monthly data into comparing the data on new particle formation (NPF) days and non-new particle formation (non-NPF) days. During the field measurement at TMS, our SMPS instrument was malfunctioned during middle September to early October, but the condensational particle counter (CPC) was always working in these three months (September-November). Due to much SMPS data loss in September and October, we classified three different types of events based on the levels of ultrafine particle and/or ozone using data collected from 25 October to 29 November to investigate the chemical and meteorological conditions for each type of event. At page 12, Table 1 summarizes the three different types of events including all NPF events (class Ia, Ib and II events) on O_3 episode days (maximum hourly O_3 mixing ratio $\geq$ 90 ppbv), non-NPF events on O_3 episode days (maximum hourly PN concentration $<10^4$ cm^{-3}) and non-NPF events on high particle number concentration days (PN concentration $\geq 10^4$ cm^{-3} with a maximum hourly O_3 mixing ratio $\leq$ 90 ppbv) throughout the 35 sampling days. The hourly average O_3 mixing ratio, nucleation mode particle number concentration and total PN concentration in the size range of 5.5-350 nm were higher on most NPF event days than the corresponding values on non-NPF event days with O_3 episodes. For non-NPF events on high particle number concentration days with a lower O_3 level than the other two types of events, the elevated particle number concentration was probably attributed to primary emissions from local sources, i.e. vehicle emissions. The detailed discussion is shown in section 3.2. Additionally, we correlated the particle formation rate, growth rate and condensation sink with gas phase pollutants, meteorological parameters, BVOCs, AVOCs and carbonyls in all NPF events, instead of only examining the correlations between gas phase pollutants and particle number. The R values for all correlation analysis based on hourly or minute data-points were given with statistical significances (*p*-values).

2) In addition to analytical deficiencies, the manuscript suffers from several spelling and writing mistakes and incomplete reference list. It is not easily readable and it seems lengthy considering the amount of results presented.

Response: Thanks for pointing it out. We agree with the reviewer's comments and have (1)modified and simplified our conclusions; (2) corrected grammatical mistakes and re-constructed sentences where necessary in the revised manuscript.

More specific comments:

Introduction:
Introduction has several writing mistakes and incomplete sentences, please check.

Response: Thanks for pointing it out. We have checked writing mistakes and incomplete sentences in the introduction and corrected them in the revised manuscript.

The whole chapter starting on p. 12121 L25 onward is confusing and full of loose sentences. Maybe it would be enough to state out the most important issues regarding this specific work on the current knowledge of different compounds participating and on the formation mechanisms, such as the role of organics?

Response: We agree with the reviewer's comments. This chapter has been simplified to mainly state out the most important issues such as the participation of different compounds in NPF and the NPF formation mechanisms, especially the role of sulfuric acid and organics vapor. The whole chapter starting on p. 12121 L25 onward is replaced (page 3: L44-59) with the following statement:

"A variety of formation mechanisms have been suggested for atmospheric aerosols (Kulmala *et al*., 2000). Generally, the formation of nucleation mode particle requires two processes: the nucleation of stable atmospheric clusters (1-3 nm) and the growth of these clusters into observable sizes (> 3 nm). Altogether, the driving force for nucleation and the growth of freshly formed particles is the sufficiently high concentration of condensational vapors, such as sulfuric acid and possibly other organic compounds with a low saturation vapor pressure formed by photochemical oxidation reaction. Sulfuric acid has been found to be a key compound in atmospheric nucleation in many studies (Kulmala *et al*., 2006; Riipinen *et al*., 2007; Sipilä *et al*., 2010). Also recent study (e.g. Kerminen *et al*., 2010) found that some organic acids produced from monoterpene oxidation can nucleate with sulfuric acid to form very stable clusters. However, for particle growth, observations suggest that the contribution of sulfuric acid to particle growth is typically from a few percents to some tens of percents of the observed particle growth rate (Boy *et al*., 2005; Nieminen *et al*., 2010; Riipinen *et al*., 2011), while organics with a very low saturation vapor pressure (Tunved *et al*., 2006; Jimenez *et al*., 2009) can be considered as the most probable candidates of the vapors responsible for the fraction of nucleation mode growth that is not explained by sulfuric acid. For example, boreal forest observations in Finland indicated a connection between nucleation mode growth and ambient concentrations of monoterpenes (Laaksonen *et al*., 2008). In Hong Kong, no study has been undertaken to study the characteristics of NPF events. The potential mechanisms and compounds participating in atmospheric NPF and growth in this region have remained unclear. Therefore, it is important to enrich the database of particle number size distribution, and to investigate the NPF and growth processes in this urban area."

2. Methodology:
2.1 Could the authors add here from where the clean air masses originated?

Response: Thanks for pointing this out. The sentence was revised in the methodology section (page 4: L72-73):

"Generally the dry monsoon season covers September, October and November when the north and northeast synoptic winds from inland PRD and eastern China coast dominate."

2.2 "polluted air from inland often reaches the sampling site" is contradictory to what was said above at 2.1

Response: Sorry for the confusion. As replied in the above question, this sentence has been changed in the text (pages 4-5: L82-84) as follows:

"The prevailing north/northeast synoptic winds in October – November bring polluted air on some days and clean air on some other days from inland PRD and eastern China coast to the sampling site, depending on the weather conditions at upwind locations."

2.3 How was the SMPS sample RH controlled/dried?

Response: Thanks for pointing this out. The following text has been added (page 6: L96-98) for clarification:

“In order to control the relative humidity (RH) during sampling campaign, the aerosol samples taken from ambient air have been dried with a 0.6 m long diffusion silica gel drier (GRIMM) before entering the sampling system. Meanwhile, the sheath air in DMA was dried with a sheath-air dryer (GRIMM).”

2.4.1:
Maybe it is not necessary to explain in so much detail how modal concentrations were calculated. But how the modal diameter limits were chosen?

Response: We agree with the reviewer’s comment. We have deleted this part and added the way how the modal diameter limits were chosen into the text (page 8: L137-141) with the following statement:

“Typically, the sizes of submicrometer particles are categorized into three modes: a nucleation mode, representing quite newly formed particles; Aitken and accumulation modes, representing aged particles. In this study, we divided the size distribution into 5.5-10 (nucleation mode, N_{nuc}), 10-100 (Aitken mode, N_{Ait}), and 100-350 nm (accumulation mode, N_{acc}). The PN concentrations in nucleation mode, Aitken mode, and accumulation mode were calculated with a 95% confidence level ($p < 0.05$). The correlation coefficients and *p*-values between the different tested parameters were calculated.”

“some data from late September to early October were unavailable”.. It seems there is no data missing on number concentrations during this period based on figs. S1-S3.

Response: During the 3-month field measurement at TMS, our SMPS instrument malfunctioned from middle September to early October, resulting in only a few data points in September and October. On the other hand, the condensation particle counter (CPC) was always working in these three months (September-November). So we obtained three month data for total number concentration, but only 35 days integrated SMPS data for particle size distribution in this sampling session from 25 October to 29 November.

If the instrument suffered from high RH, was the sample not dried? What is meant with “power correlations”?

Response: Our SMPS instrument suffered from high RH at the beginning of the sampling campaign, which actually damaged the SMPS instrument. After the SMPS was fixed and before the field measurement was re-started, we added a sheath-air dryer in the SMPS and a diffusion silica gel drier in front of the inlet of SMPS to dry the aerosol samples taken from ambient air. So the SMPS data we presented in the paper were for the dried samples.
“Power correlations” is a writing error, and has been revised to “power-law correlation” in the updated manuscript.

2.4.3:

Authors could calculate 5.5 nm particle formation rates with proper methods, taking into account the coagulation losses (and growth losses). The presented formation rate underestimates the real formation rate, especially if the background concentration is high. At most, it should be stated that this is "minimum estimate".

Response: We agree with the reviewer's comments on the method to calculate the particle formation rates. We have changed the estimated minimum formation rate in original paper into 5.5 nm particle formation rates, taking into account the coagulation losses and growth losses (page 8: L152-154). 5.5 nm particle formation rate was calculated by Eq. (1), presenting in the revised manuscript as follows:

"In this study, 5.5 nm particle formation rate (FR, $J_{5.5}$) was represented and quantified by the following equation (Sihto *et al*., 2006), taking into account the coagulation losses and growth losses:

$$J_{5.5} = \frac{dN_{5.5-10}}{dt} + CoagS_{d_{p=7nm}} \cdot N_{5.5-10} + \frac{1}{4.5nm} GR_{5.5-10} \cdot N_{5.5-10} \qquad (1)$$

I assume the GMD here means only nucleation mode GMD? Which sizes were included?

Response: The GMD is a modal geometric mean diameter obtained as a result of the fitting procedure (Dal Maso *et al*., 2005). In a log-normal particle number size distribution, the fitted GMD is close to the median diameter which is a size with the majority of the particles. In this study, the fitted GMD is the size with the highest particle number concentration in each size distribution with a 4-minute resolution. The evolution of fitted GMD < 25 nm for each size distribution was used to calculate the particle growth rate. This sentence has been added in the text (page 9: L161-163) with the following statement:
"The evolution of modal geometric mean diameters (GMD) (Dal Maso *et al*., 2005) in a size range of 5.5-25 nm for each size distribution with a 4-minute resolution was used to examine particle growth processes:"

Was any RH correction applied in size distributions when CS was calculated?

Response: Thanks for pointing it out. We calculated the CS taking into account the impact of RH. The following text has been added in the revised manuscript (page 9: L168-170):

"For the particle diameter D_{pi} used in the Eq. (3), the measured dry size spectra were converted to wet size spectra by particle growth factor (GF) according to ambient relative humidity (Laakso *et al*., 2004). "

3.1.2:

Instead of separating the particle properties by months, it might be more informative to separate them e.g. by particle formation/non-formation days; polluted/non-polluted days; different air masses; etc. Even authors seem to suggest that by discussing the reasons behind different monthly diurnal parameters in p. 12133 lines 12-24.

Response: This is excellent suggestion. We have largely improved the “Results and discussion” section and separated the days by NPF event days and non-NPF event days instead of presenting data by months. The detailed description and outline are shown in sections 3.1 and 3.2 (pages 10-20).

What do authors mean by “photochemical formation of new particles”? (p. 12133 L23)

Response: Thanks for pointing this out. This is a writing mistake. Originally, we want to say “…suggested the photochemical reaction may contribute to the new particle formation”. We have checked and modified such incorrect expressions in the text.

p. 12134 L5-12: While on O3 episode days nucleation mode concentrations were higher it seems also the total number (in all modes) increased. Maybe authors could use the measured NOx/SO2 data to show the air on O3-episode days was less polluted than on other days?

Response: Based on your first comment at 3.1.2, we have separated the days into NPF event days and non-NPF event days. Since both NPF events and some non-NPF events occurred on O_3 episode days, in order to clearly explore the characteristics and effects of NO_x/NO_2 and SO_2 on NPF event days and non-NPF event days, we compared the air pollutants on NPF event days with those on non-NPF event days, rather than the comparison between O_3-episode days and non-O_3 episode days in the revised manuscript. As such, we compared the measured NO_x and SO_2 mixing ratios on NPF event days with those on non-NPF event days, and found that the average daytime NO_x (11 ± 1.3 ppbv, daytime NO_2: 7.1 ± 0.8 ppbv) was lower on NPF event days than that (14 ± 1.6 ppbv, daytime NO_2: 9.2 ± 1.5 ppbv, $p < 0.001$) on non-NPF event days, while all the hourly average SO_2 mixing ratios were higher on the NPF event days than on the non-NPF event days, except for the values at 0800LT and 1600 LT, which were likely related to primary emissions. Hence, we have replaced this part with the comparison of NO_2 and SO_2 mixing ratios between NPF event days and non-NPF event days. The following descriptions have been added into the text (pages 19-20: L292-310):

“All the hourly average SO_2 mixing ratios were higher on the NPF event days than on the non-NPF event days, except for the values at 0800LT and 1600 LT, which were likely related to primary emissions. The average mixing ratio on NPF event days and non-NPF event days was 5.2 ± 0.2 ppbv and 4.2 ± 2.5 ppbv, respectively. The large variations of the SO_2 mixing ratio on non-NPF event days were caused by some high SO_2 levels observed on non-NPF days with high PN concentrations (Table 1), due to regional transport and/or local emissions. When the non-NPF days with high PN concentrations were excluded from the total non-NPF event days, the average SO_2 mixing ratio on non-NPF days became 4.2 ± 0.4 ppbv, lower than that on the NPF event days. For NPF events, SO_2 is needed for the production of sulfuric acid, which participates in the nucleation and growth of stable nm-sized clusters. The higher SO_2 found in the NPF events implied that SO_2 might be favorable to the nucleation. However, by comparing the SO_2 levels in the NPF events with those in the non-NPF events with high PN concentrations, we found that the average SO_2 mixing ratio in non-NPF events with high PN concentration was higher than that in NPF events (Table 1, $p < 0.05$), indicating that only a high SO_2 level was not sufficient for NPF. Other factors such as less pre-existing large particles and strong solar radiations (see Table 1) were also required.

It was found that the average daytime NO_x value (11 ± 1.3 ppbv, daytime NO_2: 7.1 ± 0.8 ppbv) was lower on NPF event days than that (14 ± 1.6 ppbv, daytime NO_2: 9.2 ± 1.5 ppbv, $p < 0.001$) on non-NPF event days during the process of formation and growth (Figure. 2). The stronger solar radiation on NPF event days than on non-NPF event days was probably one of the reasons for the lower NO_2 levels on the NPF event days. The increase in solar radiation would promote the decay of NO_2 mixing ratios via the complex photochemical reactions, consistent with the negative correlation ($R = -0.86$, $p < 0.001$) between the daytime NO_2 values and solar radiation on the NPF event days. On non-NPF event days, the daytime NO_2 mixing ratios were higher than the corresponding hourly values on the NPF event days, and had a peak at 1800 LT, suggesting the possible influence of primary emissions transported to the site from the region and/or local urban areas via mesoscale recirculation."

How the modal peak diameters were calculated?

Response: We calculated the modal peak diameters by the equation: $D = \frac{\sum_i D_{pi} n_{pi}}{N}$

Where D_{pi} is the particle size, n_{pi} is the concentration density in size p*i* (unit dN/dlogDp), *N* is the total the number concentration in a mode with a size range.

P. 12134 L. 14-16: "On O3 episode days the Aitken mode particles were probably from condensational growth and coagulation and from primary emissions.." This is very speculative and includes practically all the Aitken mode particle sources.

Response: We agree with the reviewer's comment. In revised manuscript, we classified the sampling days into three types of events to avoid such vague conclusion. For details, please refer to Table 1.

3.2: p.12134 L21: remove the word "mainly"

Response: We have removed the word "mainly" in the revised manuscript.

p. 12135 L1-3: Why there is word "hence"? Why only two events are examined and not all? The presented results don't after all identify the sources nor the mechanisms of the NPF and growth.

Response: We agree with the reviewer's comment. In the revised paper, in addition to studying a typical NPF event as a case, we have also identified 12 NPF events and examined the sources and the mechanisms of the NPF and growth, particle formation rate and growth rate, as well as their relationships with meteorological parameters, inorganic trace gas concentrations (i.e. O_3 and SO_2), biogenic VOCs (BVOCs), carbonyl compounds and condensation sink. The detailed discussions are shown in section 3.3.

Case 1 – new particle formation under a clean background:
In this section the authors use several times word “perhaps” without further justifying their assumptions. The section should be shorter and less speculative. In trajectory figures (S4-S5) authors present trajectories for 3 consecutive days instead of the examined day. Why? It would be also interesting to compare the trajectories on particle formation and non-formation days.

Response: Thanks for pointing it out and we have improved our wording in the revised manuscript. We presented trajectories for 3 consecutive days instead of the examined day because we wanted to study where the air mass originated before the examined event occurred. Furthermore, since the day before the examined event was also a NPF event, it would be helpful to present trajectories for 3 consecutive days in order to understand the history of the air masses arriving at the TMS site during these consecutive NPF events, and to investigate the variations of the boundary layer height before the start of the examined event. According to the reviewer’s comment, we also compared the trajectories on NPF and non-NPF days, and classified the air masses. The detailed description is shown as follows (page 18: L265-284):

“To investigate the transport pathways of the air masses arriving at the TMS site during the sampling period, we analyzed back trajectories for NPF days and non-NPF days. The analysis was done by using HYSPLIT 4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model developed by NOAA Air Resource Laboratory (ARL) (Draxler and Hess, 1998). Back trajectories arriving at 10:00 with 1000 m arrival height were calculated one day backward in time. Figure S2 shows the position of the air parcel at 24 h back in time for NPF and non-NPF days, respectively. The air masses were classified into three major categories on the NPF days: i) air masses originated from inland China (track 1, accounting for 56% of the total trajectories); ii) air masses originated from Yangtze River Delta with a faster movement than track 1 (track 2, 32%); and iii) air masses originated from the South China Sea with a very slow movement (track 3, 12%). The track 1 mainly occurred at daytime hours on NPF event days, and the average mixing ratios of SO_2, O_3, CO and N_{nuc} concentrations at TMS were 4.9 ppbv, 87 ppbv, 480 ppbv and 0.52×10^4 cm^{-3}, respectively. The air in track 1 had the highest O_3 mixing ratio and N_{nuc} concentration, followed by the air in track 3 (74 ppbv for O_3, $p < 0.001$ and 0.36×10^4 cm^{-3} for N_{nuc}, $p < 0.05$) and air in track 2 (66 ppbv for O_3, $p < 0.001$ and 0.17×10^4 cm^{-3} for N_{nuc}, $p < 0.001$), indicating that air masses originated from track 1 were favorable to the NPF events. On the other hand, there were two types of air masses classified on non-NPF days: i) track 1 originated from eastern China coast with a slow movement, accounting for 92% of the total air masses; and ii) track 2 originated from western Pacific Ocean and arrived at TMS with a much faster movement, accounting for 8% of the total air masses. The average mixing ratios of SO_2, O_3 and N_{nuc} concentration in track 1 were 4.0 ppbv, 87 ppbv, and 0.05×10^4 cm^{-3}, respectively, while they were 3.6 ppbv, 56 ppbv, and 0.02×10^4 cm^{-3}, respectively in track 2. The higher O_3 (87 ppbv) and CO (640 ppbv) values in track 1 air were mainly due to regional transport from eastern China. In contrast, low SO_2 (3.6 ppbv), CO (421 ppbv), O_3 (56 ppbv) and high RH (83%) levels in track 2 were caused by the strong winds originated from western Pacific Ocean, which brought clean marine air and scattered rain to the sampling site. The back trajectory results are consistent with the rose plot analysis which found that air masses associated with NPF events were mainly from northwestern to northeastern directions.”

p. 12136 L10: It should also be noted that particle formation here is observed with a delay as being measured only at 5.5 nm. So this delay must depend also on the GR.

Response: Good question. We agree with the reviewer's comment. We have changed the text according to reviewer's suggestion (page 22: L357-359):

"…there is a time delay before a VOC turns to condensable species that could promote particle to grow to the detectable size of 5.5 nm for the instrument. The delayed time depends on the production rate of the condensational vapor from VOCs and on the growth rate of the particle from cluster into 5.5 nm."

Case I:
What does the sentence "The various temporal variations and correlations: : :" mean?

Response: Thanks for pointing it out. Due to the change of data analysis method as discussed above, this sentence has been removed in the revised manuscript.

p. 12138 L20-30: The authors should calculate the H2SO4 concentrations from the proxy (Petaja et al., 2009) instead of speculating with SO2 concentrations. They could also calculate the fraction of GR explained in maximum by sulphuric acid condensation (see e.g. Nieminen et al., 2010, ACP).

Response: We thank the reviewer for making this important point. Based on global solar radiation, SO_2 concentration, condensation sink and relative humidity, we calculated the sulfuric acid concentrations by the equation (4) (Mikkonen*et al*., 2011) (pages 9-10: L172-176).

$$Q_{SA} = 8.21 \times 10^{-3} \cdot k \cdot \text{Radiation} \cdot [SO_2]^{0.62} \cdot (CS \cdot RH)^{-0.13} \quad (4)$$

And we also calculated the maximum fraction of GR contributed by sulfuric acid condensation (Nieminen *et al*., 2010) in Table 2. The detailed discussion is shown in section 3.3.2.

3.3.1:
p. 12140 L21-25: The sentence "In this study, the similar start time for all the NPF: : :" is too general and speculative

Response: We agree with the reviewer's comment. We have paid more attention to avoid presenting such speculative conclusions throughout the text. We revised this part as follows (pages 16-17: L242-248):

"In this study, the observed start time of NPF events was defined as the time when the 5.5 nm size particle concentration (the minimum detectable size for our aerosol instrument) remarkably increased. Since it takes time for newly formed particles (about 1 nm in diameter) to grow into 5.5 nm, the real start time of these NPF events could be earlier than the observed start time, and the time lag varies under different atmospheric conditions. The fitted time lag was defined in this study using the time series of the formation rate of 5.5 nm particles and the sulfuric acid concentration in each NPF event (Riipinen *et al*., 2011) (see Table 2). Based on the observed start time and the fitted time lag for each NPF event, the estimated start time of these NPF events were ranged from 0950 to 1040 LT during this sampling session. "

p. 12141 L1: "low SO_2 mixing ratios on NPF days revealed that clean air masses were favorable to the NPF" is contradictory to p. 12135 L1: "NPF events were often associated with elevated SO_2 and O_3"

Response: Sorry for the confusion. In original paper, due to the fact that we did not classify the NPF days and non-NPF days, we mixed up the comparison of SO_2 mixing ratios on NPF events with those on non- NPF days. These two statements were made based on the comparison between NPF days and non-NPF with high O_3 days, and between NPF days and non-NPF events with high particle number concentration days, not on the comparison with the total non-NPF days. For example, the conclusion of "low SO_2 mixing ratios on NPF days revealed that clean air masses were favorable to the NPF" was drawn after the comparison of air pollutant levels between NPF days and non-NPF events with high particle number concentration days; and the statement of "NPF events were often associated with elevated SO_2 and O_3" was based on the comparison between NPF days and non-NPF days with high O_3 levels. In the revised paper, in order to clearly demonstrate the SO_2 levels on NPF event days and non-NPF event days, we summarized three different types of events including NPF events on O_3 episode days, non-NPF events on O_3 episode days and non-NPF events on high particle number concentration days to compare their SO_2 levels respectively. The following descriptions have been added into the text on page 19: L292-302:

"All the hourly average SO_2 mixing ratios were higher on the NPF event days than on the non-NPF event days, except for the values at 0800LT and 1600 LT, which were likely related to primary emissions. The average mixing ratio on NPF event days and non-NPF event days was 5.2 ± 0.2 ppbv and 4.2 ± 2.5 ppbv, respectively. The large variations of the SO_2 mixing ratio on non-NPF event days were caused by some high SO_2 levels observed on non-NPF days with high PN concentrations (Table 1), due to regional transport and/or local emissions. When the non-NPF days with high PN concentrations were excluded from the total non-NPF event days, the average SO_2 mixing ratio on non-NPF days became 4.2 ± 0.4 ppbv, lower than that on the NPF event days. For NPF events, SO_2 is needed for the production of sulfuric acid, which participates in the nucleation and growth of stable nm-sized clusters. The higher SO_2 found in the NPF events implied that SO_2 might be favorable to the nucleation. However, by comparing the SO_2 levels in the NPF events with those in the non-NPF events with high PN concentrations, we found that the average SO_2 mixing ratio in non-NPF events with high PN concentration was higher than that in NPF events (Table 1, $p < 0.05$), indicating that only a high SO_2 level was not sufficient for NPF. Other factors such as less pre-existing large particles and strong solar radiations (see Table 1) were also required."

3.3.2:
p. 12141 L26: "The threshold was calculated at representative.." I don't understand what this means.

Response: The threshold (line) is calculated according to the model-based correlations in Pirjola *et al*. (1999). This model was designed to predict the required H_2SO_4 production rates for nucleation and growth as a function of condensational sink, relative humidity, and temperature, using a proportional relationship between UV and OH, with full summer sun of 36 Wm^{-2} UV corresponding to an OH concentration of 10^7 molec cm^{-3}. The threshold used in our study is the correlation under the ground-level conditions which are several orders of magnitude more polluted than those required to induce binary nucleation and growth of fresh particles by sulfuric acid. We added sentences as follows (page 26: L413-415):

"The threshold (line) was calculated according to the model-based correlations in Pirjola *et al*. (1999) under the ground-level conditions. This model was designed to predict the required H_2SO_4 production rates for nucleation and growth as a function of CS, RH and temperature."

Non-NPF days should be added to Fig 7.

Response: Thanks for pointing this out. Non-NPF days have been added into the Figure 5 in revised manuscript.

p. 12142 L7-9: How is it showed that low temp and RH were favorable conditions for nucleation?

Response: After we classified and compared the data on NPF days and non-NPF days, we clearly found lower temp and RH on NPF events than on non-NPF days. We have included this discussion in the section 3.2.2.

p. 12143 L12-14: Would be nice to see these exponent correlations shown in a figure.

Response: Due to space limit, we have presented the exponent correlations for one event case in Figure S4.

Conclusions:
"dry monsoon .. created favorable conditions for NPF" is quite speculative since seasonal data is not available

Response: We agree with the reviewer's comment. We have deleted this sentence in the revised manuscript.

Why it is said that NPF occurred on 12 out of 35 days? In three months there should be more than 35 days?

Response: As mentioned earlier, only 35-day integrated SMPS data for particle size distribution were obtained in this sampling session from 25 October to 29 November.

"The SO_2 products might dominate the nucleation process while the VOCs could mainly involve in the condensation growth. Further investigation on correlations : : : showed that isoprene, a-pinene and b-pinene might be the major potential BVOCs responsible for the NPF events at the mountain site" seems also very speculative and not fully justified by the results presented.

Response: We have largely improved the "Conclusions" section to avoid any speculation with the following statements (page 32: L495-500):

"It was found that the formation rate of 5.5nm particle had a power-law dependence on sulfuric acid concentration (with time lag $\Delta t_{J5.5}$), with the typical power between 1 and 2, and the contribution of sulfuric acid vapor to the particle growth rate ranged from 9.2% to 52.5% on these NPF event days. The examination of various nucleation parameters revealed that high sulfuric acid production with low condensation sink could be indicators of the occurrence of a potential NPF event. Moreover, based on the correlations of GR with ambient concentrations of BVOCs and their oxidation products, i.e. condensable organics, we found that monoterpenes seemed to be the most important BVOC species related to the GR of particles on the NPF event days."

Interactive comment on “Observation of aerosol size distribution and new particle formation at a mountain site in subtropical Hong Kong” by H. Guo et al.

Anonymous Referee #2

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In their manuscript, the authors present data from a measurement campaign that covers quite well a lot of parameters that are interesting for investigations on particle formation in the planetary boundary layer, such as aerosol number size distributions, BVOC and AVOC concentrations, SO2, O3, and radiation. As the authors state, such observations are far from ubiquitous in Asia, and therefore such reports are generally welcome.

However, despite the fact that the measurements and the data obtained are interesting, the manuscript has some shortcomings that in my opinion would require some major work before it could be published in ACPD. I will list them in the following:

Response: We thank the reviewer for his/her constructive comments. Our replies follow each of the specific points raised by the reviewer below.

1) Throughout the results and discussion part, the authors present several conclusion type sentences, (as an example. p.12135, l24-l26: "Obviously...", or p12136, l23–26: "In this event..."), which are generally formulated quite conservatively so that the evidence suggests some processes or pathways, quite often photochemistry being involved in a non-specific way. The large number of suggested possibilities makes it quite difficult for the reader to get a clear picture of what is/are thought to be the main process/es causing particle formation. It also makes the whole manuscript very speculative, and the conclusions seem very vague.

Response: Thanks for pointing this out. We agree with the reviewer’s comments and have removed such conclusion type sentences. According to the reviewers’ comments, we have significantly revised the “Results and discussion” section, in which we tried to provide a clear picture about the formation mechanisms and compounds participating in the NPF processes. For instance, we have focused on the discussion of “***3.2.2 Effect of meteorological parameters on new particle formation***” and “***3.2.3 Effect of gas concentrations on new particle formation***”. We have also discussed the association of sulfuric acid vapor and VOCs with the NPF in section 3.3. In the conclusions, we provided a clear picture about the main causes of the NPF at the sampling site.
Please refer to sections 3.2 and 3.3, and section “Conclusions” for details.

2) Linear correlation coefficients of particle numbers and different trace gases are the main tool used by the authors to back up their suggestions. As in the atmosphere many parameters are correlated, in my opinion the correct way to use such correlation coefficients would be to compare correlations of different factors, and take into account the processes possibly leading to such correlations, and based on such analysis concentrate on the process of interest. Correlation between two parameters alone does not imply or mostly even suggest a direct link between two parameters. Additionally, the use of the R2 was not done very convingly, with no discussion of eg. the confidence level given. Generally, I think that if

correlations are used to elucidate the particle formation process, it is important to include days with no particle formation also in the analysis; for example, even though isoprene is positively correlated with particle number on event days, if isoprene is also elevated on some non-event days, it cannot be considered a critical parameter for NPF without some explanation for this. To summarize, I think a more focused approach with some mechanistic and process-oriented analysis is needed, where possible particle formation mechanisms are ranked by their likelihood based on the observations made.

Response: The valuable comments are greatly appreciated. We have significantly improved the correlation analysis throughout the text. We have done correlation analysis on both NPF and non-NPF events; we have also calculated the confidence levels (p value, t-test) for all correlation analyses. In addition, we conducted correlation analysis between NPF and particle formation rate, growth rate and condensation sink. The "Results and discussion" section has been largely revised by classifying the sampling days into NPF event days and non-NPF event days, and separately analyzing the data on NPF event days and non-NPF event days. For details, please refer to Sections 3.1, 3.2 and 3.3.

For instance, on the discussion of correlation between BVOCs and NPF, the following paragraph was added (page 29: L438-450):

"In this study, it was found that monoterpenes were positively correlated with GR, while other VOCs species, i.e. isoprene, aromatics and carbonyls including formaldehyde, acetaldehyde and acetone showed poor and negative relationships with GR (Table 3). However, the analysis on the correlations of isoprene with total PN concentrations and nucleation mode PN concentrations on NPF event days and non-NPF event days indicated that isoprene had linear correlations with PN and power-law correlations with N_{nuc} on both NPF event days ($R_{PN} = 0.82$ and $R_{Nnuc} = 0.71$, $p < 0.001$) and on non-NPF event days ($R_{PN} = 0.70$ and $R_{Nnuc} = 0.75$, $p < 0.001$), suggesting that isoprene might be not a critical parameter for NPF. Instead, the negative correlations of isoprene with FR ($R = -0.40$, $p<0.05$) and GR ($R = -0.38$, $p<0.05$) implied that the increase in isoprene might have a negative effect on NPF. Indeed, a recent chamber study found that large isoprene emission could suppress biogenic NPF (Kiendler-Scharr *et al*., 2009). They claim that NPF rate depends on the concentrations of OH radical which could react with BVOCs to form particles. Due to the strong reactivity of isoprene with OH radicals, OH concentrations are significantly constrained in the presence of isoprene. Moreover, the oxidation products from the reaction between isoprene and OH radical do not contribute to the nucleation process due to their high volatility (Kiendler-Scharr *et al*., 2009). Therefore, the increased isoprene emission would inhibit the reaction of non-isoprene VOCs with OH radicals which could produce condensational organic vapors."

In addition to these, I have some detailed comments on the manuscript:
p12120, l 25: "Especially... " This sentence is strange, I'd consider reformulating

Response: Thanks for pointing this out and we have revised the sentence as follows (page 2: L27-30):

"The freshly formed aerosols become climatically important when they are able to grow to sizes of 50 nm and larger. Particles in this size range can act as cloud condensation nuclei (CCN), significantly increasing the indirect radiative effect of cloud (e.g., McMurry*et al*., 2011)."

p12121, l1: "radioactive"->radiative

Response: Thanks for pointing this out. We have replaced the word “radioactive” with “radiative” in the revised manuscript.

p12122, l1 "While...": this sentence does not go well with the surrounding text

Response: Thanks for pointing this out and we have revised the sentence as follows (page 3: L55-59):

“…For example, boreal forest observations in Finland indicated a connection between nucleation mode growth and ambient concentrations of monoterpenes (Laaksonen *et al*., 2008). In Hong Kong, no study has been undertaken to study the characteristics of NPF events. The potential mechanisms and compounds participating in atmospheric NPF and growth in this region have remained unclear. Therefore, it is important to enrich the database of particle number size distribution, and to investigate the NPF and growth processes in this urban area.”

-"- l 11: what is meant with "low VOCs"?

Response: Thanks for pointing this out and we have revised the wording as “organics with a very low saturation vapor pressure” (page 3: L53) in the revised manuscript.

P12124 l19: "The sampling site is..." this sentence duplicates the info on l6.

Response: Thanks for pointing this out and we have deleted the sentence.

p12127-12128: Data processing: to my understanding, the formula to get the number concentration in a size interval, given in eq 1, holds if N(dp) is the concentration density in size space, which is the way number size distributions are usually given (unit dN/dlogDp). In the case that N stands for number concentration (as stated in the text), then no normalization factor is needed in the summation. This is important also for the calculation of the condensation sink (eq 4), as the number concentration N in that formula should already have the normalization (ie. the transformation from concentrations density to concentration) factored in. This should be checked.

Response: For the calculation of the condensation sink, the particle number size distributions (5.5 – 350 nm) measured by SMPS with unit dN/dlogDp were used, and the number concentration in this formula had the normalization. However, when we calculated the nucleation mode particle number concentration in a size range from 5.5 - 10 nm, normalization factor is needed to convert the data in unit dN/dlogDp to that in particles/cm^3 (e.g. Mejia *et al*., 2009 ACP).

p 12128, l 13-> "The mean PN concentrations..." I did not understand what was done here.

Response: Thanks for pointing this out. The sentence "The mean PN concentrations in different size classes were calculated with a 95% confidence level ($p < 0.05$)" in original paper has been revised as follows (page 8: L139-140):

"The PN concentrations in nucleation mode (5.5 – 10 nm, N_{nuc}), Aitken mode (10 – 100 nm, N_{Ait}), and accumulation mode (100 – 350 nm, N_{acc}) were calculated with a 95% confidence level ($p < 0.05$)."

p12134, l25: To my experience, the growth rates cannot be determined from field data to an accuracy of 0.01 nm/h, so using such high accuracy to report them is not appropriate.

Response: We agree with the reviewer's comment. We have revised all the growth rates with an accuracy of 0.1 nm/h.

p 12136, l28: as a note, I would like to note that the correlations for SO_2, CO and NO reported here are mostly representing no correlation at all; this could be discussed.

Response: We have added the discussion on the correlations as follows (page 21: L344-347):

"Additionally, correlation of N_{nuc} with secondary pollutant O_3 (R = 0.70, $p < 0.001$) was much higher than that with primary pollutants i.e. SO_2 (R = 0.17, $p < 0.01$), CO (R = 0.06, $p < 0.01$) and NO (R = 0.23, $p < 0.01$), suggesting that the NPF event was likely associated with the photochemical formation via VOC oxidation processes, rather than direct emissions from urban sources."

p. 12137, l20: In my opinion, the anti-correlation of N_{nuc} with surface area is not an explanation of the N_{nuc} increase, merely an observation.

Response: Thanks for pointing it out. In original paper, we intended to say that nucleation events often occur after a sharp decrease in concentrations of pre-existing particles with large surface area (Guo *et al*., 2008; Liu *et al*., 2008). Large surface area of pre-existing aerosols may inhibit nucleation processes. Due to the change of data analysis method, the "Results and discussion" section including this sentence has been significantly revised as follows (page 22: L329-331 & L342-344):

"New particle formation event (nucleation mode) on 28 October was clearly observed after raining on 27 October, in line with the fact that nucleation events often occur after a sharp decrease in concentrations of pre-existing particles with large surface area (Guo *et al*., 2008; Liu *et al*., 2008)."; and,
"After 1400, the GR decreased whereas the CS increased from 0.021 s^{-1} to 0.053 s^{-1}, suggesting the increase in large surface area particles might have scavenged potential condensable vapors responsible for particle growth."

p. 12139, l11&12: the "weak linear correlations" seem to me to be more no correlation at all

Response: Thanks for pointing it out. Due to the change of data analysis method, we have removed most of the analysis on the correlations between gas phase pollutants and nucleation mode particle number concentrations. This sentence has been deleted in the revised manuscript.

p 12143: There has been discussion of the role of the power exponent in explaining the nucleation mechanisms. Whether it can be reliably used or not is still open, but in my understanding it should be computed for the relation between the concentration of the vapour in question and the formation rate J, not the concentration of small particles.

Response: We agree with the reviewer's comments. We have correlated the particle formation rate, growth rate and condensation sink with gas phase pollutants and meteorological parameters in all NPF events, instead of directly examining the correlations between gas phase pollutants and nucleation mode particle number concentrations. For more details, please refer to the "Results and discussion" section.

p12144: the section "Particulate Matter" seems quite disconnected from the rest of the text.

Response: We agree with the reviewer's comment. We have removed this section in the revised manuscript.

In addition, I would suggest careful proofreading for the use of English, as I found a number of examples where the language was not used correctly.

Response: Thanks for pointing this out and we have corrected grammatical mistakes and re-constructed sentences where necessary in the revised manuscript.