Review report on

Oxidation-driven acceleration of NPF-to-CCN conversion under polluted atmosphere: Evidence from mountain-top observations in Yangtze River Delta

By Zhu, W., Shang, S., Wang, J., Wu, Y., Deng, Z., Ran, L., Kuang, Y., Tang, G., Huang, X., Pan, X., Liu, L., Xu, W., Sun, Y., Hu, B., Wang, Z., and Liu, Z.

Zhu et al.'s manuscript examined the new particle formation (NPF) mechanism at the top of the boundary layer, as this remains poorly understood in polluted environments. To this end, they took measurements at a mountaintop site in southeastern China, characterized NPF under different air masses, and assessed its contribution to cloud condensation nuclei (CCN). The authors identified 8 NPF events, during which significantly higher rates of particle formation and growth were observed in polluted conditions, driven by elevated levels of sulfuric acid and ammonia. Polluted air masses produced higher CCN enhancement and faster NPF-to-CCN conversion, which was accelerated by nitrate-induced particle growth. Their results show that, air masses influenced by pollution intensify and accelerate CCN production at the top of the boundary layer through enhanced atmospheric oxidation capacity.

However, several details are missing, and a more thorough discussion is required in specific sections. The paper is poorly written and too complex for readers to study, particularly part 3.4. Furthermore, the authors should use a revised version in better English. That version should be rejected. Other than that, the paper can be recommended for publication once the major issues listed below have been addressed. This will enhance the manuscript.

Abstract

L20: "… exploring the nucleation mechanism …" --> Do the authors solely examine the nucleation mechanism throughout the manuscript? This means that they only consider the formation of the initial clusters and not the growth process. Please rephrase.

L25-26: According to the authors, ammonia generally enhances the nucleation process of sulfuric acid alone. This is vague. Please rephrase.

L31-32: Does nitrate have a significant effect on cloud formation? The authors are discussing the impact on CCN. While the CDNCs are indeed related to the CCN budget, this relationship is not straightforward. Please revise.

The Abstract should be rewritten.

Introduction

L40-42: Please rephrase. Furthermore, ensure that you use important references in your scientific sentences (e.g. Kulmala et al., 2001; Kerminen et al., 2018).

L42-46: Studies that report the significant impact of the NPF mechanism on CCN alone should also be included (e.g. Laaksonen et al., 2005; Kalkavouras et al., 2017; Kalkavouras et al., 2019).

L52-54: A reference is needed to confirm the negative impact of CS on the formation of nanoparticles (e.g. Kalivitis et al., 2019).

L56-57: However, many studies worldwide have used long-term measurements to demonstrate the role of NPF on CCN. This study only uses data from 8 NPF days. Please be more cautious.

L59-61: Please highlight the regional character of the NPF mechanism by including references from Aktypis et al. (2024) and Kalkavouras et al. (2021).

L67-70: It is vague. Which analysis is limited? Please rephrase and provide references.

L75-76: The authors argue that studies avoid determining the growth rate of small particles to CCN. However, it is quite common for this "growth speed" to be related to the start of the NPF and the time at which the CCN "feel" the NPF. Perhaps this sentence could be revised.

L76-79: Please emphasize the impact of anthropogenic pollutants on the rate of condensational growth by including the relevant references (e.g. Kalkavouras et al. 2020; Dinoi et al., 2023).

L84-86: A reference is needed.

L88-92: References are also needed.

L103: "… NPF nucleation and growth processes … " → What does NPF nucleation mean? The NPF mechanism consists of atmospheric nucleation and the gradual growth of freshly formed particles. Therefore, this part of the sentence is incorrect. Please revise it.

L106-107: Could you please explain what "cloud processes" means?

L107-108: "… particle number size distributions (PNSD, 2nm~20 μm), …" → There is probably a typo here (i.e. "~").

The Introduction should be revised. It lacks references, and better English should be used.

Methodology

L116-120: Please provide a map showing the exact location of the study area, even in the supplementary material. It would be useful for readers to have an idea of the location and to see pictures of your station. If possible, could you also add some references about this location? It is probably not the first time that a campaign has taken place there.

L126-131: There is a lot of missing information regarding the PNSD measurements. How many size bins does each instrument have? What are the aerosol and sheath flows? Was any calibration performed prior to the campaign? Please provide significant information about the quality of the experimental measurements.

L142-145: Please see the previous comment. The authors should provide more detail regarding the instrumentation setup. More information about ACSM measurements and data analysis should be provided: Standard/capture vapourizer? Did you apply any collection efficiency correction?

L149-150: Which instruments were calibrated? Did the authors mean the analyzers for the standard gaseous species (SO_2, O_3, NO_x) and ammonia?

L153: This information should perhaps be included alongside the sentences on gaseous pollutants, rather than after the $PM_{2.5}$.

L219-223: Firstly, the authors should avoid terms such as "mainstream" metric. Moreover, what exactly is the innovative approach, when using only 8 NPF episodes? According to Kalkavouras et al. (2019), when a **7-year dataset is used (162 NPF events were analyzed)**, the period from the start of NPF until the "wave" of new particles activated into CCN-relevant sizes is expressed through t_{start} and $t_{decoupling}$. Therefore, what valuable information is provided here? Furthermore, I find the hygroscopic growth confusing. The critical diameter is derived from kappa, however the authors state that κ is constantly changing. It is unclear.

The Methodology section definitely needs revising, as it is missing significant information.

Results

L231-233: There is a repetition here. See lines 164–167.

L233: Could you please provide the dates of these events? Given that this information is missing, it is likely that the authors mean typical Class I NPF events.

L235: What do "nucleation-mode particles" mean? The authors should provide all the relevant information in the methodology section. They should also explain what nucleation, Aitken and accumulation-mode particles are, and how they are calculated. Furthermore, please use a frame to present the 8 NPF events on the contour plot (Fig. 1), noting the dates of each event. The frame should include all the information, i.e. extend it to Fig. 1d, 1e and 1f.

L241-243: It would be helpful to provide a table containing all the NPF-related information. This table should show the dates, NPF frequency, the starting time, meteorological parameters on NPF days, the number concentrations of each particle mode, formation and growth rates, and so on, as well as a discussion of the information provided.

L248-253: "The data shows that he in-cloud formation of biogenic terpenoid" → Something is missing. Moreover, to which data are the authors referring? See the previous comment. The discussion is rather complicated.

L248-253: "… significant variations in 2~6 nm Nucleation mode particles were observed among …" → The 2-6 nm size range belongs to the nucleation mode.

L272: In other words, does this mean that only particles in the 2–6 nm range belong to the nucleation mode? This is vague. Particles above 6 nm are considered to be in the Aitken mode. It is crucial that all this information is integrated into the Methods section.

Section 3.1 should be rewritten, as it is rather vague. The authors should present all the information in a clearer way, for example using tables, and the discussion should focus on this. Several gaps must be addressed.

L279-280: The authors began section 3.2 with the following sentence: "To further explore the chemical difference between NPF-P and NPF-C events, diurnal variation and average values of NPF parameters for NPF-C and NPF-P events were analyzed.". They then discuss the formation rate and the precursors (e.g. H_2SO_4) that enhance it. Where exactly is the discussion of the chemical composition? Please be consistent throughout your manuscript. This seems quite complex.

L280-283: Poor English. Please rephrase.

L283-284: Are all three NPF-P events in peak at 10:00 LT? According to Fig. 2a, the time appears to be 12:00 LT.

L289-290: Are these the mean values of NH_3? Please could you clarify and rephrase? Furthermore, the authors discuss the results from Fig. 2d. Following the discussion of H_2SO_4 in Fig. 2a, NH_3 should be illustrated in Fig. 2b in the correct sequence.

L291-292: Do the values refer to the average? Moreover, there is a difference in O_3 concentrations when NPF is taking place (10:00–12:00 LT), but it is not marked. The figure for O_3 should be Fig. 2c, as discussed after ammonia.

L293: Could you please explain why "consequently" the growth rate is higher in NPF-P events than in NPF-C events? Please elaborate. Is there any reference to this outcome?

L295: The authors said: "Compared with European forested sites …". However, they only used data from Hyytiälä in Finland. Please rephrase and use more references from forest and remote sites in China.

L298-300: "Collectively, the above results indicate that there are significant differences in the intensity of nucleation and growth processes of NPF events under different atmospheric conditions, and these differences are caused by different regional transport processes." → Please rephrase as: "These differences suggest that the intensity of an NPF event can vary significantly depending on the atmospheric conditions and the regional transport processes involved.". Atmospheric nucleation and subsequent growth are the NPF mechanism. Therefore, it is incorrect to refer to the "nucleation and growth processes of NPF events".

L302: Ammonia? The authors probably mean ammonium (NH_4^+).

L301-302: Here, the authors examine the role of chemistry in growth rates. How does the above statement that GR is "consequently" higher in NPF-P episodes hold up?

L303: To show the difference more clearly, please use the first y-axis for organics and the second y-axis for the other components.

L303-304: Is there any scientific explanation for this? Please provide a scientific discussion, rather than just presenting numbers.

L307: Was the ACSM used as a $PM_{2.5}$ cyclone? Where is this information located in the manuscript? The SMPS recorded measurements in the size range of 2.5 nm to 16 μm. The authors suggest that half of $PM_{2.5}$ consists of organic matter. However, this size range differs from that on which the chemical analysis was based. Please elaborate.

L309: What are the latter stages of growth, and how do nitrates impact them?

L310-311: Provide some references. For instance, the comprehensive and holistic study by Trechera et al. (2023) revealed that the growth of nucleated particles is driven by the condensation of semi-volatile organic compounds.

L311-313: How did the authors reach this conclusion? Why are nitrates more active than organics? How was this outcome achieved?

L314: Since a CCN can be mainly activated at Aitken mode diameters, the focus will be on the chemical composition of PM_1 rather than $PM_{2.5}$. How scientifically sound is this approach?

Section 3.2 should be revised. There are many scientific omissions and errors in English. Furthermore, the figures presenting the diurnal variability of $PM_{2.5}$, RH, SO_2, NO_2 and WS are not discussed at all.

L319: Provide a reference for the crucial role of H_2SO_4 in the NPF mechanism (e.g. Garcia Marlès et al. (2024)).

L320-324: However, the authors have already discussed H_2SO_4 in lines 284–289.

L321: Please provide comparisons with similar environments. Your station is not categorized as "urban".

L323: Please, see the previous comment.

L323: Which value remains significantly higher than those reported for clean sites? The *R*? Or is it something else? Please clarify.

L326-327: But why do the authors discussing the role of H_2SO_4 refer to ammonia and amines at this point?

L331-332: Please revise Figure 3a. The legend is captured with the data points. What is the $J_{1.7}$ in the y-axis? There is no information about it in section 3.3. What does the "DMA" stand for? The authors should provide all the information.

L345-346: The authors have already discussed the scatter plot between $J_{2.5}$ vs. H_2SO_4 in lines 321–324.

L339-344: The authors used the MALTE-BOX model to evaluate the formation mechanism in the presence of high levels of ammonia. But where is the discussion of these results? Why did they use this model when they had direct ammonia measurements during the campaign? In lines 345–351, they discuss the role of measured ammonia on NPF days. This discussion is vague.

Section 3.3 requires substantial scientific enhancement and a more detailed discussion.

L354-355: "To elucidate the relationship between the growth processes of the two types of NPF events and the formation of CCN." → Something is missing here. Please be aware of this throughout the manuscript.

L360: What does "Da" mean? It is d_c; it is referred to as "critical diameter" above at which point all particles can act as CCN. Please rephrase.

L364-368: What about the condensation sink (CS)? The authors neither discuss nor calculate this decisive metric in the NPF mechanism. CS calculations should be performed for the entire study period and the results discussed.

L370: What does "TD" mean?

L368-369: "HNO_3 enhances low-volatility organic compound production, further suppressing the hygroscopicity of NPF-P ultrafine particles" → It is not clear to me. How does the enhancement of organic compounds suppress the hygroscopicity when the κ consists of organic and inorganic substances? Please could you elaborate?

L373-374: The authors write about figure 4b and then discuss figure 4d. This makes it difficult to follow the discussion.

L374-375: "During initial nucleation (0~2 hours), elevated non-volatile fractions (Figure 4d) suppress hygroscopic growth, maintaining D_a at higher levels (~120 nm)." → This is difficult to follow. Where does this outcome stem from? It is quite vague.

L375-377: Where does this outcome come from, and how is it depicted?

L377-380: This makes it difficult to follow the discussion. I am unable to see all this information on the figures.

L380: Could you please add a tint to show the NPF days? It is difficult to examine the figures 4a, 4b, and 4c as they are.

L386-389: What are the main differences when compared to Figures 2h and 2i?

L390-393: How is this outcome supported? It seems to be a general conclusion that lacks scientific argumentation.

L428-431: I cannot understand what is being said. What and where is the role of nitrate?

Section 3.4 should be completely revised. It is unclear and difficult to read. It needs to be improved scientifically.

References

Aktypis et al. (2024), https://doi.org/10.5194/acp-24-65-2024

Dinoi et al. (2023), https://doi.org/10.5194/acp-23-2167-2023

Garcia Marlès et al. (2024), https://doi.org/10.1016/j.envint.2024.109149

Kalivitis et al. (2019), https://doi.org/10.5194/acp-19-2671-2019

Kalkavouras et al. (2017), https://doi.org/10.5194/acp-17-175-2017

Kalkavouras et al. (2020), https://doi.org/10.1016/j.atmosres.2020.104911

Kalkavouras et al. (2021), https://doi.org/10.3390/atmos12010013

Kerminen et al. (2018), DOI 10.1088/1748-9326/aadf3c

Kulmala et al. (2001), https://doi.org/10.3402/tellusb.v53i4.16622

Laaksonen et al. (2005), doi:10.1029/2004GL022092

Trechera et al. (2023), https://doi.org/10.1016/j.envint.2023.107744