We thank the reviewer for the helpful and constructive comments, which have led to significant improvements in the manuscript. We have carefully revised the text. Our point-by-point replies are given below (blue), following the referees' comments (black). Changes to the manuscript are marked with green and underlines. In our replies, the line numbers refer to the revised manuscript.

Reviewer 4:

New particle formation (NPF) can play an important role in urban smog formation, and thus has a considerable impact on air quality and public health. However, it is still unclear when and where sulfuric acid nucleation will cease to dominate urban particle formation as sulfur emissions continue to decrease. This study investigated the characteristics and mechanisms of frequently occurring NPF events in the polluted Po Valley region through a 2-month measurement using a suite of mass specs and particle sizers. The authors first calculated particle formation and growth rates of NPF events based on the measured particle number size distributions. In addition, the authors discussed the role of measured gas-phase sulfuric acid, highly oxygenated organics, and base compounds (ammonia and amines) in particle nucleation growth, through comparisons with results from the CLOUD chamber experiments. Finally, the author concluded that sulfuric acid and base compounds remain the primary driver of the frequent NPF, while oxygenated organics may play a more important in particle growth.

The research topic of this paper is novel and has important implications of interest to a broad range of atmospheric scientists, the measurement techniques are state-of-the-art, and the results are comprehensive. Overall, this is a relevant study that fits well within the scope of the ACP. However, the way the results are interpreted and discussed needs minor revision to improve the clarity for non-specialist readers. Here are my comments:

Response: We appreciate the reviewer's positive feedback on manuscript, and we carefully revised the manuscript accordingly to the reviewer's comments.

The key point: My understanding is that the lower levels of condensation sink and amine concentration are the two main differences in the Po Valley, compared to previous urban measurements, such as those taken in China. And interestingly, these two factors offset each other, resulting in somewhat comparable particle formation rates. This is actually a very important message that emphasizes the need to further reduce amine emissions as we reduce aerosol pollution in both Europe and China. These differences were discussed in the text, but were less clear in the abstract. I would suggest that the author modify the abstract and conclusions extensively to highlight the key point of this work.

Response: Thanks for the reviewer's suggestion for the highlights of this work. We have addressed the unique environment in Po Valley area than Chinese megacities, such as lower condensation sink and metrological conditions in the introduction section (please refer to the response to Reviewer3, Comment 3). The importance of reducing key species to suppress secondary particle formations is also added in the abstract and conclusion section as suggested by the reviewer.

Abstract

Line 31-42

"Our results demonstrate that in this area, frequent NPF events (66% of all days during the measurement campaign) are primarily driven by abundant sulfuric acid (8.5×10^6 cm^{-3}) and basic molecules. In contrast, oxygenated organic molecules from the atmospheric oxidation of volatile organic compounds (VOCs) appear to have a minor role in the initial cluster formation but contribute significantly to the consecutive growth process. Regarding basic molecules, amines, typical species contributing to NPF in highly polluted areas such as Chinese megacities, are insufficient to stabilize all sulfuric acid clusters. Ion cluster measurements and kinetic models suggest that ammonia (10 ppb) must therefore also play a role in the nucleation process. Generally, the high formation rates of sub-2 nm particles (87 cm^{-3} s^{-1}) and nucleation mode growth rates (5.1 nm h^{-1}) together with the relatively low condensational sink (8.9×10^{-3} s^{-1}) will result in a high survival probability of newly formed particles, making NPF crucial for the springtime aerosol number budget. Our results also indicate that reducing key pollutants such as SO_2,

amine and NH_3, could substantially help to decrease the particle number concentrations in the Po Valley region."

Conclusions

Line 521-544

"In this study, we conducted a continuous two-month measurement campaign in the Italian Po Valley during springtime, where frequent NPF events were observed on 66% of all days. Through direct ion cluster measurement, kinetic models, and the comparison with the CLOUD chamber experiment, we have determined that sulfuric acid-base nucleation is the dominant formation mechanism in the Po Valley region. Abundant sulfuric acid and basic molecules, including amines and ammonia derived from agriculture activities, provided ample precursors for NPF events. In contrast to megacity environments, CS showed no significant difference between NPF event and non-event days, indicating that in Po Valley it is more the abundance of precursors than the variations in the sink controlling the occurrence of NPF.

Furthermore, we observed that apart from DMA, a typical basic precursor, NH_3 and other amines were also likely to be involved in NPF in the Po Valley. This was supported by the high abundance of SA-NH_3 and SA-amine-NH_3 clusters measured by the APi-TOF during NPF events. DMA, while more efficient than ammonia, was insufficient to stabilize all SA during our sampling period. This resulted in a more scattered correlation between sulfuric acid concentrations and measured formation rates compared to Chinese megacities with higher DMA concentrations. In that sense, we could show that the clustering during NPF is clearly distinct between polluted megacity environments and polluted semi-urbanized regions such as Po Valley. Similar to Beijing, we found that OOMs did not play a decisive role in the initial growth processes, likely due to the absence of ultra-low volatility organics (typical OOM dimers) in the ions and neutral cluster measurements. However, low-volatility organics were abundant enough to induce fast growth processes above 3 nm. The comparable GR and formation rates, along with lower efficient CS compared to megacity environments, indicate a high survival probability for newly formed particles. Therefore, NPF is likely to play a significant role in the fine particle concentrations and pollution levels in the Po Valley region. Further reductions of key NPF species, including SO_2, amines and NH_3, can contribute to suppressing NPF event frequency and lowering particle numbers. This, in turn, would improve air quality in the Po Valley region."

Other amines: In Fig. 3(b), most of the data points fall between DMA concentrations of 0.5 -1.8 pptv, which is close to the measured DMA concentration in Fig. 5(d). Is there any other evidence to support the conclusion that DMA is not sufficient? Or are there other amines measured by the H3O+ CIMS? If there is no strong evidence, I would suggest that the authors tone down this assertion.

Response:

We draw the conclusion that DMA alone is not sufficient to stabilize all sulfuric acids based on the following observations:

1) In the ion cluster measurement by Api-TOF, if DMA is enough to stabilize all sulfuric acids (e.g., DMA=10 ppt), as indicated by the recent CLOUD chamber experiments, a significant fraction of SA should cluster with DMA given its stronger basic properties, and SA-NH_3 clusters can be neglected in the ion cluster measurement (Yin et al., 2021). However, our measurement does not align with this expectation (Fig. 4a).

2) As mentioned by the reviewer, in Fig 3b, SA-DMA cluster formation rates do not reach the kinetic limit during our measurement, indicating that gaseous DMA is insufficient to stabilize all SA during NPF events.

3) According to co-located Vocus-CIMS measurement, ambient DMA signals were close to background levels, despite the detection of a DMA peak in the mass spectra (Fig. S4).

We think other amines, such as TMA may also involve since the present of SA and other amine clusters in the Api-TOF measurement during NPF events, which were further discussed in the section 3.3.

Additionally, based on previous studies at the same site, other amines (e.g., methylamine and trimethylamine) were also observed in the particulate phase (Decesari et al., 2014; Paglione et al., 2014). Therefore, other gaseous amines were also likely involved in the NPF.

However, we agree in general with the reviewer that the discussions on the involvement of other amines and the lack of DMA should be tonged down due to the lack of quantitative gas-phase amine measurement in our campaign. In this study, our gas-phase amine measurement lacks quantitativeness due to the absence of a suitable calibration method and the Vocus-CIMS needs to be specially tuned for good performance with amines (Wang et al., 2020), which was not applied in our campaign. We, therefore, revised the manuscript as follows:

Line 340-346

"It implies that other factors, for example, the abundant ambient NH_3 concentrations (~10 ppb) during our study period may also participate in cluster formation. It is consistent with the Vocus measurement, which suggests the ambient DMA signals were close to the background levels (Fig. S4). The reason for not reaching SA-DMA limit during the campaign could be 1) the relatively lower DMA emissions (such as vehicle flows) than Chinese megacities (Ge et al., 2011; Zhu et al., 2022), and 2) the quickly scavenge caused by photolysis and nighttime high RH (85%) (Leng et al., 2015; Yao et al.,2016)."

Line 344: "…the higher formation rates at 1.7 nm (87 cm-3 s-1) may be the decisive factor to overcome the CS and determine if a growing mode can be observed leading to a classification of the day as an NPF with growth day." This is more speculation than fact – other factors such as meteorological conditions may also play an important role. I would suggest that the authors tone down this assertion.

Response:

We have revised the sentence as follows:

Line 371-375

"Considering the similar CS and GR levels for NPF with and without growth days, the higher formation rates at 1.7 nm (87 cm^{-3} s^{-1}) may be a more important factor to surpass the CS. In stable meteorological conditions, a higher formation rate may significantly elevate the possibility of newly formed particles overcome the CS and continuous grow to larger sizes."

Line 352: "Acid-base clusters were not observed in monomer (SA1), dimer (SA2), or trimers (SA3), likely due to declustering effects in the APi-TOF instrument". This is not true – pure SA3 is energetically more stable than SA-base clusters.

Response:

The sentence has been revised as follows to make the statement clear:

Line 382-384

"In Api-TOF measurement, the absence of basic species in the smallest sulfuric acid clusters is likely attributed to the loss of base molecules within the mass spectrometer (Cai et al., 2022b; Zha et al., 2023; Alfaouri et al., 2022)."

Reference

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