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Response to Referee #1

Spiro D. Jorga et al.

Author comment on "New particle formation and growth during summer in an urban environment: a dual chamber study" by Spiro D. Jorga et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-554-AC1, 2022

(1) *This work investigates the NPF and growth with a dual chamber. The manuscript fits well to the scope of ACP. The role of ammonium in particle nucleation and growth is widely reported, however, it is very hard to conclude the innovation and new findings. This paper might be worth to be published, but not in its current form. Thus I recommend it to be resubmitted after the following comments listed below have been adequately addressed.*

To the best of our knowledge, this is the first study that demonstrates that in a sunny area, with moderate to low pollution levels and available sulfur dioxide and volatile organic compounds (both anthropogenic and biogenic) in which nucleation is infrequent addition of ammonia leads to nucleation and growth of new particles. The experimental approach used is quite innovative and the findings are quite important regarding the relative role of ammonia, amines, organics, etc. in atmospheric nucleation. We thank the reviewer for the comments and suggestions. Our responses (in regular font) follow the comments of the reviewer (in italics).

Comments

(2) *The major comment is about the conclusion or innovation of this study. NPF and growth processes involving ammonium have been intensively investigated. So what is the aim or new findings of this study? If the authors introduce a new method to investigate NPF, which is good, then I would suggest more description should be included to characterize the dual chamber system.*

The experimental approach used in this study is innovative. Perturbing “the atmosphere” (a few cubic meters of it to be exact) in a location in which nucleation is infrequent, to identify the reactant that is limiting new particle formation is attempted for the first time. The use of two chambers to correct for the various complications arising from these challenging measurements is an additional novelty of the study. We do agree with the suggestion of the reviewer and additional information has been added about the chamber system and the experimental procedure.

There have been indeed several previous studies that have pointed out the potential role of ammonia for atmospheric nucleation and growth. At the same time there have been several studies about the role of amines, biogenic secondary organic vapors, nitric acid,

iodine, etc. All of these studies both in the laboratory and in the field do not explain why nucleation and growth does not happen in areas similar to the Eastern Mediterranean site used in our work. This is one of the areas with the lowest new particle formation frequency in Europe during the summer, even if it combines strong sunlight intensity, rapid photochemistry, moderate to low particle levels, there is available sulfur dioxide and also there are reasonable levels of both biogenic and anthropogenic VOCs. Our work demonstrates for the first time that ammonia is limiting new particle formation in this area. We have additional text both in the Introduction and the Conclusions to point out the originality of this work, because based on the comments of the reviewer the main points of our study were not sufficiently clear for its intended audience.

(3) *The injected ammonia concentration is 20-200 ppb, what is the ambient ammonia concentration in this area? I am worried about the high concentration could not represent the ambient condition.*

The gas-phase ammonia concentrations used in this study are relatively high but they are still in the range of observed concentrations in the atmosphere. For example, Dammers et al. (Atmos. Environ, 2017) measured ammonia concentrations in the Netherlands up to 300 ppb. The fact that we have several measurements at concentrations higher than those used by Kirkby et al. (2011) but still relevant to the atmosphere is actually a nice feature of this work. The area has often low ammonia levels, because there are high sulfate levels and the available ammonia is transferred to the particulate phase to neutralize the available sulfate. Please note that our goal in these experiments was not to reproduce the ambient conditions. In that case regular field measurements would be sufficient and no chambers would be needed. Our goal has been to change the prevailing ambient conditions, investigate the system response and gain this way valuable insights about atmospheric processes. These points are now made in the revised paper.

(4) *What is the difference between the reference chamber and ambient measurement? The UV light?*

The major difference is that due to losses in the sampling system the reference chamber has a little lower particulate concentration than the ambient atmosphere. The UV light is also a difference in some experiments, while other experiments used natural sunlight. Other differences include the interactions of the pollutants inside the reference chamber with the walls of the chamber (for example losses of particles but also some vapors to the walls). Finally, the ambient air in the site may changing as the wind may bring a new air mass to the area, while the air mass inside the reference chamber remains the same as that present in the site at the time of the filling of the chamber. A brief discussion of the above differences has been added to the paper in the system description section.

(5) *Line 120-121: I do not understand the connection between wind speed and UV light.*

The two chambers were located inside an enclosed structure that protects the chambers from the elements and especially high wind and rain. When the wind speed is low the top cover of the structure can be removed and the chambers can be illuminated by natural sunlight. If the wind speed is high, even if only the top cover is off, the chambers may be destroyed by the wind. So during these conditions the chamber system was kept completely covered and the UV lights were used instead of natural sunlight for the corresponding experiment. This issue is now explained better in the paper.

(6) *Line 125-126: how long you flush the chamber and how to make sure there are no pollutants stick to the wall?*

The chambers were flushed with ambient air for approximately two hours before and after each experiment. Pollutants unavoidably stick to the walls (for example particles are always lost to the walls of a Teflon chamber). The potential interactions of our experimental system with the chamber walls is the reason for the use of the second (reference) chamber. Any interactions will also be present there and will be observable and therefore we can correct for them. At the same time, we performed several blank experiments to make sure that the system did not have any memory of past experiments. This information has been added to the manuscript. A similar point has been made by Reviewer 2 (comment 2).

(7) *Line 221-222: I do not understand this sentence.*

There was a typo in the sentence. We have rewritten it and it now reads "Nucleation and growth of the new particles to sizes above 9 nm in the perturbed chamber and not in the reference chamber were observed in 6 out of the 13 experiments".

(8) *Line 240-241: Have you calculated the nucleation rate (J9) ? How about the correlation?*

We now clarify at this point that we calculated the nucleation rate J_1. Calculating the nucleation rate J_9 would require changing the model to use 9 nm as the lower particle size and then repeating the fitting exercise. This would require repeating the full modeling exercise with little benefit.

(9) *Line 272-280: How about the ammonium concentration from AMS measurements? Is there any difference between Class A and Class B experiments?*

We followed the advice of the reviewer and analyzed carefully the ammonium concentrations in the different types of experiments. The average ammonium concentration for the class A experiments was only 20% higher than that of Class B-experiments. The ammonium levels in this area are determined to a large extent by the sulfate levels. So it is quite difficult to gain any additional insights from this relatively small difference in ammonium levels. A brief discussion of this point has been added to the manuscript.

(10) *Line 290-291: I do not understand why.*

Another possible explanation for not observing nucleation in the Class C experiments is that new particles were formed but they did not grow to sizes big enough to be detected by our available instrumentation. We were able to measure only particles larger than 9 nm. If the growth rate in those experiments was less than 2 nm h^{-1} then the particles would not be reaching the 9 nm threshold during the experiment. This point is better explained in the revised text.

(11) *Line 339-340: The estimated nucleation rate is too high, is this due to the high injected ammonia concentration? Then how could we connect the chamber study with the real ambient event?*

The estimated nucleation rates in this work were between reported rates in ambient measurements and those of the CLOUD lab experiments (Figure S3). Nucleation was observed even at the lower ammonia levels used in this work (20 ppb), and the estimated nucleation rate was quite high. This result is applicable to environments with high ammonia levels like the Netherlands or the Po Valley. The ammonium levels in these areas are often similar to those in our experiments. A discussion of this issue has been added to the paper.

(12) *Line 369: what do you mean ammonium nitrate formation?*

We did not observe any increase in the ammonium or nitrate concentrations in the AMS in any of our experiments. This suggests that ammonium nitrate was not formed in the perturbed chamber after the ammonia injection, and did not contribute to the particle growth in our experiments. This explanation has been added at this point of the paper.