Reply to the Interactive comment by referees #1 and #2 on „Laser filament-induced aerosol formation“

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We thank both Referees #1 and #2 for their careful reading, detailed comments and positive evaluation of our manuscript. Below, we answer to all comments, referencing them with the same numbering as in the Interactive Comment. Furthermore, to ease the reading, we reproduce the referees' comments in *italics* above each answer.

Answers to Referee #1

Detailed comments on the abstract and conclusion

The authors present in their manuscript a description of a series of experiments in which laser filaments were introduced into an aerosol chamber, and the resulting particle formation was studied using several instruments. In the abstract, the authors introduce as their main findings

1. a quantification of particle formation rates in the plasma volume

2. the observation that particle formation increases exponentially with the concentration of water vapour

3. the increase of the particle yield by number for the addition of trace gases (SO_2, α-pinene, toluene, NH_3?)

4. the increase of particle mass with the addition of α-pinene

5. that particle formation is efficiently supported by acids produced photo-ionization of both major and minor components of the air (examples given are N_2, NH_3, SO_2, organics)

In their conclusions, the authors additionally draw attention to the following findings:

6. oxygen addition reduces the particle production rate due to its high electron scavenging efficiency, which in turn reduces the plasma reactivity

7. nitrogen species do not cause significant increase in particle formation compared to Argon

8. growth and particle formation are dependent of different physio-chemical processes

9. dilution of the laser plasma affected particle production rates except in the case of ambient air

10. laser-generated particles "homogeneously nucleate water close to water saturation"
Regarding these points, I have the following comments:

1. The quantification of the particle formation rate is done assuming either

a. All particles are formed in the plasma volume and transported to the measurement inlet without additional particle formation or losses on the way

b. Particle formation rates, as they are given now, should be understood as the overall formation rate in the vicinity of the ionized region, and can then be scaled by this ionized region.

Case a. seems rather unlikely to me; case b. is more likely, but as the formation rates were calculated from a single point in the chamber without mixing, quantitative reproduction of these experiments will be quite hard. This is not a problem inside this study (as the experiments were performed with fairly identical setups), but should maybe be mentioned for the benefit of anyone wishing to reproduce the results herein.

Also, if I understood correctly, the particle formation rate was calculated by dividing the total increase of particle number by the total experiment time. This does not take into account the losses during the experiments, which at these very high rates could be quite substantial due to *both self-coagulation and wall losses. The authors should at least indicate some of these uncertainties in the description of the derivation of the formation rates, if no estimate of the size of the uncertainty is given.*

Indeed the correct one is b. Or, in other words, the important aspect is not whether the particles are formed in the filament and during the laser pulse. They may very well be formed slightly later and/or around the filament volume, once the species generated by the pulse have scattered out of the filament volume. In fact, the important information we want to put forward is the formation of particles *due to* the considered filament volume.

We expanded the description of the calculation of the provided particle production rate to provide more details about it and the corresponding limitations, and moved it to the Experimental setup section:

"Effective particle formation rates per unit plasma filament volume (hereinafter denoted as cm^{-3} plasma s^{-1}) were calculated as the increase in measured particle number concentration (particles > 3 or 2.5 nm if not stated otherwise) during the laser firing period, divided by the time during which the laser was fired, and by the estimated plasma volume of 0.08 cm^3. This effective particle formation aims at quantifying the final result of a specific laser-ionized volume in the cloud chamber. It therefore provides a lower limit to the actual formation rates, since particle losses, e.g., due to self-coagulation or wall losses, directly impact the calculated value. Furthermore, the calculation rates per unit plasma volume do not imply that particles are actually produced within the filament volume itself. They can also be produced in the subsequent evolution of the atmosphere around the filaments, depending on the diffusion of the produced species, as well as their dilution by the mixing fan. While allowing comparisons among the present study, in which all experiments were performed using the same experimental configuration, these limitations should be kept in mind when comparing our data with other experimental arrangements."

2. The observation of particle number (and mass in some cases) increasing with increasing water vapour concentration is very clear and a nice result. However, as it has become quite evident recently, small amounts of impurities can be the cause of particle formation in chambers; do the authors have an estimate whether the purified water could contain impurities such as amines in significant amounts (leading to vapour concentrations of the order of 10^6-10^8 #/cc)?

Assuming a typical water concentration in the order of $1.8*10^{17}$ cm^{-3} (283 K, 1 atm) amine vapour concentrations of 10^6-10^8 cm^{-3} would correspond to impurity levels in the water of ~5-555 ppt. Although our water purification system (Barnstead Nanopure) meets type 1 water standards we can't exclude impurities in this range especially if considering the water handling to humidify the simulation chamber (transfer to and evaporation in the humidifier). Although we never measured amines in the AIDA chamber it is know from other simulation chambers (e.g. the CERN CLOUD chamber) that amine levels in the order of some 10 ppt are hard to avoid even if no water is added. It is however quite interesting that the experiments with ambient air (no extra water added to the chamber) seem to be in line with the water dependence of the particle production observed in humidified synthetic air (Figure 8). This is one indication, that not impurities in the water, but rather the interaction of active species (e.g. $^{\bullet}OH$ radicals) generated in the plasma and depending on water concentration, promote particle formation.

To clarify this issue we added the following sentences to section 3.2.2: "Although we have no evidence that our purified water (Barnstead Nanopure) contains significant amounts of impurities we can't exclude them on a ~50 ppt level which could potentially impact nucleation. However, experiments with ambient air (no extra water added to the chamber) seem to be in line with the water dependence of the particle production observed in humidified synthetic air (Figure 8). This provides an indication that the interaction of active species (e.g. OH radicals) generated in the plasma and depending on water concentration, rather than impurities in the nanopure water, promote particle formation."

3. The increase of the particle yield by number for the addition of trace gases (SO_2, α-pinene, toluene, NH_3?) This seems clear, qualitatively.

4. The increase of particle mass with the addition of α-pinene. This seems clear, qualitatively.

No answer to comments 3. & 4.

5. That particle formation is efficiently supported by acids produced photo-ionization of both major and minor components of the air (examples given are N_2, NH_3, SO_2, organics). This statement is quite vague. Was there direct proof of the acids supporting the nucleation, or is this more of a (well-justified) speculation? If not direct evidence of the acids exists, I would *suggest that this is reworded to reflect that particle formation is supported by compounds produced in the plasma reaction products of the specified trace gases.*

Answer to comment 5. The formation of acids promoting the nucleation is not directly observed in the present work. However, formation of HNO_3 was characterized in previous works in both the real atmosphere and in laboratory experiments (Henin et al., 2011). Furthermore, the laser-induced plasma is well-known to be highly oxidizing, so that production of acids from both major components (N_2) and trace gases (NH_3, SO_2, trace organics) is most likely. To clarify this issue, we rephrased the manuscript abstract and the main text for more clarity:

- In the abstract, we replaced the mention of acids by the phrase "oxidized species like acids" in the sentence: "Our findings suggest that new particle formation is efficiently supported by oxidized species like acids generated by the photo-ionization of both major and minor components of the air, including N_2, NH_3, SO_2 and organics." Note that this is also the phrasing of the conclusion.
- in 3.1.3, we cite Henin et al, 2011, to justify the formation of nitric acid and its impact on laser-induced condensation
- Section 3.3.2 (SO_2) rephrased for more clarity. In particular, we have added in the second half of the last paragraph: "The contribution SO_2 from beyond the filament volume itself is evidenced by considering that, operating 52 min at 10 Hz, the laser filaments process only about 2496 cm^3 of the chamber volume of 84,5 m^3 ($2.95x10^{-5}$)." and "Most of the SO_2 must therefore be oxidized by reactive species that are produced in the filament and subsequently dispersed around them by transport and diffusion."

In their conclusions, the authors additionally draw attention to the following findings:

6. Oxygen addition reduces the particle production rate due to its high electron scavenging efficiency, which in turn reduces the plasma reactivity. This is clear, again qualitatively.

7. Nitrogen species do not cause significant increase in particle formation compared to Argon. I agree with this, too.

No answer to comments 6. & 7.

8. Growth and particle formation are dependent of different physio-chemical processes. This statement is again quite vague (true, of course, but not really a conclusion). It could be better to state the relevance of the participation of some specific vapors to each process, which has been the topic in recent discussion of particle formation and growth.

Hints about the different pathways leading to particle formation and growth are listed in the sentences preceding this statement. The sentence quoted by the referee was not meant to bear new information, but rather to summarize this part of the discussion. To clarify this point, we rephrased it as: "This different behaviour underlines that several pathways contribute to laser-induced new particle formation and growth: Understanding and quantifying the full physico-chemistry of the laser effect will require extensive experimental and modelling work well beyond the scope of the present paper."

9. Dilution of the laser plasma affected particle production rates except in the case of ambient air. This is actually something that I find very interesting. The actual mechanism that causes the particle formation rate dependence on the fan activity is not really clear to me. As particle formation is strongly non-linear, the dilution effect that the authors propose is easy to accept as one reason. As it is presented now, the fan effect is in my eyes a major reason that makes quantification of the particle formation uncertain. This could be highlighted more in the article. For future experiments, understanding the dilution effect, both in the particle phase and the gas phase, is a point that should be addressed with much care.

We concur to the statement that the dilution by the fan is a strong limitation to the quantitativity of our results. We now explicitly mention it as a factor influencing the particle production rate, in the paragraph describing the calculation of this production rate (Experimental setup section):

“They can also be produced in the subsequent evolution of the atmosphere around the filaments, depending on the diffusion of the produced species, as well as their dilution by the mixing fan.”

10. Laser-generated particles "homogeneously nucleate water close to water saturation". To my knowledge, homogeneous nucleation refers to nucleation directly from the gas phase, so the phrase 'particles homogeneously nucleate water' does not really make sense. If heterogeneously is used instead of homogeneously, the sentence would make sense and the statement would be ok.

We agree with the reviewer and changed the sentence to: "Considering a potential impact of the laser-generated particles on clouds we conclude that these particles nucleate water close to water saturation as typical for soluble species."

General comments

Additionally, the discussion on atmospheric nucleation rates in comparison with the rates obtained in these experiments seems out of place for this manuscript. The experiments presented here are valuable for researchers trying to understand particle formation from the gas-phase species present in the atmosphere, and these types of experiments are a good tool for understanding the processes involved in particle formation. However, a direct comparison of the formation rates is not really useful in my opinion, first, because of the non-uniform formation process in the chamber (including the fan effects), and because the exact situation occurring in the experiments does not really occur in the atmosphere.

We agree that the present particle formation rates cannot be directly compared with those recently reported in the atmosphere, since the conditions are clearly different. To avoid any confusion on this aspect, we drastically reduced the discussion about this comparison. Still, we kept a mention of it, in terms of orders of magnitude, to illustrate the local efficiency of the laser-induced process as compared to natural ones.

In general, very interesting paper with a lot of substance and many very interesting results, that are understandably quite qualitative. Clarifying the qualitative nature of the paper at the relevant sections should suffice for publication, as well as answering the points raised in reference to some of the conclusions. If these are done, I think that this study will be valuable *to the atmospheric research community. In my opinion, the quality of the results here is very good, but due to the very complexity of the phenomenon that is being studied, the presentation of the results, especially the quantification, should be done with care. I do think that the revisions needed are not very big (I will suggest minor revisions), but they are important.*

We really tried to avoid any over-interpretation of our experimental findings and therefore attempted quantification only for those cases were this was really possible. We think the reader can understand the reasons for the qualitative nature of many of our results. We added one sentence to the conclusions to clarify this issue: "Understanding and quantifying the full physico-chemistry of the laser effect will require extensive experimental and modelling work well beyond the scope of the present paper".

Specific comments

I have a few specific comments, given below:

P 29856: l7: reults-results

P29861, line 2: what is meant by 'larger particles seemed to be less stable'? Is there some observed break-up of particles, or does the concentration fluctuate? Clarify.

P 29867, l 20: I would reformulate this as 'laser filaments generate new particles that grow to sizes of 3 to 130 nm during the experiment', as this more exactly reflects the nature of the process

P. 29856: Typo fixed

P. 29861: To clarify this issue we modified the sentence to: "The larger particles formed at 97% relative humidity seemed to be less stable than the small ones which is reflected in a relative fast decrease of the integrated particle mass concentration from initially 90 ng m^{-3} to 35 ng m^{-3} over two hours (cf. Figure 6a)."

P. 29867: We rephrased the sentence as suggested by the Referee so as to clarify the statement.

Answers to Referee #2

The discussion paper by Saathoff et al. describes the nucleation of particles induced by laser-filament plasma. Several atmospheres are studied at the AIDA aerosol chamber: ambient air, humid synthetic air, humid nitrogen, argon-oxygen mixture, and pure argon as well as including trace gases such as SO_2 and alpha-pinene. Temperature and relative humidity are varied.

The paper is well-written, well-structured and clearly suitable for publication in ACP. It presents a number of original and interesting findings on aerosol nucleation under the special condition of laser-induced plasma. A number of results represent rather qualitative findings, nevertheless, I clearly recommend publication. Only a few minor comments should be addressed:

- Some of the measurements are influenced by contaminants in the chamber. As the contaminants are not identified and their concentration levels are unknown (and probably change with time and chamber conditions), these experiments are not reproducible (p29858, l. 17). This fact should be mentioned in the text.

This comment overlaps to a large extent the comments 2 (impurities), 9 (dilution by the mixing fan), and the last general comments by Referee #1. We therefore refer to the corresponding answers. Furthermore, we specifically addressed the issue regarding the contaminants on p. 29858 by explicitly mentioning this uncertainty at that location in the text.

We added the following sentence to section 3.1.1: "The uncertainties about the potential contaminants are of course a limiting factor for the quantitative reproducibility of our experiments e.g. in other experiments."

- The authors state the formation rates as number of particles per cm^{-3} plasma s^{-1}, i.e. as the particle formation rate per plasma volume. These stated formation rates in the filament are upper limits only. Most likely the nucleation is not only confined to the filament itself but is taking place inside the expanding plume that consists of the mixture of air in the filament and the surrounding air. Conditions inside this plume are rather inhomogeneous and are changing fast as the plume dilutes (especially when the fan is operated). Therefore it should be discussed in how far it is appropriate to state the formation rate as particles per cm-3

plasma s-1 and that this is most likely an upper limit or a proxy for the actual formation rate. The observed formation rates will also depend on the mixing conditions and therefore again, the results are mostly quantitative.

We concur to this statement, and amended our manuscript to make this aspect clearer. We kindly refer to our answer to the Comment #1 of Referee #1 for more details.

- it should be stated more clearly that the measurements are often qualitative and that it will be difficult or not possible to systematically derive quantitative nucleation rates or growth rates as a function of conditions such as vapor concentrations which are independent of the specific chamber conditions.

To clarify this point, besides the changes described in the answer to the general comments of Referee #1:

- We added "for the given experimental conditions" to the following sentence in the abstract:" Terawatt laser plasma filaments generated new particles in the size range 3 to 130 nm with particle production rates ranging from $1x10^7$ to $5x10^9$ cm^{-3} plasma s^{-1} for the given experimental conditions."
- We added: "While allowing comparisons among the present study, in which all experiments were performed using the same experimental configuration, these limitations should be kept in mind when comparing our data with other experimental arrangements." near the end of Section 2.
- We added: "these rates depend on the actual experimental conditions" to the conclusion (first paragraph).

References

Henin, S., Petit, Y., Rohwetter, P., Stelmaszczyk, K., Hao, Z.Q., Nakaema, W. M., Vogel, A., Pohl, T., Schneider, F., Kasparian, J., Weber, K., Wöste, L., and Wolf, J.-P., Field measurements reveal mechanism of laser-assisted water condensation, Nat. Commun. **2**, 456, doi:10.1038/ncomms1462, 2011.