Response to Reviewers for “Quantified ice-nucleating ability of AgI-containing seeding particles in natural clouds” by Miller et al.

We thank the reviewers for taking the time to carefully read and provide feedback on our manuscript. Please see our responses to each comment below in blue (line numbers refer to the final corrected manuscript).

Reviewer 1

I support publication of the manuscript.

The authors present a detailed study of the effect of silver iodide containing flares on supercooled liquid water clouds, during an experiment conducted in Eriswil, Switzerland as part of the CLOUDLAB project. The primary result reported in this manuscript is the fraction of silver iodide containing particles which nucleated ice in the experiments.

As noted just above, I support publication. I also think there are alternative perspectives for some of the results that should be considered.

Thank you for supporting the publication of our manuscript. We are happy to consider alternative perspectives for our results.

The flares were carried by drones, and burned while the drone was in-cloud. This is a very important point to keep in mind, in my opinion. In many cloud seeding studies, the seeding material (usually some sort of flare) is released (i.e. burned) below cloud base, or on on the leading edge of the cloud deck, with the expectation that wind or updraft will carry the material into the cloud. There is definitely a dispersion problem to contend with in these cases. (More on dispersion below)

We agree that this is an important aspect of our work.

1.1. The authors make the assumption that saturation ratio in the cloud is 1. I disagree with this assumption on two levels. I think that the mean saturation ratio is slightly above 1 (a quasi-steady state supersaturation). See for example, Yang et al, 2019, in particular figure 4. I agree that the saturation ratio is certainly close to 1, but exceeding 1 by just a tiny bit could be very important for this case. The flare material includes some very hygroscopic components and even a slight supersaturation could be enough to activate those particles. The second level of my disagreement with the assumption that the saturation ratio is 1 is that the cloud is turbulent, so there must be fluctuations in the temperature and water vapor concentration, and thus the saturation ratio. Figure 4 in Yang et al shows a distribution of values. You can also see it in Figure 8 of Siebert and Shaw, 2017. The fraction of ice nucleating particles that the authors are deriving is very likely to be a convolution of the fraction of particles that encountered a supersaturation high enough (in the fluctuating environment) to activate them, AND the fraction of particles that had a silver iodide particle within them sufficient to catalyze nucleation. The authors state that a saturation ratio of 1 is enough to hydrate the particles by some substantial amount, and I agree with that. That said, they also appeal to a freezing point depression. If droplets are activated, they will be getting steadily more dilute, even in a slightly supersaturated environment.

Yes, the saturation ratio could sometimes be slightly above 1 due to small local turbulence. In this case, the INF may indeed depend on the number of particles which happen to encounter high enough supersaturation to activate and which contain sufficient AgI, as you said. Still, once ice is created and starts growing, the water-supersaturation cannot be maintained, and saturation is reduced to below 1, as evidenced by the evaporation of cloud droplets (see the depletion of cloud droplets in the seeding plume in Fig. 2d). The leftover droplets which have not nucleated, as well as the solution droplets which did not activate or nucleate, will shrink/evaporate under these subsaturated conditions, which makes further nucleation unlikely due to the freezing point depression effects.

We've amended our discussion in Sections 4.1, 4.2, and in the Conclusions to include this discussion (***bold italics*** represent the newly added or changed text; the rest is reprinted here for ease of reviewing):

Lines 321-343 (Section 4.1): "Based on the composition of our seeding particles, our experimental setup, and the results we have outlined thus far, we propose that our particles cause ice nucleation in the following way: Upon emission of seeding particles in the cloud at (assumed) water saturation (RH≈100%), the seeding particles grow hygroscopically into solution droplets due to the hygroscopic material in the flare. Then ***(or perhaps simultaneously)***, some of these droplets freeze immediately if cold enough. Once there are ice crystals, the ambient saturation ratio is locally reduced as the ice crystals start growing and consuming water vapor. The larger (and/or more numerous) the ice crystals become, the more the saturation ratio is decreased and the more strong updrafts would be needed to reach water saturation (Korolev and Mazin, 2003). ***Note that the depletion of cloud droplets visible in Fig. 2d is evidence for water-subsaturated conditions in the seeding plume when ice is present.*** Therefore, in water-subsaturated conditions, the remaining solution droplets shrink and become less dilute, i.e., their water activity (a_w) decreases. A decreased a_w means there are stronger freezing point depression effects: with every percentage less RH, there is approximately 1°C of freezing point depression (Koop et al., 2000; Zobrist et al., 2008). Thus, new ice nucleation becomes unlikely. In this way, most of the nucleation occurs at the beginning of the experiment and only the best 0.1-1% of particles initiate freezing. The "best" particles are likely the largest, having the most surface area (more active sites) for ice nucleation (i.e., the deterministic component of heterogeneous nucleation), and/or the ones that grow fastest to dilute solution droplets with a_w≈1 (i.e., the kinetic/stochastic component).

An alternative ice nucleation pathway may occur if some local supersaturations exist in the cloud or in the seeding plume. There may be local supersaturations created by updrafts from natural small-scale turbulence or from the burning of the flare, which also introduces water vapor. As the particles are hygroscopic, small supersaturations could be enough to activate them into cloud droplets, whereby freezing occurs simultaneously to activation or immediately thereafter. However, since droplet activation just leads to further dilution at almost constant water activity, it is unlikely to stimulate more ice nucleation, as compared to freezing of unactivated dilute solution droplets. Nevertheless, after the first ice crystals start to grow, consuming water vapor, the saturation ratio will be reduced, shrinking/evaporating the leftover droplets, making continued ice nucleation unlikely, as described above."

Lines 407- 409 (Section 4.2): "***Alternatively, if the ice nucleation in our experiments relies on some particles encountering high enough supersaturation to activate into cloud droplets before freezing, then the lower INFs as compared to $C24_{imm}$ may be due to the fact that only few particles encountered such conditions, unlike in IMCA-ZINC.***"

Lines 449-459 (Conclusions): "We next presented our hypothesis for the nucleation mechanism in our seeding experiments (Sect.4.1). We expect that the polydisperse seeding particles grow hygroscopically upon emission into the cloud at water saturation***, and/or some particles may activate into cloud droplets if encountering local regions of supersaturation, and then the "best" particles (largest and/or most quickly reaching a_w≈1) then initiate freezing.*** We do not rule out the possibility that contact freezing may also occur, but we do not consider it to be dominant due to the fact that there were no positive correlations found between INFs and background CDNC nor between INFs and residence time, and because the collision rates are expected to be very low (particle sizes are in the Greenfield gap). Furthermore, we also suggest that ice nucleation occurs mostly at the start of the experiment because once there is ice***, the reduced saturation ratio causes shrinking/evaporation of leftover droplets,*** inducing freezing point depression and reducing the likelihood for further nucleation. ***These effects of more limited water vapor may explain why our observed INFs were an order of magnitude lower than the recent measurements of the same seeding flare particles by Chen et al. (2024).***"

1.2. I appreciate the inclusion of Table 1 in the manuscript. Could the authors comment on cases 58 and 62? I note that the aggregation factor in case 58 was 7.35 when the residence time was 8.2 minutes. In case 62, the aggregation factor was 4.36 (substantially lower) even though the residence time was five minutes longer. Was there some significant difference in conditions for case 58 that would cause the aggregation factor to be so much higher?

Co-author Huiying Zhang is currently investigating the aggregation processes in the CLOUDLAB experiments and will share the results soon in an upcoming manuscript. Possible influences are temperature, residence time, turbulence, or the crystal's aspect ratio.
Please note however that we've since realized that some of the residence times listed in Table 1 were not correct, including SM062 (residence time is 10.5 min not 13.3), just due to a copy-paste error. The times are corrected now. The residence times used in the data analysis and shown in the figures were correct to before and thus no changes in the analysis/results were needed.

1.3. In line 193, the authors state that their derived ice nucleating fraction should be representative of the initial conditions despite the fact that they are measuring ice crystal concentration and interstitial aerosol after an elapsed time of about 10 minutes. The stated rationale for that statement is that both aerosol and ice crystals will disperse, and the dispersion will be similar. I disagree. The crystals are growing – becoming much larger. Their gravitational settling will be much more pronounced. That's acknowledged later in the paper, but it should be mentioned here as an uncertainty.

It's true that this is an uncertainty. We've added a sentence in this section as suggested: "***However, we additionally note that, because ice crystals and aerosol particles have different sizes, their differences in dispersion behavior likely lead to uncertainties in the calculated INF.***" (Lines 194-196)

Minor points

1.4. line 17: the reference to Pruppacher and Klett. That's a 900+ page book. At least provide a chapter in the reference, please.

We've updated the reference to include the chapter title (Homogeneous Nucleation).

1.5. Line 325: "…the deterministic component of heterogeneous nucleation…" There is no deterministic component to nucleation. Nucleation is stochastic. Ice nucleation does tend to be favored in certain places for some samples, but even there, ice doesn't always form in the same place. See figure 3 in Holden et al., 2019. (I know the title of the paper is that it proves the existence of active sites, but figure 3 clearly shows that ice may form at one spot with a preference, but it isn't deterministic.)

Ice nucleation has both stochastic and deterministic components. While classical nucleation theory treats ice nucleation as purely stochastic, the purely stochastic approach cannot explain the behavior of INPs. The presence of active sites, i.e., that some sites tend to be more favored for nucleation than others, as Holden et al (2019) show, is precisely evidence for the deterministic component. The fact that these active sites don't *always* initiate nucleation means that the stochastic component is there too.

References

Holden, M.A., Whale, T.F., Tarn, M.D., O'Sullivan, D., Walshaw, R.D., Murray, B.J., Meldrum, F.C. and Christenson, H.K., 2019. High-speed imaging of ice nucleation in water proves the existence of active sites. Science Advances, 5(2), p.eaav4316.

Siebert, H. and Shaw, R.A., 2017. Supersaturation fluctuations during the early stage of cumulus formation. Journal of the Atmospheric Sciences, 74(4), pp.975-988.

Yang, F., McGraw, R., Luke, E.P., Zhang, D., Kollias, P. and Vogelmann, A.M., 2019. A new approach to estimate supersaturation fluctuations in stratocumulus cloud using ground-based remote-sensing measurements. Atmospheric Measurement Techniques, 12(11), pp.5817-5828.

Reviewer 2

Overall this manuscript describes an extensive set of airborne seeding experiments with downwind sampling capturing changes in cloud properties within the seeding aerosol plume. These experiments are difficult to perform and uncommon in the literature, and provide a very useful validation of seeding techniques in an appropriate real-world environment and some deeper mechanistic insights. The manuscript is publishable as-is, though I will suggest some edits for clarity and minor expansion of discussion:

We are glad you see the value in our work and appreciate your suggestions!

2.1. Introduction or Section 2.2: Ice nucleation by silver iodide based seeding materials will vary with exact aerosol composition, which can be impacted both by burn material formulation and burn conditions. At least a brief discussion of this seems appropriate in one or both of these sections.

It's true that the particle composition impacts the ice nucleation, and we discuss this in Section 4.2 while comparing the different laboratory measurements that used different types of silver iodide particles. This is also why we focus on the Chen et al (2024) measurements to compare to ours, because they use the same flares and similar burning conditions, as noted in Line 398. We have also now referred the particle composition in the added sentence in Line 364-366: ***"We further note that although the experimental setups, exact particle composition, and measurement techniques are not the same, and thus the measurements are not directly comparable, we still find it beneficial to discuss the data together in order to contextualize our work."*** Overall, it is still rather unknown how exactly the AgI-particle formation and composition impact their ice nucleating ability, so we prefer to not go too in-depth about it.

2.2. There is almost no discussion of secondary ice production in the manuscript, but a few words in the introduction would be welcome considering that there is evidence of secondary ice in some similar clouds to those observed in your study (https://doi. org/10.1029/2021JD036411 and https://doi. org/10.5194/acp-2021-686). Further, Fig 4b shows inverse correlation (or no correlation removing endpoints as discussed) between INF and residence time, which to me implies SIP is not occurring under your study conditions, which seems worth drawing attention to.

We do not expect any significant secondary ice processes to be occurring in our seeding experiments, at least to the extent that would affect our measurements, for the following reasons: a) SIP usually requires large droplets, which we did not have very much of (droplet mean radii are ~10 micron); b) all ice crystals were manually visually classified and very few splinters were observed; c) an indication of SIP is a higher ICNC than INP concentrations, whereas we have orders of magnitude more seeding particles than ICNC. The lack of positive correlation of INF with residence time in Fig. 4b is indeed another indication of no significant secondary ice production.

We've added to Section 2.4 a short discussion of SIP and why we discount it, and how it would affect the INF: ***"Furthermore, this INF relies on the assumption that no significant secondary ice production occurred in our experiments, which is based on the fact that very few large droplets (radii >20 μm) were present and very few splinters were observed. If there would have been secondary ice production, our estimated INF would be an overestimation."*** (Lines 196-199)

We've also added a sentence in the discussion of Figure 4b regarding SIP: "***The negative correlation (or even lack of any correlation) also supports the absence of secondary ice production in our experiments, i.e., if there was secondary ice production, we would expect more ice crystals to grow to a detectable size with increasing time, rather than the opposite.***" (Line 304-306)

2.3. Eqn 2 – perhaps a few words around this equation to clarify that the seed_conc is background subtracted to remove ambient aerosol, as discussed at the end of section 2.3.

We've added the suggested clarification: "The denominator represents the total seeding particle concentration because seed_conc consists of the measured particles that did not nucleate ***(i.e., the background-subtracted total particle number concentration, as described in Section 2.3)***, and the $ICNC_{adj}$ is assumed to be equal to the number of seeding particles that nucleated."(Line 189-191)

2.4. Do any of these experiments have measurable background ice? The example case does not, but do any of the other 15? Impacts of background ice on the analysis methods should be discussed if it is present.

No, none of these experiments had any background ice. We've added this explicitly to the text in line 128: ***"Note that for all 16 experiments, there were no ice crystals in the background."***

2.5. Line 267-8: Suggest wording change to something like "more seeding aerosols will act as INPs at colder temperatures" rather than discussing activation probability of individual INPs, there is a whole can of worms with heterogeneous classical nucleation theory that you don't need to get into for this paper. Not a critical change in my opinion though.

We see your point. We've changed the sentence to the following:
"With decreasing temperatures (more supercooling), it is expected that more seeding particles will be able to initiate ice nucleation." (Line 273)

2.6. Line 271 point a: if this were the primary reason, you could fit an exponential to your data with higher significance. I recommend either including a metric of how fit significance changes here or removing this explanation. I find explanation b more compelling in absence of that, so I think it stands on its own.

Good point. The exponential fit in Fig. 6 is only marginally better than the linear fit in Fig. 4a (r of 0.41 instead of 0.40), and we agree that explanation b is more compelling, so we've removed explanation a as suggested: "The linear correlation is weak likely because of the amount of natural variability and possible confounding factors in experiments in natural clouds." (line 276-277)

Section 4.1:

2.7. There is a lot of interesting speculation here, but it feels a little out of place in that it only loosely ties to the experimental results that are presented. I think there is some opportunity for streamlining here, and building this section out to start with results first and how they constrain the potential freezing mechanisms.

Yes, it's true that it's mostly speculation, as it's nearly impossible to know exactly what occurred, but we consider that addressing this question is a relevant discussion point in the paper. This is why we've added some more discussion regarding other possible ice nucleation pathways in the case of local supersaturations (see reviewer response 1.1) and modified the section accordingly.

2.8. The flares generating the particles will locally heat the air and add water vapor from combustion. These thing coupled together makes it very likely that as the flare plume cools to ambient conditions it will generate supersaturated conditions to some extent, so it seems unavoidable that at least some particles will activate through an immersion freezing mechanism, but figuring out what fraction will be difficult.

Please see reviewer comment 1.1 and our response. We've now included a short discussion about what would occur in case of local supersaturations, which could be caused from updrafts and/or water vapor input from the flare burning.

2.9. Can you reach effectively water subsaturated conditions without first depleting all your liquid cloud droplets? I'm not sure this explanation makes sense in light of your data that seems to mostly show persistence of mixed-phase clouds.

There must be water-subsaturated conditions in order for cloud droplets to shrink/evaporate, and we do see cloud droplet depletion locally in the seeding plume, shown in Fig. 2d. While the overall stratus clouds are persistent, the local structure in the seeding plume implies water subsaturated conditions there. We've added a reference to Figure 2d in the discussion of our freezing mechanism: "***Note that the depletion of cloud droplets visible in Fig. 2d is evidence for water-subsaturated conditions in the seeding plume when ice is present***." (Line 327-328)

2.10. Regarding condensation v immersion freezing: My understanding of the general difference is that in immersion freezing, water uptake occurs at a temperature where a given aerosol will not immediately freeze, then drops are cooled until the freeze. For condensation freezing, water uptake occurs at cold temperatures, so as soon as liquid water condenses on an INP it is capable of freezing (as soon as it reaches a requisite water activity). The discussion in this section of the manuscript seems to split these two mechanisms in a different way, however, with liquid water uptake occurring at the same temperatures for both, but the condensation mechanism requiring higher supersaturations for some reason. Some clarification here and in the introduction as to how the authors understand these different mechanisms would be appreciated, but given that the conclusions of the manuscript don't greatly depend on this interpretation I don't see this as a major issue.

We agree that the distinctions can be a bit convoluted. Our definitions are based on Vali et al (2015), as we write in the introduction: "In immersion freezing, the INP is fully immersed in a cloud droplet or aqueous solution droplet before ice nucleation takes place. Condensation freezing, however, is thought to occur when the particle activates into a cloud droplet concurrently to the ice phase forming, ***at high enough supersaturations for the particle's activation***" (Lines 44-47). The italics part was added now to emphasize that supersaturation is needed for activating the particle into a cloud droplet.

In response to Reviewer comment 1.1, we've since adapted our discussion on the possible freezing mechanisms in Section 4.1 and 4.2 and we hope that it is now more clear. Furthermore, we have moved away from trying to fit a specific freezing mode label onto our experiments, because none fit very perfectly, but rather instead explain the freezing pathway. For example, we've removed the term "immersion freezing" from Section 4.1, the abstract, and the conclusion, and rephrased the last sentence in Section 4.2: "***However, as explained***

previously, we suggest that the most likely, most dominant mechanism is that freezing occurred after water uptake on the seeding particles, rather than through contact with pre-existing droplets." (Line 430-432)

2.11. Section 4.2: this section is a challenging one to discuss, because the different measurements are not directly comparable, as you spend the section outlining, but there is still an understandable desire to compare your measurements to previous literature. Ultimately I think this section is still helpful for the explanations it offers for the discrepancies observed between different studies, but I wonder if the framing at the beginning of the section could be changed to make that clear from the beginning?

We've added the following sentence to the beginning of Section 4.2 to add this clarity: "***We further note that although the experimental setups, exact particle composition, and measurement techniques are not the same, and thus the measurements are not directly comparable, we still find it beneficial to discuss the data together in order to contextualize our work."*** (Line 364-366)

2.12. For example, lines 350-3: Perhaps it is better to directly state here that the different frozen fraction metrics aren't directly comparable, but are placed on the same graph for the sake of discussion.

We've added to line 363: "***and we place all data on the same graph for the sake of discussion."***