To the editor and reviewers,

Thank you for the comments regarding the manuscript titled “Fast and sensitive measurements of sub-3 nm particles using Condensation Particle Counters For Atmospheric Rapid Measurements (CPC FARM).” We appreciate the time and effort that the editor and reviewers have dedicated to providing valuable feedback on our manuscript. We have incorporated the changes as suggested by the reviewers.

Below is a point by point response to the reviewers’ comments along with changes made in the manuscript colored in red.

Editor Comments:

The paper is very well written and the graphs are clear. However, Fig.6 and Fig. S6 need to be replotted using a color scale that is color-impairment-friendly. Please do so prior to resubmission following review.

We thank the editor for this observation. The color maps for Figures 6 and S5 have been changed to Turbo, a replacement for Jet created by Google Research. They found that the color maps used in Turbo are smooth and distinguishable for all conditions except total colorblindness, a condition that affects 0.00003% of the population. (https://research.google/blog/turbo-an-improved-rainbow-colormap-for-visualization/)

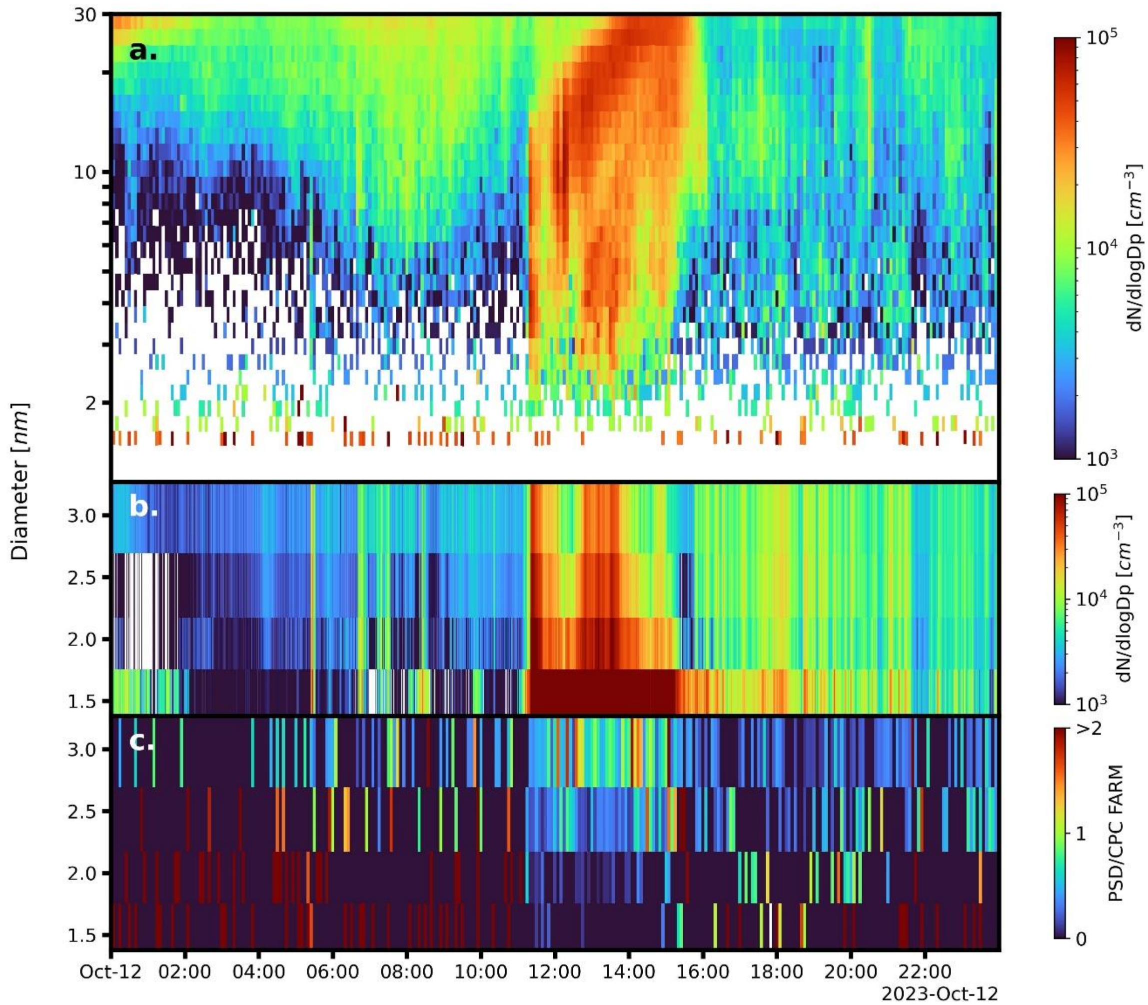
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Figure 6

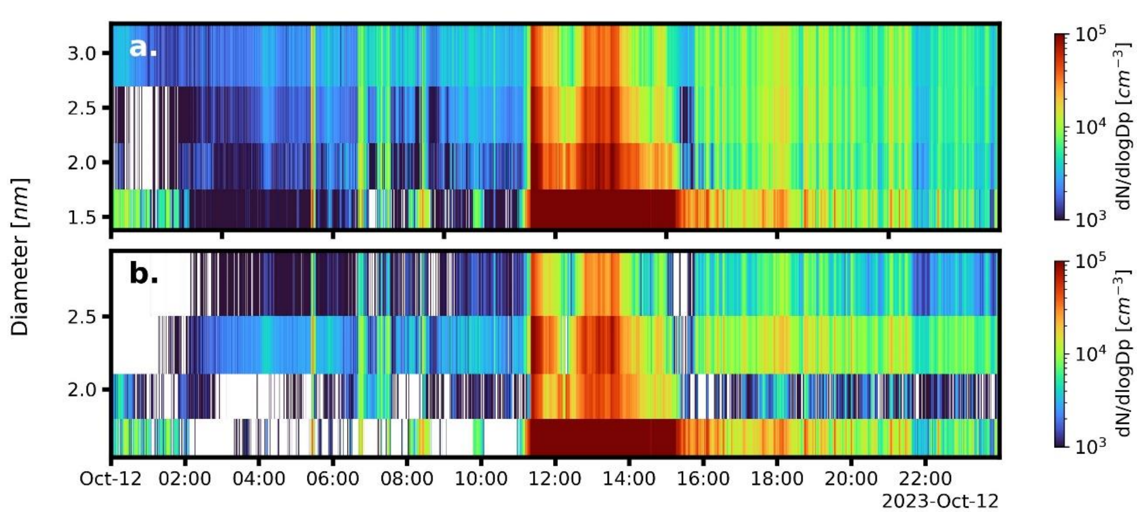
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Figure S5

Reviewer 1 Comments:

Reviewer 1 Summary:

The manuscript entitled "Fast and sensitive measurements of sub-3 nm particles using condensation particle counters for atmospheric rapid measurements (CPC FARM)" by Darren Cheng and colleagues reports on a new device capable of size-resolving particles with diameters below 3 nm utilizing condensation techniques. The authors use a battery of water-based condensation particle counters based on the design of the MAGIC 250 from Susanne Hering but operate the individual devices at different temperature settings to obtain a range of cut-off diameters. By taking differences of the measured number concentrations in the different channels the size distribution is recovered without the help of pre-size selected differential mobility analyzers. As concentrations are therefore much higher in the detectors the sampling rates allow much faster monitoring of the dynamics during new particle formation compared to an SMPS system suffering from low counts for several reasons.

The manuscript starts with an introduction of current techniques relevant to atmospheric aerosol sizing in the smallest possible size range which very much goes along my own thinking. Followed by a brief description of the general features of the CPC FARM, the instrument's performance is characterized by calibration studies using state-of-the-art techniques. Extensive analysis of potential uncertainties in the CPC detection is performed and subsequently data inversion procedures are described in detail. The performance of the CPC FARM has been tested with ammonium sulfate particles and ambient air and comparison to an SMPS has been made demonstrating the improvement in detection for particle sizes below 3 nm. Furthermore, data inversion techniques are discussed using synthetic particle size distributions and simulated instrument responses. Overall, the manuscript is of very high quality and clearly fits the scope of Atmospheric Measurement Techniques. Below I'm listing a few mostly minor things that might be considered before final publication.

We thank the reviewer for their comments on our manuscript. We have incorporated those comments into our work as outlined below.

Comment 1:

Section 2.1 describes the CPC FARM in a very general way. I understand it is based on the MAGIC 250 instrument (and the TSI 3789) but still some more details would be helpful. I'd recommend putting a schematic into the supplemental material illustrating the core setup of a single channel. Also, the temperature tuning of the different channels could be addressed in this section. It is described later on in section 2.4 (Pittsburgh Campaign Setup) but I assume

the same settings have been used already for the CPC FARM experimental characterization (section 2.2).

We have added a schematic of a single channel's growth tube in the supplemental information. We respectfully disagree with the reviewer's comment concerning moving the temperature tuning to section 2.1. The temperatures were tuned based on the CPC calibration, which is discussed in section 2.2. We believe the manuscript is clearer if we first discuss the methods to tune the CPC and then follow by the results of the calibration.

Supplementary Text Changes:

S1. CPC FARM Single Channel Schematic

Figure S1 shows a schematic of a single channel of the Condensation Particle Counters For Atmospheric Rapid Measurements (CPC FARM). Each channel samples at 3.3 L min^{-1}. Prior to entering the first stage of the growth tube, 3 L min^{-1} of transport flow is removed. The remaining 0.3 L min^{-1} continues into the 7.1 cm long x 4.7 mm ID, cold conditioner stage. In this study the conditioner stage was set between 1 – 5 °C. Next, the flow enters the 2 cm long, hot initiator stage which was set between 35 – 99 °C. The final cold moderator stage is 7.1 cm long and set at 1 °C. The flow is then directed through a nozzle before entering the optics which counts particles by collecting the light diffracted by particles passing through a laser beam.

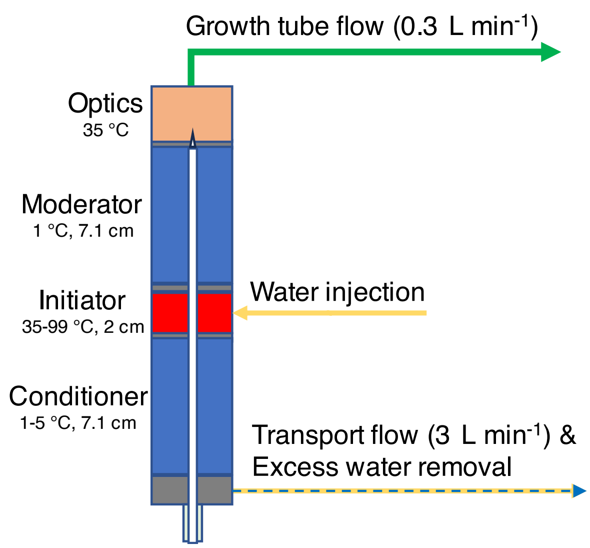

Figure S1. Schematic of a single channel of the CPC FARM showing the dimensions of each stage and the operating temperature ranges of each stage. The green arrow indicates the sample growth tube flow. The blue arrow indicates the transport flow. The yellow arrows indicate the injection and ejection of water.

Comment 2:

One thing that should be further discussed with respect to the performance of different channels in the CPC FARM is the behavior of detection efficiencies. It appears to me that channel 3 systematically shows larger cut-off diameters and reduced slopes of the detection efficiency curves compared to all other channels (figure S1 in the supplemental material). Does this in any way impact the data inversion? It is also interesting from a technical point of view as the same geometry and operating conditions not necessarily gives the exact same output in laminar flow devices.

Would different tuning (flow rates, temperatures) in this channel help in getting results closer to the other channels?

Differences in the slopes of the detection efficiencies, as fitted by the curve, are taken into account in the numerical inversion and thus will not influence the inverted size distribution. However, differences in the detection efficiency slope will affect the inverted size distribution determined from the approximate data inversion method, as this method assumes each detection efficiency curve is a step function. In addition, the channels do not need to be tuned (via flow rates or temperature differences) such that their detection efficiency curves match since the numerical inversion approach considers non-ideal detection efficiencies.

We are not surprised by the relatively small variations between the third channel and the other channels. While all channels were designed to the same specifications, the final, physical form differs from channel to channel due to manufacturing (growth tube nozzle dimensions), assembly (rolled Durapore wick thickness), and component tolerances (critical flow orifices). We believe that small differences within the instrument tolerances can cause differences in the detection efficiency curves, especially since we are operating at large supersaturations to activate sub-2 nm particles. These differences necessitate the calibration of each channel, as we have performed and demonstrated here. We've also added a phrase to clarify that the detection efficiency curve with the highest variation between channels, the ΔT=30 °C setting, was not used.

Main Text Changes:

The cut-points of the five channels were very similar at a given temperature setting except for the smallest ΔT=30 °C which had d_{50} ranging between 5 and 7 nm. This temperature setting was not used in the field study nor inversion.

Comment 3:

Regarding Figure 2: is this the same as Figure S1a.? I'm wondering whether for the main text it would make more sense to show the detection efficiencies for the different channels at which they have been finally operated during the ambient measurements.

The reviewer brings up a useful point. We have added the interpolated detection efficiency curves for each of the five channels at the field operating conditions into the main text.

Main Text Changes:

~~Figure 2 shows t~~The detection efficiency of ~~a~~ each CPC FARM channel ~~on the CPC FARM measured~~ was determined experimentally over a wide range of temperature differences (ΔT=30 °C to ΔT=97 °C~~,~~) between the initiator and conditioner stages. ~~All detection efficiency curves of the CPC FARM are shown in Fig. S1.~~ The moderator stage was held at 1 °C. An analytical function, consisting of a particle activation term combined with a diffusion loss term Eq. (S1) (Stolzenburg and McMurry, 1991), was fitted to the experimentally measured detection efficiencies as shown in Fig. S2. The d_{50} of each channel, defined as the diameter at which the detection efficiency corrected for diffusion loss, reaches 50% of the plateau value, was calculated based on the fitted curve. The lowest d_{50}~~,~~ was approximately 1.5 nm mobility diameter~~, was achieved~~ at the maximum ΔT=97 °C. The cut-points of the five channels were very similar at a given temperature setting except for the smallest ΔT=30 °C which had d_{50} ranging between 5 and 7 nm. This temperature setting was not used in the field study nor inversion.

The operating temperatures of the CPC FARM were selected based on the experimentally determined relationship between d_{50} and ΔT for each channel such that the resulting d_{50} values were spaced evenly in log scale over the 1.5 – 3.0 nm range. Figure 2 shows the resulting modeled detection efficiencies of the CPC FARM channels. The curve fit parameters were calculated by interpolation of the corresponding parameters at measured ΔT settings. Note that all curves shown in Figure 2 are normalized to a common plateau efficiency of 1 for visual clarity. Actual plateau efficiencies of the modeled curves varied between 0.93 – 0.98.

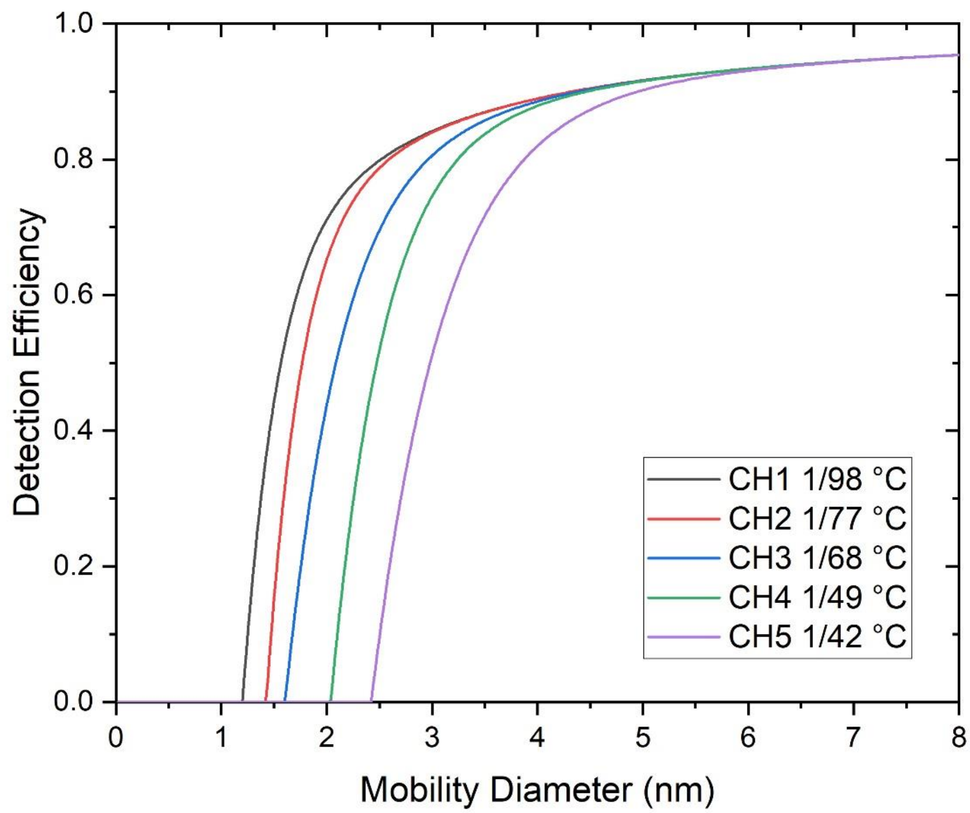

Figure 2: ~~Detection efficiency as a function of mobility diameter for the channel used for the smallest cut-point measurements on the CPC FARM. Each color/symbol represents a different set of conditioner and initiator temperatures. Solid lines represent the fitted model.~~ Interpolated

and normalized detection efficiencies as a function of mobility diameter for each channel of the CPC FARM. Each color represents a CPC FARM channel set at the indicated conditioner/initiator temperatures to achieve the targeted d_{50}.

Comment 4:

Figure 1 might benefit from some more explanatory figure caption. What do the colours in the figure indicate?

We have added text to the Figure 1 caption to elaborate on the color scheme.

Main Text Changes:

Figure 1: Schematic displaying PSD and CPC FARM sampling setup during the Pittsburgh measurement campaign. The PSD is enclosed by the purple box. The CPC FARM is enclosed by the green box. Blue arrows indicate instrument sample flows. Red arrows indicate instrument exhaust flows.

Comment 5:

In the supplemental material preceding equations S1 and S2 it's written "Eq. Eq. (S1)" and "Eq Eq. (S2)". One "Eq." can be removed there.

Thank you for catching this typographical error.

Supplementary Text Changes:

A fitted model, given in ~~Eq.~~ **Error! Reference source not found.**, is shown as solid lines in **Error! Reference source not found.**.

A fitted model, given in ~~Eq~~ **Error! Reference source not found.**, is shown as solid lines in **Error! Reference source not found.**.

<u>Reviewer 2 Comments:</u>

The article presents a new instrument consisting of five water CPCs in parallel (CPC-battery) intended for fast measurements of the particle size distribution in the 1-3 nm size range.

The study is rigorously done, including laboratory and field testing, inversion development and error analysis. The writing is very clear and easy to follow. I do not have major concerns with the study, but the authors could consider the following minor comments/questions

We thank the reviewer for their comments on the manuscript. We have addressed those comments below with manuscript changes as highlighted.

Comment 1:

were there any counts from homogenous nucleation at the channel(s) with lowest cut-off size and how was that monitored?

There was no homogenous nucleation on any of the channels. Homogenous nucleation was monitored by filtering the incoming air with a HEPA filter. This is in line with what was observed in (Hering et al., 2017). Ion-induced nucleation can occur at the highest temperature differences. We do get counts from cosmic rays, around a count every ten seconds, at the highest temperature differences which can be reduced by having the instrument cover on.

Comment 2:

Figure 2. I would find it more useful that the main article would show those curves that were used for the final CPC Farm instrument, instead of different temperature settings for one channel.

Thank you for your suggestion. Please see the changes made in response to Reviewer 1 Comment 3.

Comment 3:

In Fig 6c there is a lot of white, where the PSD did not record any counts (I assume), meaning it underestimated by a lot. Would it make sense to assign a very dark blue color to those points, so that it is visually easier to read the plot? Currently the red points which are due to noise in PSD stand out from the white background, although that is not the main point of this plot.

We thank the reviewer for this suggestion. In Figure 6c, we have changed the color scaling of the color bar from log to linear and limits from 0 to > 2.

Main Text Changes:

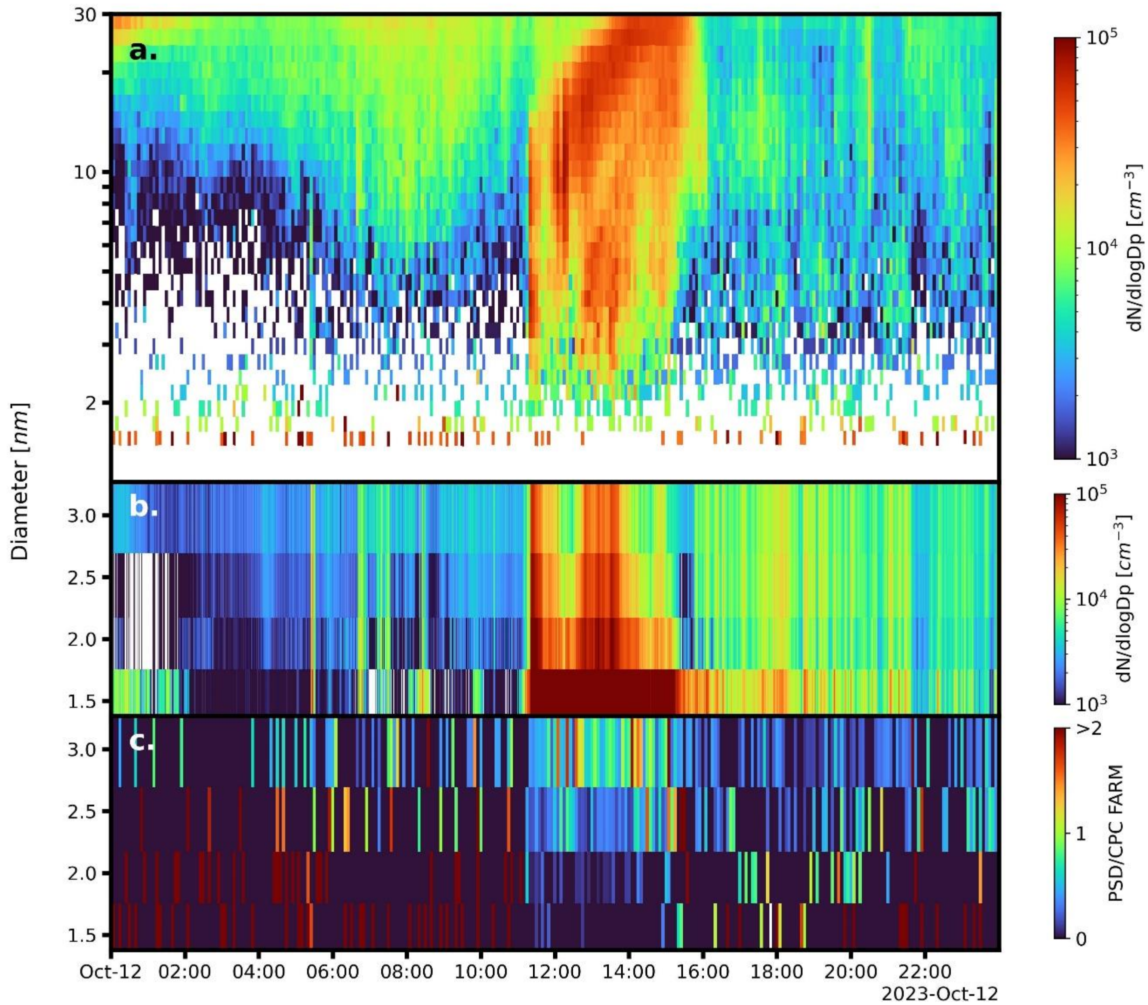

Figure 6

Comment 4:

row 33. I don't really get how the undetected NPF events could influence the growth of existing particles to larger sizes

We have changed the phrasing of the sentence as shown below.

Main Text Changes:

NPF events that occur rapidly and at diameters and concentrations below the detection limits of the instruments are obviously not observed but could still contribute significantly to atmospheric particle number concentrations and produce clusters that can ~~influence the growth of~~ help grow existing particles ~~to larger sizes~~.

Comment 5:

row 55. This is major limitation/uncertainty in some instruments.

We have changed the phrasing of this sentence to the following.

Main Text Changes:

Significant uncertainty can arise ~~Some uncertainty arises~~ from ~~bipolar~~ charging ions which are able to pass through the mobility analyzer and ~~to~~ be counted by the CPC (Hering et al., 2017);

Comment 6:

row 135. Can this be generalized to other environments than boreal forest where the observations in Riipinen et al. 2009 were made and is there newer studies on the hygroscopicity of 1-3 nm particles?

We are not aware of other studies that have examined the hygroscopicity of sub-3 nm particles. The hygroscopicity of sub-3 nm is difficult to determine as very few observations exist on the composition/properties of freshly formed particles. The composition of 1-3 nm particles likely varies to some extent between locations and is dependent on precursor gases that initiate nucleation. For urban Pittsburgh, NPF is driven by sulfuric acid-base nucleation as suggested by our observations and previous studies (Saha et al., 2018; Stanier et al., 2004). Ammonia sulfate is a good proxy for particles formed via sulfuric acid-base nucleation.

In addition, ammonium sulfate is a common calibration particle for sub-5 nm CPCs. For example, the Particle Size Magnifier (PSM) (Lehtipalo et al., 2014), the DEG boosted ultrafine CPC (Iida et al., 2009), and water CPC (TSI 3789) (Hering et al., 2017). We have added this information to the main paper.

Main Text Changes:

Ammonium sulfate particles were chosen for calibration as these have similar hygroscopic properties as newly formed atmospheric particles (Riipinen et al., 2009). In addition, ammonium sulfate particles are the most commonly used calibration particle for sub-10 nm CPCs including the PSM and TSI 3789 (Hering et al., 2017; Lehtipalo et al., 2014).

Comment 7:

Chapter 3.4. could changing particle composition also play a role in why some events/plumes are better detected than others or why the ration between the different instruments varied?

Certainly, the composition-based dependencies of detection efficiency curves differ for water and butanol CPCs in the sub-10 nm range. We have made note of this point in the main text.

Main Text Changes:

These plumes appear to be real events as there is a corresponding increase in the smallest size bins observed on the CPC FARM over the same periods. One potential explanation is that the concentration of particles in the plume is around the PSD detection limit of around $3x10^4$ cm^{-3} at 2.4 nm (Figure S6c). Another explanation is that different plumes could contain particles of different compositions. The water CPCs used in the CPC FARM and the butanol CPCs used in the PSD have been shown to exhibit different composition-based detection efficiencies in the sub-10 nm size range (Kulmala et al., 2007).

<u>Citations for this Reviewer Response:</u>

Hering, S. V., Lewis, G. S., Spielman, S. R., Eiguren-Fernandez, A., Kreisberg, N. M., Kuang, C., and Attoui, M.: Detection near 1-nm with a laminar-flow, water-based condensation particle counter, Aerosol Sci. Technol., 51, 354–362, https://doi.org/10.1080/02786826.2016.1262531, 2017.

Iida, K., Stolzenburg, M. R., and McMurry, P. H.: Effect of Working Fluid on Sub-2 nm Particle Detection with a Laminar Flow Ultrafine Condensation Particle Counter, Aerosol Sci. Technol., 43, 81–96, https://doi.org/10.1080/02786820802488194, 2009.

Kulmala, M., Mordas, G., Petäjä, T., Grönholm, T., Aalto, P. P., Vehkamäki, H., Hienola, A. I., Herrmann, E., Sipilä, M., Riipinen, I., Manninen, H. E., Hämeri, K., Stratmann, F., Bilde, M., Winkler, P. M., Birmili, W., and Wagner, P. E.: The condensation particle counter battery (CPCB): A new tool to investigate the activation properties of nanoparticles, J. Aerosol Sci., 38, 289–304, https://doi.org/10.1016/j.jaerosci.2006.11.008, 2007.

Lehtipalo, K., Leppä, J., Kontkanen, J., Kangasluoma, J., Franchin, A., Wimmer, D., Schobesberger, S., Junninen, H., Petäjä, T., Sipilä, M., Mikkilä, J., Vanhanen, J., Worsnop, D. R., and Kulmala, M.: Methods for determining particle size distribution and growth rates between 1 and 3 nm using the Particle Size Magnifier, 2014.

Saha, P. K., Robinson, E. S., Shah, R. U., Zimmerman, N., Apte, J. S., Robinson, A. L., and Presto, A. A.: Reduced Ultrafine Particle Concentration in Urban Air: Changes in Nucleation and Anthropogenic Emissions, Environ. Sci. Technol., 52, 6798–6806, https://doi.org/10.1021/acs.est.8b00910, 2018.

Stanier, C. O., Khlystov, A. Y., and Pandis, S. N.: Nucleation Events During the Pittsburgh Air Quality Study: Description and Relation to Key Meteorological, Gas Phase, and Aerosol Parameters Special Issue of Aerosol Science and Technology on Findings from the Fine Particulate Matter Supersites Program, Aerosol Sci. Technol., 38, 253–264, https://doi.org/10.1080/02786820390229570, 2004.

Stolzenburg, M. R. and McMurry, P. H.: An Ultrafine Aerosol Condensation Nucleus Counter, Aerosol Sci. Technol., 14, 48–65, https://doi.org/10.1080/02786829108959470, 1991.