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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Spatial and vertical extent of nucleation events in the Midwestern USA: insights from the Nucleation In ForesTs (NIFTy) experiment" *by* S. C. Pryor et al.

S. C. Pryor et al.

spryor@indiana.edu

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Comments from the reviewers are in black, responses are in red (this formating did not survive cut-and-paste thus have manually edited to indicate where responses start).

Reviewer 1: This manuscript aims to investigate the spatial and vertical extend of new particle formation events in the Midwestern USA, as well as the role of H2SO4, NH3 and organics in new particle formation and growth. Although the study contains interesting results, additional work is required before the manuscript can be considered for publication in ACP. Main Comments: 1.) The Information content of the paper does not

justify the length of the article and attempts should be made to shorten the manuscript. There is a lot of unnecessary information that was already presented in a previous paper (Pryor et al., 2010). It seems that excerpts have been copied "word by word" from that manuscript (sections 3.32-3.34)! This is unnecessary! Please justify why the analysis of the back trajectories, nucleation parameter and condensation sink is presented again, though it was discussed in great detail previously (Pryor et al., 2010). Further, the manuscript should be restructured. There is a lot of duplication/repetition in the manuscript which can be avoided. The discussion is scattered throughout the paper (parts in Chapter 2, 4 and 5). I recommend deleting chapter 2 and moving the relevant text to the introduction/method and discussion sections. Reorganize Chapter 4 and reconsider the number of figures (e.g. figures 12 and 13 needed?). Chapter 5 is simply an extended list of points already made in the main text. Delete and replace with conclusions! Any additional discussion of the results that is -at the momentgiven in section 5 should be included in section 4. Table 1 and 2 could be moved to supplementary? 2.) The authors aim to assess the relative role of H2SO4, NH3 and organic compounds in atmospheric nucleation. This would be a significant development but would require a systematic analysis of the correlation between the new particle formation rate and sulfuric acid (e.g. Kuang et al., 2008;Sihto et al., 2006) and organics (e.g. Kerminen et al., 2010;Paasonen et al., 2010). A more quantitative analysis of the data should be considered! Especially the use of the Fractional Aerosol Coefficients (FAC) to estimate the low volatile organic vapor concentration is questionable and needs further justification. As stated correctly, the approach neglects the availability of oxidants (OH/O3) as well as the loss to the preexisting aerosol surface/mass. Why using it, especially since OH was measured? It is stated: "OH measurements for three nucleation days and two nonevent days show a substantial diïnĚĞAĚŸ erence in OH distribution throughout the day". Therefore I would expect that the true organic oxidation products vary accordingly (probably showing a diurnal cycle more similar to H2SO4). The lack of any correlation between FAC and particle number is not surprising and (most likely) mean- ingless for new particle formation! Since OH (and probably O3) was measured,

a more detailed analysis taking into account the oxidation capacity of the air mass and the loss to the preexisting aerosol could be conducted! RESPONSE STARTS HERE: 1) It is correct that we specify the event classification of Dal Maso et al. 2005 that we use (3.3.2). Since we want to be clear about the definitions they gave of the event characteristics we did not change the wording. We also state how the nucleation parameter was specified by Boy and Kulmala. Again this is definitional but perhaps the wording could be tweaked. The NP of Kuang was not discussed or used in our prior analysis. The description of the back-trajectory analysis (3.3.4) is not duplicated from the earlier paper (but rather is much abridged). The analysis presented in the ACPD paper is for the NIFTy field campaign not for the long-term measurement period (of 2 years). Second part of 1). It is not entirely common to have objectives in the results section of a paper, but this reorganization could be done if the editor approves it. It was intended that section 2 provide the objective and the substantiation of why those objectives were selected. I have identified a number of sentences that could be removed to remove any redundancy. Figure 12 could be removed if deemed unnecessary. Figure 13 contextualizes the NIFTy data with the limited amount of existing data. Section 5 – could be abbreviated if the structure which refers back to the objectives is deemed undesirable.

2.) OH was only measured on a very limited number of days (and not throughout the diurnal cycle) and ozone was not measured. Thus alas we have no data on which to base more mechanistic analyses of the oxidation of VOCs. We noted that the use of FAC is speculative, thus the analysis/discussion of the VOCs will be moved to supplementary materials.

The overall length of the manuscript will be reduced by moving three figures (Figure 5, Figure 12 and Figure 15) to supplementary materials along with associated text (and Table 2), and the abbreviated sections described herein. RESPONSE ENDS HERE

Specific/technical comments:

P23290, L19-24: “There are indirect indications that the growth in locales with high sulfur dioxide emissions is dominated by sulfuric acid (Sakurai et al., 2005; Stolzenburg et al., 2005; Petaja et al., 2007). Generally in less polluted regions the growth is dominated by other compounds (Boy et al., 2005; Wehner et al., 2005), but the role of organics in the growth can also be substantial in polluted environments (Smith et al., 2008).”: Unclear, please rephrase! RESPONSE STARTS HERE Rephrased to; “Particle growth in locales with high sulfur dioxide emissions is dominated by sulfuric acid (Sakurai et al., 2005; Stolzenburg et al., 2005; Petaja et al., 2007). However, the role of organics in the growth can also be substantial in polluted environments (Smith et al., 2008). Generally in less polluted regions particle growth is dominated by compounds other than sulfuric acid (Boy et al., 2005; Wehner et al., 2005).” RESPONSE ENDS HERE

P 23291 Lines 1-21: “but although regional new aerosol particle formation events are frequently observed at locations separated by up to 300 km, “they are rarely identical” (Hussein et al., 2009).”: Unclear, please rephrase! RESPONSE STARTS HERE Hussein et al. (2009) summarized a number of studies over Scandinavia and concluded that regionally coherent events were observed but “they are rarely identical”. Rephrased the entire sentence to; Prior research has shown regionally coherent new aerosol particle formation events covering distances of upto 300 km are frequently observed in Scandinavia (Dal Maso et al., 2007), but these events while nearly coincident in time have site-specific characteristics (Hussein et al., 2009). RESPONSE ENDS HERE

3-2.1: P 23296 line 20 – p 23297 line 9: The whole paragraph is confusing, please rephrase! The discussion on previous inter comparisons is irrelevant and misleading. P 23296,line 20 - p 23297,line 2 could be deleted. RESPONSE STARTS HERE Paragraph in question is; “Prior inter-comparison of FMPS and SMPS (operated with an ultrafine water-based CPC) has indicated good correspondence when the diffusion correction is applied to the SMPS data, with a high correlation in time series of total

aerosol particle concentrations (r2=0.91) and generally similar size distributions (Asbach et al., 2009; Jeong and Evans, 2009). The inter-comparison of aerosol particle sizing instruments used at the different sites during NIFTy indicate relatively good correspondence in the average size distribution derived from three of the instruments – the SMPS system deployed in Bloomington and the FMPS and SMPS deployed at MMSF, though as in prior research (Jeong and Evans, 2009), sub-30nm aerosol particle concentrations are slightly lower from the FMPS (Fig. 2). Equally, as shown in a prior inter-comparison using diesel soot (Asbach et al., 2009), the particle concentrations at approximately 100nm diameter are higher in both FMPS systems. There are evident discrepancies between size-resolved aerosol particle concentrations from the two SMPS systems, the FMPS as operated at MMSF and the FMPS that was deployed in Indianapolis (Fig. 2). The source of the discrepancy is unclear but may derive from noise on the electrometers (specifically mis-counting aerosol particles at smaller sizes with the FMPS due to residue on the electrometer stages), or slight mis-alignment in the aerosol flow within the FMPS deployed in Indianapolis. In light of this discrepancy, the aerosol particle size distributions from Indianapolis must be viewed with caution." The purpose of having this discussion was to contextualize the instrument inter-calibration we conducted. We have abbreviated the discussion to; "The inter-comparison of aerosol particle sizing instruments used at the different sites during NIFTy indicate relatively good correspondence from three of the instruments – the SMPS system deployed in Bloomington and the FMPS and SMPS deployed at MMSF. As in prior research sub-30nm aerosol particle concentrations are slightly lower from the FMPS (Jeong and Evans, 2009), while concentrations of approximately 100nm diameter particles are higher in both FMPS systems (Asbach et al., 2009) (Fig. 2.). Size distributions from the FMPS deployed in Indianapolis differ substantially from those derived from the other instruments (Fig. 2). This discrepancy may derive from noise on the electrometers (specifically mis-counting aerosol particles at smaller sizes with the FMPS due to residue on the electrometer stages), or slight mis-alignment in the aerosol flow within the FMPS deployed in Indianapolis. In light of this discrepancy, the aerosol

particle size distributions from Indianapolis must be viewed with caution, and growth rates computed there from are deemed too uncertain to present herein." RESPONSE ENDS HERE

Chapter 3.2.1: Why are Grimm and the CPC's not included in an inter comparison? RESPONSE STARTS HERE Regrettably they were not available. RESPONSE ENDS HERE

Chapters 3.3.2-3.3.4: Already presented in Pryor et al.,2010 (see comments above). If discussed, parameters could be introduced in the same way as the "condensation sink". RESPONSE STARTS HERE The event classification could be moved to supplementary information presuming it is common knowledge. Suggested reword of the NP of Boy and Kulmala: Boy and Kulmala (2002) developed a "nucleation parameter" (NP): Section 3.3.4 suggested rewrite; "Analyses of other long-term data sets have indicated preferential occurrence of nucleation with specific back-trajectories (Young et al., 2007; Coe et al., 2000; Komppula et al., 2006; Fiedler et al., 2005; Hussein et al., 2009). Thus, 24-h back trajectories were computed for every classified day of data from MMSF using the HYSPLIT model for receptor heights of 50 and 500m a.g.l.. " RESPONSE ENDS HERE

Chapter 4.1.1: Why no growth rates given for Indianapolis? RESPONSE STARTS HERE See above – the particle size distributions are deemed too uncertain. RESPONSE ENDS HERE

Chapter 4.1.2: The results presented in chapter 4.1.2 are closely related to chapter 4.3 (P23310-lines 1-26). Move to Chapter 4.3 to avoid unnecessary repetitions? Does the double event add any addition information? RESPONSE STARTS HERE We were not aware of any major work describing double-peaked events, and wanted to denote both their presence, and provide a physically consistent explanation for their presence. RESPONSE ENDS HERE

Chapter 4.2: Back trajectories, reference to Pryor et al., 2010? RESPONSE STARTS

HERE Surely suggested rewrite; However, as in Pryor et al. (2010) there is something of a tendency towards a greater prevalence of northerly flow on the days on which evidence of nucleation was observed at MMSF (cf. Fig. 9c vs. d) consistent with cold front passages from the north and northwest. RESPONSE ENDS HERE

Chapter 4.3: Subheadings would be very helpful. RESPONSE STARTS HERE Ok, suggestions; Add subheading 4.3.1. Chemical controls on nucleation on line 21 of 23308 Add subheading 4.3.2. Chemical controls on growth on line 8 of 23312 Add subheading 4.3.3. Mass closure on line 21 of 23312 RESPONSE ENDS HERE

P23308 line 1- p23309 line 28 and Figure 12: The general relation between CS, NP was already discussed in Pryor et al.,2010 (see comments above). RESPONSE STARTS HERE CS and the NP of Boy and Kulmala were presented earlier for the long-time period. Here we present these calculations for NIFTy data because they are a standard way of evaluating controls on nucleation and provide a context for use of the nucleation parameter of Kuang et al. We propose to abbreviate the discussion to; "The condensational sink (CS) was computed using data from the SMPS and FMPS at MMSF, by assuming the condensing vapors have a very low vapor pressure, an accommodation coefficient of 1, and exhibit properties similar to sulfuric acid (Kulmala et al., 2001). In keeping with prior research (Kulmala et al., 2005), these results do not indicate a very strong influence of CS on the occurrence or intensity of nucleation (as measured using the total number concentration of sub-30nm aerosol particles) (Fig. 12). This is also consistent with relatively high aerosol particle loadings in the region and the high regional emissions of SO2 and NH3 that may mean nucleation can be initiated and sustained even when the condensational sink is comparatively strong. Average NP values at MMSF are demonstrably higher on event than non-event days (Fig. 12), although there is one event class B day that was characterized by relatively low NP values and one non-event day that exhibited high NP but no evidence for enhanced ultra-fine aerosol particle concentrations. Excluding those two outliers, NP values in excess of $3\times10-23$Wmmolecules-1 K-1 was observed on event days, while values

below that threshold characterized non-event days." RESPONSE ENDS HERE

P23309, lines 25: Correlation of those 5 data points seems to be questionable. What is the meaning of this correlation? RESPONSE STARTS HERE As I stated; "Further, in this small data set from the NIFTy experiment, there is some evidence that the intensity of particle production is inversely correlated with LÈ (the correlation coefficient for LÈ vs. total aerosol particle number concentration _-0.8)." Naturally it is hard to make any firm conclusions from such a small sample size, but the statistical realtionhsip is physically consistent. Suggested rewording: "The intensity of particle production is inversely correlated with LÈ (the correlation coefficient for LÈ vs. total aerosol particle number concentration _-0.8), though the small sample size precludes detailed interpretation." RESPONSE ENDS HERE

Figure 5a: Datapoints missing: H2SO4 before 13:00, NH3 after 10am. Figure 5 lower panels: VOC data hard to read. Needs improvement. RESPONSE STARTS HERE Yes, there are some missing data. This figure will be moved to supplemental information. RESPONSE ENDS HERE

Figure 14: needs improvement. Vertical bars indicating the variation in the composite data should be included. Figure 5 indicates some strong variation in ammonia throughout the day. This seems to average out in the composite data. Again vertical bars indicating the variations would be helpful. RESPONSE STARTS HERE Addition of vertical bars to Figure 14 makes it virtually illegible. The variability from day to day is of course higher than in the mean and is why we chose to present Figure 5. RESPONSE ENDS HERE

In References/Citations: IPCC reference correct?, Plass-Dulmer>Plass-Dülmer RESPONSE STARTS HERE All non-English letters will be corrected manually (apologies). Endnote does not seem to recognize them. RESPONSE ENDS HERE

Reviewer 2: Statement for the article Spatial and vertical extent of nucleation events in the Midwestern USA: insights from the Nucleation in forests (NIFTy) experiments

by S.C. Pryor and co-authors. In complete agreement with referee number 1, I see no reason why most of the results presented already in the publication New particle formation in the Midwestern USA: Event characteristics, meteorological context and vertical profiles also by Pryor and coauthors in Atmospheric Environment has to show up in nearly similar way in this article. I'm willing to read and refer a new improved version of this manuscript after the authors have removed all the results published in the last paper. As referee Nr. 1 already pointed out the manuscript is too long and should be rewritten by only concentrating on the new results. So making the story short I'm willing to review the paper again after major revision with a more scientific, shorter version of the results which were not published 5 month ago in a different journal. RESPONSE STARTS HERE Response: 1) Trajectory analysis for the long-term measurements at this site were presented in the earlier paper for a single receptor height of 50-m. We plotted the results for the entire year as trajectory density plots. We cited quite clearly this manuscript, and in no way sought to obfuscate the prior analysis. In the current work, we present specific back trajectories terminating at 50 and 500m for each day of the field experiment – different depiction and specifically information about the height above ground. 2) Also CS were computed for the long-time series of particle size distributions. We cited quite clearly this manuscript, and in no way sought to obfuscate the prior analysis. We presented these calculations for NIFTy data because they are a standard way of evaluating controls on nucleation and provide a context for use of the nucleation parameter of Kuang et al. We have abbreviated both the description of method and results. RESPONSE ENDS HERE

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