Atmospheric
Chemistry
and Physics
Discussions

Open Access

Interactive comment on "Evolution of gaseous precursors and meteorological parameters during new particle formation events in the Central European boundary layer" *by* J. Größ et al.

J. Größ et al.

birmili@tropos.de

Response to Anonymous Referee #1

This paper addresses factors controlling new-particle formation events at Melpitz, Germany using long-term observations. The authors develop an automated method to classify the strength of NPF (unfortunately with no explicit influence of growth in the classification), and use a large pool of classified days to look at the timeseries of factors that may influence NPF. The work is well-suited for ACP and the results are generally interesting.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Reply: Referring to your comment *"unfortunately [they use] no explicit influence of growth in the classification"* we would like to point out that the focus of this present analysis has been to examine the circumstances of fresh particle formation (i.e., gas-phase chemical and meteorological factors). We acknowledge that the important questions related to particle growth, i.e. how many Aitken particles, CCN and optically active particles will be produced as a result of NPF, are of vital interest. The importance of the latter process has not escaped us. However, such analysis needs more extended and refined methodology. We confirm that we have more suitable data sets and case studies at hand for the latter topic, and these are currently in progress of being analysed with a clear focus on the growth process. In this paper, however, we took major advantage of the NAIS instrument, which provides readings of particles down to 2 nm, which is most suited to investigate the circumstances of fresh new particle formation.

The writing is often sloppy (e.g. comma usage) and could use additionally proofreading.

Answer: Thank you for your suggestion. We will make sure to proofread the revised manuscript as carefully as possible.

I have specific scientific and writing comments below that should be addressed before publication in ACP.

P2309 L12: I'm not sure how large-scale atmospheric models currently parameterize growth.

Answer: Some sentences were added to the manuscript for clarity: "Due to restraints with regard to computing power, global chemistry transport models can treat aerosol particle growth due to condensation of organic precursors only in highly simplified form. In an exemplary fashion, we reiterate the mechanisms used in the representative state-of-the art model GEOS-Chem-TOMAS (D'Andrea et al., 2013). That model assumes that 10% of monoterpene emissions will convert to secondary organic aerosol (SOA). This aerosol yield is distributed onto the pre-existing sectional size distribution accord-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ing to either the mass in each section (thermodynamic limit) or the Fuchs-corrected surface area (kinetic limit). The work of D'Andrea et al. (2013) includes even a variant where the growth of particles by SOA condensation is highly size-dependent in the nucleation mode range, based on experimental evaluations (Häkkinen et al., 2013). The rough estimate of an aerosol yield as well as the inclusion of two alternative condensation mechanisms confirm the considerable uncertainties of current knowledge with regard to these condensation processes."

P2309 L17: Percentages are fractions, not frequencies.

Answer: Thank you, this will be corrected accordingly.

P2311 L6 vs. L2312 L23: is the lower limit of the APS 0.5 or 0.8 microns?

Answer: Technically, the lower limit of the APS is 0.5 μm in aerodynamic diameter. This is the technical limit of the instrument. Converting this aerodynamic diameter into a mobility diameter yields a lower cut-off of 383 nm. However, comparison with mobility size spectrometers suggests that the APS becomes increasingly unreliable at the lower end of its measurement range. (By measurement principle, the APS is performing well for large particles that are separated by their inertia in the instrument's counterflow.) Smaller particles tend to separate only to a poor degree in the separation unit of the instrument. Therefore, between 20 and 800 nm, the TDMPS data were used exclusively, with the APS data continuing the size distribution above that point. This is now clarified in the text.

P2314 L20: Shouldn't the units for A be m2 W-1 cm3 in order to get the concentration of OH correct?

Answer: Sorry for this oversight, indeed, $cm^3 \, W^{-1} \, m^2$ needs to be the correct unit.

P2316 L18-19: *By definition* H2SO4 production depends equally on [OH] and [SO2] (k[OH][SO2] for the rate-limiting step), it's just that here [OH] varies more. Please be more accurate in this description.

Answer: Thank you. Of course, you are right. This has now been reformulated in the text.

P2317 L14: "maxima" should be "maximum" here (not plural).

Answer: Thank you. This was corrected.

P2319 L9: I'm guessing that g(tau) should be g(t) since you're defining "g" in a general sense (as a function of time).

Answer: Thank you. This was an oversight, and has been corrected.

L12: The event in 2a doesn't grow to sizes close to 100 nm.

Answer: This number was checked by lognormal fitting, yielding a nucleation mode diameter of 70 nm at midnight and 90 nm on the next day (not shown in the Figure). These diameters are now mentioned in the text.

L23-24: How does the event in 2d do in the filter? It extends for a long time but does not grow. It seems like these events could have strong responses from the filter too, but aren't necessarily the events you want to find.

Answer: You are right in noticing that these are rather different types of NPF events. In principle, we can distinguish between events with subsequent particle growth, and events without particle growth. Next, there are also different time spans during which NPF events are observed.

Identifying and classifying NPF events can be done, perhaps, with two major intentions in mind:

1. Examine the circumstances of fresh particle formation (i.e., gas-phase chemical, meteorological)

2. Evaluate the potential of NPF events to deliver total particle number concentration, CCN number concentration, and radiative forcing effects.

The main objective in this paper is to examine aspect 1), i.e. the circumstances of fresh particle formation. Our filter is sensitive towards high numbers of small particles (N[2-20]) as well as a long duration of an event. The filter either indicates that there were many small particles observed, and/or if this was the case for a long time. The event in Figure 2d performs well under this method, and for the purpose of examining aspect 1), we consider the performance of our filter adequate. Aspect 2), i.e. the examination of particle growth, how many Aitken particles, CCN and optically active particles will be produced as a result of NPF is another issue — perhaps ultimately more relevant than aspect 1), but this needs a more extended analysis that includes particle growth. In this paper we took major advantage of the NAIS instrument, which provides readings of particles down to 2 nm, which is most suited to investigate aspect 1). The discussion raised here will be considered in the revised version of the text.

P2324 L15-17: You bring up the turbulence and flux here but you haven't introduced Figure 5 yet.

Answer: Figure 5 is now introduced earlier.

Figures 4 and 5. What are the sigma values on the plot. They are never defined or discussed, I [...] believe.

Answer: The sigma values indicate the standard deviation of the mean parameter calculated for the three event classes. (Technically, it is calculated by standard deviation divided by the square root of n-1.) The purpose of the sigma values is to obtain a feeling for the significance of the difference that the shown atmospheric parameters exhibit between the three event classes. They correspond to the whiskers depicted in the plot. Technically the whisker interval represents the range in which the true mean value can be expected with 66% probability.

P2324 L22-24 and P2325 L6-8: Why can't the high CS overnight be due to primary emissions into a shallow night time BL that?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Answer: We checked your question. In the surroundings of Melpitz, primary particle emissions could be emitted by traffic sources. Traffic could then be seen, for example, by NOx or black carbon. Our original statement was: "(3) Class I and II events show a condensation sink CS above average". Figure 1 shows the diurnal cycles of CS, temperature, NOx and black carbon. Note that this graph is plotted without normalisation of the Figure by the start time of the event, as was done in Fig. 4 of the manuscript. In this kind of display, the effect of CS that was mentioned in our text disappears. It can be observed that for all event classes, CS has a similar magnitude around 05:00 (night-time high) and around 13:00 (day-time low). (CS changes by a factor of around 5 between them.) A decline in observed CS starts when temperature starts to rise (black line). The decline in CS seems to terminate when temperatures above 290 K are reached (brown line, for Event class I). There is a diurnal cycle in NOx and BC which is similar to the overall pattern of CS (see the diurnal cycles in Figure 1). There is also a peak in NOx and BC in the morning, which we attribute to local anthropogenic emissions but this tends to be noticeable only quite some time after the decline in CS has started. BC makes up less than 10% of total particle mass at Melpitz, so that it is unlikely that this can account for the diurnal effect in CS. For the reasons stated above we will weaken our original statement about the importance of CS for new particle formation (NPF). In fact, there seem no arguments available for CS playing a relevant role in the environment presented at Melpitz.

P2326 L9: How can something be proportional to a class?

Answer: This text was reformulated, to "[...] rise with ascending event class".

P2326 L22-23: Did you check that the small particles (Dp<20 nm) actually don't contribute significantly to the CS? Sometimes they can if the nucleation event is strong and the background is clean.

Answer: Thank you for this suggestion. This has now been checked. Figure 2 shows an expanded version of Manuscript Fig. 4 (d), indicating the fraction of CS calculated

for particles smaller than 20 nm. It is clear that the fraction CS[2;20] remains very small in comparison to total CS except, perhaps, in the case of event class I. There, CS[2;20] amounts to about 1/6 of total CS at the time of maximum N[2;20]. This peak is actually visible in the shape of the curve of total CS. As a consequence of this finding, we will formulate the text accordingly: "CS is correlated most strongly with the number of bigger particles, i.e. in the Aitken and accumulation mode. It is our interpretation that in these cases, CS originates from the same or similar pollution sources that emit SO2. (The newly formed particles <20 nm contribute only little to CS, about 15% at event peak time for event class I, and less for the rest of the periods.)"

P2326 L26 and other places: What do you mean by "mean levels"? Mean for the day for each class individually? Mean across all three classes?

Answer: this was clarified to "...decrease to their pre-event levels within a matter of a few hours ...".

Section 5.3: I'm very confused by this section. Where are the results of these tests? Are these the sigma values in the figures? What do they mean? Why no discussion?

Answer: Sorry for this oversight from our side. We now insert the missing text: " We performed statistical tests in order to identify the degree of significance regarding the differences between the three NPF event categories in terms of the measured atmospheric parameters. Student-t tests were conducted at a significance level of 99% for every 15 min interval for the parameters shown in Fig. 4. The result was that class I and class II are significantly different from class III (weak events or non-events) in terms of OH (aka solar radiation), SO2 and H2SO4 for every 15 min interval of the period between 4 hours prior peak event time and 6 hours past event time. Significant differences could even be confirmed for CS most of that time and, in addition, for the differences between class I and class II regarding OH, SO2 and H2SO4. These statistical tests serve to confirm that the atmospheric conditions found during class I, class II, and class III events were indeed substantially different, and can thus be interpreted

as influential factors for the occurrence of a NPF event of the corresponding class."

Section 5.4: I have concerns with using only the 2-3nm bin for determining J2. (1) If particles are formed above and brought down through mixing, couldn't the particles be larger than 2-3nm before reaching the surface. Events being first observed at sizes larger than 3 nm are not uncommon at some sites. (2) Are the counting statistics good enough for a single bin (esp. the smallest one)?

Answer: Thank you for this remark. (1) Indeed, particles seem to be able to grow to considerable sizes before they are observed at the measurement site. Very recently, Platis et al. (2015) reported such findings for Melpitz using unmanned aircraft observations of total particle number concentration. That work suggests that NPF events may start some few hundred meters aloft, to be measured near the ground only after considerable delay. During this delay time, it is possible that particle may grow to diameters up to 20 nm before they are detected at the ground-based site. (2) This is hard to answer, because the NAIS instrument measures particles by means of an electric current in an electrometer, and not by an absolute count rate, such as a CPC. It is normally assumed that the NAIS measurement bears significance even at 2.06 nm when the concentrations are high. In the manuscript Figure 2 (a) it can be seen that the NAIS signal is clearly visible and pronounced during NPF events down to 2.06 nm. We therefore trust these measurements, especially when they are averaged to the 15 min intervals as was done in this work.

Section 5.4 second paragraph: What to take from this? What might a correlation of N with [H2SO4] but not N with J2 mean?

Answer: We agree that the presentation of the matter in the paper has been confusing. The basic correlation of N with [H2SO4] is interpreted as H2SO4 being a main factor responsible for the formation of new particles. The correlation of N with [H2SO4] being more solid than the correlation of J2 with [H2SO4] is somehow surprising, because J2 refers to the particles in the range 2-3 nm that should actually be more close to the

process of nucleation, which is thought to be initiated by [H2SO4]. We have one suspicion, which relates to your previous statement above. If one assumes that particles are formed aloft and only subsequently mixed down to the ground (Platis et al., 2015) this would mean that many of the smallest of particles have already grown into bigger sizes. Hypothetically, the actual nucleation could have terminated already when the particles from the burst reach the ground, and the particle number size distribution could well be shifted to the bigger sizes of the 2-20 nm interval. (When looking at the NAIS observations from this paper (Figure 4) we almost always see new particles in a wide size range (2-10 nm or even bigger) when they first appear at the ground.) This would then imply that the statistical connection between J2 and [H2SO4] is weakened, because the smallest particles have already dynamically evolved at the time of measurement, while N appears to be a better representative of the outcome of the nucleation process that happened at a previous time upwind. This would have the consequence that ground-based measurements of the 2-3 nm channel might not necessary be a useful indicator for nucleation processes happening at higher regions of the boundary layer, and that N might actually be a better representative of the outcome of the nucleation process. These conclusions are very tentative since to date, no reliable four-dimensional ambient data set has been obtained to verify the complete four-dimensional evolution of a boundary layer NPF event (cf. Platis et al., 2015). As a solution to your questions, we propose to insert the above discussion in the manuscript text.

P2330 L6: Similar to a comment as before... CS is *by definition* important for [H2SO4]; however, it's the lack of CS variability (relative to [SO2] and [OH]) that you observe.

Answer: Thank you, this will be clarified in the text.

P2330 L18: What do you mean by "larger-scale particles"? Larger-diameter particles or particles observed on a regional scale?

Answer: We meant ". . . larger particles (10-20 nm) . . .", which will be amended in the

text.

Wolfram Birmili, on behalf of all co-authors.

References

D'Andrea, S. D., Häkkinen, S. A. K., Westervelt, D. M., Kuang, C., Levin, E. J. T., Kanawade, V. P., Leaitch, W. R., Spracklen, D. V., Riipinen, I., and Pierce, J. R.: Understanding global secondary organic aerosol amount and size-resolved condensational behavior, Atmos. Chem. Phys., 13, 11519-11534, doi:10.5194/acp-13-11519-2013, 2013.

Häkkinen, S. A. K., Manninen, H. E., Yli-Juuti, T., Merikanto, J., Kajos, M. K., Nieminen, T., D'Andrea, S. D., Asmi, A., Pierce, J. R., Kulmala, M., and Riipinen, I.: Semi-empirical parameterization of size-dependent atmospheric nanoparticle growth in continental environments, Atmos. Chem. Phys., 13, 7665-7682, doi:10.5194/acp-13-7665-2013, 2013.

Platis, A., Altstädter, B., Wehner, B., Wildmann, N., Lampert, A., Hermann, M., Birmili, W., and Bange, J.: An Observational Case Study on the Influence of Atmospheric Boundary-Layer Dynamics on New Particle Formation. Boundary-Layer Meteorology. Online version September 19, 2015. http://dx.doi.org/10.1007/s10546-015-0084-y

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2305, 2015.

Full Screen / Esc

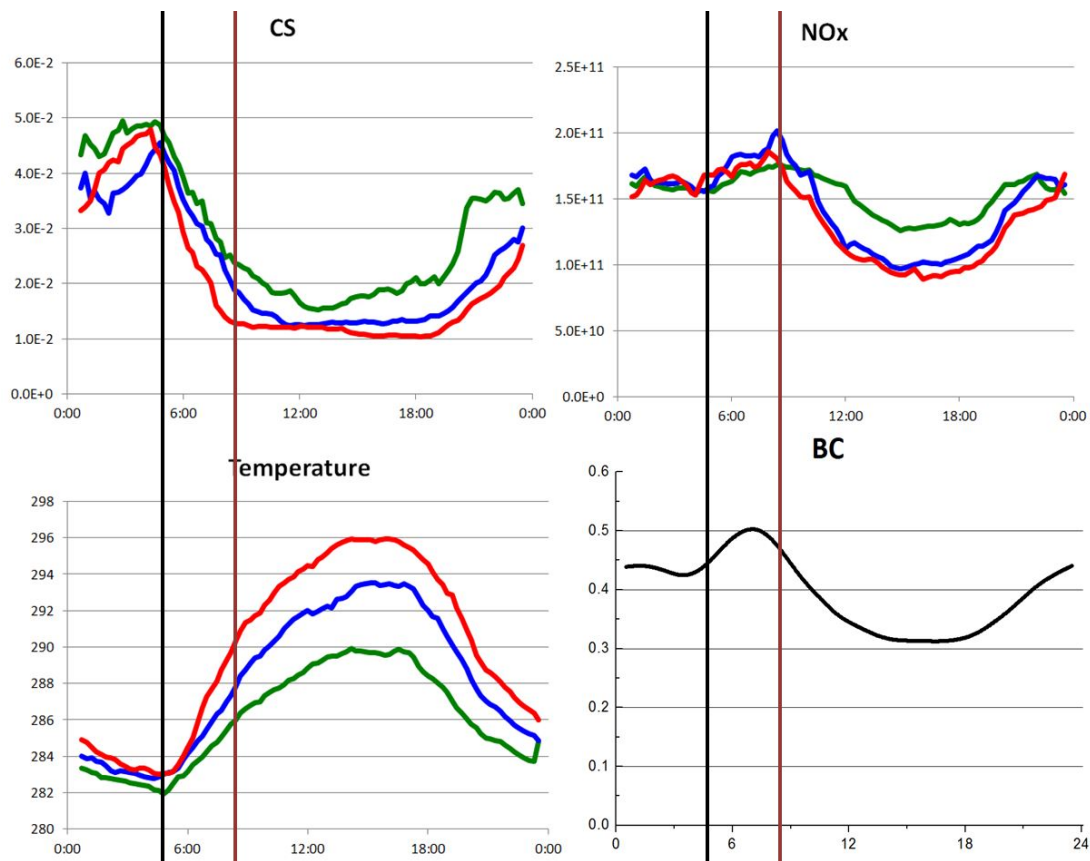Printer-friendly Version

Interactive Discussion

Discussion Paper

Fig. 1. Average diurnal cycles of CS, in s-1, NOx, in molec./cm^3, ambient temperature in K, and equivalent BC mass concentration in μg/m^3. Colour code like in the manuscript.
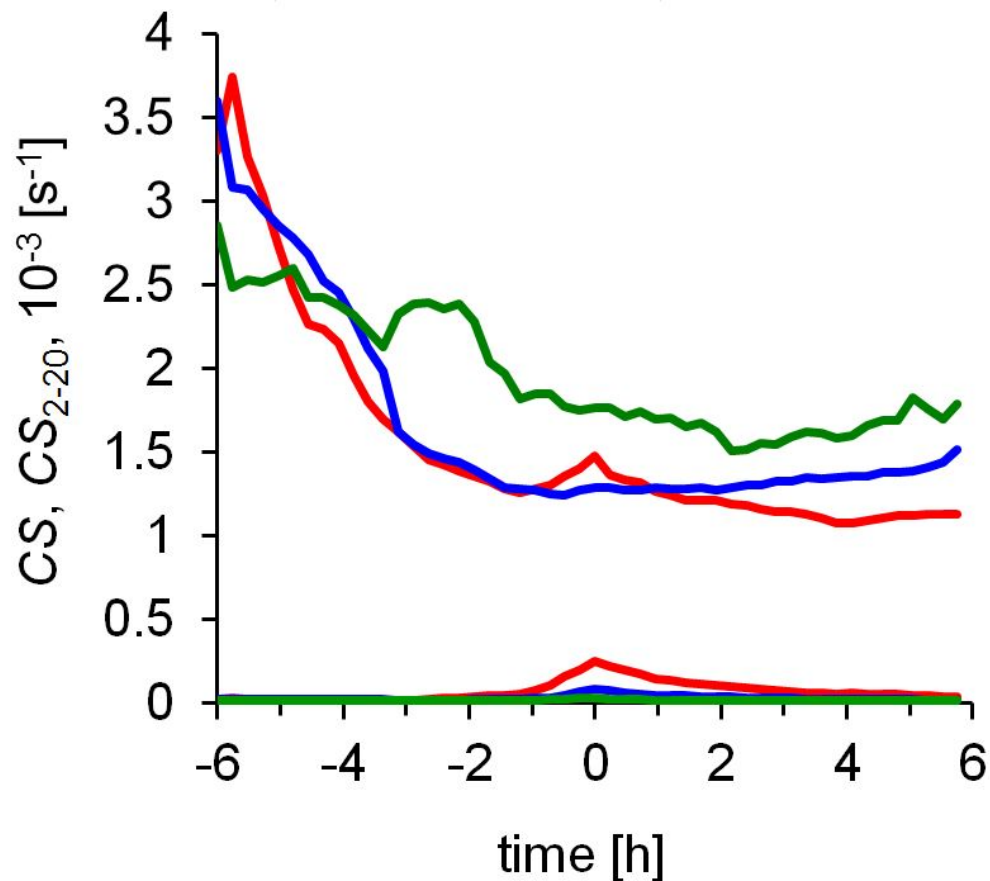
Fig. 2. Time series of the Condensation Sink (CS), in s-1, highlighting the fraction of CS attributed to 2-20 nm particles. Colour code like in the manuscript.