

Author's response to referee (MB Enghoff) comments on:

Ion - particle interactions during particle formation and growth at a coniferous forest site in central Europe

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The review is in general positive and did only demand minor revisions.

We greatly appreciate the thoughtful comments and suggestions that helped to improve the manuscript. Thank you very much for your time and effort! We trust that all suggestions have been addressed accordingly in the revised manuscript. We respond to the specific comments as follows:

1: Elevated growth rates of neutral particles

Referee's comment:

Six of the eight analysed events occur in the morning. From Fig. 2 I estimate that there is about a 1 hour delay between the onset of ion growth (looking at the black circles) and the growth of neutrals. In the morning concentrations of condensable gas (sulphuric acid) is increasing due to photolytic production. I therefore suggest that the observed difference in growth rate could be due to differences in condensable gas concentrations - since the ions grow earlier in the morning where less material is available for growth they grow slower than the neutrals. Looking at Table 2 it seems that the enhanced growth of neutrals is indeed only observed in the morning events (except Aug. 17 – maybe this was a cloudy day?), whereas the two noon events do not show this difference in growth rates – in fact they show the opposite behavior as predicted by theory. From Fig. 7 and 8 it also appears that the growth rate anomaly is most pronounced in the events with a large Δt . Maybe the authors have some direct measurements of condensable gas concentrations that can be used to test if this idea has merit or not, but I think it should be considered in any case.

Author's response:

The reasoning of the referee is very plausible. The lower GRs of the earlier occurring ions may be related to differences in available gas phase precursor concentrations. The exact identity of the involved gas phase components cannot be deduced from our data. Likely, sulfuric acid and oxidation products of volatile organic compounds are involved. Of these, only sulfur dioxide, being the main precursor of sulfuric acid, was measured during the campaign. Sulfur dioxide concentrations mostly showed an increase in early morning and reached peak concentrations before noon. During all considered events, the morning hours were sunny (except the 19th June), with sunrise between 5 and 6 AM local time. As the production of sulfuric acid depends strongly on photochemistry, H_2SO_4 concentrations are expected

to increase strongly with sunrise. Further, oxidation products of volatile organic compounds are also expected to exhibit an increase in concentration during the morning. Therefore, in the early morning, when the first intermediate ions are formed, the precursor gases are expected to be still at relatively low concentrations. Due to less available precursor gases, the ion growth is likely to be slower compared to neutral particles which form later. Nevertheless, the ions are likely to have an accelerating influence on the later occurring neutral particles, as presented in the manuscript.

We added the following paragraph to the Discussion (p. 186 line 16):

A possible explanation for the slower ion GR could be the diurnal variation of gas phase precursors like sulfuric acid or oxidation products of volatile organic compounds (VOC). In the early morning hours, when the first intermediate ions are formed, the precursor gas concentrations are expected to be low. On sunny days, as were most of the considered event days, the precursor gas concentration will increase during the day. This is due to increasing VOC emissions from the forest with rising air temperature, as well as due to photochemical processes leading to the formation of sulfuric acid and oxidation of VOCs. Therefore, the neutral particle growth which occurs later could be enhanced due to higher concentrations of precursor gases.

Additionally, ion-ion and ion-particle interactions enhance neutral particle GRs. As the potential precursor gases were not measured in this study, the focus to explain our observation will be on ion-particle interaction processes. Nevertheless, it is not expected that the observations can be explained fully by ion-particle interactions.

2: Estimation of ion production

Referee's comment:

Due to limitations in the NAIS the ion production rate Q is underestimated, as explained by the authors. I was wondering if it was possible to estimate the expected ionization rate, depending on if Radon measurements are available. For cosmic rays the muon flux would need to be known. If so then the ionisation can be estimated using the energy deposition ($\sim 2 \text{ MeV}/(\text{g}/\text{cm}^2)$) and ionisation energy (34 eV/ion pair). Something similar was done by Laakso et al (ACP 4, p. 1932, 2004).

Author's response:

Unfortunately, radon concentrations were not measured during the campaign, leaving the determination of the ionization rate solely to the measurements conducted with the NAIS.

3: Efficiency of NAIS

Referee's comment:

On p. 182-183 it is described how the AIS performs better than the NAIS – if you know the difference in efficiency (preferably size-dependent), could you use this to calibrate the NAIS-measurements? It would certainly be nice to see how much of the total particle formation could be due to the ions. Maybe you could make some kind of “best” case scenario to estimate an upper limit for the ion contribution?

Author's response:

The gain of information by performing a calibration of the NAIS with AIS data is considered to be fairly small, as measurements with the AIS were performed one year after the presented NAIS measurements. Therefore, background parameters differ significantly between the two measurements. An estimation of the “real” ion formation rate, based on NAIS and AIS measurements as well as on a publication by Hörrak et al. (2008), is given in the last paragraph of p. 183. Under the given circumstances, we don't consider a calibration to be more reliable than the already presented estimation.

4: Figure 2

Referee's comment:

Are the smoothed fits used to find the growth rates? If so I suggest splitting the fit for total and neutral particles in 2 parts since there appears to be a very steep part up to ~ 7 nm followed by a more flat line.

Author's response:

The referee is right, the smoothed “fits” are used to find the growth rates. However, the “fits” are the result of smoothing the times of maximum concentration by means of a running least square polynomial smoothing filter (Savitzky and Golay, 1964). Therefore, the method does account for changes in GR with particle diameter. When inspecting the black “fit” line in Fig. 2, a change in GR somewhere around a diameter of 7 nm is also visible.

Moreover, the aim of our analysis was to compare the GRs of ions and neutral particles by applying the same method to all our data. This objective is met with this approach.

5: Technical comments

Author's response:

- The term "temporal advance" was substituted by "time difference" as proposed by the referee.
- p.183 l7: "bended" was substituted by "bent" as proposed by the referee.

Fig. 1: Why not show the lines for the 10 nm ions down to 1.5 nm like the solid lines?

Author's response:

Ion-ion, ion-particle and particle-particle interactions were calculated for particle sizes interacting with particles of the same size as well as larger sizes. Once all coefficients were calculated for one reference size, the reference size was shifted towards the next larger size. Therefore, the information on the coefficients for the interaction of larger particles with smaller ones is contained in the previously calculated coefficients of the interaction of small particles with larger ones. In other words, the interaction of a large particle of size A with a smaller particle of size B is the same as the interaction of a particle of size B with a larger particle of size A. Therefore, Fig. 1 does not include smaller diameters for 10 nm ions and particles.

References

- Hõrrak, U., Aalto, P. P., Salm, J., Komsaare, K., Tammet, H., Mäkelä, J. M., Laakso, L. and Kulmala, M.: Variation and balance of positive air ion concentrations in a boreal forest, *Atmos. Chem. Phys.*, 8(3), 655–675, doi:10.5194/acp-8-655-2008, 2008.
- Savitzky, A. and Golay, M. J.: Smoothing and Differentiation of Data by Simplified Least Squares Procedures, *Anal. Chem.*, 36(8), 1627, 1964.