Atmos. Chem. Phys. Discuss., 6, S4640–S4645, 2006
www.atmos-chem-phys-discuss.net/6/S4640/2006/


Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Identification and classification of the formation of intermediate ions measured in boreal forest" *by* A. Hirsikko et al.

**A. Hirsikko et al.**

Received and published: 16 November 2006

We thank the referee for his comments and suggestions to improve the manuscript.

Specific comments:

1.

*Referee: With regard to nucleation mechanisms, the authors pointed out: (1) The intermediate ions are either formed via ion-induced nucleation or via the attachment of small ions on neutrally nucleated particles (page 9193, lines 1-3). (2) The gap in the size distributions of cluster ions (subclass Ib.2) is an indication of the dominance of the neutral formation mechanisms (page 9194, lines 1-4). I think that the authors should extend their discussion on nucleation mechanisms. The intermediate ions formed via nucleation on ions and via attachment should have quite different properties in size*

*distributions.*

*(1) While the clear gap in the ion size distributions (sub-class Ib.2) may indicate that neutral nucleation dominates at the measurement site, it could also be a result of the attachments of small ions to particles nucleated somewhere else (via either ion-induced or neutral nucleation mechanisms) and transported to the measurement sites. This should be pointed out in the first paragraph of page 9194.*

*(2) I would say that the obvious continuous ion distributions in the sizes range from 1 nm to 3-5 nm (sub-classes Ia and Ib.1, see Fig. 1) are clear indications of the dominance of ion-induced nucleation. This should be pointed out explicitly in the paper. Due to the rapid decrease of equilibrium charging fraction with decreasing size of nanometer particles, dominance of neutral nucleation should always lead to a clear gap in the sizes range from 1 nm to 3-5 nm.*

*(3) The authors have pointed out that sub-class Ib.2 days, which may be associated with neutral nucleation, are rare. Table 3 also shows that more than half of the BSMA identified particle formation event days belong to sub-classes Ia and Ib.1 which are clearly associated with ion-induced nucleation. Thus, it appears reasonable to conclude that at least half of the BSMA identified particle formation event days are clearly associated with ion-induced nucleation while only a few of the BSMA identified nucleation event days are probably associated with neutral nucleation. This should be pointed out in the text and reflected in the abstract.*

Answer: The referee could be right when saying that gap in the charged particle size distribution may be due to the attachment of cluster ions to particles nucleated elsewhere (by either neutral or ion-induced mechanism). The gap in the size distribution during the subclass Ib.2 particle formation was around 2 nm, with the width of approximately 0.5 nm. However, the gap was seen two-three times more often with the positive intermediate ions than with the negative ones (19 times for positive ions and 7 times for negative ions). Furthermore, during the most of the class-Ib.2 events for positive



ACPD
6, S4640–S4645, 2006





EGU

ions the negative intermediate ion events were of class Ia or Ib.1, with no gap in their size distribution.

The referee recommends us to conclude that ion-induced nucleation dominates on days with the particle formation event of subclasses Ia and Ib.1. The domination of ion-induced nucleation would mean that ion-induced nucleation makes more than 50 per cent of the new intermediate ions. Just based on the ion size distributions we can only say that ion-induced nucleation could be important on those days, but not necessarily dominating.

To find out the relative contribution of ion-induced and neutral nucleation mechanisms we should apply additional measurement methods to obtain the charging state of small particles (e.g. < 6 nm in diameter) during the particle formation (see Laakso et al., 2006, reference in the manuscript) and models/calculations to obtain nucleation rates for neutral and charged particles (Laakso et al., 2006b,c). The charging state is defined as the ratio of naturally charged particles to particles charged to bipolar charge equilibrium. If the aerosol particles are overcharged (ratio over 1) it indicates the important contribution of ion-induced nucleation, whereas the undercharged state (ratio below 1) indicates the dominance of neutral nucleation mechanism.

Based on their measurements in Hyytiälä, Laakso et al. (2006) found correlation between subclass Ib.2 events and the dominance of neutral nucleation (undercharged state), but there was a large variation in the contribution of ion-induced nucleation during other particle formation days (days in subclasses Ia, Ib.1 or II). The model calculations by Laakso et al. (2006b,c) showed that ion-induced nucleation clearly dominated (the fraction of ion-induced nucleation of the total nucleation rate was over 50 per cent) only on one day in Hyytiälä during one year of measurements and the corresponding calculations. In addition to that, the ion-induced nucleation was important on many days.

To extend the particle formation analysis with charging state measurements and nu-



ACPD

6, S4640–S4645, 2006

cleation rate calculations for charged and neutral particles will be topics of our next papers.

2.

*Referee: In Table 2, the authors should add an additional column showing the number of days in each sub-class suggested by both BSMA (either BSMA+ or BSMA-) and DMSP measurements. Fig. 4 gives some information but it will be useful to list the numbers for different classes in the table for direct comparisons.*

Answer: Adding the column that shows when we observed simultaneously particle formation events, undefined days and non-event days with the BSMA and DMPS could offer important and interesting additional information. We will consider adding such a column.

3.

*Referee: In Tables 2, 3, and 4, the authors presented number of days in each sub-class based on BSMA+ and BSMA- measurements. It will be very useful to add another column showing the number of days that both BSMA+ and BSMA- are in the same sub-class. This will give information about the number of days in each sub-class containing BSAM+ or BSMA- only.*

Answer: We agree with the referee, and consider adding the column that shows the number of days when particle formation based on BSMA- and BSMA+ was of same class.

4.

*Referee: After addressing comments 2 and 3 above, the authors may want to add some discussions on the possible reasons leading to the differences in the values derived based on BSMA+, BSMA-, and DMSP measurements. On page 9197 the authors gave several reasons briefly (including the suppression in the growth of nucleated particles associated with low concentrations of condensing vapors). The authors should*



ACPD

6, S4640–S4645, 2006

*give the concentrations of precursor gases measured to support the argument. Actually, it will make the paper more significant if the authors can present statistics on the meteorological (temperature, relative humidity, solar irradiance, etc.) and chemical (concentrations of SO2, H2SO4, NH3, certain organics, etc.) data measured during the same period. I believe that analysis of meteorological and chemical data will provide useful insight on possible reasons behind the difference in the values for each sub-class derived from BSMA+, BSMA-, and DMSP. For example, is there any statistical difference in key meteorological and chemical parameters between the days only BSMA- shows the event and the days only BSMA+ shows the events?*

Answer: In Hyytiälä we measure continuously: O3 and SO2, but not H2SO4, NH3 or organics, which are measured only during campaigns. However, we have available calculated H2SO4 concentrations (Boy et al., 2005), which we consider utilising to some extend together with the meteorological data before resubmitting the paper. However, the main focus of this paper was to identify and classify the particle formation days. To further study the relationship of all the meteorological and vapour precursor parameters on each particle formation day in detail would be a topic of other paper since we observed 269 and 226 particle formation days for negative and positive intermediate ions, respectively.

5.

*Referee: Page 9198, lines 12-14 and page 9200, lines 16-17. The authors emphasized that the negatively charged particle formation were generally more favorable at the measurement site. However, the data presented in the paper clearly show that nucleation on positive ions is also significant. I think that it is equally important to point this out in the text.*

Answer: We agree with the referee. Since we observed the positive intermediate ion formation events during our measurements also the positive ion formation was important on our site.



ACPD

6, S4640–S4645, 2006

6.

*Referee: Page 9196, lines 4-6 and Page 9200, lines 1-3. The conclusion about the decrease in the relative number of DMPS detected particle formation events may change if the authors re-organize the year from April to March as suggested by referee 1.*

Answer: We plan to change the presentation of statistics so that each year begins in the beginning of April and ends at the end of March as suggested by both referees.

Minor comments:

We will improve the text according to the technical comments. However, we do not have measured H2SO4 concentration only simulated/calculated concentration is available (Comment 7).

References

Boy, M., Kulmala, M., Ruuskanen, T.M., Pihlatie, M., Reissell, A., Aalto, P.P., Keronen, P., Dal Maso, M., Hellen, H., Hakola, H., Jansson, R., Hanke, M., and Arnold, F.: Sulphuric acid closure and contribution to nucleation mode particle growth, Atmos. Chem. Phys., 5, 863-878, 2005.

Laakso, L., Hirsikko, A., Dal Maso, M., Kerminen, V.-M., Vana, M., and Kulmala, M.: Effect of Ion-Induced Nucleation on Particle Formation in a Boreal Forest, in Proceedings of 7th International Aerosol Conference, 10-15 September, St. Paul, Minnesota, USA, pp. 1639-1640, 2006b.

Laakso, L., Hirsikko, A., Gagné, S., Dal Maso, M., and Kulmala, M.: Contribution of ion-induced nucleation on Tropospheric nucleation, in Proceedings of the workshop on Formation and Growth of Atmospheric Aerosols, 8-9 September, Minneapolis, USA, 2006c.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9187, 2006.