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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Kinetic nucleation and ions in boreal particle formation events" *by* L. Laakso et al.

L. Laakso et al.

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Interactive comment on "Kinetic nucleation and ions in boreal particle formation events" by L. Laakso et al. Anonymous Referee #2

Received and published: 21 August 2004

I was looking forward to reading this paper. In my initial quick review I saw that it was a serious study of an interesting phenomenon and felt that it deserved to be published in JACP. However, after a more careful reading, I realized that the paper can not be accepted for publication in its present form. This is not to say that the paper is not without considerable merit, because it presents an excellent comparison of measured and calculated quantities. The problems with the paper are more in the line of "technical difficulties." I will not go into the problems with English grammar and usage as those can be easily remedied by a careful reading of the manuscript by the co-authors. (Some

of whom have a perfect command of English!) It is, however, imperative that the errors in usage be corrected before publication can be recommended. (Many of these are simple omissions of articles.)

Comment: Language is now checked by one of the authors having a good command in lingua franca.

More serious are the problems I encountered in trying to understand the paper. My problem is primarily concerned with the way some things are explained and with a few of the figures. In general I do not have problems with the techniques or conclusions reached.

The paper describes measurements and analysis related to the nucleation of aerosol particles in a forest in Finland. The point of the study is to get a more comprehensive understanding of nucleation under realistic conditions, and to elucidate the role of ions in particle formation. An underlying question is the competition between the growth of new particles and the scavenging of new particles by pre-existing aerosols. The theoretical part of the work was carried out with a box model. My first problem with the paper (albeit a minor one) has to do with the title, “Kinetic nucleation and ions in boreal particle formation events." The word “boreal" in my dictionary has six meanings, all having to do with the northern region of earth and only when you get to the sixth definition is word forest mentioned. Therefore, I would suggest that the title should include the words "boreal forest" instead of just “boreal." That is, boreal should not be seen as modifying the word “particle" because, I assume, particles are particles the world over and there is nothing special about particles formed in the north.

Comment: Done

The conclusions reached in this paper are, basically, that the nucleation of particles in a boreal forest is a kinetically limited process that generates a large number of small stable clusters. When these clusters reach a diameter of 2 nm they become "activated" and begin to absorb organic vapors. This will not happen in the presence of a large

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number of pre-existing particles because the newly formed clusters will be scavenged away. The small particles are observed to be mainly negative ions. The authors suggest that this shows that ions are involved in particle formation, or that sulfuric acid condenses preferably on negative ions. They conclude that ion-induced nucleation is not as important as the kinetic nucleation of neutral clusters. The work relies on a variety of rather interesting measurements. I will not go through them in any detail, but let me mention that the instruments used were (1) BSMA = a mobility analyzer to measure ions, (2) AIS = another mobility analyzer (3) DMPS = mobility analyzer for neutral particles (4) a special DMPS to measure charging state (5) CIMS, a mass spec to measure sulfuric acid concentration. (6) DSFIA to measure ammonia (7) Instruments to measure ionizing radiation. The mobility analyzers were used to obtain size distributions for ions and particles. The BSMA makes measurements of particle in the 0.4 to 6.3 nm range. The AIS measures ions up to 55 nm in diameter. The DMPS measures neutral particles from 3 to 500 nm in diameter.

I found the discussion on the measurement of charging state to be somewhat confusing. When I first read the section I was convinced that the authors had made a mistake, but then after carefully re-reading the relevant sections I decided that their description is probably correct. However, I would suggest they rewrite the sections involved, giving a clear definition of charging state and a clear discussion of how it was determined. (I know that "charging state" is a term used in the field, but many general readers will not be familiar with it.)

Comment: A new chapter explaining the charging state is added.

The box model described in section 3 seems to be quite appropriate. I have a small problem with the section called "Nucleation" where the authors state that the kinetically limited nucleation is determined by the collision rate of ammonium bisulphate clusters. The formation of ammonium bisulphate clusters is limited by the concentration of sulfuric acid molecules. So, they say, the nucleation rate is J=KC2. Maybe I am missing something here, but shouldn't C be the concentration of the ammonium bisulphate

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clusters? Or if C = [H2SO4] then I would think that K should not simply be the coagulation kernel between ammonium bisulphate clusters, although it might be proportional to that kernel.

Comment: The kernel is for ammonium bisulphate clusters whereas the concentration of ammonium bisulphate clusters is approximated by the concentration of sulphuric acid. This problem is discussed in article by Vehkamäki et al., 2004 (Hanna Vehkamäki, Ismo Napari,Markku Kulmala and Madis Noppel; Stable ammonium bisulphate clusters in the atmosphere. Accepted for publication in Phys. Rev. Letters, 2004)

The next section is called "Coagulation." The authors refer to Figure 2 which is unfortunately almost unintelligible. There are many red and blue lines on the figure. There is a black diamond with the words, "Negative condensation enhanced." What does this mean? Some lines have words or symbols next to them. For example, there are lines labeled dp1 = dp2 and others dp2 = 0.68 nm. What does that mean? Why is this figure presented anyway? It does not seem to have relevance to the rest of the paper! I would suggest the words used in the body of the text tell the reader all he/she needs to know about the coagulation coefficients.

Comment: Explanations are improved.

The section on "Condensation" was a bit confusing. The authors state that "condensation of ammonium and sulphuric acid is treated as in coagulation between molecules and particles." Also, "the organic vapour condenses ... without any thermodynamic barrier."

However a bit later they state that "The condensation rate of the organic vapor ... was calculated using the Fuchs Sutugin formula." I would think that the Fuchs Sutugin approach involves thermodynamics, the condensation and evaporation of molecules, the dependence of vapour pressure on temperature, etc. etc. So, all in all, I am uncertain exactly how the model treated condensation.

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Comment: A paragraph discussing this topic is added.

In Section 4.1.1. on meteorology we read that, "Only during the night 84-85 there were some changes due to the temperatures below zero which made the air drier." According to the figure, the air was very slightly drier on day 85 than on days 87 and 88, but I do not think this difference is significant. So I do not know why the sentence was included.

Comment: This sentence refers to night-time RH. Text improved.

Section 4.1.4 discusses fractional concentrations of ions and particles with reference to Figure 9. This figure (and figure 11) are difficult to interpret because there are so many curves and so little explanation of them. The caption for Figure 11 says "fractional" concentrations but the figure shows concentrations.

Comment: More explanations added to the text. This figure was constructed after careful thinking. We have decided to show all curves in one figure in aim to make it easier to compare different curves together. It is difficult; the authors agree and needs some effort to be understood. However, we wanted to give a reader a possibility to compare for example the heights of peaks in different size intervals, time lags between the peaks and also the relationship between charging state and the behavior of ions.

In Section 4.1.3 there is an example: "...if we have 105 neutral clusters..." This example is trivial and probably should not be included. Furthermore it has an error.

Comment: Dropped out.

Finally, the authors show that the model results do a very nice job of generating results similar to the measurements. For me this is the nicest aspect of this paper because the model has very few ad-hoc assumptions. This is not a case of "fitting" the results, but rather, starting with basic principles and showing that the theoretical analysis agrees with observation.

In conclusion, the paper has many interesting points and it discusses an important

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problem. On the negative side, it is somewhat difficult to read, it has problems with English usage, and the figure captions are inadequate. I recommend publication after revision.

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