Atmos. Chem. Phys. Discuss., 7, S5160–S5168, 2007
www.atmos-chem-phys-discuss.net/7/S5160/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of positive air ions in boreal forest air at the Hyytiälä SMEAR station" *by* U. Hõrrak et al.

U. Hõrrak et al.

Received and published: 21 September 2007

Final Author Comments

The authors thank both referees for their high rating of the measurements carried out by the authors and Anonymous Referee #1 for many constructive comments intended to improve the quality of the paper. Below, we consider all the comments in the same order as given in the Interactive comment by Anonymous Referee #1.

General comments by Anonymous Referee #1

Referee: This paper reports measurements of positive ions and aerosol in Finland, and more specifically, attempts to close the ion balance between production and loss terms. The measurements carried out are of fundamentally good quality, though some *of the techniques applied and conclusions drawn are not adequately justified given the uncertainties. The authors have adopted new and not always clear terminology to describe standard terms in ion-aerosol physics, and this makes the paper harder to understand than it needs to be.*

Authors: The authors are very thankful for the high rating of the measurements. The constructive criticism by the Referee is discussed below in the section "Specific comments".

Referee: The paper title is not really relevant to its contents and implies a detailed study of the chemical or electrical properties of positive ions, which has not been carried out here. A new title, perhaps including the words "ion balance" or "ion concentration" and mentioning aerosol would make the topic of the paper much clearer. The paper is also rather long and some aspects could be shortened and clarified, see specific comments below.

Authors: The suggestion is accepted; the title of the revised paper will be "Variation and balance of positive air ion concentrations in a boreal forest". We agree that the paper is rather long and the revised paper will be shortened according to the Referee's recommendations.

Specific comments by Anonymous Referee #1

Referee: 1. Nomenclature. a. Ion naming. In my opinion the first author is the world expert in the classification of air ions by their electrical mobility. He has written several papers and a landmark thesis in which detailed classification of air ions by their mobility categories has been carried out. However, in the paper, atmospheric charged particles are referred to as cluster ions, small/intermediate/large ions, charged nanometer particles, aerosol ions, charged ultrafine aerosols, charged nanometer particles etc. Horrak has previously defined all these types as small, intermediate and large ions, but perhaps this broader collaboration of authors has led to the use of less rigorously defined

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categories. Returning to the Horrak terminology throughout, with just one name for each type of ion, would make the paper much easier to follow.

Authors: The three ion classes are traditionally called the small/intermediate/large ions in the literature about atmospheric electricity. Today, the air ions are in the focus of aerosol research, but atmospheric electric terminology is not common in aerosol physics. So far, the synonyms are sometimes unavoidable. Due to this fact, we tried to be as punctual as possible using the aerosol particle terminology in parallel with ion terminology in different sections of the paper. The recommendations by the Referee will be considered when explaining the usage of parallel terms in the revised paper.

Referee: 1. Nomenclature. b. Charged aerosol nomenclature. The use of the term ”ion sink” is only defined relatively late (p9475) as an attachment rate. In the abstract it is referred to ambiguously as a ”loss”. Only after equation (3) on p 9473 it is possible for the reader to work out that it actually has units of rate. The authors appear to be unaware of the basic aerosol literature which already defines and discusses attachment rates at length. It is confusing for the reader to be presented with an alternative, poorly defined term when a perfectly good one already exists. Similarly the use of the word ”overcharging” appears to be another re-definition. Though it is not defined in the text, it seems to refer to a non-equilibrium charge distribution; again, this is use of a confusing new term in place of an existing definition.

Authors: The authors thank the Referee for pointing out careless usage of some words and terms in the paper. The short term ”sink” is used in the atmospheric aerosol research instead of the clumsy term ”relative loss rate” (see e.g. Pirjola et al., 1999; Kulmala et al. 2001). The ion sink due to the aerosols (measured in s^{-1}) is the product of the average ion-particle attachment coefficient (measured in m^3s^{-1}) and the particle concentration. The expression ”ion loss” has a common meaning and does not refer to any specific physical quantity. The term ”overcharging” is briefly explained in Introduction (page 9468, line 24). Actually, this term is common in aerosol research

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(e.g. Laakso et al. 2007). It refers to a specific case of non-equilibrium charge distribution with the increased amount of negative or positive particles. The terms will be better explained and their usage in the revised paper will be improved according to the recommendations by the Referee.

Referee: 2. In Section 4.2, it is suggested that fog reduces the conductivity of atmospheric air by decreasing the ion concentration. Attachment of ions to fog droplets will occur, but a change in ion mobility could also modulate air conductivity. I am surprised this is not mentioned, since the Estonian group are known for their ion mobility instrumentation, and Horrak himself has discussed this effect in his own thesis (pp 82-83). Perhaps the authors are aware of other work on this topic that they could refer to in order to exclude mobility effects.

Authors: The atmospheric-electric fog effect was discovered by means of air conductivity measurements (Dolezalek, 1963; Hoppel, et al., 1986). It is well known that the relative variation of the small ion mobility is much less than the relative variation of the ion sink due to the aerosols. Thus the variation of the mobility has a secondary role in the effect of fog on the air conductivity. However, this role is worth to be studied. Unfortunately, the small ion mobility was not measured in the present research and the estimation of the effect of ion mobility in the atmospheric-electric fog effect will remain a subject of the future studies.

Referee: 3. The authors determine the ionisation rate q by closing the ion balance equation, i.e. by calculating ion loss due to self-recombination and attachment (nucleation is, quite reasonably, excluded on the basis of their data). The values of q calculated are lower than is usually measured. This discrepancy is then used as a basis on which to infer there must be an additional loss term. This approach requires q, and indeed all the other parameters of the balance equation, to be very well known in order to accurately estimate the residual and its error range. Errors in q are not stated,

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but on page 9485 the errors in air ion concentration are quoted as ∼10%. The ion uncertainty alone in eq (1) therefore implies a fractional error in q of ∼30%, which could account for he "pine needle effect" and hygroscopic aerosol growth that are invoked by the authors to increase q. To justify the introduction of a different mechanism it must be clearly shown that the discrepancy in the ion balance is greater than the possible errors in q, which need to be discussed as follows:

a. Errors in N (aerosol number concentration) measurements

b. Errors in beta: discussion of the attachment coefficient formulation chosen and its errors over other approaches (e.g. see Gunn, 1955; Fuchs, 1963, Marlow and Brock, 1975; Clement and Harrison, 1992).

c. Errors in alpha: The self-recombination coefficient alpha is also assumed to be constant throughout the paper, which is probably inappropriate for a detailed closure of the ion balance. An expression for alpha should be specified and the errors estimated.

Authors: The statement that the 10% uncertainty in the ion concentration implies an about 30% uncertainty in q when estimated according to Eq. (1), is not relevant. Eq. (1) follows in a steady state equation $q = \alpha n^2 + \beta N_{tot} n$. Therefore, the implied uncertainty of q could approach as a maximum the limit of 20% in the fictitious situation of particle-free air. However, the second term in the equation above 5-12 times exceeds the first term (see Table 1) and thus the implied uncertainty is typically 11-12%.

a) The aerosol measurements and calibration of used instruments is thoroughly discussed in the referred paper by Aalto et al. (2001) where uncertainty of measurements in typical atmospheric conditions was estimated to be about 10%. Repeating of the referred discussion would lengthen the present paper by many pages and thus it seems to be unreasonable. We accept the standard rule to present the measurements so that the uncertainty is of the same magnitude as the least significant digit. Few lapses violating this rule will be corrected in the revised paper.

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b) We are aware that there are no numerical uncertainty estimates of attachment coefficients available in literature, including the publications suggested by Referee (Gunn, 1955; Fuchs, 1963, Marlow and Brock, 1975; Clement and Harrison, 1992). The estimates of attachment coefficients used in the present paper are justified according to the results by Reischl et al. (1996), who compared different theoretical models with the experiment. The differences between the accepted theoretical models and the experiment are considerably less than the uncertainty of atmospheric measurements, thus the effect of the errors in the estimates of the attachment coefficients is expected to be insignificant.

c) The theory of the ion-ion recombination is quite complicated (e.g. Bates, 1985) and not able to provide reliable numerical results for cluster ions, whose chemical composition is unknown. The first model, which results in a realistic estimate of the recombination coefficient of atmospheric ions, was published only a few months ago (Stommel and Riebel, 2007). Theoretical estimates of the ion-ion recombination in the atmospheric air are considered less exact when compared with experimental results. The published experimental values of alpha vary between 1.4×10^{-6} and 1.6×10^{-6} cm^3/s. The uncertainty of the value of 1.5×10^{-6} cm^3/s, which is used in the paper, is estimated to be about 7%. The ion-ion recombination sink typically makes up about 10% of the total sink of small ions. Thus the effect of the uncertainty in the value of the recombination coefficient is suppressed by about 10 times and makes a negligible value of about 1% in the ion balance.

Referee: 4. The paper is rather long and this is partly because well-known facts are repeated, for instance demonstrating that the atmosphere always contains air ions, and explaining the recombination limit in clean air, are not necessary and referencing e.g. review papers would suffice. The discussion of precipitation (p9481) is qualitative and should be removed. Also, figures 3a, 3b and 4 do not all seem to be needed.

Authors: The paper will be shortened in the process of revision considering the pro-

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posals by the Referee.

Technical corrections suggested by Anonymous Referee #1

Referee: Equation 4 uses radius whereas Figure 1 shows diameter.

Authors: Figure 1 will be complemented in the revised paper to include the axis of the particle radius.

Referee: Epsilon 0 is the permittivity of free space, not the electric constant.

Authors: ISO 31-5 allows using of any of the terms ”permittivity of free space” and ”electric constant”. CODATA and NIST use the term ”electric constant”, see http://physics.nist.gov/cuu/constants, category ”Universal”. The permittivity of free space equals the electric constant. We are not considering free space and use the ”epsilon 0” only as a fundamental physical constant. Thus the term ”electric constant” is still to be preferred in the present paper.

Referee: P9474 line 17 define ”diameter concentration”.

Authors: The definition will be added into the revised paper.

Referee: Figure 9 - it is impossible to resolve the shape of individual points.

Authors: The problem will be solved in the revised paper by resizing the Figure 9.

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