Atmospheric Chemistry and Physics Discussions

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Interactive comment on "**Ambient sesquiterpene concentration and its link to air ion measurements**" *by* **B. Bonn et al.**

Anonymous Referee #3

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The authors have developed a model to estimate the concentration of sesquiterpenes in a boreal forest air based on air ion, aerosol particles and trace gases measurements. They have proposed a new method to estimate the sesquiterpene concentration with a high time resolution and high sensitivity with concentrations in pptv-range, which is highly relevant for emission budget estimates of regional importance. In this study, the authors have assumed a link between the concentration of cluster air ions and the so-called stabilized Criegee biradicals, formed in the reaction of biogenic sesquiterpenes with ozone and predominantly destroyed by its reaction with ambient water vapour. They have used the "maximum approach" assuming that all the negative ions in a tiny size range of 0.56-0.75 nm, in which the cluster ion mode is commonly located, consists of stabilized Criegee biradicals. After the charged fraction of the Criegee

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biradicals (ions) has theoretically been derived, the concentration of sesquiterpenes can be found from the steady-state balance equation of the Criegee biradicals. In order to obtain a sesquiterpene mixing ratio at the inlet of the air ion spectrometer (2m in height above the ground), the emission measurements at the top of the forest canopy (at about 12 m height) were applied and a logarithmic vertical wind profile below the canopy was assumed. The subject of the paper is relevant for ACP. However, the present manuscript requires major revision before it can be published. The authors are asked to consider the following particular comments and recommendations.

1) The authors should know (considering the list of co-authors) that the cluster ions in the atmosphere have different chemical compositions and complicated structures. The cluster ion formation and evolution is relatively well known (Mohnen, 1977; Viggiano, 1993; Beig and Brasseur, 2000; Nagato and Ogawa, 1998). According to current understanding, the primary air ions generated by the ionizing radiation (e-, N_2^+, O_2^+, O_2^-) undergo numerous ion-molecular reactions to become the cluster ions (e.g. $H_3O^+(H_2O)_n$, $NH_4^+(NH_3)_m(H_2O)_n$, $C_5H_5N^+(NH_3)_m(H_2O)_n$, $CO_3^-(H_2O)_n$, $NO_3^-(HNO_3)_m(H_2O)_n$, $HSO_4^-(HNO_3)_m$). Here the sign (+, -) indicates the ion polarity, m and n the number of ligands. Almost all the cluster ions have some water molecules around the core ion. The number of molecules surrounding the core ion depends on the thermodynamical properties of the cluster and the air. Therefore, we cannot agree that the cluster ions in the investigated size range of 0.56-0.75 nm are mainly simple compounds consisting of a single molecule as described in Section 5.1 in page 13175 and afterwards.

2) In addition to a rather arbitrary speculation about the link between the concentrations of Criegee biradicals and cluster ions in the size range of 0.56-0.75 nm, the derivation of the charged fraction of the neutral particles in the investigated size range (supposed to be Criegee biradicals) is the most problematic. This derivation is based on Eq. 20, where the concentration of cluster ions is found from the balance equation Eq. 7 in pages 13175-13176. The source term or the formation rate of the cluster ions (0.56-

0.75 nm) in Eq. 7 is "the production by collisions of the neutrals, matching the size range of interest (N0) with present ambient air ions (Nions), including charged aerosol particles as well". The separate growth term of even smaller ions was ignored. Thus, any new ion in the investigated size range is assumed to be formed by the collision of a neutral particle or cluster with any "ambient air ion" (e.g. molecular ion, cluster ion or charged aerosol particle) and a subsequent charge transfer. This is an interesting approach, but the authors have ignored a generally accepted growth and evolution path of primary air ions via ion-molecular reactions (Mohnen, 1977; Viggiano, 1993; Beig and Brasseur, 2000; Nagato and Ogawa, 1998). The ion-molecular reactions can contribute to the ion concentration in the size range of 0.56-0.75 nm, as well as decrease this concentration due to the evolution towards large sizes and, therefore, these reactions cannot be just ignored. Also, the ion (0.56-0.75 nm) losses in Eq. 7 are probably overestimated because the condensation sink takes into account the losses due to all pre-existing aerosol particles and, thus, accounts also for some losses that have already been taken into account by the ion recombination term. The condensation sink is also not a proper parameter to account for the losses of air ions on aerosol particles, but neutral vapours (see e.g. Pirjola et all., 1999). The so-called "ionic condensation sink" is introduced later in Eq. 26 in page 13180. In principal, the "ambient ions" (Nions) in the recombination term should also include the ions of opposite polarity of the investigated size range (N), but this would complicate significantly the solution of the differential equation (see Eq. 11) and can be ignored due to its small contribution. The authors should explain in more detail the validity of the balance equation (Eq. 7) with respect to ignoring the ion-molecular reactions. In Introduction, they should also give a brief overview of the ion formation and evolution via ion-molecular reactions, which is very important in a chemical point of view.

3) We are also concerned about the simplification of Eq. 19. The simplified equation for the calculation of charged fraction (Eq. 20), as well as the assumption of the initial conditions (zero ion concentration in the beginning), are not valid in general because of the contribution of small ions, generated by ionizing radiation and growing

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via ion-molecular reactions. Eq. 20 and Eq. 21 are valid only in the case of initially neutral particles in the investigated size range, but this is certainly not a case in the real atmosphere. An amount of neutral clusters (Kulmala et al., 2000) could be formed by molecular ion and cluster ion recombination (see e.g. Yu and Turco, 2001), but their concentration in a common situation should be small due to the sink on aerosol particles. The authors have assumed that there is a zero ion (0.56-0.75 nm) concentration in the beginning (N= 0 cm-3, if t= 0 s), but what about the other "ambient air ion" concentration and the size range where they are located? The "ambient air ion" concentration (Nion) and also the ion production rate are important factors of the charging of aerosol particles (see Laakso et al., 2004). We did not find a relevant discussion in the paper about how these parameters affect the results, and whether the balance of "ambient air ions" (see Tammet et al., 2006) should be taken into account in the model.

4) The theoretical charged fraction was derived separately for long-lived and short-lived species, Eqs. 30 and 31, respectively in page 13182. To specify the chemical nature of the air ions, the authors had to distinguish between possible candidate groups of long-lived (i.e. thermodynamically stable clusters or chemically unreactive molecules) and short-lived compounds (e.g. volatile organic compounds). For this purpose, they have used the ratio of negative to positive ions in the investigated size range of 0.56-0.75 nm and interpreted the variation of the ratio in terms of the effect of compounds of different lifetimes. As a result, the long-lived species (ions) were ruled out and short-lived compounds with the lifetime of about 1 s or less were selected as possible candidates. Later, only one compound called Criegee biradical was selected. We found such an approach to be rather qualitative and not well argued regarding the seasonal variation of the ratio. It is well known that the mobility of ions depends on the chemical composition of the air (on trace gases), as well as on the meteorological parameters (air temperature and pressure). Therefore, the changes in meteorological parameters should be taken into account in the mobility-diameter conversion procedure. The complexity of conversion and its uncertainties were discussed in the paper by Tammet (1998) and, therefore, the authors should be aware of the problem. Also, according to the published

results (Mohnen, 1977; Hoppel and Kraakevik, 1965; Nagato and Ogawa, 1998; Iida, et al., 2006), the ratio of negative to positive ions commonly differs from unity also in locations different from the boreal forest, and was explained by differences in the cluster formation due to ion-molecular reactions and by different structure of positive and negative cluster ions (e.g. the different number of polarized water molecules around the core ion). The ratio of small ions is also affected by the electric field close to the Earth surface known as the electrode effect. The latter depends on local meteorology: stability of atmosphere and the presence of cloud cover, which can reverse the electric field close to the ground compared to fair weather conditions. In interpretation of the measurements, the attention should be paid to this as well.

Summarizing the discussion given above, we suppose that the separating of cluster ions into two groups - ions in the size range of (0.56-0.75 nm) and the remaining "ambient air ions", or extracting one ion group from the whole cluster ion group measured by the aspiration type spectrometers (Tammet, 2006) with the aim of finding out its chemical composition in uncontrolled atmospheric conditions is too complicated a task.

Some minor remarks:

Page 13170. Regarding Eq. 6. According to Hoppel and Frick (1986) and Laakso et al. (2002), instead of the diffusion coefficient of the particle (D1), there should be the radius of the particle.

Page 13180. Regarding the condensation sink and ionic condensation sink equation derivation. There is an error in Eq. 23 and 24. Instead of the particle diffusion coefficient (D1), there should be the diffusion coefficient of air ion (Dion). Further, Eq. 24 is not exactly the same as Eq. 25, but an approximation. The equals sign should be replaced with the approximation sign.

Page 13180, Eqs. 26 and 27. The enhancement factor A depends on particle size (Laakso et al., 2002). How significantly does the simplification of Eq. 26, using the constant enhancement factor A instead of the size-dependent Aj affect the ionic con-

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densation sink given by Eq. 27? This simplification is needed for deriving Eq. 29 from Eq. 21.

Pages 13187-13191. In Section 5.4 "Electron and proton affinity", the electron and proton affinities were calculated by applying different quantum physical-chemical models. This is a highly rated innovation, but very hard to understand due to a large number of abbreviations used. For example see pages 13189-13190.

Page 13196. It is not clear for the reader, what kind of chemical sink (Kchem) was used in Eq. 31, when calculating the charged fraction data given in Figure 8. Reading the text on page 13196, we can guess that only reactions of the stabilized Criegee intermediate with water vapour have been considered. However, the exact value of the rate constant used among many constants given in page 13196 still remains unknown. We are also concerned about that both charged fractions found from Eq. 29 and Eq. 31 give very similar results (see Fig. 8). Could the authors explain the fact?

Page 13196. When calculating the concentration of Criegee biradicals from the air ion (0.56-0.75 nm) concentration by dividing it by the charged fraction (Eq. 31), it should be kept in mind that the charged fraction was calculated for the non-steady-state conditions, for the time tau (mean lifetime of ions supposed to be charged Criegee biradicals). If this time (about 1 s) differs significantly from the mean lifetime of real ions measured by the ion instruments, the concentration of Criegee biradicals would be significantly over- or underestimated. The average lifetime of cluster ions in the boreal forest given by Tammet et al. (2006) was about 130 s for positive and about 110 s for negative ions.

In many places in the text we can find that the ion (0.56-0.75 nm) source was assumed to be similar throughout the year (e.g. page 13175, line 11, page 13183, line 12) with a short explanation given in page 13185, lines 8-18. In Conclusions (page 13203, lines 18-20), the authors state that the ion source was also assumed to be constant: "Note as well that we considered the major source of the air ions in the size section studied

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to be constant for all seasons, which remains an issue to be studied in the future, but this seems to be reasonable for the conditions found at Hyytiälä". Should the reader understand that the "constant ion source" means the constant ion production rate?

Some misprints:

Page 13175, line 12 "can be then be".

Page 13176, line 15 "invetigated".

Page 13188, line 15, instead of "secies" should be "species".

Page 13188, line 15, " by CS*, The ratio", note the capital letter.

Page 13177. The Eq. 10 is not correct; the term Nions,j should be in the denominator.

Page 13186, Eq. 36, instead of 'subtraction', there should be 'sum' in the denominator.

Page 13220, Fig. 8 caption, superfluous word "(left)" should be removed.

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