

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

**B. Bonn et al.**

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### **General**

First of all, we would like to thank all reviewers for their critical comments on the present study. It is very interesting to have reviewers of such a different opinion, probably because of a different scientific background and focus. Since we believe this topic to be of high atmospheric relevance, we fully agree with William Stockwell's (first reviewer) comments and like to thank him for his excellent transfer to a broader point of view. The presented topic is certainly of relevance not only for the boreal forest area but also on the global scale. The short lifetime of sesquiterpenes makes it indeed necessary to implement a subgrid scale for regional and global studies, because variations are to be expected on the scale of even a few meters horizontal as well as vertical not treated

correctly by the coarse resolution of a regional or a global model. Hence as pointed out by William Stockwell a shoot emission study will give an indication of a very small scale emission of a compound. But it is definitely a challenge to transfer single shoot measurements to a broader area or even a global models grid box size. Here we need to stick to the present data obtained at a boreal forest site in this first study only. But we would be glad to see this method to be applied elsewhere too.

The second reviewer (no. 3) was rather sceptical about the presented approaches, assumptions and conclusions made. Every critical comment is welcome to check the validity of the described method. Nevertheless, we are convinced that the presented approach, the results shown and the conclusions drawn are valid and we will give a detailed explanation, why this approach is reasonable. By doing so we hope to convince the sceptical reviewer of the results given.

## Detailed comments

For answering the detailed comments of reviewer no. 3 we will give the specific answers according to the number of the reviewer's comments given.

1. First, it was claimed that we did not take into account the 'cocktail' of a multitude of different chemical compounds and especially clusters in the size range of interest. This is definitely wrong, since charge affinities were checked for all available trace gases including  $\text{NO}_x$  and sulphur compounds ( $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HSO}_3$ ,  $\text{H}_2\text{SO}_4$ ). Additionally correlations of the accessible trace gases with the air ion concentration in the section of interest were made. These revealed no correlation at all except for two gases, namely ozone and water vapour. Especially the correlation of water vapour (negative correlation) gave a clear indication for our hypothesis, since this is expected opposite for sulphuric acid or nitric acid compounds and

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thus clusters derived from these. The anticorrelation with present water vapour clearly indicated the role of the stabilized Criegee Intermediate stated in the paper. Volatile organic compounds are of major importance in the boreal zones too. Emissions of terpenes such as sesquiterpenes are of remarkable importance (Hakola et al., 2003; Hakola et al., 2006). These will much more affect the local atmospheric chemistry than nitrate or sulphur compounds in the  $\text{NO}_x$ -limited situation at Hyytiälä. By contrast to the terpenes importance less is currently known about their ambient concentrations, especially with respect to sesquiterpenes. This is caused by its high reactivity and the linked problems during detection. In our method this reactivity is not treated as a disadvantage but as a benefit, because of the intense production of the biradicals (stabilised Criegee intermediates).

And second we guess that the difference between the reviewer 3 and us is mainly linked to the question of atmospheric air ions to be either single molecules or multicomponent clusters. Since the referee applies the method of Tammet et al. (2006), a chemically well mixed cluster, including a multitude of different compounds with sufficiently high charge affinity, is assumed to make the derivations independent from the charge affinity of single compounds. From Israel (1960) it is known that negative charges are of about 40% higher mobility (smaller size) but not above. However, the difference of small ionization rate and collision rates between small molecules or clusters with ionized ones to the collision rates of molecules with charged larger particles should be noted. There are orders of magnitude difference. The charging of single molecules by doubly charged particles is much more efficient, because of higher concentration of particles compared to ionized molecules and clusters and because of the higher collision rate. This all leads to the conclusion that in general no remarkable excess of a single charge should be seen.

We have done the seasonality plot of negative to positive charge ratio not only for the second size section (0.56-0.75 nm, shown in Fig. 3 of the manuscript) but for

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the first six size sections: (1) 0.4-0.56 nm, (2) 0.56-0.75 nm, (3) 0.75-1.00 nm, (4) 1.00-1.33 nm, (5) 1.33-1.78 nm and (6) 1.78-2.37 nm in mobility derived diameter. These seasonality plots revealed a strong seasonal pattern for the first two sections with a higher concentration of negative ions and a much weaker one for the following two with an excess of positive air ions, mainly apparent below 1 nm in mobility derived diameter. Above 1.78 nm only a scattering around unity can be seen, indicating that this is about the starting size for which the assumptions of Tammet et al. (2006) can be made. Not below. Below 1 nm it appears that mainly single molecules or very tiny not well-mixed clusters (probably two molecules) compete for the charge. In order to reveal the measured excess of a single charge the molecules or clusters of interest must have a sufficiently short atmospheric lifetime as it is expected for the stabilised Criegee intermediates destroyed mainly by reactions with ambient water vapour.

2. We partly refer this point to the statements given above. Furthermore, the validity of ignoring the growth of smaller ions (first size section) is questioned. Again this is related to the e.g. sulphuric acid cluster approach, forming small clusters which take up further gases to grow (Kulmala et al., 2000). However, similar correlations with atmospheric traces as done for the second size section have been done for the first size section. Again no correlations with ambient acid concentrations but a moderate anticorrelation with water vapour can be found. Most likely the compounds (let us call it that way furtheron) are radical species to explain the high excess of negative charges. They also have a notably lower concentration making it unrealistically to cause a higher concentration at larger sizes. Growth cannot stop at a certain point of size. Only a smaller stabilised Criegee biradical such as derived from monoterpenes would have been able to grow. This we have checked within our study, revealing that concentrations and reactivities of monoterpenes are too low. Furthermore, if the cluster would have been formed at e.g. 0.4 nm in mass diameter and grown furtheron, the excess

- of a single charge should be apparent for all the subsequent size sections. But there is a clear change between the second and the third size section. Hence, there is no need to take into account any growth.
3. The reviewer is concerned about the assumption of initially zero ions during integration of the general dynamic equation for air ions between 0.56 and 0.76 nm. Certainly there is an ionization rate in the ambient atmosphere, which is about 6 ions  $\text{cm}^{-3} \text{s}^{-1}$  at maximum. But there are two aspects to consider: (a) The much higher collision rate with a large aerosol particle than with a single molecule (size aspect) and (b) the concentration of air ions in the section of interest. This would require at least a lifetime of more than a minute to explain the observed air ion concentration. This disagrees with the other results given, namely the lifetime of stabilised Criegee intermediates and the remarkably higher concentration of negative charges. Therefore, we are convinced of the assumptions made. One comment is needed for the period in December 2004, which is discussed in the paper. At that time additional sources might be available (really stable boundary layer, local pollution) and because of that the period was excluded.
  4. We are aware of meteorological impacts on the mobility and have taken this into account. Nevertheless, the results shown are not explainable by cloudy and non-cloudy conditions. There is no rainy season during winter and a dry season during summer in Finland. But there is certainly a temperature effect for example on the collision rate as formulated in Eqs. (3)-(6). However, this effect is not able to explain the ion ratio measured. Nevertheless, the chemical influence is able to.

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## Minor remarks

p. 13170: Correct. This will be changed.

p. 13180: No. The condensation sink is first given for neutral particles only. Therefore, there is no need to include diffusivity of air ions. Later on (Eqs. (26f)), the enhancement factor  $A$  is considered to take this into account. However, the equal sign of Eq. (24) will be changed to an approximation because of the change from integral to summation.

p. 13180: Reviewer 3 emphasizes the effect of using a constant  $A$  instead of  $A_j$  in Eq. (27). Of course  $A$  is not constant for ion ion interactions. However, in this study we assume the stealing of the charge from a doubly charged aerosol particle by a neutral molecule. Even if the molecule would be a cluster, this results in an  $A$  value equal to unity for all particle sizes (compare Eq. (7)).

p. 13187-13191: In order to make understanding of the quantum chemistry calculations easier, we will provide a detailed appendix including the common abbreviations used in the text and refer to standard textbooks, in which more detailed information can be obtained.

p. 13196: The chemical sink considered is certainly the reaction of the stabilised Criegee intermediates with water vapour. Although there are multitudes of possible reactions, the others are of negligible importance for that. We will emphasize this in the text. The published reaction rates for the reaction of the stabilised Criegee intermediate with water vapour is indeed not well-known, although we use the value of the most recent study of Großmann (1999).

The individually charged fractions, i.e. positive and negatively charged, of stabilised Criegee intermediates (sCIs) are certainly dependent on the air ion mobility, which differs for both charges (Israel, 1960). In this context we aimed to get the neutral concentration from the totally charged sCIs, thus summing both and this effect is hidden in the average term for both polarities. The excess of a single polarity is determined by

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the charge affinity of the molecules and clusters of that size and by their lifetimes. This effect is obvious for the second size section (0.56-0.75 nm) throughout the year.

p. 13196: Sure. The lifetime is one of the critical parameters. However, please note the different approach of Tamm et al. (2006) assuming long-lived, well-mixed clusters instead of the short-lived radicals. Most likely their approach is valid above ca. 1.7 nm in mobility derived diameter only.

The term 'constant ion source' is meant differently. It refers to a production via a single way (sesquiterpenes + ozone) mainly. If there is any additional source reaction neglected so far, which can usually not be excluded, the approach overestimates the concentration of sesquiterpenes (maximum approach). This was aimed to investigate with the emission measurement intercomparison, which yielded similar values. Consequently we are confident in the assumptions stated and will reformulate "to be constant" to "to be formed by the same source throughout the year".

The misprints except below will be corrected for the final version.

p. 13177: No. We are not aware of the reviewers aim: The lifetime is the reciprocal sum of the individual sinks which are the following: (i) The sink because of chemical reactions ( $K_{chem}$ ), (ii) the condensation sink ( $CS$ ), (iii) the sink on forest surfaces ( $K_{forest}$ ) and the collision with further ions in different size sections  $j$  to neutralize ( $\sum_j \beta_j \cdot N_{j,ions}$ ).

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