

Dear Dr. Nizkorodov

We thank the referees for valuable comments on the manuscript “Acidic reaction products of mono- and sesquiterpenes in atmospheric fine particles in a boreal forest”. The comments were very useful, they have all been carefully considered when revising the manuscript and we think they improved the quality of our manuscript a lot. The changes made to the manuscript are described in detail below following the chronology of the comments by the respective referees.

Response to the comments from referee 1.

-Spelling and grammar has now been checked by the native English speaker.

-Abstract: The average, median and max/min concentrations of all measurements are now mentioned in the abstract.

-Sampling strategy has been described better.

-Appendix A1 has changed into Table 3.

-List of sampling periods has been checked and ordered.

-We are sorry about the mess in the table. Some dates were not correct. Some back-up filters were also included in the table. We accidentally uploaded a wrong table. There was no parallel sampling.

-The values below LODs were taken as half of the detection limit. This has now also been added to the text.

-In figure 2, the samples were considered to belong to the month where most of the sampling took place. The figure 2 was redrawn as requested by the referee 2. In cases of all the measurement values were below detection limit, monthly mean were left out from figure 2.

-The reviewer asked more specific information concerning the uncertainty, especially of the calibration curve. We added the following sentence to describe our procedure to the experimental section: “The samples were analysed, using external standards on a four-point calibration curve representing the entire measurement area. The uncertainty of the analysis based on duplicate analysis was less than 50% close to the detection limits, and less than 20% for higher concentrations. The uncertainties of average concentrations were added as standard deviations into table 1 and figure 2”.

- The reviewer asked us to add medians and standard deviations to the Table 2. The values were taken from the literature and the medians and standard deviations were not provided in the original papers by Warnke et al and Parshnitsev et al. In Kourtchev et al medians and ranges were given, but since this was the only one giving medians we decided not to include them.

-The reviewer reminded that we should keep in mind the work in recent years on volatility and influence of aerosol mass, which affect yields of the compounds with different vapour pressures. Therefore we added the following sentence: “Also background aerosols, often present in ambient air, complicates the comparison with smog chamber results. Pre-existing aerosol mass is known to effect yields of compounds with differing vapor pressures (e.g. Chan et al., 2007)”

P. 2858 line 2 . We rephrased the sentence as suggested by the reviewer.

P. 2858 line 7 Place where standard was synthesized was removed from the abstract

P. 2859 line 9. We added “occurrence of” to the sentence.

P 2860, line 19 The samples were analyzed in a negative ion mode.

P.2860 L19 The results of the efficiency tests are added. The efficiency of the denuder was checked by taking samples of more volatile organic compounds (aromatic hydrocarbons and monoterpenes) than measured in this study using pumped adsorbent tube sampling and their concentrations were found to be negligible after denuder.

P2861 L5: The word fast was replaced by the word “quickly” and in L10: matrice is replaced by matrix

P2861 L13: The standard deviation of detection limits was lower within compounds than between compounds. This sentence has been added to the text.

P2861 L23 for→as

P2861 The sentence in L26 has been removed

P2862 calcd→calculated

P2864 L.14: The reviewer wondered if other tree species, such as birch, would be responsible for limonene emissions in this area? This is indeed true. There are few birches in the area. The following sentence was added to the text:” There are also few birches growing in the area and birches emit limonene early summer (Hakola et al., 2001)”.

P2864 L. 24: with -> at. Kamen -> Kamens.

P2864 L28. typography checked, correlation changed to “somewhat correlated”.

P2865 L1: ‘averagely’ was changed to ‘on average’ as suggested by the reviewer

P2865 L8: References requested were added to the last sentence i.e. Warnke et al. 2006, Kourtchev et al.2008, Parshintsev et al. 2010

P2865 L18: The reviewer was worried about our comparison in VOC and acid concentrations although the measuring times were not matching together all the time. This is true and we clearly state that our calculated ratios are approximates only. We also added a sentence: “In the on-line VOC measurements, there were several breaks due to malfunction of the instrument and because the sampling times of the acids where sometimes several days, the overlapping of VOC and acid analysis are not complete. Thus comparing these seasonal means represents approximates only. However, since the daily variation in VOC mixing ratios is quite modest compared to the seasonal variability, it is justified to compare VOC and acid concentrations.”

The reviewer stressed that when comparing our data with previous smog chamber studies, we should be careful and consider differences in reaction conditions (seed aerosol yes/no, temperature) and quantification. We agree and added the following sentence:” Background aerosols, often present in ambient air, also complicated comparison with the smog chamber results. Preexisting aerosol masses are known to affect the yields of compounds with differing vapour pressures (e.g. Chan et al., 2007).” It is also mentioned in the text that temperature is a controlling factor in phase partitioning of organic acids. In addition to this we are not claiming these ratios are production yields, but only concentration ratios in the air.

P2866 L. 1-2: Limonic acid was detected by Glasius et al. in 2000 (Environ. Sci. Technol., 34, 1001). This reference has been added.

P2866 L5-6: Due to the large associated uncertainties the reviewer proposed to change "suggests" to "could indicate" or a similar term. This has been changed as suggested.

P2866 L. 27-28: The description of the sampler was asked to be moved to the experimental section. This was moved.

P2867 L25-26 The word "concomitant" is not the right word here, as noticed by the reviewer. We replaced it with the sentence "The results were compared with"

The standard deviations were added to the Table 1.

Table 2: The reviewer wanted to add medians and standard deviations to the Table 2. The values were taken from the literature and the medians and standard deviations were not provided in the original papers by Warnke et al and Parshnitsev et al. In Kourtchev et al medians and ranges were given, but since this was the only one giving medians we decided not to include them.

In Figure 1 the isomeric form of pinonic acid was added, but our standard for limonic acid did not specify the isomeric form.

Response to the comments from referee 2.

-The text has been corrected by native English speaker

-The reviewer was worried about our comparison in VOC and acid concentrations although the measurements were not completely overlapping. This is true and we clearly state that our calculated ratios are approximates only. We also added a sentence "In the on-line VOC measurements, there were several breaks due to malfunction of the instrument and because the sampling times of the acids were sometimes several days, the overlapping of VOC and acid analysis are not complete. Thus comparing these seasonal means represents approximates only. However, since the daily variation in VOC mixing ratios is quite modest compared to the seasonal variability, it is justified to compare VOC and acid concentrations. "We are not claiming these ratios are production yields, but only ratios in the air.

- When calculating the monthly mean values, the samples were considered to belong to the month where most of the sampling took place.

-We have added standard deviations to the figures and they are also tabulated. We removed figure 2, since we thought it is similar compared to the Fig.3. We added caryophyllenic acid concentrations to the fig.3.

-The reviewer 2 claims that "If terpenes and their acid products are derived from emissions from the industry (e.g., sawmills) then one would expect no correlations with aerosol. In addition, might it be possible that for some terpenes a local source would skew the concentrations towards the precursors. ." This is not true, they are strongly correlated as shown by Liao et al. (2011). Aerosol particle concentrations substantially increased during episodes and monoterpene mixing ratios showed strong connections with Aitken mode particles both in number and volume concentrations. We added this to the text.

The reviewer 2 thinks that the correlation between caryophyllenic and caric acids are poor. They are not good, but we think that correlation exists and correlation coefficients are shown in figures. We added a word "somewhat" in front of "correlated" in the text.

The detailed corrections are all taken into account and corrected as suggested by the reviewer 2.

P2858 L6 inserted “respectively” in the end of the sentence.

L13 added “from”, L15 corrected “precursors”, “winter, indicating”

L16 added “the” in sentence “during the cold”., L24 added “,”.

P2859 L10 deleted “the”, L24 “the reaction products” was changed into: “specific acid reaction products”

From line 24, the paragraph is changed to: ”In this study, specific acid reaction products of biogenic VOCs, which affect the formation and growth of fine particles, were analyzed from ambient aerosol from boreal forest. Fine particle filter samples were taken at the SMEAR II station (Station For Measuring Forest Ecosystem-Atmosphere Relations; Hari and Kulmala, 2005) in Finland from June 2010 until October 2011.”

P2860: L6: changed to “The most common vegetation on the sampling site...”

L11 added “A”, “Before sampling, “ L16 added “a”, L24:”electrospray”...

L19: changed to: “Efficiency of the denuder was checked by taking samples of more volatile organic compounds (aromatic hydrocarbons and monoterpenes) than measured in this study using pumped adsorbent tube sampling and TD-GCMS analysis.”

P2861 L 3: ACN is defined, L17 “it’s” changed to “its”.

The reviewer suggested that “a brief paragraph should be provided for discussion of the standards and the details of the synthesis should be provided in the SI. “ We still think that because using of the authentic standards are one of the main things in the article, section 2.3 is needed and we would like to keep it as it is.

P2864: L4 sentence is corrected

L8 table A1→table 3

L13 added “emissions”, L28 changed into r^2 , there has been some technical issues with this.

L28 “precursors, i.e. they...”

P2865,L1 “averagely changed to “The average concentrations...”

P2865 L18: The reviewer was worried about our comparison in VOC and acid concentrations although the measuring times were not matching together all the time. This is true and we clearly state that our calculated ratios are approximates only. We also added a sentence: “In the on-line VOC measurements, there were several breaks due to malfunction of the instrument and because the sampling times of the acids where sometimes several days, the overlapping of VOC and acid analysis are not complete. Thus comparing these seasonal means represents approximates only. However, since the daily variation in VOC mixing ratios is quite modest compared to the seasonal variability, it is justified to compare VOC and acid concentrations.”

L8: added reference: “(Warnke et al. 2006, Parshintsev et al. 2010, Kourttchev et al., 2008)” .

P2866 L16 “quite” changed to “relatively good”

P2868: L2, “or” → “and/or”

The reviewer commented Figure 2: “I suggest spelling out “mean temperature” in the legend. Also I think it would be important to show the uncertainties of the measurements on this plot. Also it is quite difficult to see trends for individual species since a stacked bar graph is used. Perhaps a separate plot showing individual concentrations could be also presented here”. We removed figure 2 and added individual concentrations of all compounds in figure 3 (now figure 2), as suggested by the reviewer. The uncertainties are presented as standard deviations.

The reviewer commented Figure 4: “To be clear, the left side of the figure are the measurements from this study, and the right side is from the modeling study, correct? Please make this clearer in the plot and caption”. We have added which figure is which in Fig. 4.