

Answers to Referee #3

We thank the Referee #3 for the detailed comments and very constructive suggestions. We have corrected and improved the manuscript according to them. The referee comments are in bold, please find our answers in italic with the changes we have made to the manuscript in plain text. Updated figures 2, 6, 7 and A1 are separate files as well as added supplementary figures.

Patokoski et al. utilize a unique long term VOC data set at the SMEAR II site in Finland to analyze the possible sources of several long-lived atmospheric VOCs. HySPLIT 4.0 backwards trajectories were calculated to determine the sources of specific VOCs and the Unmix 6.0 receptor model was used to compare SO₂, anthropogenic and biogenic/combustion sources. The authors seem to have put together a novel study with relevant scientific results. However, several major issues should be reviewed and addressed to improve the quality of the presentation of the data. Of primary concern is the almost complete lack of statistical rigor. For example, in Section 3.3, p-values are stated as being equal to zero rather than less than 0.05, which was revealed in a later sentence. P-values should be stated here as well as in Fig. A1.

We thank the Referee for pointing out this inconsistency. We have revised the figure to indicate if the p-values are smaller or higher than 0.05.

More importantly, statistics are missing from almost the entire rest of the paper. The exception is within the discussion of long-term VOC trends (e.g. Table 6). Within the discussion and the conclusion statements were made using this data even though there was no statistical significance. If there is no significance, it should not be stated that the values changed over time.

We have added the results of statistical test to where they are applicable, e.g. Table 5. Our conclusion concerning the long-term trend (over six years) is that there is no significant trend. In the analysis our null hypothesis was that there is no trend in VOC VMRs and because the calculated trends are not statistically different from this zero trend, the null hypothesis remains valid.

We agree with the Referee and removed the discussion dealing with trends from the text: "...These trends are all slightly negative, except for a slightly positive trend for monoterpenes. For monoterpenes the VMR change was 8% per year for the summer monthly medians. However, one should interpret these trends with care, because they were calculated based on measured summer monthly medians whose trends were not, in fact, statistically significant (i.e. the confidence intervals included zero)."

Another major issue is the organization of the paper. Methods were often included in the results and discussion sections and the conclusion section was mainly a simple recap of the paper rather than extending the significance of the papers findings. The description of source areas in section 3.4 (page 14607 line 23) is a good example of method details that were placed in the results section.

We have re organized the paper to make it more fluent.

We added description of wider significance to the conclusions:

“The trajectory analysis indicated the importance of especially Eastern Europe and Russia for elevated VMRs of long-lived VOCs in Southern Finland, and lack of significant sources in Scandinavia and North Sea.”

“Both the trajectory and Unmix analyses showed that air masses coming from a northerly direction had fewer pollution events with the studied trace gases than the air-masses arriving from easterly and westerly directions with higher anthropogenic influence. The long-range transport from easterly directions may explain at least partly the lack of declining trend in the VOC VRMs observed here and by Hellén et al. (2015) in northern Finland, in spite of emission reductions in European Union. The result stresses the importance of global emission reductions for cleaner air.”

“This study showed that forest fires can cause elevated levels of atmospheric VOCs hundreds of kilometers downwind, and can pose a threat to the air quality. With changing climate the frequency and strength of forest fires are expected to increase. Thus any efforts to prevent forest fires or develop early detection and extinguishing methods would be beneficial for future air quality and health.”

We added to the methods, end of the section 2.3 Trajectory analysis, description of the the source areas selection method:

“We selected ten square shaped source areas for a further comparative study. The selection of source areas for further analysis was done subjectively, based on the trajectory maps and demographic information and information on industry and other possible sources in different geographical areas.”

Detail on the Unmix model at the beginning of 3.5 is another example of methods in the results/discussion.

We moved three sentences from section 3.5 to the to the methods part to the end of the section 2.5 Unmix 6.0.

“For the Unmix analysis, VOC VMR and trace gas data were divided into three sectors according to the wind direction measured at SMEAR II. The division was made based on the findings of the VOC source fields as revealed by the trajectory analysis and described above in section 3.4. The three sectors were: (1) North (0°-5° and 300°-360°), Urbanized continental (5°-210°) and Urban and sea (210°-300°).”

Lastly, it seems that the inclusion of monoterpenes is forced into the paper and should be removed, since it is excluded from most of the analyses and doesn't add enough to the one section to be included in the entire paper. It also does not fit with the Title of the paper.

Similarly to temperature and inorganic trace gases, such as CO, SO₂ and NO_x, monoterpenes are used as ancillary data in the comparison to the anthropogenic VOCs source. However long lived VOCs are the main focus of the study and we feel that the title represents the manuscript.

The presentation of the hypotheses starting on page 14596 line 20 are confusing, several seem to be rather similar. It might clear it up to closely follow the section heading used in the paper.

We clarified the hypothesis and changed their order. See also the answers to the referee #2.

Regarding the use of the PTR-MS, I have two questions/concerns. First, did the 4 VOC mixtures used contain all of the VOCs in this study?

Yes, the VOC mixture used in calibrations included all VOCs in this study.

We added a sentence to clarify this:

“Calibration gas mixture included all the studied compounds.”

Although PTR-MS does have a low fragmentation profile compared to other techniques there are clustering issues that should be accounted for, either by using standards or accounting for clustering ions (such as m/z 51 for methanol). Secondly, did you account for water clustering in your calculations? Low E/N ranges can increase the clustering of reagent clustering (see de Gouw et al. 2003 “Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry” and others) and if they are not accounted for will cause over calculations of VMRs.

The fragmentation and clustering are taken into account in VMR calculations and we added a sentence to the text:

“Thus the fragmentation and clustering was always taken into account when calculating VMRs.”

In general there were many grammatical errors within the paper. Tenses were often changed throughout the paper between past and present instead of staying in the past tense (e.g. Page 14605 Lines 20-23). Also, the use of “e.g.” was often used in place of a description/statement rather than as an example of a description/statement (e.g. Page 14598 Line 4). Prepositions were often missing throughout the paper.

Thank you for the comment, the manuscript was proofread and we hope it improved the readability of the text.

Some specific comments/questions:

+ Page 14598 Line 24 – move “were measured” to after “seven masses”.

Yes, we moved “were measured” to after “seven masses”.

+ Page 14599 Line 1 – What about the years from 2009 to 2011? It is unclear from this paragraph.

In line 7 is said that

“...in May 2010 sampling protocol changed when the instrument was transported to the another hut. At the same time the sampling inlet was moved about 50 m to another tower, 33.6 m above ground.”

We added a sentence after that to clarifying where the measurements were done during 2009-2011:

“This sampling height was used for measurements during years 2010-2011. During the years 2010-2011 the atmospheric VMRs used in this work were measured every third hour.”

+ Page 14599 Line 21 – were these measured at 33m throughout the entire experiment?

The other trace gases than CO were measured from 33 m throughout the entire experiment. Only CO was measured from 16.8 m in 2010.

+ Page 15602 Line 4 – it is unclear what observations are being referred to in this sentence.

*We meant the observations by Rinne et al. (2012) and clarified that to the text:
“The summertime OH concentration presented by Hakola et al. (2003) agreed well with the observations by Rinne et al. (2012). . . .”*

+ Page 15602 Line 1 – Why wasn't the OH and NO₃ concentrations estimated the way the O₃ concentrations were?

The O₃ concentrations were measured directly while as the OH and NO₃ concentrations are orders of magnitude smaller and were not measured during the observation period. Thus we had to rely on the estimations of concentrations concerning the OH and NO₃ concentrations. The estimates were adjusted based on the available observations as described in the text.

+ Section 3.3 – It is unclear why there is such a concentration on SO₂ and not much mention of other trace gases or VOCs. Others should be included or the section should be renamed.

We removed sentences from the end of this paragraph:

“According to the EMEP database SO₂, emissions in the European Union have decreased from about 25.8 to 4Gg over the period 1990–2012. Emission data from Eastern Europe for the same time period is scarce. Riuttanen et al. (2013) also observed a general decreasing trend of SO₂ of -5.2% per year at SMEAR II during 1997–2008. Anttila and Tuovinen (2010) observed a decreasing trend of SO₂ of -2.2% 20 per year for the whole of Finland during the years 1994–2006.”

The VOCs and the other trace gases are studied in the beginning the section 3.3 and thus renaming the section is not needed. SO₂ is discussed in more detail since it is an important tracer and has been studied a lot and in this study it supports the analysis of different VOC sources such as burning and traffic as well as removal processes.

+ Page 14607 Line 21 conflicts with the statement made on Page 14609 Line 9-10. Are they different or similar?

Thank you for pointing this out. We apologize and removed a word a similar from the sentence which is on the page 14609 line 9-10.

+ Page 14609 Line 2 – It is unclear what is meant by “the latter”.

Yes, we agree that this is unclear and replaced “the latter” by “the background field”.

+ Tables and Figures – Statistics need to be included in most

Yes, this is true and we marked if the p-values are smaller or higher than 0.05 to the Figure the A1. In Table 5 and Figure 7 we have now indicated if the differences are statistically significant.

+ **Figure 1 – “Medians of summer months” was a little confusing. It might be clearer to say “Median of each summer month”**

We rephrased this to the Figure 1.

+ **Figure 2 – Color the star (asterisk?) for the SMEAR II site a different color than the fire locations. It is difficult to see.**

We agree and we changed star to the white triangle.