Answers to the Referee #2

We thank the Referee #2 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.

General comments:

A source analysis excluding the fire events would be an important part of this manuscript to make sure that the results are not masked by the fire events. From the text it is not clear for now if this analysis is shown or if the fire events were not removed (specifically in figure 5).

Thank you for pointing this out. In figure 5. all data has been used. The forest fire periods are removed from seasonal analysis (summertime) analysis. Figure 5. shows all analyzed source areas and forest fire episodes are included in the Figure in order to give the all-inclusive picture of VOCs sources. There are also probably other less pronounced forest fire events during our measurements so excluding the major forest fires from the analysis could be misleading. This further supports the inclusion of them in the source area analysis and Fig. 5.

The specific aims of the paper should be clearer. The reader expects those to be the main questions that will be addressed in the mentioned order. In this manuscript many big specific aim items are given that are later mostly mentioned in half sentences. E.g. specific aim (2) the biogenic vs. anthropogenic origin of the VOCs at the site is not well covered in the paper.

Thank you for pointing this out, we have clarified the aims to make them more explicit to the reader. The aims are now described in the revised manuscript as follows:

The specific aims of this study are (1) to identify the main source areas of VOCs observed at SMEAR II, (2) to investigate how these sources coincide with e.g. wildfires and biomass burning, and major urban and industrial areas and to (3) to determine the biogenic vs. anthropogenic influence by determining the source profiles of VOCs in relation to other trace gases.

Biogenic versus anthropogenic influence is studied by UNMIX, discussed and covered in section 3.5 and we conclude that the urban sectors contribute to high concentrations due to higher anthropogenic activity. However, the analysis of population density in the source area against VOC concentrations did not result in a significant correlation. We have added population density paragraph to the table A1. Biogenic influence did not depend so much on the source area rather on the season and thus biogenic activity was found to be higher during summer.

In specific aim (1) the reader is prepared to find some information about that beyond the fact that the correlations are not significant. The possibility that the trends are mostly influenced by temperature is interesting and should be investigated with the available data rather then just mentioned. Also, what causes the lack in significance of trend? Is it measurement uncertainty or is the available data series not long enough?

Thank you for your suggestion. We agree with the referee and we have removed the aim (1) and renumbered the remaining ones.

We studied the dependence of temperature and VMRs of studied VOCs by correlating temperature and monoterpene, methanol and acetone VMRs. Correlation coefficients were 0.79, 0.79 and 0.76 respectively for the whole data set including summers and winters. For summertime the respective correlation coefficients were 0.53, 0.30 and 0.58. Furthermore, we have done the trajectory analysis separately for summertime and wintertime (Supplement). The source field is broadly similar during winter and summer, even though in winter the continental air masses are associated with colder air and summer with warmer air.
However, correlation coefficients do not reveal if the correlation is due to causality or that two variable correlate with a third one. For monoterpenes the emissions are driven by temperature (Guenther et al. 1995). Whereas summertime biogenic methanol emissions are related to the expansion of cell walls (Jacob et al., 2005) during the growth at the start of the summer leading to a smaller correlation coefficient. Atmospheric acetone has various sources dominated by biogenic emissions and forest fires (Singh et al., 1994) coinciding with the warmest summers of the observation period. We added temperature to the Fig. 1 and the following to the text:

"The source areas of many/most VOCs are broadly similar in summer and winter-time (Supplement) even though in winter the continental air masses are associated with colder than average temperatures and in summer with warmer. This indicates that the temperature is not the main driver of the spatial patterns revealed by the source area analysis."

The reasons for lack of significant long term trend are the ones the Referee pointed out: VOC VMRs are often at the limit of detection and six years is rather short time period for this sort of analysis, so only very pronounced trends would show up. We agree with the Referee that our period is too shot to study trends. We have removed trend analysis from the text and the Table 6. as well as the trend lines from the Figure 1. Please also see answer to Referee 3.

Specific/technical comments:
Text in general: VOC VMR, VOCs VMR, VOCs VMRs and VOC VMRs are used in the text in different places. The authors should make sure their use is always grammatically correct.

Thank you for pointing this out. We corrected these to the text.

page: 14594 line: 5 It should be mentioned here that the method was the HYSPLIT 4 backward trajectory

We added to the backward trajectory method to the text
"HYSPLIT 4"

page: 14595 line:18 An article ("a" or "the") is missing for boreal forest

We added the article.

page: 14596 line: 13 "but in both measured" should be "but both measured"

We corrected this to the text.

page: 14596 line: 16 "long-lived VOCs" might be grammatically better then "long lifetime VOCs"

We rephrased "long lifetime VOCs" to "long-lived VOCs".

page: 14596 line: 21 long term changes in sources affecting the VOC concentrations was not possible as no significant long term trend was found. Specific aim (1) should be rephrased to the fact that only long term concentration changes were quantified but not the change of sources was investigated. Or at least it needs to state later in the text that you think you found that there were no long term changes in the sources.

We removed aim 1 which was: " to investigate long term changes in sources affecting the VOC concentrations and to quantify their trends (biogenic and anthropogenic) over six-year period…" Please see previous answer.

page: 14596 line: 29 Article is missing for "boreal climate zone"

We added the article.

page: 14597 line: 8 Article is missing for "boreal forest"

We added the article.

page: 14597 line: 9 Be consistent with the use of 'degree' in the description of the site location

Thank you for pointing this out. We corrected these to the text.

page: 14598 line: 15 Please explain what you mean with 'cancelling effects'. What is canceled on the measured VMRs?

"Cancelling effects" we mean that we are cancelling changed E/N effect on the measured VMRs. We added to the text "…..of changed E/N…." *and also added* "Thus the fragmentation and clustering was always taken into account when calculating VMRs."

page: 14598 line: 17 Technically more correct would be the usage of mass to charge ratio m/z as that is the measured quantity.

We added to the line 5 on page 14598 …."mass to charge ratio, m/z 33 (later denoted m)…"

page: 14598 line: 23 Please mention what kind of back trajectory (HYSPLIT 4.0) was used

We added **"**HYSPLIT 4.0**"** *to the text*

page: 14599 line: 28 "for the purposes" should be "for the purpose"

We rephrased "for the purposes" to "for the purpose"

page: 14601 line: 20 Does this statement together with the earlier statement that biogenic emissions are stronger in summer and anthropogenic emissions are stronger in winter infer

that all compounds other then benzene are mostly dominated by biogenic sources? This seems the case, as their annual trend resembles biogenic rather then anthropogenic trends.

These compounds are not originated only from biogenic sources. However also other sources such as forest fires and atmospheric chemistry have seasonality similar to that of biogenic sources.

We added to the text:
"…indicating the possible importance of biogenic and photochemical sources as well as other seasonal sources such as forest fires.."

page 14604 line 7. To make the point that acetonitrile is clearly coming from the burning areas the backward trajectory time and therefore the map should be extended into the area of the burnings. The backward trajectory does not reach all the way back to the burning areas in Russia. As lifetimes and reaction rates of acetonitrile (Table 3 & 4) are missing it is not clear if this could help or if acetonitrile lifetimes are too short to extend the method.

Thank you for pointing this out. Study focuses on the forest fires within observed trajectory fields/areas. This is not only due to the lifetimes of the studied compounds (acetonitrile has a long lifetime as discussed below) but also on the reliability of the trajectories, which is generally thought to be poor for period longer than four days. We clarified the figure 2. by pointing out which burning areas are studied in this manuscript.

We calculated lifetime of acetonitrile (which is in winter day 29 years, winter night 5300 years and in summer day 1 year, summer night 1500 years) and added the reaction rate coefficients to acetonitrile towards OH ($2*10^{-14}$ molec/s·cm^3) and NO_3($5*10^{-19}$ molec/s·cm^3)and lifetime to the Table 3 and 4.

We also recalculated lifetime acetaldehyde and corrected the reaction rate coefficient.

page 14605 line 5. At the beginning of this subsection (3.3) it has to be made clear if the whole measurement period includes or excludes the fire events!

We clarified this and added to the text:
"These include the forest fire episodes described above, as well as other more dispersed fires."

page 14605 line 12: It is not clear to me if the correlations in this section are for data with or without the fire period. As the fire periods are special events influencing acetonitrile and others (discussed previously) the reader expects in this section data that is removed from fire events to study the regular source fields. After removing the fire events (if not done so already) does acetonitrile still correlate similarly well to the methanol and the benzene group? If fire events were previously removed from this analysis (and Figure 5) this should be noted accordingly.

As we stated earlier in Figure 5. it was purpose to give a big picture of sources. Refer to the earlier answer to this in general comments.

page 14605 line 14: Why is this called Figure A1 and not Figure 6?

The figure is an appendix and it is named according to journal practices.

page 14605 line 20: Should this reference go to Figure 5 instead of Figure 4? As this section describes Fig 5.

Thank you for pointing this out. We changed the reference to the correct one.

page 14605 line 23: Also acetone and benzene seem to have higher values in the Northern area.

We clarified this to the text and rephrased the sentence from
"…except methanol and acetonitrile, the other VOCs do not have any elevated…." to
"…With the exception of methanol and acetonitrile, the VOCs did not have source areas in the Northern area.…."

page 14606 line 15. The acronym EMEP needs to be introduced.

*We added introduction of the acronym EMEP (*The European Monitoring and Evaluationing Programme*) in the text.*

page 14606 line 24. Why are fire episodes only removed for analysis in section 3.4 and not already in 3.3? Just as the authors argued that the fire events can mask other source areas that is true also in section 3.3 and should therefore be already excluded there.

As we stated earlier in section 3.3 there was purpose to give a big picture of sources. Fire episodes are one important source to be shown but there are certainly other fire events outside the selected periods and thus fire episodes were not removed in section 3.3 where the all data is discussed.

We rephrased the sentence from.
*"*Data of the short forest fire episodes were removed prior to this analysis so that they would not mask other source areas."
to "Data during the short forest fire episodes during summers 2006 and 2010 were removed prior to this analysis so that they would not mask the differences due to other seasonally altering sources."

page 14607 line 6 The authors mention a possible temperature dependence with the VOC VMR trends. Can this be investigated further? Can you show a temperature trend in your data? This would give the statement more value then just mentioning a possibility of a temperature trend. Very likely temperature measurements at the site were present for all times.

See answer in the general comments

We added to the page 14607 row 2 to the sentences:

"…The climatic conditions in summers during the measurement period were different from each other, which may have led to differences in biogenic source strength, source area distributions, and VOC VMRs…"

"…The source areas of many/most VOCs are broadly similar in summer and winter-time (Supplement) even though in winter the continental air masses are associated with colder than average temperatures and in summer with warmer. This indicates that the temperature is not the main driver of the spatial patterns revealed by the source area analysis.

Detecting the inter annual differences in source areas was problematic because e.g. in summer 2006 air masses arrived from Western Russia, but there were no arrivals from Central Europe. Summers 2006 and 2010 were both influenced by continental climate, and air masses arrived from Western Russia (area 1) bringing warm air as well as elevated VOC VMRs from the coinciding forest fires…"

page 14607 line 26: Why is this called Table A1 and not 6? It seems like a supplement was planned but not carried out. This should be fixed before final publication.

Yes, table A1 and figure A1 are Appendixes.

page 14609 line 11-25. It would be helpful for the reader that is not familiar with the region if the same numbers as used in Figure 6 are mentioned together with the area names in the results discussion so that reading and looking at the figures is made easier.

That's a very good suggestion. We added the numbers referring the areas.

page 14609 line 18. This statement seems to be true in summer not in winter. This should be noted in () at the end of the sentence.

We clarified this. The sentence reads now as:

"…From Fig.7, it can be seen that nearly all of the selected areas are sources of methanol especially in the summer."

page 14609 line 19. 'Eastern Europe' was not defined in the source areas in Figure 6 before. Be more specific which area you mean or at least mention all the areas as numbers that you define as Eastern Europe.

We added the numbers to referring the Eastern Europe to the text.

page 14610 line 9: Earlier was mentioned that the fire episodes were excluded for this analysis to eliminate possible masking of other source areas. But here (and in Figure 7) those periods appear again. Also why not show acetonitrile in summer? And the way you show acetonitrile in winter here is not useful because due to the high fire influence the other source areas are masked. (Too small to see in the plot)

Did you mean ….why not …..<u>in winter</u> and …acetonitrile <u>in summer</u> ? Unfortunately we have measurements of acetonitrile only during one of the winters.
We rescaled the Figure 7. However, the VMR values are very small outside fire episode and indicating that the influence of other sources to acetonitrile VMRs in Hyytiälä is very small and thus too low to be seen in the plot.

We also added a sentence to the end of Figure 7. caption:
"Forest fire data were removed from summer data and analyzed separately."

page 14611 line 25: What data is exactly used for figure 9? It was mentioned that this includes data from the urbanized continental sector. Is this data filtered by wind direction? Or how exactly did you come up for a filter for this data? And why did you choose to only show this particular sector? A wind rose of the site would be good.

The sector with most anthropogenic source influence was selected to show the clearest influence. The data used was selected by wind direction from urban continental area (5°-210°). Wind distribution has been studied e.g. Lappalainen et al. (2009) and Liao et al. (2011) and we added to the text, page 14612, line 14:
" Wind arrivals are distributed in all directions (Lappalainen et al., 2009)."

page 14611 line 25 to page 14612 line 5: It is not clear to me why this figure was chosen and what point the authors want to make with this. Any number of compounds, areas and seasons could have been shown so there should be a reason to why exactly this and what point it is supposed to make.

We chose monoterpenes as they are compounds with relatively short lifetime and thus represent the compound, which has local biogenic sources and is not influenced by long distance transport. Thus they are used in the comparison of biogenic and local anthropogenic source.
We added clarification to the text:
"Monoterpenes, representing local biogenic sources,…"

page 14612 line 14: Wind directions are mentioned here. It would be good for the reader to see a wind rose from the site to give this analysis more significance.

Please, see previous clarification about wind directions.

page 14613 line 1: Toluene is forgotten in the list. It was also discussed in this paper.

Thank you for finding this mistake, we added it to the text.

Figure 2: I would suggest a different color for the site to clearly distinguish between the fires and the star for the site location.

Good point, we have clarified the Figure 2 in the revised manuscript by replacing the red star for site location by white triangle, we have also added the white boxes to pronounce the areas which have been used in calculations. Thank you for pointing it out, this clarified the message of the figure.

Figure 3: It is not clear why the authors decided to multiply the data by factors of 10 or 100. Obviously this can be helpful if two compounds would not be able to be visible on the same color bar but not otherwise. E.g. in row 1 all are multiplied with 10 which is not necessary (same for row 3). In row two the multiplications are justified and can be kept.

We agree and clarified the figure caption to e.g. only benzene is multiplied in top row of Fig. 3.

Table 4: The lifetime of acetonitrile is missing.

We added to the table.

Table 3: Reaction rate coefficients of acetonitrile are missing.

We added to the table.

Table 5: Both SDs and std are used without explanation. Why use two different acronyms for standard deviation and not explain them. Decide on one and use it consistently!

Thank you for finding this inconsistency, we replaced std by SD and added the explanation ***standard deviation*** *for SD. In addition we have also indicated where the difference between VMR during the fire to pre-fire is statistically significant.*

Table 5: Why are not all VOCs shown in this table? It seems like acetone and acetaldehyde have similar source areas and should be taken into account both in this table and the discussion.

We added values for acetone and acetaldehyde to the table.

Figure 5: It is not clear if this data excludes fire events. If not it would be good to have an additional (similar) plot but without the fire events as fire events might include artificial correlations that are not part of typical correlations.

Please see previous answers. Removal of all forest fires during the period is not possible. Removing forest fire events from years 2006 & 2010 would be misleading and we might still see forest fires or something masked by them.

Figure 6: There are two rectangular boxes within area 1 with thinner line with. What do they mean? If not mean anything they should be removed.

These two boxes depict the forest fires events and we have colored them by pink in the revised manuscript. We changed it to the figure 6. caption also.

Figure 7: text to the left of the figure is too small to read. The text to the right is a bit better but still too small.

Yes, we agree and enlarged the fonts.

Figure 7: Acetaldehyde and acetonitrile should be zoomed in better. There is no need for a large negative value on the y-axis setting as there are no values there. That makes a lot of the plot white and the rest hard to see. Please change this.

Thank you for pointing this out. We scaled the y-axis again.

Figure 7: What do the negative numbers in the sources mean (many in yellow but also others present)? Does that mean these areas are sinks for given VOCs?

The value in Figure 7. is the difference from median. Negative values means that VMR from air arriving from these areas are lower than median VMR and positive values that VMRs of arriving air masses are higher than median. We clarified the figure y-axel to $VMR_{measured}$-$VMR_{interpolated}$ [ppb_v].

We added to the text:
"…the calculated differential source is clearly positive for nearly all compounds (Fig.~7). The negative differential source of many compounds in e.g. area 6 indicates that their VMRs are below the seasonal median in air masses arriving from this area…"

References:

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron,C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873--8892, 1995.

Jacob, D. J., Field, B. D., Li, Q., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H. B., and Guenther, A.: Global budget of methanol: Constraints from atmospheric observations, J. Geophys. Res., 110, D08303, 2005.

Singh H. B., O'Hara D., Herlth D., Sachse W., Blake D. R., Bradshaw J. D., Kanakidou M., Crutzen P. J. Acetone in the atmosphere: Distribution, sources, and sinks, J. Geophys. Res., 99, 1805–1819, 1994