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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sources of long-lived atmospheric VOCs at the rural boreal forest site, SMEAR II" *by* J. Patokoski et al.

Anonymous Referee #2

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The paper entitled "Sources of long-lived atmospheric VOCs at the rural boreal forest site, SMEAR II" presents one of the rare multi-year VOC datasets and analyzes trends and sources of the long-lived VOC species. Both HYSPLIT 4.0 backward trajectories and Unmix 6.0 receptor model are used to identify and characterize the sources. These methods are tested first on two events where elevated concentrations of fire related tracers were observed at the site and traced back to fires occurring in Eastern Europe and Russia. After evaluation of the methods they are applied to the entire data set so make conclusions on long lived VOCs and their seasonal source areas.

The paper has clearly improved from its last version but is in many places still needs attention to detail hence a large number of specific/technical comments

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).

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.

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?

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.

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

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

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

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

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

page: 14597 line: 8 Article is missing for “boreal forest”

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

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

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

page: 14599 line: 28 “for the purposes” should be “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.

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.

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!

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.

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

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

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

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

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.

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.

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.

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.

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.

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.

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)

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.

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.

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.

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

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

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.

Table 4: The lifetime of acetonitrile is missing.

Table 3: Reaction rate coefficients of acetonitrile are missing.

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!

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.

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.

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.

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.

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.

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 14593, 2015.