Dear Editor,

We thank the reviewers #2 and #3 for their detailed comments and very constructive suggestions. We appreciate a lot that they have worked so specifically. We have corrected and improved the manuscript according to them. Please find our answers to the comments in italic to the reviewer comments. The changes for the manuscript are marked by track changes.

Sincerely yours, on behalf of the coauthors,

Johanna Patokoski

Answers to the Referee #2

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 reviewer 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 reviewer 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·cm³) and NO_3($5*10^{-19}$ molec/s·cm³)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 …..in winter and …acetonitrile in summer ? 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

Answers to Referee #3

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 reviewer 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 reviewer 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, SO$_2$ 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 O_3 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 NO_3 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. SO$_2$ 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.

Sources of long-lived atmospheric VOCs at the rural boreal forest site, SMEAR II

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Abstract. In this study a long-term volatile organic ~~compounds~~ compound (VOCs) concentration data set, measured at the SMEAR II (Station for ~~measuring~~ Measuring Ecosystem–Atmosphere Relations) boreal forest site ~~at~~ in Hyytiälä, Finland during the years 2006–2011, was ~~investigated~~analyzed in order to identify source areas and profiles of the observed VOCs. VOC mixing ratios were measured using proton transfer reaction mass spectrometry. Four-day HYSPLIT 4 backward trajectories and the Unmix 6.0 receptor model were used for source area and source composition analysis. Two major forest fire events ~~, one in Eastern Europe and one in Russia ,~~ in Russia took place during the measurement period. The effect of these fires was clearly visible in the trajectory analysis, lending confidence to the method employed with this data set. Elevated volume mixing ratios (VMRs) of non-biogenic VOCs related to forest fires, e.g. acetonitrile and aromatic VOCs, ~~related to forest fires~~ were observed. Ten major source areas for long-lived VOCs (methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene) ~~were identified~~ observed at the SMEAR II site were identified. The main source areas for all the targeted VOCs were Western Russia, Northern Poland, Kaliningrad and the Baltic countries. Industrial areas in Northern ~~Continental~~ continental Europe were also found to be source areas for certain VOCs. Both trajectory and receptor analysis showed that air masses from Northern Fennoscandia were less polluted with respect to both the VOCs studied and ~~with~~ other trace gases (CO, SO_2 and NO_x)~~than~~, compared to areas of Eastern and Western ~~Continental~~ continental Europe, Western Russia and Southern Fennoscandia.

1 Introduction

Volatile organic compounds (VOCs) in the atmosphere have several sources, both biogenic and anthropogenic. On a global scale the ~~emissions of biogenic VOCs~~ biogenic emissions are estimated

to be an order of magnitude higher than the anthropogenic ones (Guenther et al., 1995). The main biogenic sources are forests (Simpson et al., 1999), ~~and~~ to a lesser degree, crops (Guenther et al., 1995), and algae in aquatic ecosystems (Fink et al., 2007). However, in ~~the northern latitude winter~~
~~and during~~ many circumstances, including winter in northern latitudes and air pollution events, anthropogenic emissions can be dominant. The most important non-biogenic VOC sources are traffic, biomass burning (especially forest fires), ~~the~~ extraction and refining of fossil fuels, and ~~the~~ evaporation of solvents (Blake et al., 2009). Once emitted, the VOCs may ~~be~~ are transported and oxidized in photochemical processes during this transport. The main oxidants for VOCs in the atmosphere are
ozone (O_3), and the hydroxyl (OH) and nitrate (NO_3) radicals (Atkinson and Arey, 2003). Depending on their reactivity with these oxidants, some VOCs have a relatively long lifetime, from a few days to a few months, and can be transported over long distances. In order to study this atmospheric transport and to identify the source areas of the measured concentrations, trajectory analysis has been widely used (Stohl, 1996; Stohl and Seibert, 1998).

~~In source areas~~, The source areas which VOCs are emitted ~~, for example, from forest fires (de Gouw et al., 2006) or industrial sourcesor, on the other hand, from~~ from may comprise of areas with well defined industrial sources, of densely-populated urban areas ~~: these have~~ with a mixture of various source elements such as industry, power plants and vehicles (Baker et al., 2008)~~. The locations of~~, or of areas with high biogenic emission rates. Furthermore, areas with forest fires may show up as important source areas during fire episodes (de Gouw et al., 2006). Thus, the importance of different source areas may vary temporally~~and spatially~~, due to ~~e.g.~~ seasonal variations in the biogenic activity of plants~~or~~, variations in anthropogenic activity or forest fire episodes, and meteorological conditions.

The SMEAR II (Station for ~~measuring~~ Measuring Ecosystem–Atmosphere Relations) site, located in a rural environment in a boreal forest in Southern Finland, has been used for two decades to investigate atmospheric processes leading to aerosol particle formation and growth. At this site winters typically are characterized by stronger anthropogenic influence e.g. from heating, whereas biogenic activity is more pronounced in the summer. There is ample evidence that biogenic VOCs contribute to these processes at this site (e.g. Tunved et al., 2006; Ehn et al., 2014). However, there is also evidence that emissions and atmospheric concentrations of some VOCs generally labeled as biogenic, such as monoterpenes, are occasionally affected by anthropogenic processes (Liao et al., 2011; Haapanala et al., 2012). ~~Many VOCs~~ Furthermore, many VOCs observed at the site, with a relatively long lifetime, are known to have both biogenic and anthropogenic sources. These VOCs include e.g. methanol, acetone and acetaldehyde~~which lifetimes for Southern Finland have been estimated to be in spring 16, 33 and 4 days, respectively by Patokoski et al. (2014).~~ As these compounds can be transported over thousands of kilometres, their atmospheric concentrations observed at SMEAR II are likely to be influenced by distant anthropogenic emissions in addition to more local biogenic and anthropogenic sources. Previously, Ruuskanen et al. (2009) have observed that there is ~~an~~ indica-

tion of long-range transport of VOCs from continental Europe to Finland. Also Hellén et al. (2006)

60 ~~studied the source areas of VOCs in Helsinki urban air, and found out~~ observed that most of the ~~benzene was~~ atmospheric benzene in urban site in Helsinki originated from distant sources. During long-range transport, the VOCs in air masses coming to the SMEAR II site are often at least partly oxidized. ~~The~~ Thus the observed VOCs may ~~thus have both primary and secondary sources~~ have also secondary chemical sources in addition to direct emissions.

65 The volume mixing ratios (VMRs) of VOCs have ~~earlier~~ been studied at SMEAR II earlier, e.g. by Rinne et al. (2005); Ruuskanen et al. (2009); Hakola et al. (2009, 2012) and Hellén et al. (2004). These studies have only made use of short data sets, with the exception of ~~that~~ those by Hakola et al. (2009, 2012), thus not allowing ~~a study of~~ for studies of variations from annual to inter-annual ~~variations.~~ scales. Of the two long term studies, Hakola et al. (2012) ~~made continuous measurements~~

70 ~~using~~ utilized continuous measurements by an in situ gas-chromatograph and Hakola et al. (2009) ~~using~~ used noon-time air samples and laboratory analysis~~, but in both measured only terpenoids~~. Both of these studies measured only terpenoid compounds with short atmospheric lifetimes. The analysis of source areas of oxygenated compounds with longer atmospheric lifetimes has not been ~~possible without employing larger data sets comprising several compounds~~ previously feasible, as

75 long-term data sets on VMRs of several compounds have not been available.

Thus our aim in this study is to ~~use VOC VMR data covering several years (2006–2011) and to~~ investigate the source profiles and source areas of relatively ~~long-lifetime~~ long-lived VOCs (methanol, acetaldehyde, acetone, toluene, benzene) observed at the SMEAR II site ~~. Winters are characterized by stronger anthropogenic influence e. g. from heating whereas biogenic activity is more pronounced~~

80 ~~in the summer.~~ by using VOC VMR data covering several years (2006–2011). The specific aims of this study are (1) to ~~investigate long term changes in sources affecting the VOC concentrations and to quantify their trends (biogenic and anthropogenic) over a six-year period, (2) to determine the biogenic vs. the anthropogenic influence from defining the source profiles of VOCs in relation to other trace gases for SMEAR II, (3) to identify the~~ identify the main source areas of VOCs ~~in~~

85 ~~air masses arriving from Northern Fennoscandia, Northern Continental Europe and Western Russia within the lifetime of the long-lived VOCs, such as acetone and benzene,~~ observed at SMEAR II, (~~4~~2) to investigate how these sources coincide with e.g. wildfires and biomass burning, and major urban and industrial areas ~~. The~~ and to (3) to determine the biogenic vs. anthropogenic influence by determining the source profiles of VOCs in relation to other trace gases.

90 The focus of the research conducted at SMEAR II ~~'s focus is atmosphere-biosphere interaction and define~~ station is atmosphere-biosphere interactions and the aerosol formation and growth processes in the boreal climate zone. While many studies have focused on the influence of local to regional sources on the observed trace gases concentrations (Patokoski et al., 2014; Liao et al., 2011; Eerdekens et al., 2009; Hakola et al., 2009, 2012), this study aims at identifying source areas in

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95 regional to continental ~~source areas and focuses~~ scale and focuses also on characterizing the effect of long range transport.

2 Methods

2.1 Measurements site

~~VOCs~~ VOC VMRs were measured at the SMEAR II site in Finland during the years 2006–2011.
100 SMEAR II is a rural measurement station located in ~~boreal forest at~~ a boreal forest in Hyytiälä, Southern Finland ($61°51'$ N, $24°17'$ E, 180 m a.s.l.). A detailed description of the site is given by e.g. Hari and Kulmala (2005). The site is located 220 km north-west of Helsinki and 60 km northeast of Tampere~~which~~, which, with a population of about 200 000, is the largest city near the site. Continuous long-term measurements of trace gases, aerosol particles and gas exchange between the
105 atmosphere and the biosphere have been carried out at the SMEAR II since the mid-1990's (Vesala et al., 1998). The forest ~~surrounding~~ at the station is dominated by Scots pine (*Pinus sylvestris*), sown in 1962 (Bäck et al., 2012). There is also some Norway spruce (*Picea abies*), aspen (*Populus tremula*) and birch (*Betula* sp.) at the site (Hari and Kulmala, 2005). The canopy height is about 18 m. Within a square of $40 \text{ km} \times 40 \text{ km}$ centred on the station 23 % of the area is covered by pine
110 forests, 26 % by spruce forest, and 21 % by mixed forest (Haapanala et al., 2007). Agriculture and water bodies cover 10 and 13 %, respectively.

2.2 Instrumentation and sampling

The VOC VMRs were measured with a quadrupole proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria, Lindinger et al., 1998a). PTR-MS uses the hydronium ion
115 (H_3O^+) as a primary reactant ion. VOCs with a larger proton affinity than that of water will readily react with H_3O^+ (Lindinger et al., 1998a, b). ~~The PTR-MS uses a~~ This is a a soft ionization technique, and most compounds ~~hardly fragment at all~~ are not fragmented by it (Tani et al., 2003). The reactant and the product ions are mass filtered with a quadrupole mass spectrometer and detected with a secondary electron multiplier (SEM). Product ions are protonated~~and thus e.g. methanol~~, and,
120 therefore, methanol, for example, is identified at ~~molecular mass m~~ mass to charge ratio (m/z, later denoted m) m of 33. During the measurements ~~,~~ the PTR-MS was calibrated with a VOC calibration gas mixture at regular weekly or biweekly intervals. During the period 2006–2011 four different VOC mixtures, which all included 16–18 VOCs and were all manufactured by Apel-Riemer Environmental Inc., USA, were used. Calibration gas mixtures included all the compounds studied here.
125 A detailed description of the calibration procedure and the VMR calculation methodology is presented by Taipale et al. (2008). The following settings were used during the measurements: U_{drift} varied from 450 to 525 V (mean value 479 V), temperature of drift tube was 50 °C, E/N range varied from 105 to 130 Td (mean value 110 Td) and normalized sensitivity for e.g. acetone varied from

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18 to 40 ncps ppb$_v^{-1}$ (mean value 28 ncps ppb$_v^{-1}$). Detection limits for studied VOCs are presented in Table 1. The instrument was calibrated every time when settings were changed, taking into account the changes in the sensitivity and cancelling ~~effects on the~~ the effect of the changes in E/N to the measured VMRs. Thus the fragmentation and clustering was always taken into account when calculating VMRs.

~~Seven masses~~ Six of the measured masses were analyzed in this study: m 33, m 42, m 45, m 59, m 79, ~~m 93~~ and m ~~137~~93 a.m.u, which have been identified as methanol, acetonitrile, acetaldehyde, acetone, benzene, ~~toluene and monoterpenes~~and toluene, respectively (de Gouw and Warneke, 2007)~~, were measured.~~. In addition m 137, attributed to monoterpenes, was used as ancillary data in the analysis.

PTR-MS and GC-MS ~~concentration measurements~~ (Gas chromatography mass spectrometer) concentration measurements conducted previously in Hyytiälä have agreed well for monoterpenes (Rinne et al., 2005., Ruuskanen et al., 2005), as well as ~~of~~for methanol, acetaldehyde, acetone, benzene and toluene (Kajos et al., 2015). These VOCs, excluding monoterpenes, have relatively long lifetimes, and ~~the behaviour of their VMRs was investigated with~~ their sources were investigated with HYSPLIT 4 trajectory analysis and the Unmix 6.0 receptor model. One-hour median mixing ratios were calculated for the analysis. All the data are presented in local standard time (UTC +2 h). There are some gaps in the data due to maintenance, some technical problems, and the usage of the PTR-MS in other measurement campaigns (Fig. 1). Data quality was checked, and data were filtered by removing values below the detection limit. The detection limits for the measurement periods are presented in Table 1.

During the years 2006–2009 the VMRs of the VOCs were measured from a scaffolding tower at a height of 22 m above the ground. From summer 2006 to spring 2007 the measurement sequence consisted of one-hour of atmospheric VMR measurements followed by one-hour of disjunct eddy covariance measurements~~(Rinne et al.~~. Thus, ~~2007). Thus~~VMR data were obtained every second hour. The sampling protocol was changed in March 2007 when a ~~chamber with a~~ branch chamber measuring emission from a Scots pine shoot ~~enclosed~~ was included in the measurement cycle~~;~~. Thereafter the atmospheric VOC VMRs were ~~then~~ measured every third hour instead of every second hour. In May 2010 the sampling protocol was changed again when the instrument was transported to another measurement ~~hut~~cabin. At the same time the sampling inlet was moved about 50 m ~~to~~into another tower, with the inlet at 33.6 m above ground. 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. These measurement heights were chosen for analysis because they are more representative for ~~depicting concentrations due to transport, rather~~ atmospheric surface layer concentrations affected by e.g. long distance transport, than concentrations inside the canopy ~~. The canopy height was about 16 .~~which may be affected relatively more by local emission and deposition processes.

Nitrogen oxides (NO$_x$), carbon monoxide (CO), sulphur dioxide (SO$_2$) and ozone (O$_3$) mixing ratio data were used in the analysis as ancillary data. The mixing ratios of NO$_x$ were measured with a chemiluminescence technique (TEI 42C TL, Thermo Environmental Instruments, MA, USA), and CO was measured by an infrared light absorption analyzer (HORIBA APMA 360, Horiba, Japan).

170 SO$_2$ was measured with a fluorescence analyzer (TEI 43 BS, Thermo Environmental Instruments, MA, USA) and O$_3$ by an ultraviolet light absorption technique (TEI 49, Thermo Environmental Instruments, MA, USA). CO, NO$_x$, O$_3$ and SO$_2$ were also measured at a height of 33 m except in 2010, when CO was measured at 16.8 m.

2.3 Trajectory analysis

175 HYSPLIT 4 (HYbrid Single Particle Lagrangian Intergrated Trajectory) was used ~~for~~ to calculate the air mass trajectories (Draxler and Hess, 1998). The arrival height of the calculated trajectories ~~at SMEAR II~~ used for the analysis was 100 m a.g.l., thus representing air masses arriving at SMEAR II in the surface layer, in which the VOC VMR measurements were ~~made~~conducted in. Backward trajectories of 96 h (4 days) were calculated for every hour from 2006 to 2011. ~~For the purposes~~

180 ~~of the trajectory analysis the VOC VMR data were interpolated~~ In order to be able to remove the seasonal cycle from VOC VMRs, the monthly median values were interpolated for each hour of each day. The monthly median value was given to the day in the middle of the month and interpolation done for the periods between the mid-points of subsequent months using a Piecewise Cubic Hermite Interpolating Polynomial (PCHIP) ~~to cover every hour and thus match the trajectory data. Each time~~

185 in order to achieve a smooth curve.

Each time a measured VOC VMR data were available at SMEAR II, they were associated with a trajectory arriving at the site at the same time. The path of the back trajectories was considered with a $1° \times 1°$ spatial resolution. The VMRs were assumed to remain constant during the whole transport time. The grid cells over which ~~trajectories~~ a trajectory traversed prior to ~~the observation~~

190 ~~of high VMR values~~ its arrival at SMEAR II were associated with ~~high values~~in the source field. ~~Thus~~simultaneously measured VMR values. Finally, for each grid cell a single value for each VMR was obtained by calculating a mean of the VMRs from all the trajectories that have traversed it during the time period concerned (Stohl et al., 1995; Stohl and Seibert, 1998).

The differential source field was achieved by calculating first trajectory field using interpolated

195 monthly median VMRs and then subtracting this from the actual source field. Thus, the trajectory maps ~~are interpreted so that there is a color code corresponding to VMRs e. g. if there is an area in a map where methanol is observed to be~~ indicate the typical VMR of a given compound when the air mass is arriving to the measurement site from the grid cell in question. For example, if the color coding of a grid cell is 3 ~~this means that the measured value~~ ppb for methanol, this indicates

200 that the VMR of methanol measured at SMEAR II, when the air mass is arriving through this grid cell, is 3 ~~at the site is assumed to come from that area~~ ppb in average (see Figs. 3–5). The trajectory

analysis was limited to the area between 50 and 75° N in latitude ~~,~~ and 12 and 50° E in longitude. For reasons of statistical significance, at least 25 trajectories had to cross a grid cell in order for that grid cell to be accepted into the analysis, i.e., grid cells with less than 25 traverses were omitted from the analysis. ~~Finally, all the VOC VMRs at each grid cell were averaged to yield the VOC source field (Stohl et al. , 1995; Stohl and Seibert, 1998)~~

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.

2.4 Forest fire locations from satellite observations

The forest fire location data ~~are~~ were obtained from FIRMS (Fire Information Resource Managements System), which ~~delivers fire locations and hotspots as globally observed~~ provides fire locations as observed globally by MODIS (Moderate Resolution Imaging Spectroradiometer). Data have been collected by NASA's Earth observing system (EOS) Terra and Aqua satellites. With these two satellites global data coverage is achieved every ~~1 to 2~~ one to two days.

2.5 Unmix 6.0

Source compositions and contributions were investigated with the multivariate receptor model EPA Unmix 6.0 (Norris et al., 2007), developed by Ronald Henry at the University of Southern California. A ~~basic problem of~~ typical problem in multivariate receptor models is how to determine the optimal number of sources, the source fingerprints and their contribution from the ambient air VOC measurement data alone. ~~Some~~ Normally, some additional constraints must be added in order to obtain unique solutions. In Unmix, this is obtained by requiring the composition and contribution of the sources ~~must be~~ to be be non-negative. In addition to this, Unmix searches for periods when the data indicate that the contribution of one of the sources is missing completely or its contribution is minor. The application of Unmix to VOC VMR data obtained by gas chromatographic methods at an urban site in Helsinki ~~is~~ has been described by Hellén et al. (2003). According to the recommendations for the model, the regression of each of the species explained by the sources (R^2) should be over 0.8, while the signal-to-noise ratio should be over 2. In this study, Unmix was applied for inorganic trace gas and VOC VMR data, except for monoterpenes that were excluded also from the source area trajectory analysis (see Sect. 3.5). One-hour ~~medians of~~ median VMR values of inorganic trace gases and VOCs were used as input data to the model. Data were filtered by horizontal wind speed, excluding ~~from analysis observations (~~wind speeds below $1 \, \mathrm{m \, s^{-1}}$ from the analysis. As a result 30 % of data were excluded from ~~analysis) with wind speed below 1 . All~~ the analysis. All of the results exceeded the recommended R^2 and signal-to-noise values, indicating that the receptor modelling results ~~that~~ were applicable and valid.

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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 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°).

3 Results and discussion

The VOC VMRs of most ~~compounds which were studied~~ studied compounds have maxima in ~~summertime~~ summer and minima in winter (Fig. 1)~~. However, benzene behaves in the opposite way. This is~~, indicating the possible importance of biogenic and photochemical sources as well as other seasonal sources such as forest fires. Benzene, on the other hand, exhibited the opposite behavior, likely due to a lack of significant biogenic sources ~~of benzene~~ and its shorter atmospheric lifetime in the summer. Of the other studied VOCs, methanol, acetone ~~, acetaldehyde and the monoterpenes also~~ and acetaldehyde as well as monoterpenes have biogenic sources ~~in~~ and around the measurement site (Rinne et al., 2007)~~, and acetonitrile is emitted~~. Acetonitrile is emitted typically by biomass burning.

3.1 Lifetimes of the observed VOCs

To estimate the ~~VOC chemical lifetimes~~(chemical lifetimes, defined as e-folding times)~~),~~ of VOCs, OH and NO_3 radical concentrations ~~, were estimated , based on data from~~ were estimated based on the values presented by Hakola et al. (2003). The summertime OH concentration presented by Hakola et al. (2003) agreed well with the observations ~~(~~by Rinne et al. ~~,~~ (2012), ~~except in the case of~~ but the summertime NO_3 ~~, whose radical concentration is~~ concentration was at least twice as high as the observations. Thus, for this study, the annual cycle of NO_3 as presented by Hakola et al. (2003) was scaled by dividing it by two. Summer- and wintertime median O_3 concentrations were calculated from O_3 measurements at SMEAR II. Photolysis values for summer- and wintertime were calculated following Hellén et al. (2004). Actinic flux values corresponding to the albedo for snow-covered forest in winter (~~α = 0.8~~albedo = 0.8) were used when photolysis values were calculated. The concentrations of oxidants and reaction rate coefficients used in calculations are presented in Tables 2 and 3.

The calculated atmospheric lifetimes of the ~~studied VOCs~~ VOCs studied here (methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene) ~~in~~ for summer- and wintertime are presented in Table 4. Compared to the lifetimes of monoterpenes (about one day in winter and one hour in summer), these lifetimes were much longer. For most compounds, the atmospheric lifetimes ~~exceed~~ exceeded the duration of the back-trajectories used in this analysis. However, in summertime both toluene and acetaldehyde ~~have a lifetime below~~ had lifetimes shorter than four days. Thus, for these compounds ~~,~~ the results of the four-day backward trajectory analysis should be interpreted with caution.

270 ~~The following sections describe the source areas of the studied VOCs: (1) during long-range transport episodes from forest fires, (2) for all VOC VMR data and (3) for summers and winters separately~~In the following first the trajectories from the two major forest events are discussed. Second, the general features of the trajectory fields over the whole measurement period are presented. Third, the features and seasonal differences of sources in a set of selected areas are discussed.

3.2 Forest fire episodes in Russia in the summers of 2006 and 2010

During the measurement periods two particularly active forest fire episodes with several fire hotspots occurred in Russia, one in summer 2006 and the other in summer 2010. They also influenced air quality in Finland (Leino et al., 2014). These fires provide temporally and spatially well-defined sources of trace gases that can be used to evaluate the ability of the trajectory analysis to identify ~~the~~
280 such source areas.

Biomass burning has previously been observed to be a source of VOCs in several field and laboratory studies (e.g. Crutzen and Andreae, 1990; Holzinger et al., 1999; de Gouw et al., 2006; Virkkula et al., 2014). Acetonitrile has commonly been used as a marker compound for emissions from biomass burning (de Gouw et al., 2003, 2006; Holzinger et al., 1999). The oxygenated VOCs
285 (OVOCs) and aromatic VOCs (benzene and toluene) have also been linked to biomass burning in different studies (Koppmann and Wildt, 2007; de Gouw et al., 2006). ~~Forest fires affect air quality; and the biggest smoke plumes can be seen in satellite images and even reduce visibility in the plume areas.~~

Forest fires, which were observed during these measurements, occurred in the year 2006 in the
290 Vyborg area near the Finnish–Russian border and in year 2010 in the Moscow area (Fig. 2). The sum of all observed fires during the two episodes are shown in Fig. ~~2; in order to be visible on the map , the forest at the given location was not necessarily burning all the time. Lappalainen et al. (2009) observed an exceptional drought at SMEAR II during summerof 2006.~~ 2. Any particular fire location show in the map has not necessarily been burning the whole summer. During the summer of 2010
295 an unusually high temperature anomaly was observed in Eastern Europe (Twardosz and Kossowska-Cezak, 2013). ~~Williams et al. (2011) also reported unusually high temperatures at SMEAR II during summer 2010.~~ These circumstances can be favourable for the ignition and development of major forest fires.

In ~~summer~~ the summer of 2006 the largest fires ~~were~~ occurred south of Moscow and in Belarus.
300 There were also fires in Karelia, in Vyborg area near St. Petersburg and the Finnish-Russian border. The first forest fire episode occurring within the time-frame of this study was in the period of 4–31 August 2006. The trajectory analysis ~~shows~~ showed the high VOC mixing ratios observed at SMEAR II during this period to have originated from ~~that~~ the forest fire area (Fig. 3). Unfortunately, acetonitrile was not ~~being~~ measured during this period. ~~During this period~~ Anttila et al. (2008) also
305 observed elevated amounts of particulate matter mass (PM_{10}, $PM_{2.5}$) and higher polycyclic aro-

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matic hydrocarbon (PAH) concentrations during this period at Virolahti, located on the Finnish ~~south~~ southern coast near the Finnish-Russian border.

During ~~summer~~ the summer of 2010 a large number of forest fires were located in ~~Northwest~~ North-western Russia. The second forest fire episode within the time frame of this study ~~was~~ occurred in 20 July–31 August 2010. During this period acetonitrile data ~~too was being~~ was also measured at SMEAR II. ~~Comparing~~ By comparing the forest fire locations (Fig. 2) and acetonitrile's mean VMR field from trajectory analysis, one can see that acetonitrile is originating from the general direction of the maximum burning area (Fig. 4). All the other VOCs and trace gases studied also had similar source area distributions~~to acetonitrile~~.

For ~~comparison between fire and non-fire VOC VMRs~~ a comparison of VOC VMRs during fires and without fire, the mean VMR values of methanol, acetonitrile, benzene, SO_2 and CO were calculated for periods both before and during the forest fire episodes in both years (Table 5). In ~~,~~ 2006 the period from 1 to 31 July 2006 was selected to represent the situation before the forest fires. In, 2010 the period from 25 June to 15 July 2010 was used for the same purpose. In both cases concentrations were calculated using data, ~~filtered by trajectories , of air~~ chosen by trajectories which had traversed the ~~burning~~ fire areas. In this study, the forest fire areas were selected to be [~~27–36~~58–62° E, 58–62N, ~~27–36°~~ N~~E~~] (area 1) in 2006 and [~~28–34~~56–61° E, 56–61N, 28–34° N~~E~~] (area 2) in 2010. ~~Before the forest fire episode in year 2010, the VMR of acetonitrile was 0.06, while during the episode it was 0.13. Benzene too had elevated VMR levels in arriving air masses that had travelled over forest fires. In, 2006, benzene's VMR before the forest fires was 0.08 $_v$ and during the episode 0.17 $_v$; in 2010 the values were 0.05 and 0.09 $_v$, respectively. Acetonitrile and benzene have earlier been observed to be emitted from biomass burning (Holzinger et al., 1999; Simpson et al., 2011; Virkkula et al., 2014). Elevated CO concentrations were also observed in air masses associated with forest fires. Before the forest fire episodes, CO was measured at 128 $_v$ in 2006 and 111 $_v$ in 2010. During the episodes, CO concentrations were 154 and 152 $_v$, respectively. However, the mean VMRs of methanol did not increase during the fire episodes, which indicates that methanol at SMEAR II has other dominant sources, such as biogenic emissions from vegetation. is usually linked to fossil fuel combustion processes rather than biomass burning (Seinfeld and Pandis, 1998). In this study, too, the concentration in 2006 was actually lower during the forest fire episode than before it; in 2010 it was only slightly elevated during the episode.~~

Many of the VMRs of VOCs were 50-100% higher when the air mass was transported from active forest fire than before it. For example, ~~b~~Before the forest fire episode in year 2010, the VMR of acetonitrile was $0.06\,\mathrm{ppb_v}$, while during the episode it was $0.13\,\mathrm{ppb_v}$. Benzene also had elevated VMR levels in ~~arriving~~air masses that had travelled over the forest fires. In 2006, benzene's VMR before the forest fires was $0.08\,\mathrm{ppb_v}$ and during the episode $0.17\,\mathrm{ppb_v}$; in 2010 the values were 0.05 and $0.09\,\mathrm{ppb_v}$, respectively. ~~Acetonitrile and benzene~~Thesecompounds have earlier been observed to be emitted from biomass burning (Holzinger et al., 1999; Simpson et al., 2011; Virkkula et al., 2014).

Elevated CO concentrations were also observed in air masses associated with forest fires ~~but~~while the difference in NOx was not significant. ~~Before the forest fire episodes, CO was measured at 128 ppb$_v$~~

345 ~~in 2006 and 111 ppb$_v$ in 2010. During the episodes, CO concentrations were 154 and 152 ppb$_v$, respectively. However~~The mean VMRs of methanol did not increase during the fire episodes, which indicates that methanol at SMEAR II has other dominant sources, such as biogenic emissions from vegetation. SO_2 is usually linked to fossil fuel combustion processes rather than biomass burning (Seinfeld and Pandis, 1998). In this study the change inSO_2 concentration ~~in 2006 was actually~~

350 ~~lower during the forest fire episode than before it; in 2010 it was only slightly elevated during the episode.~~was to different directions for the two years, indicating other processes besides forest fires affecting the concentrations as well.

3.3 ~~Differences in~~ General features of source areas~~for the whole measurement period~~

The mean trajectory fields of the VOCs studied here (methanol, acetonitrile, acetaldehyde, acetone,

355 benzene and toluene), as well as those of CO, NO_x and SO_2 from the year 2006 to the year 2011 are presented in Fig. 5. These include the forest fire episodes described above, as well as other more dispersed fires. From this figure it can be seen that methanol, acetone and acetaldehyde had very similar source areas. There was very good correlation between methanol and acetone ($r =$ 0.86, ~~$p = 0$~~$p < 0.05$). Methanol and acetaldehyde were also correlated ~~to~~with each other ($r = 0.66$,

360 ~~$p = 0$~~$p < 0.05$). On the other hand, the source areas of benzene, toluene, CO and NO_x were ~~also~~similar to each other~~and correlated well~~. Acetonitrile had similarities with both methanol and benzene, correlating ~~, however,~~better with the methanol group than with the benzene group. Both are released in incomplete burning processes (section 3.1). The correlation matrix~~and~~, Pearson's correlation coefficients and p values between all compounds are presented in Fig. A1. All p values were below

365 0.05, except those for the correlations between methanol and ~~benzene,~~NO_x and ~~CO~~acetonitrile and acetaldehyde, which were statistically insignificant. Anthropogenically-influenced source areas (benzene, toluene, NO_x, CO) were observed in the northern part of ~~Continental~~continental Europe and Eastern Europe, Fennoscandia, Western Russia, and marine and coastal areas (Baltic Sea, Barents Sea, White Sea, Norwegian Sea and North Sea) (Fig. ~~4~~5). Northern Fennoscandia seemed to be

370 quite free of anthropogenic sources of VOCs. NO_x, CO and SO_2 concentrations were also low in air masses arriving from the north. ~~Except~~With the exception of methanol and acetonitrile, the ~~other VOCs do not have any elevated~~VOCs did not have source areas in the Northern area. The occurrence of forest fires in ~~Eastern Europe~~Russia is visible in the mean trajectory fields of all ~~data~~compounds. In addition to biomass burning, some small local emissions e.g. from traffic, wood combustion and

375 biogenic emissions may also have had an effect on the results.

The source areas of SO_2 were similar to those of NO_x and CO. The main source areas of SO_2 were Western Russia, Northern Poland and Kaliningrad, while NO_x and CO had additional source areas in Western Europe. Riuttanen et al. (2013) found a similar sharp distinction in SO_2 concentra-

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tions between air masses arriving from Eastern and Western Europe. ~~They~~ The study also found that air masses coming from Central Europe were exposed to more rain and~~thus~~, thus, were subject to the wet removal of SO_2. They ~~speculate~~ speculated that this may ~~be~~ have been one reason why SO_2 source areas in Central Europe were not separable in the trajectory fields. However, in this study we found that the also water-soluble methanol and ~~also~~ NO_x were not totally washed ~~away~~out during transport from Central Europe, as there were visible source areas for methanol in the North Sea, Skagerrak and the northern Germany areas, and for NO_x in Northern Continental Europe (Fig. 5). ~~We~~ Thus we propose that wet deposition does not fully explain the absence of SO_2 in the air masses arriving from Western Europe, as interpreted by Riuttanen et al. (2013), but that the observed difference in SO_2 is probably due to more rigorous emission regulations in the western part of Europe than the eastern part. This interpretation is supported by Vestreng et al. (2007), who observed a significant difference in the reduction of emissions of SO_2 between Western and Eastern Europe during years 1980–2004. ~~According to the EMEP database , emissions in the European Union have decreased from about 25.8 to 4 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 of −5.2 % per year at SMEAR II during 1997–2008. Anttila and Tuovinen (2010) observed a decreasing trend of of −2.2 % per year for the whole of Finland during the years 1994–2006.~~

3.4 Source areas and their seasonal difference

In order to study the possible seasonal changes in the VOC source areas, these were determined separately for the summer (June–August) and the winter (December-February) periods. Data ~~of~~during the short forest fire episodes during summers 2006 and 2010 were removed prior to this analysis so that they would not mask ~~other source areas~~the differences due to other seasonally altering sources. Although there was some inter-annual variation in the observed VMRs of VOCs, no clear trends of VMRs were observed during the whole measurement period (Fig. 1). ~~The long-term trends of selected VOCs based on the summertime medians of the VMRs of VOCs studied are presented in Table 6. These trends are all slightly negative except for that of monoterpenes that seemed to be slightly positive. 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). Summers were~~

The climatic conditions in summers during the measurement period were different from each other, ~~e. g.~~ which may have led to differences in biogenic source strength, source area distributions, and VOC VMRs. For example the median temperature between summers in Finland at Hyytiälä were observed to vary from 12.9 to 17 °C, which may have an effect on the biogenic emissions of VOCs such as methanol, acetone and monoterpenes (Fig. 1).

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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 interannual differences in source areas was problematic because e.g. ~~methanol, acetone and monoterpenes.~~ 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.

The fact that there is no significant trend in monoterpene VMRs indicates that it is unlikely for local biogenic activity to have a trend affecting the VOC VMRs. As the monoterpenes have atmospheric lifetime in the range of hours to days thus corresponding to the transport from local source areas, they would be most sensitive to show such an effect.

Additionally, in the case of monoterpenes' VMRs the change of the sampling location may ~~bias the trend calculated~~ hider an observation of a trend over the whole ~~observation~~ measurement period, as monoterpenes have a short life time (1 h; Table 4).

The source areas of the VOCs also varied slightly between years due to variations in the VOC VMRs, deposition and the prevailing paths of arriving air masses. Despite these differences, all five summers (2006–2008, 2010–2011) and two winters (2006–2007 and 2008–2009) were combined in this study ~~,~~ to get as good an areal trajectory data coverage as possible for summers and winters separately. Summer ~~,~~ 2009 was not included in the trajectory analysis because VOC VMR data ~~was then~~ were only available for 18 days.

For the evaluation of the ~~VMR~~ VOC source areas, ten rectangular areas were selected for separate analysis ~~of the trajectory fields of~~ during both main seasons (summer, winter) (Fig. 6). These areas differ from each other in having e.g. different ~~industry~~ industrial structures and population densities.

The ten selected areas were as follows:

(1) Western Russia [54–61° N, 29–40° E]. In this area there are two densely-populated cities, Moscow and St. Petersburg, and also harbours on the Baltic Sea. The area includes many different industries as described in detail in Table A1~~,~~.

(2) Northern Poland, Kaliningrad and Baltic countries (Estonia, Latvia and Lithuania) [53–59° N, 18–28° E]. This area includes the port of Gdansk, which is one of the important harbors in the Baltic Sea. Similarly to the Western Russia there is also a lot of industry in this area~~,~~.

(3) Karelia and the White Sea [63–66° N, 31–40° E]. This area is a significant Russian industrial area, ~~also including~~ including also large forests and the coastal areas of White Sea. Compared to the Western ~~Russia~~ Russian source area, the Karelia and White Sea area is more sparsely populated~~,~~.

(4) The Kola Peninsula and Barents Sea [66–70° N, 29–42° E]. This area is rich in minerals and is therefore an important Russian industrial area. Around the Barents Sea there is an active petroleum

industry (Austvik, 2007) with several oil drilling sites and oil tankers present on the Norwegian and Russian coasts. ~~Four different source areas for VOCs were then defined in Fennoscandia (Denmark, Finland, Norway and Sweden) : (5) The Bay of Bothnia 64–67 N, 20–25 E was separated off as its own source area, as there are several metallurgy plants there (Skellefteå, Luleå, Tornio, Raahe) and also wood and timber industry, (6) The coast of the Norwegian Sea and Northern Sweden 67–69 N, 13–20 E. In this area the notable cities in industrial point of view are Kiruna and Narvik. Kiruna has rich iron ore deposits and Narvik has a large port, (7) The Stockholm region 58–61 N, 15–20 E is one of the most important industrial areas in Sweden. Stockholm is also the largest city in Fennoscandia, with an important harbour, (8) The Skagerrak area 54–60 N, 8–14 E includes the surroundings of Goteborg, Malmö, Copenhagen and Oslo. In addition to the Stockholm area, the Skagerrak region is also significant from an industrial point of view. There are many important ports and diverse industry in this area, (9) In~~

(9) Europe's important offshore oil and gas fields are situated in the North Sea and coastal areas [52–58° N, −1–6° E] ~~are situated Europe's important offshore oil and gas fields~~. Norway, Denmark, Germany, the Netherlands and the UK are involved in oil production in the North Sea (EIA, International Energy Outlook, 2014). The coastal areas of the North Sea are also very densely populated~~;~~.

(10) Northern Germany [52–54° N, 8–15° E]. This is one of Germany's main ~~industry~~ industrial areas, with several important harbours such as Hamburg, Lübeck and Rostock.

To evaluate the influence of the selected source areas for the ~~studied VOCs~~ measured VMR VOCs, during summer and winter, ~~two different VOC VMR trajectory fields were calculated for each compound. The momentary VOC VMR trajectory field was calculated directly from the measured one-hour median values. The interpolated VOC VMR trajectory field was calculated from a linear interpolation of the monthly median values corresponding to the same time period. This interpolated VOC VMR trajectory field is called the background field in the following discussion. By subtracting the latter from the momentary field a~~ trajectory fields for the difference between the measured VMRs and the median seasonal cycle, defined as linearly interpolated values on monthly medians, were calculated for each compound. This is called differential source field ~~was obtained~~, with the seasonal trend ~~removed from the source area analysis~~ on VMRs removed from it. The average values of the differential source field for the ten areas listed above are presented in Fig. 7. Acetonitrile was included in the source area analysis in summer only, when forest fires occurred.

In urban areas ~~, VOCs mostly originate~~ VOCs originate mostly from traffic, but are also ~~evaporated from fuels and combustion~~ emitted from other combustion processes, evaporation of fuels, and various industrial processes (Reimann and Lewis, 2007; Hellén et al., 2006) ~~and from various industrial processes~~. The ten areas investigated here were mainly located in ~~similar areas having a lot of industry~~ heavily industrialized areas and/or ~~dense population~~ areas with high population density. The strongest source areas for all the VOCs studied were located in Eastern Europe including West-

ern Russia(1), Northern Poland, Kaliningrad and the Baltic Countries (2), Karelia and the White Sea (3). In these areas, 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. In addition to these source areas, which are common to most of the studied compounds, certain compounds have specific source areas of their own. Methanol is an abundant VOC in the atmosphere having many different sources, both biogenic and anthropogenic (Jacob et al., 2005). From Fig. 7 it can be seen that nearly all of the selected areas are sources of methanol especially in the summer. Eastern European source areas (1-3) were observed to generally be large emitters of OVOCs (methanol, acetaldehyde and acetone). This is in line with earlier observations by Hellén et al. (2004), who reported Eastern Europe to be an important emitter of carbonyls. In addition to these source areas, acetone and acetaldehyde also arrived from the areas of Stockholm, the Skagerrak, the North Sea and the coastal areas and northern Germany: all of these areas have emissions from traffic and solvent use related to various industrial activities. The oxidation of hydrocarbons and the primary biogenic emission are known to be the major global source of acetaldehyde (Singh et al., 2004); these sources have not, however, been taken into account in this study. Acetaldehyde also has a relatively short lifetime (1 days) during summer. These factors can add some uncertainty to this analysis of acetaldehyde. Benzene was also found to have sources in the Kola Peninsula area, most likely connected with the petrochemical industry and mining. However, the North Sea area with its active petrochemical industry did not appear as a distinguishable source area for aromatic VOCs in this study.

As seen earlier, when comparing the VMRs of VOCs before and during the forest fires, the mixing ratios at SMEAR II for benzene and acetonitrile were found to be significantly elevated during these episodes (Table 5), Fig. 7. The forest fires are a strong sources of most of the VOCs studied here. In 2010 acetonitrile's VMR difference from the background values was 0.07 ppb_v. In other source areas, acetonitrile's differential source was near zero (Fig. 7).

The areas with strongest differential source indicated anthropogenic sources. However, the vast boreal forest zone in Northern Europe is an important emitter of biogenic VOCs (BVOCs). Most BVOCS emitted from boreal forests are short-lived terpenoids, whose high atmospheric reactivity keeps their concentrations relatively low compared to those of e.g. OVOCs, with longer atmospheric lifetimes (Hakola et al., 2003). In this study, the forest regions were not identifiable

525   as well-defined source areas~~, but probably contributed~~ ; however, they probably did contribute to background levels. During summer there were minor source areas in the Baltic Sea, where there should be no anthropogenic sources. These interesting source areas could be ~~producing VOCs from~~ due to the production of VOCs by e.g. algae or cyanobacteria. However, the VMR levels of VOCs originating from algae are low compared to anthropogenic sources (Kansal et al., 2009)~~compared to~~

530 ~~anthropogenic sources~~. With the current data and analysis it is not possible to identify the source of these marine emissions. In the future ~~,~~ their origin could be clarified by using shorter trajectories and making measurements near the Baltic Sea, or by collecting samples from over the Baltic Sea.

3.5   Low concentrations from the north, urban influences from continents and seas

   VOC ~~sources~~ source profiles were analyzed with the Unmix 6.0 receptor ~~model. For the Unmix~~

535 ~~analysis, VOC VMR and trace gas data were divided into three sectors according to the wind direction at SMEAR II. The division was made based on the findings of the VOC source areas described above. The sectors were: (1) North (0–5 and 300–360), Urbanized continental (5–210) and Urban and sea (210–300)~~Model for different wind sectors. In all sectors ~~,~~ three distinctive sources were identified: (1) ~~A~~ a source containing mainly SO_2 ~~;~~ and thus this was named the SO_2 source,

540 (2) ~~A~~ a source containing toluene, benzene, NO_x and CO. These compounds are typical of anthropogenic emissions, and thus the source was named the anthropogenic source, (3) ~~A~~ a source containing oxygenated VOCs (OVOCs, methanol, acetone and acetaldehyde), acetonitrile and a portion of CO. This source was related to biomass burning and other biogenic emissions, and was named to biogenic/combustion source.

545   The mean contributions of ~~all these sources in the~~ these sources to VMRs with wind from different sectors were similar ~~in both seasons~~ within the seasons but there was a major difference between seasons. The contribution of the anthropogenic source was dominant in winter and the biogenic/combustion source in summer (Fig. 8). The dominance of the biogenic/combustion source in summer can be attributed to two processes. First, the biogenic/combustion source included acetoni-

550 trile, and high mixing ratios of acetonitrile were observed during forest fire episodes in summer~~, secondly~~. Second, this source included OVOCs which also have biogenic sources and thus higher VMRs during summer (Fig. 1). Biogenic emissions ~~are dominant at SMEAR II in summer. The~~ of the monoterpenes measured at SMEAR II are ~~mostly emitted from biogenic~~ dominant in the summer, and due to relatively short lifetime their VMRs are dominated by the local sources. How-

555 ever, from the time series of monoterpenes ~~it can be seen~~ we can see that there are occasionally notably high VMR peaks, which are known to have an anthropogenic origin (Liao et al., 2011) (Fig. 1). ~~Monoterpenes were not included in the trajectory and Unmix analysis because they differ from the other VOCs in this study in having a short lifetime from one hour to several hours and mainly local sources. A comparison of diurnal cycles~~

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560   In Fig. 9 median diurnal cycle of the anthropogenic ~~source and monoterpenes is presented in Fig. 9. Data in Fig. 9~~ VOC source is compared to that of the monoterpenes. The data are from the urbanized continental sector. Monoterpenes, representing local biogenic sources, had a considerable diurnal variation during the summer, with higher mixing ratios at night, and no variation in winter, as also observed in previous studies in similar ecosystems (Hakola et al., 2000; Rinne et al.,

565   2005). This is due to the diurnal cycle in the surface layer mixing and the night-time emissions of monoterpenes from coniferous trees. The aromatic VOCs have shorter summertime lifetimes as compared to winter, leading to lower anthropogenic source levels in summer. The contribution of the anthropogenic source in winter was about three times higher in all sectors than in summer. Both summertime and wintertime diurnal cycles of the anthropogenic source ~~show~~ showed a maximum at

570   night, possibly due to lower night-time mixing in the boundary layer. This diurnal cycle is similar to that of monoterpenes and indicates that there is local influence on the anthropogenic source.

Histograms of the source contributions, together with their mean, median and maximum values both in summer and in winter, are presented in Figs. 10 and 11. Many of these distributions are skewed, having a tail of high contribution values. Thus the mean and median values of these source

575   contributions may have large differences. The skewness of the source distributions also indicates that the simplest statistical parameters, such as mean and median, may not adequately describe the distribution of the sources or their contribution to the local atmospheric mixing ratios of these compounds. There were considerable differences between the source distributions from different wind direction sectors. Wind arrivals are distributed in all directions (Lappalainen et al., 2009). Air masses arriving

580   from the ~~North~~ Northern sector had in general lower mean source contributions than air masses from the Urbanized continental and the Urban and sea sectors. Particularly in the summer there was a tail of high contributions in the Urbanized continental and the Urban and sea sectors for anthropogenic source (maximum values were 17.2/4.7) and biogenic/combustion ~~sources~~ source (9.8/6.1), as compared to the North sector whose maximum contributions were 1.6 and 4.9 for the anthropogenic and

585   biogenic/combustion sources, respectively. ~~Hence~~ However, the median values were much closer to each other. This indicates that air masses from the north were ~~clearly less polluted with the trace gases studied~~ had fewer pollution events with high VOC VMRs as compared to the two other sectors. These results combined with the earlier observations in this paper support the conclusion that air masses related to the highest VMRs of long-lived VOCs observed at SMEAR II have their origin

590   in Russia and the Eastern European countries, the Northern part of ~~Continental~~ continental Europe and Southern and Central Fennoscandia.

4   Conclusions

This study has focused on identifying the source areas of the long-lived VOCs (methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene) measured at the SMEAR II site in southern Fin-

595 land, and to investigate the relative influences of biogenic and anthropogenic ~~compounds arriving in~~ sources to compounds arriving to Southern Finland from areas outside of the country. The analysis is based on a data set which consisted of several years (2006–2011) of VMR measurements of ~~OVOCs, acetonitrile, aromatic VOCs and monoterpenes. Annual trends of VOCVMRs based~~

600 ~~on summer monthly medians were presented for the measurement period. The trend of VMRs for monoterpenes was slightly positive. All the other VOCs had a small negative trend in their VMRs. Trend calculations showed, however, that none of these trends could be considered as significant. The~~ VOC. The origin and sources of the ~~VOCs observed~~ observed VOCs were analyzed by the trajectory model and a multivariate receptor model.

During the measurement period, two major forest fire episodes occurred in ~~Eastern Europe and~~

605 Russia. Elevated VMR levels for several VOCs and other trace gases were observed in air masses arriving from areas in which abundant fire counts were observed. This corroborates the applicability of the trajectory analysis as a method for identifying the source areas of these trace gases.

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

610 and North Sea.

Three sources (labelled SO_2, biogenic/combustion and anthropogenic) were ~~separated~~ identified by receptor analysis both in winter and summer. The biogenic/combustion source dominated in summer and the anthropogenic source in winter. Both the trajectory and Unmix analyses showed that air masses coming from a northerly direction ~~were less polluted with the trace gases studied~~ had fewer

615 pollution events with the studied trace gases than the air-masses arriving from easterly and westerly directions with higher anthropogenic influence.

~~Ten different source area regions were~~ 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

620 the importance of global emission reductions for cleaner air.

The ten source areas selected for further analysis ~~. All the source areas seemed to have~~ showed enhanced emissions due to the anthropogenic activity: most of the areas contained ~~with abundant industry~~ industrial activity. There were some differences in the importance of these source areas between summer and winter. Western Russia, Northern Poland, Kaliningrad and the Baltic regions

625 and Karelia turned out to be the most significant source area for all the VOCs. Benzene came mainly from areas related to the petrochemical industry, such as the Kola Peninsula, while acetone and acetaldehyde were related to areas where solvents are used in industry e.g. the Skagerrak and ~~North~~ Northern Germany. Forest fire areas stood out clearly as sources for all the ~~VOCs studied~~ studied VOCs and especially for acetonitrile. This study showed that forest fires can cause elevated levels of

630 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. Even though boreal forests ~~,~~ with their high OVOC emissions ~~,~~ ~~covered~~ cover large areas in the region, these forest areas were not specifically indicated as source

635   areas. However, they probably did contribute to the regional background levels. The level of SO_2 concentration showed a clear difference between Eastern and Western European source areas, which was not seen in water soluble VOCs ~~and thus, contributed to reduction in emissions . Some biogenic influence appeared in the Baltic Sea region in summer. One potential VOC emitter there could be algae or cyanobacteria, which would be worth studying in the future.~~ . Thus, the difference in the

640   SO_2 can be attributed to reduction of its emissions in Western Europe.

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Table 1. Detection limits (ppb$_\mathrm{v}$) for one hour averages of the measured VOCs during the measurement periods. Percentages of values below detection limit are presented in brackets.

VOC	DL1 (12 Jun– 26 Sep 2006)	DL2 (29 Nov 2006– 10 Jul 2007)	DL3 (12 Jul 2007– 22 Jun 2009)	DL4 (28 May 2010– 29 Dec 2011)
methanol	0.07 (1 %)	0.06 (1 %)	0.07 (1 %)	0.1 (3 %)
acetonitrile			0.004 (1 %)	0.005 (4 %)
acetaldehyde	0.02 (2 %)	0.02 (1 %)	0.02 (1 %)	0.03 (1 %)
acetone	0.02 (1 %)	0.01 (1 %)	0.02 (1 %)	0.03 (1 %)
benzene	0.005 (3 %)	0.003 (1 %)	0.005 (3 %)	0.006 (2 %)
toluene	0.02 (73 %)	0.01 (1 %)	0.02 (22 %)	0.02 (4 %)
monoterpenes	0.01 (3 %)	0.01 (19 %)	0.01 (4 %)	0.02 (12 %)

Table 2. Concentrations of hydroxyl (OH), ozone (O_3), and nitrate radicals (NO_3) used in the lifetime calculations of the VOCs.

Oxidants	winter [molecules cm^{-3}]	summer [molecules cm^{-3}]
[OH] day	5.5×10^4 [a]	1.5×10^6 [a]
[O_3] day/night	$6.8 \times 10^{11}/5.7 \times 10^{11}$	$8.6 \times 10^{11}/7.1 \times 10^{11}$
[NO_3] night	1.2×10^7 [a][b]	4.2×10^7 [a][b]

[a] Hakola et al. (2003). [b] rescaled based on Hakola et al. (2003).

Table 3. Reaction rate coefficients (k_{OH}, $k_{\mathrm{O_3}}$, $k_{\mathrm{NO_3}}$) and photolysis rates for the measured VOCs.

	k_{OH} [cm^3 molecules^{-1} s^{-1}]	$k_{\mathrm{O_3}}$ [cm^3 molecules^{-1} s^{-1}]	$k_{\mathrm{NO_3}}$ [cm^3 molecules^{-1} s^{-1}]	$k_{\mathrm{photolysis}}$ in winter [s^{-1}]	$k_{\mathrm{photolysis}}$ in summer [s^{-1}]
methanol	9.00×10^{-13} [a]		2.42×10^{-16} [d]		
acetaldehyde	1.50×10^{-12} [a]		2.72×10^{-15} [e]	1.50×10^{-6} [f]	3.27×10^{-6} [f]
acetone	1.80×10^{-13} [a]		3.00×10^{-17} [e]	2.32×10^{-7} [f]	4.85×10^{-7} [f]
benzene	1.19×10^{-12} [a]	1.70×10^{-22} [c]	3.00×10^{-17} [d]		
toluene	5.60×10^{-12} [a]	4.10×10^{-22} [c]	6.79×10^{-17} [d]		
monoterpenes	7.50×10^{-11} [b]	1.4×10^{-17} [b]	7.06×10^{-12} [b]		

Rate constants (k_{OH}, $k_{\mathrm{O_3}}$ and $k_{\mathrm{NO_3}}$) used in calculations in Table 4: (a) iupac preferred, (b) Monoterpenes' rate constants k_{OH}, $k_{\mathrm{O_3}}$ and $k_{\mathrm{NO_3}}$ were calculated as weighted averages of individual monoterpenes typical in SMEAR II (Hakola et al., 2003), individual k values (Atkinson, 1994), (c) Atkinson, 1994, (d) http://kinetics.nist.gov/kinetics/Search.jsp, last access: 17 January 2013, (e) Rinne et al. (2007), (f) Calculated similar to Hellén et al. (2004).

Table 4. Total atmospheric lifetimes (e-folding times) of the VOCs studied, daytime and night-time in summer and winter. Daytime values are the sums of lifetimes calculated towards O_3, OH and photolysis. Night-time values were calculated towards O_3 and NO_3.

VOC	total lifetimes on a winter day	total lifetimes on a winter night	total lifetimes on a summer day	total lifetimes on a summer night
methanol	~~234~~ 230 d	1 y	9 d	~~113~~ 110 d
acetonitrile	29 y	5300 y	1 y	1500 y
acetaldehyde	~~7~~ 5 d	1 y	~~2~~ 1 d	~~101~~ 100 d
acetone	48 d	88 y	15 d	25 y
benzene	~~177~~ 180 d	69 y	6 d	27 y
toluene	38 d	29 y	1 d	11 y
monoterpenes	1 d	3 h	1 h	0.9 h

Table 5. Mean VMRs of studied trace gases (ppb_v) and standard deviations (SDs) before and during the forest fire episodes in 2006 and 2010. The VMRs of the compounds were calculated from VMR data which were selected using trajectories from the burning areas. Area 1 is [58–62° N, 27–36° E] in 2006 and area 2 is [56–61° N, 28–34° E] in 2010. Asterisk indicates when VMR of a trace gas differs significantly from pre-fire VMR (two-sided t-test)

Compounds	in 2006 before episode	SD	in 2006 during episode	SD	in 2010 before episode	SD	in 2010 during episode	SD
methanol	4.9	0.78	3.2*	1.21	3.7	0.75	3.7	2.10
acetonitrile					0.06	0.01	0.13*	0.07
acetaldehyde	0.86	0.31	0.94	0.41	0.55	0.09	0.76*	0.40
acetone	3.0	0.40	3.0	0.88	2.0	0.32	2.8*	1.44
benzene	0.08	0.03	0.17*	0.13	0.05	0.03	0.09*	0.06
toluene	0.05	0.03	0.09*	0.07	0.21	0.09	0.28*	0.11
sulphur dioxide	0.23	0.14	0.16*	0.15	0.20	0.12	0.35*	0.42
Nitrogen oxides	1.3	0.56	1.3	0.51	0.60	0.47	0.47	0.28
carbon monoxide	130	5	150*	49	110	9	150*	45

Table A1. Main industries of source areas.

Source area	Main industries	Mean population density of area [persons km^{-2}]
1. Western Russia	Oil and gas trade, shipbuilding yards, machine building, heavy machinery, mining, ferrous and nonferrous metallurgy, chemical industry and energy and paper production[1]	55
2. Northern Poland, Kaliningrad and Baltic countries	Machinery and chemical industry: chemicals, petroleum and refining, shipbuilding and coal mining[2], forestry with wood and processed wood products, chemical, pharmaceuticals, plastic and rubber industry, metal and electronics industry[3]	63
3. Karelia and White Sea	Forest industry, ferrous and non-ferrous metallurgy, coastal areas of the White Sea: oil production and processing[4]	3
4. Kola Peninsula and Barents Sea	Mining, iron industry (iron-ore enterprises and separators), apatite production and other metal industry such as aluminum and nickel plants and smelters[5], petroleum industry[6]	5
5. Bay of Bothnia	Metallurgy and wood and timber industry[7]	15
6. Coast of Norwegian Sea and Northern Sweden	Machinery, metal industry and mining [7,8]	3
7. Stockholm area	Electronics and chemical industry, machinery[7]	48
8. Skagerrak	Machinery, metallurgy and chemical industry[7]	117
9. North Sea and coastal areas	Oil production[9]	358
10. Northern Germany	Chemicals, plastics, electronics and automotive industry[10], dockyards for shipbuilding, metal industry and machinery[11]	203

[1] Ria Novosti (2010); World Factbook (2014a); [2] World Factbook (2014b); [3] Industries (2014c); [4] Artic Centre (2005); [5] Hansen and Tønnessen (1998); [6] Austvik (2007); [7] Internship to industry (2009); [8] Bothnian green logistics corridor (2012); [9] EIA (2014); [10] GTAI (2013); [11] GTAI (2011).
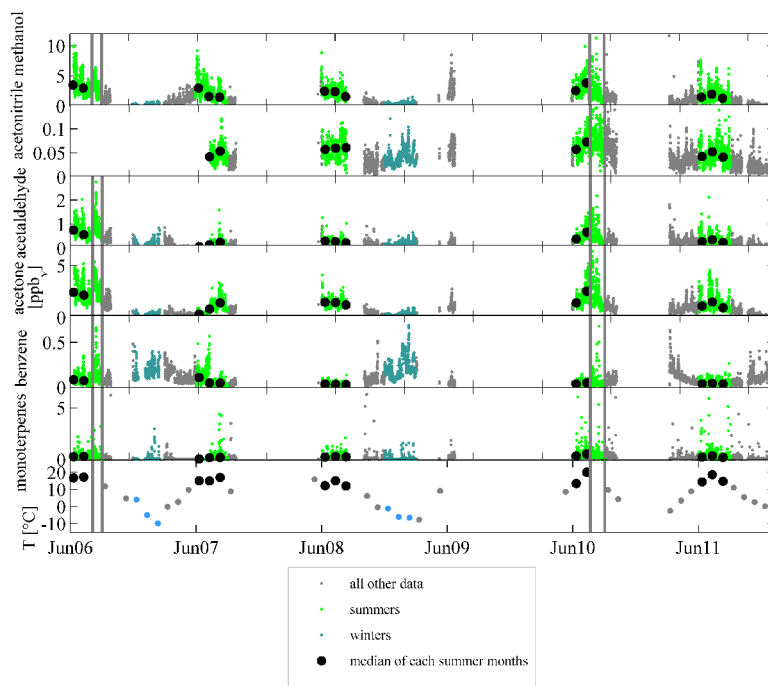
Figure 1. Time-series of the VMRs of the VOC studied during the measurement period. Summertime data used in source area analysis are marked in green and winter data in light blue. Data from other seasons are marked in grey. The monthly medians of the summer months are marked with black dots~~, and a linear fit based on summer-month medians is marked with a black dashed line~~. The forest fire periods in the summers of 2006 and 2010 are marked with grey vertical lines.
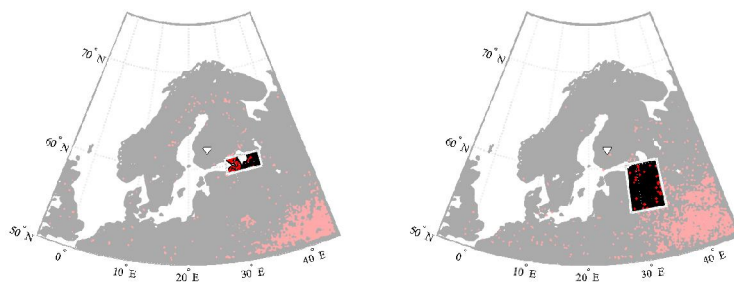
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Figure 2. Map of forest fire locations during the forest fire episodes of the summers of 2006 (left) and 2010 (right). In 2006, the forest fire event occurred during 4–31 August and in 2010 during 20 July to 31 August. These maps depict the sum of all observed fire spots during the burning periods, each being shown by a dot. Data of forest fire locations are taken from the Fire Information Resource Managements System (FIRMS). The SMEAR II site is marked by a ~~star~~ white triangle in the map.
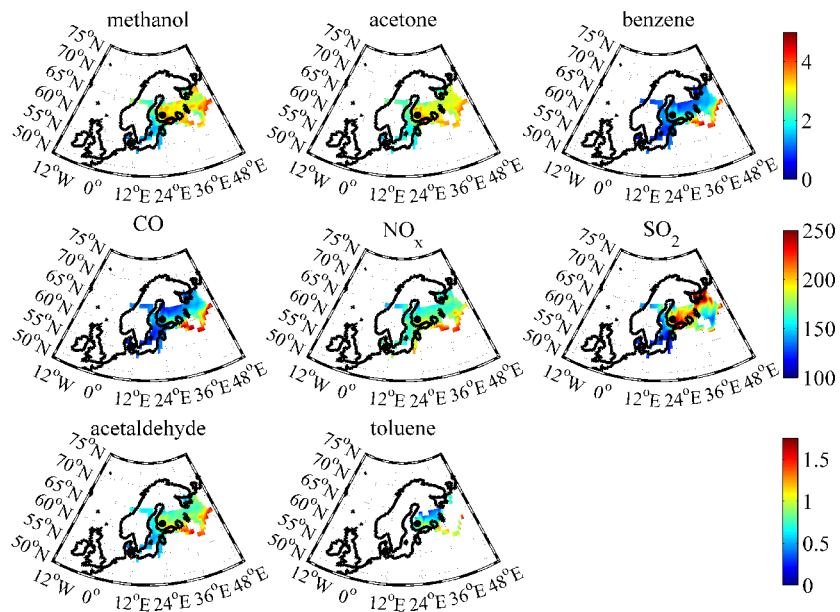
Figure 3. Mean trajectory fields for selected VOCs and trace gases (ppb$_v$) during the forest fires in summer 2006. VMR scales are presented on the right, with the scale for each compound being multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, acetone and benzene (benzene multiplied by 10). Middle row: CO, NO$_x$ (NO$_x$ multiplied by 10) and SO$_2$ (SO$_2$ multiplied by 100). Bottom row: acetaldehyde and toluene (toluene multiplied by 10). The SMEAR II site is marked by a dot in the map.
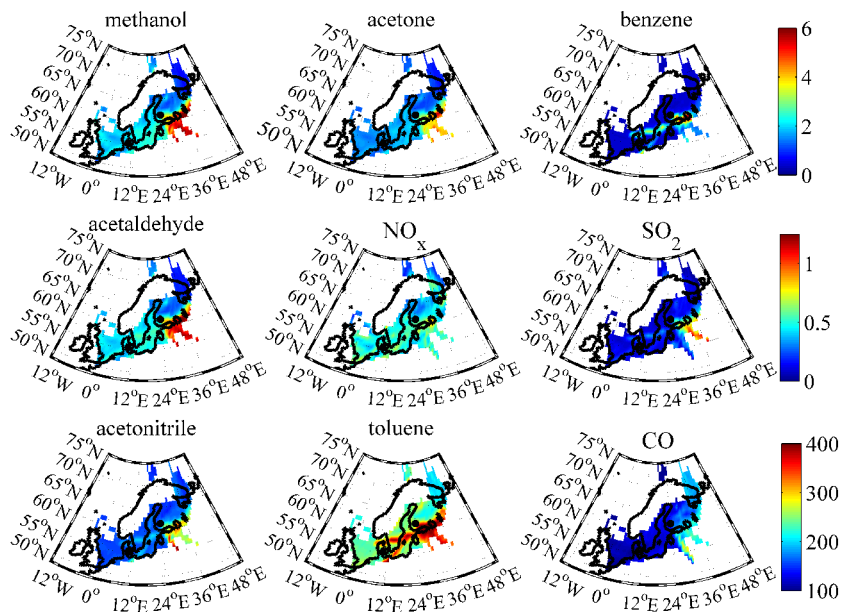
Figure 4. Mean trajectory fields for selected VOCs and trace gases (ppb$_v$) during the forest fires in summer 2010. VMR scales are presented on the right, with the scale for each compound being further multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, acetone and benzene (benzene multiplied by 10). Middle row: acetaldehyde, NO$_x$ and SO$_2$. Bottom row: acetonitrile (acetonitrile multiplied by 1000), toluene (toluene multiplied by 1000) and CO. The SMEAR II site is marked by a dot in the map.
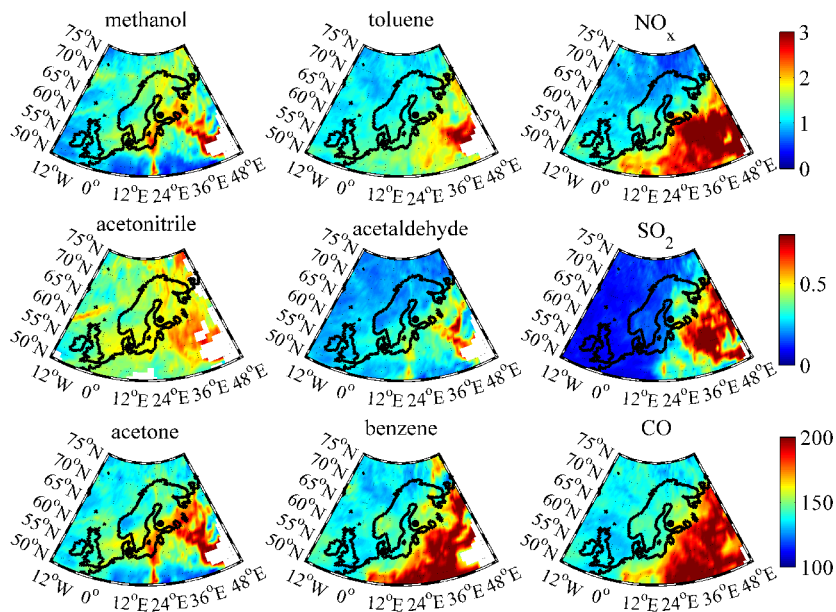
Figure 5. Mean trajectory fields (2006–2011) of selected VOCs and trace gases (ppb$_v$). VMR scales are presented on the right, with the scale for each compound being further multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, toluene (multiplied by 10) and NO$_x$. Middle row: acetonitrile (multiplied by 10), acetaldehyde, SO$_2$. Bottom row: acetone (multiplied by 100), benzene (multiplied by 1000) and CO. The SMEAR II site is marked by a dot in the maps.
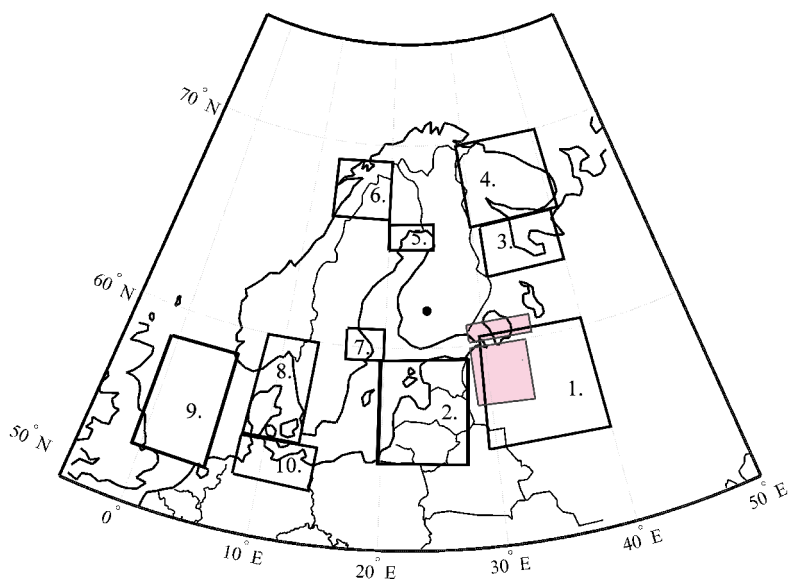
Figure 6. Main source areas of VOCs: (1) Western Russia, (2) Northern Poland, Kaliningrad and Baltic countries, (3) Karelia and the White Sea, (4) Kola Peninsula and Barents Sea, (5) Bay of Bothnia, (6) Coast of Norwegian Sea and Northern Sweden, (7) Stockholm area, (8) Skagerrak, (9) North Sea and coastal areas, (10) Northern Germany. Two forest fire source areas, limited in time, are marked by ~~grey~~ pink boxes. These are treated separately for the episodes (see Table 5) The SMEAR II site is marked by a dot in the map.
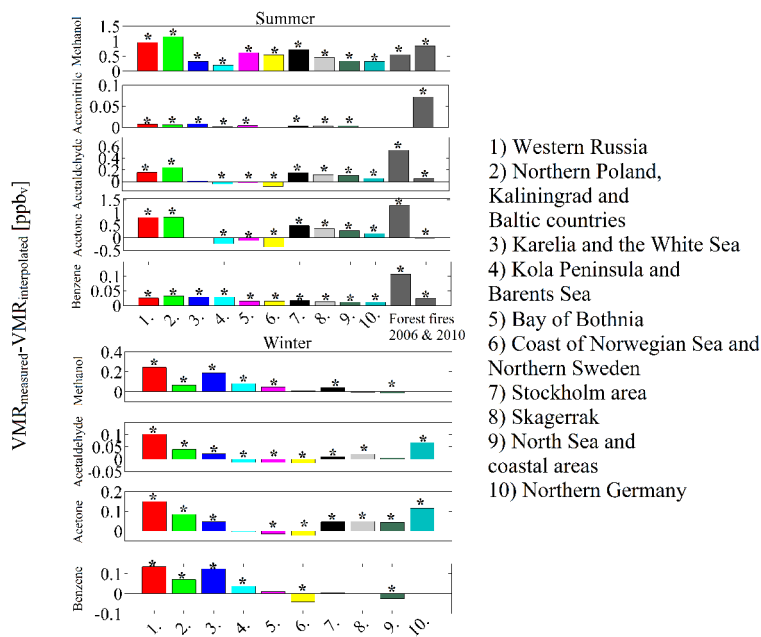
Figure 7. Differential source fields VMR$_{measured}$-VMR$_{interpolated}$ (ppb$_v$). Hourly VMR values of source areas interpolated from monthly medians were subtracted from directly-measured hourly values of source areas during summer (upper panel) and during winter (lower panel) for methanol (m 33), (acetonitrile (m 42), in summer only), acetaldehyde (m 45), acetone (m 59) and benzene (m 79). Forest fire data were removed from summer data and analyzed separately. Asterisk indicates when differential VMR fields of a trace gases differ significantly from zero (two-sided t-test).
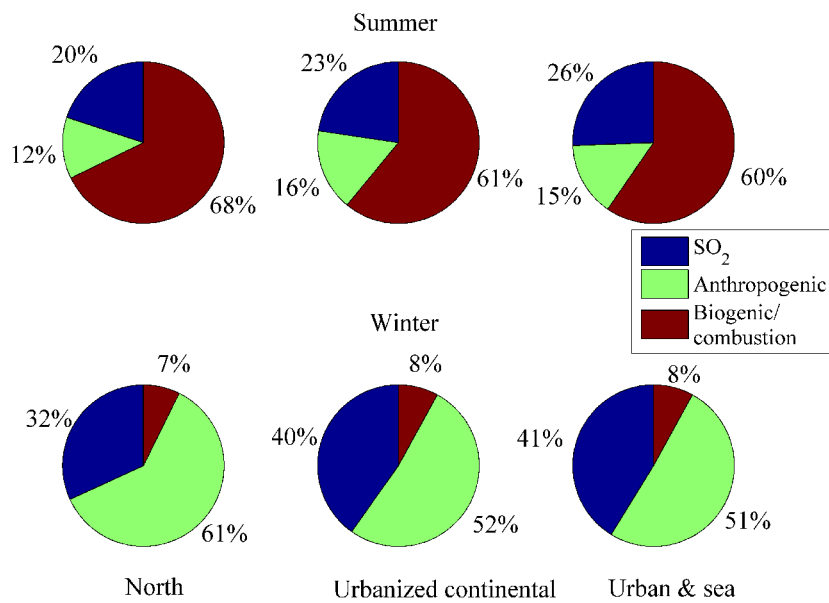
Figure 8. Pie charts of mean values of sources in each sector during summer (June–August) (topmost row) and during winter (December–February) (bottom row). The North sector includes data from direction 0–5 and 300–360°, Urbanized continental from 5–210° and Urban and sea sector from 210–300°.
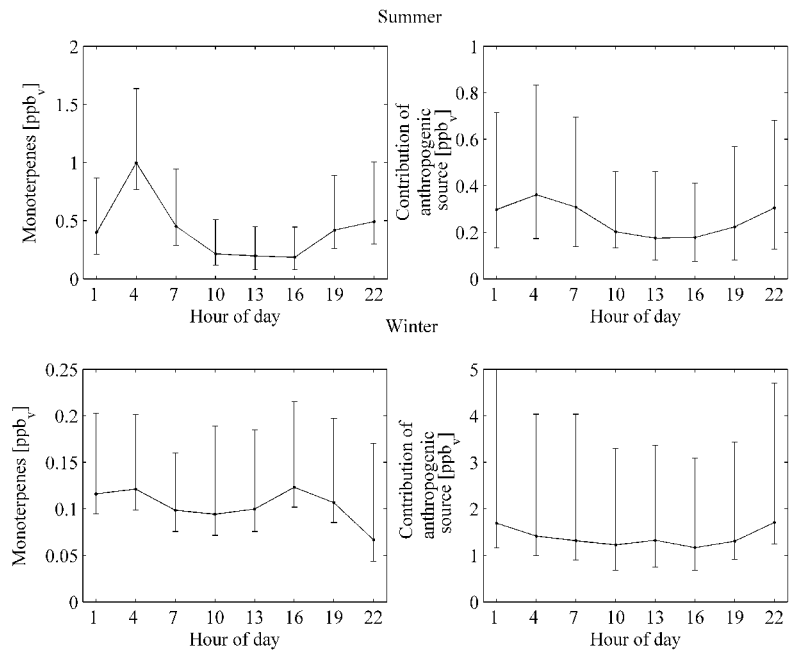
Summer

Winter

Figure 9. Diurnal cycles of monoterpenes (left) and the diurnal cycle of the anthropogenic source's contribution (right) in summer (top row) and in winter (bottom row) are presented as mean values and 20 to 80 percentiles. Data in all figures are from the urbanized continental sector.
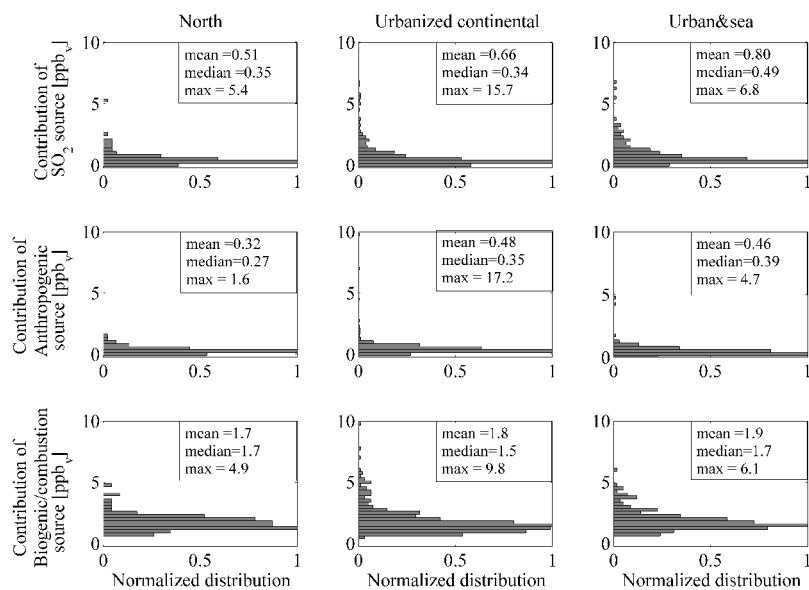
Figure 10. Normalized distributions of different sources in three sectors during the summer. The first column is the North sector ($N = 338$), the second column is the Urbanized continental sector ($N = 1817$) and the third column is the Urban and sea sector ($N = 952$). In the topmost row all panels are distributions of the SO_2 source, the middle row the anthropogenic source and the lowest row biogenic/combustion source. Each sector has been normalized with the maximum value of the observations. Mean, median and maximum values of source contributions are shown for each sector.
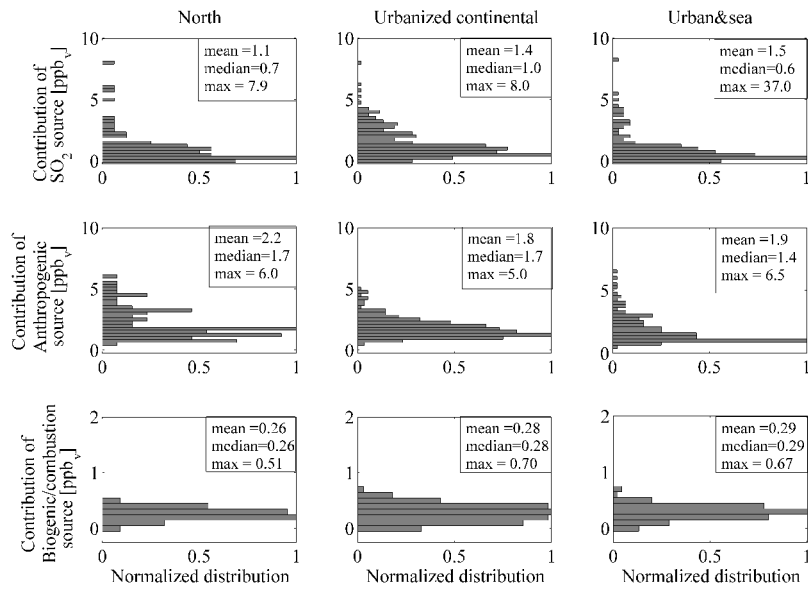
Figure 11. Normalized distributions of different sources in three sectors during the winters. The first column is the North sector ($N = 142$), the second column is the Urbanized continental sector ($N = 714$) and the third column is the Urban and sea sector ($N = 391$). In the topmost row all panels are distributions of the SO_2 source, the middle row the anthropogenic source and the lowest row the biogenic/combustion source. Each sector has been normalized with the maximum value of the observations. Mean, median and maximum values of source contributions are shown for each sector.
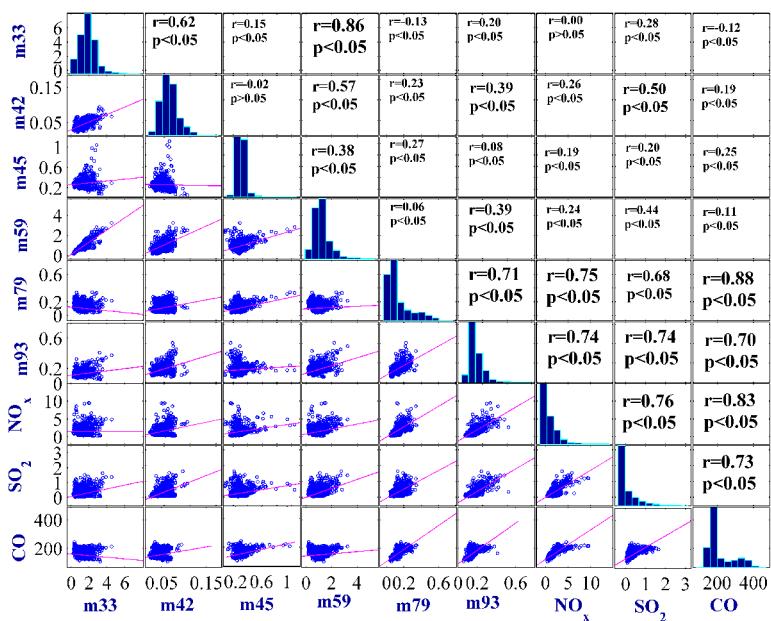
Figure A1. ~~Correlation~~ The correlation matrix~~for~~, Pearson's correlation coefficients and p values between calculated trace ~~gas~~ gases (m 33 (methanol) m 42 (acetonitrile) m 45 (acetaldehyde) m 59 (acetone) m 79 (benzene) m 93 (toluene) NO_x (nitrogen oxides) CO (carbon monoxide) and SO_2 (sulfur dioxide)) correlations. Diagonal in the matrix is distribution of data.