

We thank both Referees for the excellent reviews and good suggestions. We have adapted and answered all the comments and the revised manuscript has been significantly improved. Below detailed answers to the comments can be found. The referee comments are bolded whereas our replies are written in a normal text.

REFeree #1

Rantala et al present long term flux measurements of VOCs, CO₂ and periodically CO from an urban background site in Northern Finland. This represents the first such data set from a city in the northern latitudes and is therefore of interest as it builds upon our still very sparse collection of urban VOC flux data sets. I am therefore keen to see this work published, but I have some reservations about the methods used and in particular the simplicity of the division of the footprint into road, built and vegetation sectors. The authors must address these points before I can recommend publication. Main Comments: The authors segregate their measured fluxes into three distinct sectors (built, road and vegetation; defined in figure 1) and try to establish differences between the emission rates observed in each. I think this is a worthwhile exercise as it goes beyond what has been published in previous urban VOC flux studies. However, in order to do this properly I would expect a much more detailed analysis of the flux footprint that allows the footprint contributions to be mapped to specific areas surrounding the tower e.g. major roads, buildings and vegetation. I have seen this type of analysis applied to fluxes measured over agricultural land (Neftel et al, 2008) and also urban areas (Helfter et al, 2011) and feel this might offer more meaningful results than your current approach of segregating sectors on the basis of wind direction (based on a study by Vesala et al. (2008)) which appears overly simplistic. For example, on occasions when the wind comes from the south the flux footprint would encompass both the road (i.e. the major highway) and vegetation sectors. Perhaps it is uncommon for the wind to come from the boundaries between sectors, but this information is not included. How do the authors treat such periods where the footprint is likely to span two sectors? It would be very useful if the authors could supply wind roses for the different measurement periods in a supplementary information section so we can judge for ourselves whether this is an issue or not.

We agree that calculating proper footprint estimates would allow a much more detailed source analysis. However, the parameterized analytical footprint models (such as Kljun or Kormann and Meixner) commonly used in EC studies do not function well in heterogeneous surroundings and therefore dividing the source area into detailed patches of different land uses is not meaningful. This is particularly true at the Kumpula site where calculation of flux footprints using a bit more sophisticated model in neutral conditions has shown somewhat different pattern (Vesala et al. 2008) when compared to the simple elliptic footprints commonly obtained from the analytical models. Unfortunately the problem with this model (and commonly with more complex models) is that only neutral conditions can be calculated. Nevertheless, we added the cumulative 80% footprint to the Fig. 2 calculated using the Korman and Meixner model to give some indication about the source area of the measurements.

We also think that flux footprints can be spanning over two sectors and thus we now filtered the data based on the footprint estimates. A measured flux value was defined to be, for example, from the road sector if maximum 30% of the 80% flux footprint area covered other than the road sector. Thus, periods when wind blew close to a sector border, were rejected from further analysis. The total rejection rate was around 30%. On the other hand, disregarding data decreased also statistical significance, especially in the case of the built sector. Nevertheless,

we decided to do the division into different sectors based on the footprint estimated source areas to avoid the problems pointed out by Referee #1. All the Figures and Tables were changed correspondingly and text related to the method was added on P10, L24-28.

We added the median fluxes from different wind directions (20° bins) to the supplementary material.

On page 6, line 27 the authors state "Other quality controlling, such as filtering flux data with flux detection limits or with stationarity criteria was not performed because applying these methods for the noisy DEC data would potentially bring other uncertainty sources". Could you please elaborate on this and define what you mean by "other uncertainty sources"? My interpretation is that you did not want to remove individual fluxes that fell below the limit of detection because your averaged fluxes would then be biased high. I would agree with this, but not filtering the raw data for data below the limit of detection means you subsequently need to convince us that your averaged fluxes are significantly different from zero. From page 5, line 20 we already know that the average of the data sets between calibrations are significant, but the same assurance is needed when you average the data for your various analyses e.g. by time of day. For example, in figure 3 (m/z 42), the red and blue traces do not look significantly different from zero to me. I would recommend calculating an averaged limit of detection (which others have done, see Valach et al. 2015) for each of your analyses so we know for sure. This does not necessarily need to be added to the plots in the main manuscript but should certainly be shown in the SI.

We mean that removing flux values based on, for example, detection limits, can easily bias average values so the interpretation of the Referee #1 is correct. In our opinion, somewhat noisy DEC data should be filtered using only independent data, such as friction velocities. We would not like to do any filtering based on the DEC data itself because we are not sure if this can create systematic error sources. Only exception is that measurement periods with lot of spikes were of course disregarded from further analysis. This was clarified in the revised manuscript.

We agree with the referee that acetonitrile flux does not differ statistically significantly from zero except from the built sector. This is also mention in the original manuscript (page 12, line 7–8; page 14, line 1). Furthermore, we admit that detection limits would be very useful information for the reader, thus we added mean flux detection limits ($\overline{\text{LoD}}$) to Table 4 (revised manuscript) for each season. Individual LoDs were defined to be $1.96 \times \sigma_{ccf}$, where σ_{ccf} is the standard deviation of the cross covariance function tails (see Taipale et al. 2010). The mean $\overline{\text{LoD}}$ was then calculated using a formula $\overline{\text{LoD}} = 1/N \sum \text{LoD}^2$ as discussed in Valach et al. (2015). Single flux values were of course under detection limits more often but the average fluxes were not.

The method used to calculate time-lags is clearly critical to determining the flux. A recent publication by Langford et al. (2015) demonstrated that significant bias (both positive and negative) can be introduced to noisy eddy covariance data when methods are used that search for a maximum in a cross-covariance function. They also suggest that the problem is exacerbated at high measurement points and when sampling through long inlet lines and especially for disjunct data which has poorer statistics and hence a higher random error. Your data set would appear to fit into this higher risk category and therefore I think it is important for you to demonstrate that your data are not affected by this bias. I appreciate that you suggest the potential bias is minimised through the use of a relatively small

lag-time window and the use of the smoothed cross-covariance but depending on the signal-to-noise ratio of your data a significant bias could remain. This is important to know since you state in at least two sections that some of your fluxes were very close to the detection limit (Page 10, line 6 and Page 11, line 11). Given the length of your data set, recalculating the fluxes using a prescribed lag time is perhaps unrealistic, but it would certainly be interesting to see how the different time-lag methods compare over a shorter period of a few weeks and to see the flux distributions in the supplementary information. Such an analysis would give us further confidence in the fluxes you present. Related to this, on Page 5, line 18 please could you give more details on the method of smoothing you applied? Was this a running mean? How many data points were used for the average?

Yes, determining the lag-times properly is one of the most important tasks in flux calculations. In our case, the cross covariance functions were usually quite noisy due to low fluxes and limited amount of data points for each 45-min-period. Thus, single flux values were usually close to a detection limit or below it. As the Referee mentions, this behaviour may lead to a strong bias if the maximum method with a wide time-time window is used for searching the lag-times.

However, we tried to minimize this behaviour by determining first a mean lag-time for each compound, and then seeking the individual lag-times using a short ± 2.5 s lag-time window and smoothed cross covariance functions. On the other hand, according to Taipale et al. (2010), a constant lag time should be avoided as well because then fluxes are then easily underestimated. Langford et al. (2015) mentions that the problem can be partly avoided by controlling the flow rate, heating the inlet line and recording wind and concentration data to a same computer. However, our flow rate was not controlled via a mass flow controller and the data was also recorded to two computers. Thus, small variations in lag-times can be expected and using a constant lag-time would probably underestimate the fluxes. On the other hand, we did not want use wider lag-time window because then the mirroring effect would become more visible.

We added to the supplementary material the flux distributions for each compound. The distributions were calculated using a constant (mean) lag-time, and using a lag-time window of ± 2.5 s around the mean (this study). The period was May 21 – June 4 2013. The distributions were quite equal for many compounds. The average fluxes with a constant lag-time were typically lower (up to 30%) but we think that this is caused by the fact the actual lag-time does not stay totally constant. Of course, random variation affects also the results as only 147 data points were used in the study. After that said, we admit that when dealing with fluxes close to the detection limit, values can be somewhat biased. We added more discussion about the topic to the revised manuscript (Section 2.2.1).

The smoothing applied in the study was based on a running mean with an averaging window of ± 2.4 s, i.e. 49 data points. We added this information to the text (Section 2.2.1).

The method section 2.2 seems a little muddled and could do with restructuring and there is some important information missing. You start by introducing the DEC equation, but then immediately follow up with a discussion of high frequency loss corrections. It would make more sense to me for you to follow the equation with an outline of your flux calculation procedure. For example, you should mention at this point what the length of the averaging period was, what the typical value of n was, what the duty cycle length was, what the typical time-lag was and how you calculated it etc. Once you have fully outlined how you

calculated the fluxes you can then start your discussion of the flux corrections and QA/QC procedures you applied. Most of this information is there, it's just a case of restructuring in a more logical order.

We thank for the suggestion and re-organized Section 2.2.1. First, we present the DEC equation and the measurements with the PTR-MS. However, basic details about the measurements are already discussed in Section 2.1.1. High frequency corrections and potential flux uncertainties are discussed at the end of the section.

Page 10, line 21. The emission potentials are not shown in figure 10. Figure 10 shows the regression between measured and modelled isoprene/furan fluxes from which the emission potential can be derived. In the text you need to make it more clear how you derived the emission potentials from figure 10, unless you are familiar with this type of analysis it is not obvious. In deriving the emission potentials did you set the intercept to equal zero? This information should be included. I like the fact you have calculated isoprene emission potentials for urban vegetation, but in their current format I don't think they are particularly useful. Strictly speaking the G93 algorithm is used for leaf-level emission potentials on a mass per gram of dry leaf basis. While it can be used to derive area based emission potentials as you have done, the values are not likely to be compatible with the more recent BVOC emission models such as MEGAN that use area based emission factors, in part because these newer algorithms use a different set of standard conditions. In order to maximize the usefulness of these results I would suggest also converting your area based emission potentials to leaf-level potentials ($\text{ng g}^{-1} \text{ s}^{-1}$) by first estimating the foliar density for your flux footprint. Estimating the foliar density will of course introduce additional uncertainty and this should be factored in to your presented emission potentials. These values could then be compared to the standard urban isoprene emission potentials used in Guenther et al., (1995) and to those derived for other European cities (Valach et al. 2015).

The emission potentials were calculated using the G93 algorithm, i.e. the parameter E_0 was fitted to the data. Intercept was defined to be zero. Of course, other than biogenic isoprene emissions contributed also to the flux at m/z 69. However, these emissions were estimated to minor compared with the biogenic ones, thus, no intercept etc. was allowed when the emission potentials were determined. We clarified this in the text (Section 3.2.2).

We agree that the emission potentials are not very useful from the modelling point of view as the vegetation coverage is heterogeneous. However, our purpose was to show that the flux at m/z 69 consists mostly of biogenic isoprene as the results agree well with the G93 algorithm. In addition, we wanted to point out that the (normalized) isoprene emissions are quite uniform from all wind directions. Indeed, the results would be more useful if they were scaled to leaf-level. In this approach, they could be also compared with other urban studies. Unfortunately, we think that estimating the dry leaf masses would be very inaccurate because tree species diversity around the site is large, partly due to the University botanical garden. Therefore, we would avoid to do such analysis. We also think that more complicated MEGAN algorithm would bring no benefit for our purposes.

As a conclusion, we left Fig. 12 in the revised manuscript but removed the wind direction separation as Referee #2 suggested. The zero lines were also added. However, we removed the Table 5 and also discussed in the text that the emission potentials cannot be compared with the other studies due to the problems pointed out by the Referee #1 (Section 3.2.2).

Minor Corrections

In the main text you discuss the fluxes and concentrations using the specific names of the compounds measured, whereas you refer to the measured m/z ratio in your figures. As you have spent time in Section 2.2.2 identifying the m/z ratios I would suggest harmonising the figures with the text and using the compound(s) names.

We agree with this. In the revised manuscript, compound names are used in all figures instead of mass-to-charge ratios. We used the actual names also in Tables 3–4 in the revised manuscript. However, naming in Table A1 was not changed because otherwise the table would have become too large.

Please can you clarify why you separate your data into Jun-Aug and Sep-May? While this isolates the warmest summer months, autumn, spring and winter are all wrapped together. With such an extensive set of measurements could you not have looked at the variation of VOC and CO₂ fluxes at a much finer temporal resolution (e.g. monthly... or at least by season) and compared with monthly variations in traffic and temperature? This would be very interesting as none of the previous urban VOC flux work published have shown monthly variations across a full year.

The separation was done because we wanted to see if the warmest season differs from other months. Traffic rates were also lowest during summer while they stayed otherwise quite constant. We agree the conditions vary a lot between September and May, thus the separation was not perfect from that point of view. We decided to present the seasonal cycles in the revised manuscript because the flux data coverage was not good enough to present data in monthly basis. The results and discussion was changed accordingly. See also response for the Referee #2.

Page 2, line 4: suggest you change to "...have generally major effects on the chemistry of the atmosphere"

Changed.

Page 2, line 9: change to: "...conducted in the UK where winters are relatively mild."

Changed.

Page 2, line 13: please add the reference to which you are referring to.

We added the reference (Langford et al., 2010). In addition to that, Harrison et al. (2012) studied also relationships between CO and VOCs, thus, that reference was also included to the introduction.

Page 2, line 21. The climate zone descriptions given in Stewart and Oke are very brief so I would suggest adding a line to describe the characteristics of climate zone 6 so the reader doesn't have to look it up.

The site is classified as local climate zone, which corresponds to "open low-rise" (see Stewart and Oke, 2012) with detached buildings and scattered trees and abundant vegetation. We described the climate zone better in the revised manuscript (Section 2.1).

Page 3, line 2, change "blew" to "was"

Fixed.

Page 3, line 8, please change to "For the rest of the time..."

Changed.

Page 3 line 14. Please add somewhere to this paragraph the Reynolds number for the two flow regimes used

We added the Reynolds numbers to the paragraph.

Page 3, line 22. Please add the \pm uncertainty of the Apel-Reimer gas standard used for calibration

The uncertainty of the standard gas ($\pm 5\%$) was added to the text.

Page 5, line 22. Please can you define what you mean by "...its flux values were defined to be insignificant". Does this mean the data were set to zero or rejected? If it was the latter did you use gap-filling?

We tried to say that those mass-to-charge ratios with no significant peak values at all were rejected from the further study. This concerns mass-to-charge ratios 31, 89 and 103. We clarified this in the text.

Generally, no gap-filling was used because the procedure would be very complicated above the heterogeneous terrain with multiple sources.

Page 6, line 17. Can you infer the low frequency flux losses from the co-spectral analysis applied to your CO₂ fluxes?

The corrections were $< 3\%$ and we mentioned this in the text.

Page 9, line 23. The measured CO/CO₂ flux ratios could be further compared to those measured above London by Harrison et al. (2012).

We thank for the reference. Harrison et al. (2012) found a CO/CO₂-ratio of 0.32–0.55% whereas in our study the ratio was 0.34%. We added this comparison to the text.

Page 13, line 9. The monoterpene fluxes in figure 3 don't look any more or less scattered than any of your other diurnal cycles. Please rephrase this sentence to better reflect the data shown or remove.

We agree with this statement and removed the sentence from the text.

Page 13, line 20. I think it's worth adding a line here to make it clear that you are using the intercept as a measure of the non-traffic related emissions.

We clarified the section to point out that the intercept was used as a measure of the non-traffic related emissions.

Page 13, line 26. Again, please be clear about how you arrived at this estimate.

We admit that the procedure was not well described. The estimate was rough and was based on the intercepts of the linear fits between the OVOC fluxes and the traffic rates. The intercepts were compared with the measured average fluxes. Considering relatively high uncertainty estimates, we concluded that the emissions from traffic and other anthropogenic sources were around the same.

However, we improved the source identification as was asked by Referee #2, and the procedure is currently better explained in the revised manuscript. We also tried to give more accurate value with uncertainty estimates. We concluded that the traffic can explain $65 \pm 25\%$ of the measured OVOC flux at the site (Table 6).

Page 13, line 34. Please change to "Nevertheless, the contribution from non-biogenic isoprene+furan emissions...."

Changed.

Page 14, line 29. I would presume the ambient temperature also has a large effect on VOC emission rates? Was the ambient temperature higher in Mexico compared to London and might this have resulted in larger evaporative emissions? If so, I wonder if temperature can be incorporated into figure 11 in some way or mentioned in your discussion.

We agree with this statement. The average temperature was around 13°C (12.2°C at the 95 m tall tower) in London during the campaign whereas in Mexico city, the ambient temperature was somewhat higher, varying diurnally between 10 and 25°C (Fast et al., 2007). For example evaporative solvent emissions might increase as a function of the ambient temperature. We added discussion about the topic to the text (Section 3.3).

Page 29: Figure 1, please add the zero line for temperature.

The zero line was added for temperature.

Page 31: Figure 3 please add the y axis zero line to each plot

The zero lines were added to each plot.

Page 33: Figure 5. I would recommend changing the blue circles to open circles. I would also expect to see error bars and a zero line shown on the y axis.

The blue circles were changed to open circles as suggested. Error bars and a zero line were also added. See also the response for Referee #1.

Page 34: Figure 6. I was interested to see that the CO fluxes are zero at night time but the CO₂ flux is still showing emission. Can you provide some comment on this? Secondly, could you also provide some further comment as to why the two peaks in CO flux do not correspond temporally with the peaks in CO₂ and traffic counts? It would be interesting to see how the ratio of the two change throughout the day. In addition please add the zero lines to the CO and CO₂ plots.

The non-negative nocturnal CO₂ fluxes origin mainly from the soil and vegetation respiration from the vegetation near the station (see Järvi et al., 2012). We mentioned this in the revised manuscript.

CO-flux is also peaking during the rush hours (see upper quartiles in Fig. 6, original manuscript) but interestingly the highest median fluxes were observed couple of hours later. As the amount of CO-flux data was quite limited, this is might be also coincidence. Some CO emissions could originate also from a residential building area behind the road. We studied the CO/CO₂ relations more in the revised manuscript (Section 3.2).

The zero lines were added to the CO and CO₂ plots.

Page 35: Figure 7. Please add the zero lines.

Page 36: Figure 8. Please add the zero lines.

Page 38: Figure 10. Please add the zero lines.

The zero lines were added to Figs. 7, 8 and 10 (Figs. 10–12 in the revised manuscript).

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REFeree #2

General Comments: This paper describes >1.5 year long-term flux measurements of VOC, CO and CO₂ in the urban environment of Helsinki, Finland. As was shown in the paper and also expected for an urban environment, most VOCs have large traffic related emissions, but other anthropogenic sources are also important for some VOCs. In addition, during summer biogenic isoprene and monoterpene emissions and CO₂ uptake are evident in the data. Overall VOC fluxes in the specific location of these measurements were rather small compared to other cities. Long-term flux measurements, especially in an urban area, have not been reported in the literature very often and therefore this dataset is very interesting and unique and I think a dataset like this is worth exploring and publishing, but the analysis presented here needs major improvements before it is acceptable. **Major Issues:** 1. The organization of the discussion section: I found this paper very hard to read, because of a constant mix of topics in the first part of the discussion. I would suggest to re-organize the chapters 3.1 and 3.2., before discussing the individual emission sources (traffic, biogenic, and others). The seasonal and diurnal cycles for all VOCs, CO and CO₂ should be discussed in detail first then discuss individual sources. I would like to see an actual figure showing the annual cycle for VOC, CO and CO₂ fluxes, although there might not be enough data for CO. Right now this important information is hidden in various figures and tables. For this discussion the data should not be separated into the three sectors. After describing these general trends in the fluxes, each emission source sector can be described: traffic, biogenic, and others; and for all of these CO and CO₂ should be included and not be shown in a separate chapter.

We thank for the good suggestion. We re-organized the manuscript so that first annual cycles (seasonal averages) of measured fluxes and concentrations are discussed (Section 3.1) and shown in Fig. 5 in the revised manuscript. Tables and figures were also modified accordingly. Even though the measurements were done between Jan 2013 – Sep 2014, some months, mainly January, February and October were underrepresented in the data sets (less than 100 data points) and no good data from November and December was recorded at all. This was caused by long measurement gaps (Fig. 1 in the original manuscript). We believe that such a small amounts of data would not represent well the monthly averages, especially when taking to account the effect of the wind direction. For example, the wind did not blow from road sector almost at all in October, leading to really small fluxes of benzene, toluene and C₂-benzenes. Therefore, we decided to present seasonal cycles in the revised manuscript.

Unfortunately, CO-fluxes were only measured between April and May 2014, thus no annual cycles for CO is shown. However, the average CO-fluxes are still shown in Table 5. We also added a diurnal cycle of CO concentrations to the revised manuscript (Fig. 6).

It would also be important to add the mixing ratios to the annual and diurnal cycles. From the paper as is, it is not possible to understand, if this is a heavily polluted location or not. I would assume that in the cold winter months, when the boundary layer is really low, mixing ratios could get rather high.

We agree with this statement. The original manuscript contained only a basic mixing ratio statistics from the summer and the other months, but we expanded Table 3 in the revised manuscript to cover all four seasons. In addition, we added 95% quantiles which represent higher end of the measured concentrations. Furthermore, we added the diurnal median cycle for each compound and expanded discussion in Section 3.1.

However, we would like to avoid of analysing the concentrations in more detail for two rea-

sons: First of all, the manuscript can easily become too long and its focus blurred if lot of concentration related material is added. We think that VOC concentrations are mostly driven by horizontal advection, not by the local emissions. Thus, these two components are difficult to analyse together. Secondly, the VOC concentrations (excluding alcohols) measured in Helsinki are already analysed in detail by Hellén et al. (2003), (2006) and (2012).

We think that the pollution episodes with high mixing ratios were quite rare due to several reasons. First of all, Helsinki is rather small city and pollution emission are generally low. Secondly, the city is located by the sea, thus, totally calm situation when emissions could accumulate near the ground are somewhat uncommon. However, concentration of many compounds peaked during morning rush hour, probably as a result of traffic peak and relatively shallow boundary layer (revised manuscript, Fig. 6).

The separation of the data into the three wind direction sectors looks like a good approach, when looking at the map and the potential emissions from those sectors, but the VOC flux data (Figure 3, 4 and 5) are actually very similar for each sector. The only substantial difference was found for CO and CO₂ in Figure 6 and for the weekday/weekend plot in Figure 9, although that is mainly due to the traffic counts between weekday and weekend. The wind sector separation complicates the discussion in many places, but doesn't really add any information, so I think Figures 3, 4, 5, 9 and 10 should be simplified by using all the data. In addition, throughout the manuscript it becomes clear that even in the road sector substantial non-traffic related emissions are evident and in all three wind direction sectors multiple sources contribute to the VOC emissions. This makes a quantitative analysis and separation of sources very difficult and this should be acknowledged clearly in the manuscript.

We agree with the referee that the differences between the sectors are not as clear as for CO and CO₂. However, the sector separation has been used in former flux publications at the site (Vesala et al., 2008; Järvi et al., 2012, 2014). Thus, we would still like to keep the separation, at least from the point of the comparison to the previous studies. In addition, differences between the sectors were clear for acetonitrile and acetone, both having most significant source in the built sector. In addition, the fluxes from the road sector were significantly higher for methanol, acetaldehyde, isoprene, benzene and C₂-benzenes. Therefore, we partly disagree with the comment that no differences between the sectors were found. However, we agree that diving the data to three sectors gives no additional information for Figs. 4, 5, 9 and 10. Thus, those figures were re-plotted without the separation in the revised manuscript (Figs. 4, 7, 8 and 12).

Based on a suggestion from Referee #1, we decided to do all calculations using a footprint analysis instead of the wind directions (see a response for Referee #1), thus minimizing the interaction between the sectors. As a result, the differences between the sectors are clearer in some cases.

We also think that the quantitative analysis of the sources is tricky and we clarified this in the text (Sections 3.2.1 and 3.3).

For some VOCs an attempt for a quasi source apportionment was done in the paper. For example, on page 13 line 10-15, the monoterpene sources are summarized and biogenic contribution was assumed to be around 40%. This type of information is to me one of the most relevant results of this paper. Unfortunately this estimation of a source apportionment was only done for monoterpenes and OVOCs and it would be important to do this carefully for all the measured VOCs. If this is possible with the data, I would like to see something like a pie chart for

each VOC or class of VOCs showing the traffic, biogenic and other anthropogenic contributions for summer and winter, which should then be presented as the main result of this paper.

We agree that this kind of information would be very useful. We expanded the discussion about sources and made a Table (Table 6 in the revised manuscript) that shows different sources of OVOCs, terpenes and aromatic compounds in summer and winter. Estimating the contributions has its uncertainties and this was pointed out in the revised manuscript (Section 3.3).

Specific comments: page 2 line 26: It would be really helpful to add the typical footprint to Figure 2. The discussion about the wind sector analysis would be much easier to follow.

We added the cumulative 80% footprint to the Figure 2. In addition, the picture was enlarged to cover the area of 2000×2000 m instead of 1200×1200 m. See also the response to Referee #1.

page 3 line 7: I assume this is 0.5s per mass per measurement cycle of about 6s each?

The measurement cycle was slightly higher, around 7 s, because switching between the masses took some time, as well as the basic measurements (m/z 21 and m/z 37). We clarified this in the text.

page 3 line 8-9: Were there any other masses with significant signal or was most of the VOC signal captured by the masses used for the presented flux measurements. Please indicate other important masses.

The additional masses were m/z 61, 71, 73, 75, 87, 99, 101, 113 and 117. Furthermore, some heavier masses than m/z 137 were measured but the data quality was really poor due to low sensitivity of the PTR-MS at higher masses. We think that the most important mass-to-charge ratios were already included to the flux measurement cycle.

page 3 line 19-21: The PTR-MS instrument settings are described here, but the actual detection limits for the 0.5s measurements and the 20-30 min flux calculations are not given. Please add those, especially taking the issues with the instrument background measurements into account.

The flux detection limits were added to the Table 4. See also the response for Referee #1. The detection limits of concentration measurement were added to the Table 2. We determined the detection limits from the zero air measurements of the calibrations, thus, the detection limits are shown only for the calibrated compounds. The determined values represent 1.96σ detection limits for individual 0.5 s measurements.

page 3 line 24: What do you mean by "correct primary ion signal"? Is this mass discrimination corrected? Shouldn't the calibration be done at the same settings as the actual measurements and not with optimized SEM voltages?

The calibrations were always done before a measurement period. Therefore, the SEM voltage was optimized (increased) before the calibration and the same value was used until the next calibration (and the measurement period). The sentence was reformulated.

page 3 line 25: Does the zero air generator change the humidity? Background measurements at a different humidity can produce significant artifacts.

No, we used the ambient air also for the zero air measurements and humidity should not have changed. The artifacts were observed for toluene only but the reason for this remained unknown. We clarified this in the text.

page 3 line 31-32: How much does the uncertain zero air measurement add to the uncertainty, please be specific.

This depends on the compound but the possible systematic errors were estimated to be small. The procedure affects individual hourly values but this kind of data is not presented in the manuscript. We included to the text a note that the effect was estimated to be negligible.

page 4 line 9: Also for CO and CO₂ measurements it would be good to add the precision and uncertainties.

The random error and detection limit of CO were $0.23 \mu\text{g m}^{-2}\text{s}^{-1}$ and $0.16 \mu\text{g m}^{-2}\text{s}^{-1}$, respectively. The corresponding numbers for CO₂ were $0.05 \mu\text{g m}^{-2}\text{s}^{-1}$ and $0.03 \mu\text{g m}^{-2}\text{s}^{-1}$, respectively. We added the missing information to the manuscript.

page 4 line 16 and page 5 line 11: Why did you use different averaging times for CO and CO₂ with 30 min compared to the VOCs with 45 min?

For VOCs, we used 45 min averaging period to include more data for the flux calculations. This is crucial issue from the point of finding correct lag times. CO and CO₂ were measured properly with 10 Hz frequency, thus, there was no need for using longer 45 min intervals. Based on previous studied at the site the optimal flux calculation time for CO₂ has been found to be 30-minutes.

page 5 line 13: Was there a reason not to use something like a time server synchronization program?

We were not able to setup such a synchronization. Therefore we needed to do the time synchronization afterwards.

page 5 line 14: Was m37 the highest flux, higher than methanol? Is that why m37 was used for the time lag calculation?

Yes, the first water cluster showed generally highest – or better to say most clear – cross covariance function peaks. However, the actual lag-times were calculated individually for each compound. The lag times of the water cluster were only used to handle the shift between the computer clocks (the anemometer and the PTR-MS).

page 6 line 31: Are those data coverages for flux measurements or do those include the mixing ratio measurements?

The data coverages are for flux measurements; mixing ratios have slightly higher coverages. We clarified this in the text.

page 7 lines 8-14: There have been a few recent papers about oil and gas emissions using PTR-MS showing that m69 can also have a significant influence from cycloalkanes.

We thank the referee for this statement. For example, part of the cyclohexane fragments to m/z 69. According to Hellén et al. (2006), the cyclohexane concentrations are around 0.10 ppbv in Helsinki during winter, thus, affecting partly also observed m/z 69 signal. We added this additional information to the text, Tables and Figures.

page 7 line 19: Are those anthropogenic monoterpene likely from the sector "solvents and other products" or more traffic related?

We do not know. Hellén et al. (2012) speculated that monoterpenes could originate also from traffic but the possible processes are unknown. We think that traffic could be the most obvious solution as no industrial areas etc. are located nearby the station but this is hard to say. Part of the monoterpene emissions could originate at least from glass cleaner liquids. We expanded the discussion about anthropogenic sources of monoterpenes (3.2.3).

page 7 line 33: Mention here that acetonitrile is often used as a tracer for biomass burning.

We expanded the sentence to cover this information.

page 8 line 6: Often biogenic inventories do not represent urban environments well, please explain where you get the E0,synth values for the measurement location from and what your confidence in this value is.

We agree with this statement. Generally, the emission potential values are not necessary very useful in urban environment without having additional information about vegetation cover. Our purpose was only to show that the G93 algorithm works well for m/z 69 fluxes, thus, biogenic isoprene emissions have probably a major contribution to the measured flux at m/z 69 during summer. In addition, we wanted to show that (normalized) isoprene emissions are quite uniform in all wind directions.

After having comments related to this topic from Referee #1 as well, we decided to delete most of the isoprene analysis because the more detailed research would be impossible. However, the basic analysis was left into the manuscript, but we pointed out that the values are not representative for further use (e.g. for models).

page 8 line 13: In Figure 3 it can be seen that acetonitrile and acetone seem to be emitted from the built sector. Could those be the result of solvent use at the University buildings?

Acetone is most probably coming from University buildings, especially from Chemistry Department. This is shortly discussed in page 13, lines 16–19 (original manuscript). Acetonitrile could also originate from similar sources and we added this speculation into the text (Section 3.2.3).

page 8 line 26: The annual trend in the concentration of the aromatics will also strongly depend on the boundary layer height. Atmospheric background mixing ratios of benzene are much higher in winter in the northern hemisphere with over 100ppt, but local enhancements in an urban area are probably more driven by the boundary layer height than lifetimes. Again it would be very helpful to look at annual and diurnal cycles of mixing ratios in detail as well.

This is true and local sources affect on diurnal trends of concentrations. Boundary layer heights do also have an effect and we discuss more about the topic in the revised manuscript (Section 3.1). We added also more discussion about annual and diurnal trends.

page 9 line 19-23: I think it is problematic to compare CO/CO₂ ratios with other studies without taking the strong decreasing trend of CO into account. Over the past decade(s) CO and VOCs have decreased by several percent every year. The discussion should take this trend into account. Also, there are other sources of CO in a city compared to cars driving in a tunnel, e.g cold starts, (as mentioned in the text), domestic burning and other residential and commercial combustion sources. I would therefore delete the comparison with the tunnel study and look at other papers that show CO/CO₂ enhancement ratios.

As suggested, we deleted the tunnel study section. Besides, a study from Harrison et al. (2012) was compared with our results. We also mention that CO emissions from traffic have had a decreasing temporal trend which may explain partly the differences between our study and Famulari et al. (2010). See also the response for Referee #1.

page 9 lines 24-31: I agree that cold starts are likely an important source of CO and VOCs in the built sector, but I am wondering if the high CO and aromatics

emissions in the afternoon could also be explained by domestic burning. Acetonitrile is generally used as a tracer for biomass burning, but it is not a good tracer for domestic burning, because N emissions are generally smaller from wood than foliage burning (e.g. Yokelson et al ACP 2014). So the lack of acetonitrile fluxes by itself is not a reason to discard domestic burning as a major source of CO and VOCs in winter. The domestic burning should have a strong annual cycle. I am not sure, if without the annual cycle measurement of CO, there is enough evidence to look for this source here.

This might be a good explanation and was added to the text (Section 3.2). Unfortunately, CO-fluxes were measured during two months only, thus, studying annual cycles was not possible. Domestic burning near the site is probably more related to warming Saunas and using fireplaces. Most of the houses in Helsinki and within the flux source area are warmed by district heating, thus, these emissions from residences do not necessarily have the annual cycle.

page 10 line 9: Why did you choose Sep-May and not Dec-Feb? Shouldn't that give you a better contrast?

The original plan was to divide the data to two classes due to a better statistics. However, as both Referees suggested, we divided the data into four classes according to the seasons to have better contrast between colder and warmer periods. The text and some results (e.g. related to biogenic contribution) were modified accordingly. See also the response for Referee #1.

page 10 line 15: I don't know about the fuels in Finland, but methanol, acetaldehyde and acetone are usually not ingredients of gasoline. In many places, especially the USA and Brazil, gasoline contains a lot of ethanol, but usually no other oxygenated VOCs.

In Finland, a popular 95E10 contains ethanol (< 10%) and methanol (< 3%). Of course, this does not mean necessarily traffic related methanol emissions but they might be possible. According to Caplain et al. (2006), acetone and acetaldehyde have also tail pipe emissions.

We added more discussion about the topic to the revised manuscript (Section 3.2.1).

page 10 lines 25-28: It is probably correct that in the road sector most aromatics are from traffic, but in general toluene and to a lesser extend C2-aromatics have large non traffic related sources such as solvents, paints and paint thinners. This should be mentioned here.

We agree with this statement and added discussion about additional sources to the text. We believe that those additional sources should have only a relatively minor effect on fluxes in the road sector but of course they might be more important in the built sector. See also the comment from Editor and our response.

page 11 line 9: The total traffic related flux of aromatics is calculated here and with this the fraction of the traffic to total aromatics flux can be estimated. As I mentioned earlier, this would be a very important result. Is the error of 1.2 ± 0.2 g/m²/yr correct? Looking at the error estimate in the equation two lines above, this seems low?

The error analysis was based on the uncertainty estimates of the slope (29 ± 5 ...) between the fluxes and the traffic rates, i.e. we assumed that the intercept described non-traffic sources and its uncertainty estimate was excluded from the calculations. The error estimate is correct but on the other hand, it excludes possible systematic errors, such as calibration or possible errors of the traffic counts. We clarified this in the text.

page 11 line 15: This is the only time Figure 9 is mentioned in this section of the text and is only briefly mentioned later on. Either this figure needs to be explained better or deleted.

We agree. We simplified the figure and added more discussion about it into the text (Section 3.1).

page 11 lines 20-28: It is clear that even in the road sector other sources besides traffic are strongly contributing to the VOC emissions, which can be seen in all the low correlation coefficients given in this paragraph. This would be a good place to mention the difficulty in the source apportionment again.

This is true and we expanded the discussion about the difficulties in the revised manuscript (Section 3.2.1). However, low correlations do not necessarily mean that also other sources than traffic have major contribution on – for example – aromatic fluxes. Flux measurements were just quite noisy for many compounds, decreasing also correlations.

page 11 lines 29-34: Here I am wondering again, if cycloalkanes are contributing to the signal on mass 69.

This is totally possible, at least cyclohexane might contribute to the measured concentrations at m/z 69. We are not sure whether cycloalkanes contribute also to the measured flux at m/z 69 or not. Nevertheless, we mention cycloalkanes in the text and Table 2 in the revised manuscript.

page 12 line 21: The isoprene emissions, at least for the road and vegetation sectors, are of the same magnitude, but the CO₂ emissions look very different. There is a very clear signature of CO₂ uptake in the vegetation sector, and therefore one would expect to have similar CO₂ uptake in the road sector and as a result the anthropogenic CO₂ flux is underestimated. Is this effect taken into account in this manuscript? Can this be used to estimate the flux and be compared to the Jaervi et al 2012 paper?

Carbon dioxide emissions from the vegetation sector are relatively low, thus, the net carbon uptake becomes visible during summer. In the road sector, this kind of behaviour cannot be seen as the CO₂ emissions from traffic dominate the net exchange during all seasons.

Järvi et al. (2012) took the possible CO₂ uptake to account by using CO₂ flux data from snow covering season only. However, in this study – for example in Fig. 6 – the CO₂ uptake was not taking to account as it would be very tricky. However, the possible uptake by the vegetation is mentioned in the revised manuscript.

page 13 lines 14-15 and page 13 lines 26-27: It is not clear to me, how these contributions are actually calculated, the biogenic monoterpene contribution and the non-traffic related contributions of anthropogenic VOCs. As I mentioned earlier, this is one of the more important results and it should be explained in detail how these contributions or "source attribution" is calculated.

In the original manuscript, the average fluxes from September–May were compared with the average fluxes from June–August. However, as we present seasonal cycles instead of two periods only in the revised manuscript, that comparison would not make sense anymore. Therefore, we decided to determine the biogenic contribution by comparing the fluxes in the range of $T < 10^{\circ}\text{C}$ with the average fluxes from summer. We could have also compared the average winter fluxes with the average summer fluxes. However, the statistics was better with the temperature criteria.

The new procedure increased the biogenic contribution (for methanol: 25% \rightarrow 40%) but

the estimate should be now more accurate and also more clear for the reader. See also the responses for Referee #1.

page 14 lines 1-8: I agree that acetonitrile from the built sector is likely from solvent use in the chemistry buildings, but again domestic burning cannot be well characterized using acetonitrile due to the low emission rate from domestic burning.

This is a good statement and was added to the text (Section 3.2.3).

Figure 2: please label the sectors and add typical footprints.

We labelled the sectors and added the cumulative 80% footprint.

Figure 3, 6 and 9: a label would make the figures much easier to look at.

Labels were added to Figs. 3, 6 and 9 (Figs. 3, 4 and 9 in the revised manuscript).

Figure 7: It would be worth showing the other sectors for comparison.

We added CO-CO₂ comparisons from other sectors as well (Fig. 9). However, comparison to traffic counts is possible for road sector only because in other directions the nearest roads were more far away and traffic counts were not counted for those directions.

Technical Comment: There are so many small grammatical errors everywhere in the manuscript, mainly missing articles and prepositions, that I can not list them all here. I would suggest an additional proofreading.

The revised manuscript was carefully proofread.

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We thank the editor for the helpful comments and suggestions. Editor comments are bolded whereas author responses are written in a normal text.

Looking at the map provided in the figure 2, the site seems to be particularly influenced by green vegetation. Even the sector identified as buildings is comprised of a fairly large fraction of vegetation, rather unique compared to the urban UK sites the authors compare their measurements with. Consistently this sector does not show a significantly different pattern of m/z 69 emissions. Perhaps a better description of this sector would be to call it 'urban residential sector with vegetation'.

This is true, the sectors have only small differences in vegetation coverage (Table 1). Therefore, the names of the sectors are somewhat vague but have been widely used in previous publications concerning the same site (Vesala et al., 2008; Järvi et al., 2012, 2014). In that sense, we would still like to use the original names. However, we expanded the discussion about the land use (section 2.1).

Temperature and PPFD normalized isoprene emissions were around the same from all wind directions. However, absolute values differ because the ambient temperature was typically the lowest when the wind blew from the built sector.

BTEX emissions: The sector identified as road borders to what it seems like an industrial complex (for example: at a distance of about 300-400 m a smoke stack is evident on google earth). It is argued that this sector is primarily influenced by road traffic. The influence of additional BTEX sources in this sector (other than traffic) could perhaps be obtained by explicitly comparing toluene to benzene fluxes during rush hour peaks with other periods. The upper limit of traffic related emission ratios should be close to 2 (1.9) based on the emission factor database for the average European fleet. The authors compare their measurements to other cities. In this context it is noted that Mexico City seems to be a special place with respect to many of the measured VOC fluxes. For example toluene measurements by Velasco et al., 2009, were thought to be influenced by local application of resin surrounding the flux tower resulting in toluene / benzene flux ratios of about 8-10. Measurements by Karl et al., 2009, reported a city wide average ratio of about 3.2 for Mexico City and concluded that about 60-70% of toluene could be due to evaporative emissions. Figure 11: It is noted that a correlation of fluxes between some compounds (such as toluene) and CO₂ needs to be discussed with caution. For example most of traffic related toluene emissions are evaporative and not produced by the ICE - thus not intrinsically linked to CO₂ tailpipe emissions. This is fundamentally different for benzene emissions for example, which are much more closely related to tail-pipe emissions.

We thank for the good suggestion. We calculated the ratio between the average toluene flux and the average benzene flux for two cases: all the data and periods when the traffic rate was over 2000 vehicles per hour. The ratios were 2.9 ± 0.7 and 3.1 ± 1.0 , respectively, indicating non-traffic related toluene sources. Interestingly, the ratio was higher for the high traffic period but the difference was statistically insignificant. On the other hand, the toluene fluxes alone followed also well the traffic counts with an intercept of $4 \pm 5 \text{ ng m}^{-2}\text{s}^{-1}$. Of course, toluene might still have evaporative emissions, but the traffic related emissions seemed to be still more important source if the offset is assumed to describe non-traffic related emissions. We expanded the discussion related to non-traffic related sources of toluene and C₂-benzenes (sections 3.2.1 and 3.3). We also added Table A2 to the manuscript which contains VOC to benzene flux ratios for each season.

We agree that the terrain is quite heterogeneous consisting of different land covers, but the old ceramic factory to which the editor likely refers to is not active anymore. The nearest industrial and workshop activities are over 800 -1000 m to the east south but these start to be already outside the flux footprint which typically expands less than that (e.g. Ripamonti et al. 2013, Figure 2). Also these emissions sources did not show up in the Fig. S2 where the average VOC fluxes are plotted as a function of wind direction.

We also agree that the VOC fluxes are not totally comparable with the CO₂ fluxes as many VOCs have also other anthropogenic sources than CO₂ does. We pointed this out more carefully in the revised manuscript (section 3.3). The message of the comparison was to show that the low VOC fluxes measured in Helsinki are rather sensible when taking to account also low CO₂ fluxes, indicating less intense anthropogenic activities, such as traffic related emissions. However, we did not want to argue that those two emissions should have necessarily a linear dependency.

We included also Karl et al. (2009) to the discussion. We admit that the study by Velasco et al. (2009) was done at a unique location, but that was one of the rare studies which provided both the CO₂ and VOC fluxes from the same urban location.

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Anthropogenic and biogenic influence on VOC fluxes at an urban background site in Helsinki, Finland

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Abstract. We measured volatile organic compounds (VOC), carbon dioxide (CO₂) and carbon monoxide (CO) at an urban background site near the city centre of Helsinki, Finland, Northern Europe. The VOC and CO₂ measurements were obtained between January 2013 and September 2014 whereas for CO a shorter measurement campaign in April–May 2014 was conducted. Both anthropogenic and biogenic sources were identified for VOCs in the study. Strong correlations between VOC fluxes and CO fluxes and traffic rates indicated anthropogenic source of many VOCs. The VOC with ~~highest emission~~ [the highest emission rate](#) to the atmosphere was methanol which originated mostly from traffic and other anthropogenic sources. ~~Traffic~~ [The traffic](#) was also a major source for aromatic compounds in all seasons whereas isoprene was mostly emitted from biogenic sources during summer. ~~Small~~ [Some amount of](#) traffic related isoprene emissions were detected during other seasons [but this might have also been an instrumental contamination from cycloalkane products](#). Generally, the [observed](#) VOC fluxes were found to be small ~~compared in comparison~~ with previous urban VOC flux studies. However, the differences were probably caused by lower anthropogenic activities as the CO₂ fluxes were also relatively small at the site.

1 Introduction

Micrometeorological flux measurements of volatile organic compounds (VOC) in urban and semi-urban areas are limited, although local emissions have [a](#) major effect on the local and regional atmospheric chemistry and furthermore on air quality (e.g. Reimann and Lewis, 2007 and references therein). Biogenic VOCs, mainly isoprene and monoterpenes, affect hydroxyl radical (OH) concentration ~~,particle growth, and formation of photochemical oxidants and aerosol particle growth~~ (Atkinson, 2000; Atkinson and Arey, 2003; Kulmala et al., 2004; Spracklen et al., 2008; Kazil et al., 2010; Paasonen et al., 2013). Long-lived compounds, such as anthropogenically emitted benzene, contribute also to [the](#) VOC concentrations in rural areas (e.g. Patokoski et al., 2014, 2015).

[The](#) VOCs may have both anthropogenic and biogenic sources in [the](#) urban areas which complicates the analysis of VOC flux measurements made in these areas. Globally, [the](#) most important anthropogenic sources are traffic, industry, gasoline evap-

oration and solvent use (Watson et al., 2001; Reimann and Lewis, 2007; Kansal, 2009; Langford et al., 2009; Borbon et al., 2013 and references therein) whereas the biogenic VOC sources within cities include mostly urban vegetation, such as trees and shrubs in public parks and at-in street canyons. Based on previous micrometeorological flux studies, the urban areas are observed to be a source for methanol, acetonitrile, acetaldehyde, acetone, isoprene+cycloalkanes, benzene, toluene and C₂-benzenes (~~Velasco et al., 2005; Filella and Peñuelas, 2006; Langford et al., 2009~~
~~Velasco et al., 2009; Langford et al., 2010; Park et al., 2013; Valach et al., 2015~~Velasco et al., 2005; Langford et al., 2009; Velasco et al., 2009; Langford et al., 2010; Park et al., 2010; Valach et al., 2015). In addition, concentration measurements connected to source models have ~~shown~~underlined emissions of various other VOCs, such as light hydrocarbons, from the urban sources (e.g. Watson et al., 2001; Hellén et al., 2003, 2006, 2012). Monoterpene emissions have surprisingly remained mainly
 10 unstudied, although the monoterpenes have generally major ~~effect on the~~effects on atmospheric chemistry. For example, Hellén et al. (2012) found that monoterpenes and isoprene together have a considerable role in OH-reactivity in Helsinki, Southern Finland. ~~Biogenic~~The biogenic emissions might have also a considerable role in ozone (O₃) chemistry in the urban areas (e.g. Calafapietra et al., 2013).

The VOC flux measurements reported in literature have been conducted in the latitudes ranging from 19°N to 53°N, but
 15 most of the measurement in the north have been conducted in ~~British Isles with their relatively mild winters~~the UK where winters are relatively mild (Langford et al., 2009, 2010; Valach et al., 2015). Thus no measurements have been reported from the northern continental urban areas. The VOC emissions from traffic are typically due to incomplete combustion. This also results in emissions of carbon monoxide (CO), and thus the emissions of certain VOCs are potentially linked with CO fluxes. However, only ~~one of the publications on~~two publications on the urban VOC fluxes ~~mentioned above~~ combine the VOC fluxes
 20 with the CO fluxes in their analysis (Langford et al., 2010; Harrison et al., 2012). Thus our aim is ~~to i)~~i) to characterize the VOC fluxes in a northern urban city over an annual cycle, ii) to identify the main sources, such as traffic and vegetation, of aromatics, oxygenated VOCs and terpenoids ~~using traffic counts, taking into account traffic volume together with the~~ measured CO and carbon dioxide (CO₂) fluxes and the ambient temperature (*T*), and iii) to compare the VOC fluxes with the previous urban VOC flux studies to assess the relation of ~~VOC fluxes to the~~VOC fluxes and the CO and CO₂ fluxes in different cities.

25 2 Materials and methods

2.1 Measurement site and instrumentation

Measurements were carried out at urban background station SMEAR III in Helsinki (60° 12' N, 24° 58' E, Järvi et al., 2009a). The population of Helsinki is around 630 000 (<http://vrk.fi/default.aspx?docid=8882&site=3&id=0>, cited in 12 ~~Dec~~December 2015). The site is classified as a local climate zone ~~6 (Stewart and Oke, 2012) and it belongs to the~~, which corresponds to
 30 "an open low-rise" category (see Stewart and Oke, 2012) with detached buildings and scattered trees and abundant vegetation. The site is in a humid continental climate zone with ~~clear annual variations between a~~clear annual variation between the four seasons: ~~the~~ monthly mean temperature varies from −4.9°C in February to 17.6°C in July (1971–2000, Drebs et al., 2002; see also Fig. 1), and daylight hours range from 6 to 19 h per day. ~~SMEAR III~~The SMEAR III site consists of a 31-m-tall lattice

tower located on a hill, 26 m above the sea level and 19–21 m above the surrounding terrain. The site is roughly five kilometres North-East from ~~the~~ Helsinki City Centre. According to ~~the~~ local wind direction, the ~~measurement~~ surroundings around the tower can be divided into three areas: built, road and vegetation (Vesala et al., 2008, Table 1, Fig. 2). However, a fraction of vegetation was significant also in the built and road sectors (Table 1). Thus, a better name for the built sector would be, for example, "urban residential sector with vegetation", but the short names are used throughout the text to keep the terminology and subsequent discussion as simple and short as possible.

The built sector in the northern direction (320°–40°) is dominated by university campus buildings and ~~the~~ Finnish Meteorological Institute (mean height 20 m) close to the tower. In the road sector (40°–180°), one of the main roads leading to Helsinki city centre passes through with the closest distance between the road and the tower being 150 m. The area in-between is covered by deciduous forest with mainly birch (*Betula sp.*), Norway maple (*Acer platanoides*), aspen (*Populus tremula*), goat willow (*Salix caprea*) and bird cherry (*Prunus padus*) (Vesala et al., 2008, Fig. 2). On the road, a typical workday traffic rate is around 44 000 vehicles per day (Lilleberg and Hellman, 2011), and the vehicles have been found to be the main source of CO₂ and aerosol particle number emissions in the area (Järvi et al., 2012; Ripamonti et al., 2013). In the vegetation sector (180°–320°), most of the surface is covered by green areas of the Kumpula Botanic Garden and the City Allotment Garden. During this study, the wind blew most often from the vegetation sector and least from the built sector.

The site infrastructure, the flux measurement conditions and the surrounding areas are described in detail ~~by Vesala et al. (2008) and in Vesala et al. (2008) and in~~ Järvi et al. (2009a).

2.1.1 VOC measurements with PTR-MS and volume mixing ratio calculations

A proton-transfer-reaction quadrupole mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Innsbruck, Austria; Lindinger et al., 1998) was measuring 12 different mass-to-charge ratios (m/z , see Table 2) every second hour using a 0.5 s sampling time between 1 January 2013 and 27 June ~~2014~~ 2014. The total sampling cycle was around 7 s (Fig. 1). ~~Rest~~ For the rest of the time the PTR-MS sampled a wider range of mass-to-charge ratios ~~from one level~~ but those measurements are not considered in this study. In addition, we had a short campaign between 27 June and 30 September 2014 when 14 mass-to-charge ratios were measured using the same 0.5 s sampling time. During the campaign, ~~those~~ the two additional mass-to-charge ratios were m/z 89 and m/z 103. In that period, the measurement cycle took always two hours so that m/z 31–69 were measured during the first and m/z 79–137 during the second hour, and the total sampling cycle was around 4.5 s. In summer 2014, there were some data gaps due to software problems (Table 2).

The PTR-MS was located inside a measurement ~~cab~~ container and sample air was drawn to the instrument using a PTFE tubing with 8 mm inner diameter (i.d.). The sample line was 40-m-long and it was heated (10 W m⁻¹) to avoid condensation of water vapour. A continuous air-flow was maintained in the tube with some variations in the flow rate: first 20 l min⁻¹ (whole year 2013), then 40 l min⁻¹ (until 30 May 2014) and then 20 l min⁻¹ (until the end of the measurements) again. The corresponding Reynolds numbers were around 3500 and 7000 for the lower and higher sample line flows, respectively. From the main inlet, a side flow of 50–100 ml min⁻¹ was drawn to PTR-MS via a 0.5-m-long PTFE tube with 1.6 mm i.d.

The PTR-MS was maintained at a drift tube pressure of 2.0–2.2 mbar and primary ion (H_3O^+) count rate of about $10\text{--}30 \cdot 10^6$ ~~eps (counts per second (cps,~~ measured at m/z 21). With these settings, E/N -ratio where E is the electric field and N the number density of the gas in the drift tube, was typically around 135 Td ($\text{Td} = 10^{-21} \text{ V m}^2$). ~~The oxygen~~ Oxygen level O_2^+ was mostly below 2% of the H_3O^+ signal.

- 5 The instrument was calibrated every second or third week using a diluted VOC standard (Apel-Riemer, accuracy $\pm 5\%$; Table 2). The volume mixing ratios were calculated using ~~the a~~ procedure described in detail ~~by in~~ Taipale et al. (2008). Before ~~a calibration, the the calibration,~~ SEM voltage (MasCom MC-217) of the PTR-MS was always optimized to get a ~~correct-high~~ enough primary ion signal level (e.g. Kajos et al., 2015). The optimized SEM voltage was also used in the measurements until the next calibration. The instrumental background was determined every second hour by ~~measuring-sampling~~ VOC free air, produced with a zero air generator (Parker Balzon HPZA-3500-220). The intake for the zero air generator was outside of the measurement cabin close to the ground, thus, the relative humidity was the same for both the zero air measurements and the ambient measurements. During the measurement period, the zero air generator was working sometimes improperly leading to contaminated m/z 93 signal. These periods were removed from the zero air measurements and replaced by the nearest reliable values. In addition, due to software problems, the zero air measurements were not recorded between 7 July and 30 September 15 2014. These gaps were replaced by a median diurnal cycle values of the zero air measured during 27 June – 7 July 2014. One should note that the mentioned problems with the zero air measurements had no effect on the flux calculations. However, they did, of course, cause ~~some uncertainties for additional uncertainties in~~ the measured concentration levels but a systematic error for the concentration levels was estimated to be negligible.

2.1.2 Ancillary measurements and data processing

- 20 An ultrasonic anemometer (Metek USA-1, Metek GmbH, Germany) was installed at 31 m, 0.13 m above the VOC sampling inlet. The ambient temperature was also measured at the VOC sampling level with a Pt-100 sensor. ~~The photosynthetic~~ Photosynthetic photon flux density was measured at 31 m in the measurement tower using a photodiode sensor (Kipp&Zonen, Delft, Netherlands). Pressure was measured with Vaisala HMP243 barometer on the roof of the University building near the site.

- 25 Hourly traffic rates were measured ~~online~~ 4 km from the measurement site by the City of Helsinki Planning Department. These rates were converted to correspond to ~~traffic rates on the~~ traffic rates of the road next to the measurement site following the procedure ~~by presented in~~ Järvi et al. (2012).

- CO_2 and CO concentrations (10 Hz) were measured with a Li-Cor 7000 (LI-COR, Lincoln, Nebraska, USA) and ~~the a~~ $\text{CO}/\text{N}_2\text{O}$ analyser (Los Gatos Research, model N2O/ CO -23d, Mountain View, CA, USA; later referred as LGR), respectively. 30 The CO_2 concentration was measured continuously between January 2013 and September 2014. The CO concentration was measured between 3 April and 27 May 2014 (Fig. 1) and the LGR was connected to the same main inlet line with the PTR-MS. During the CO measurements, the main inlet flow was 40 l min^{-1} . After the LGR was removed from the setup, the main inlet flow was decreased to 20 l min^{-1} to increase the pressure in the sampling tube and to get a higher side flow to the PTR-MS (from 50 to 100 ml min^{-1}).

Thirty minute average CO and CO₂ fluxes were calculated using the eddy covariance technique from ~~the~~ raw data according to commonly accepted procedures (Aubinet et al., 2012). A two-dimensional (2D) coordinate rotation was applied to the wind data and all data were linearly de-trended. The 2D rotation was used instead of ~~the a~~ planar fitting as the 2D rotation is likely to be less prone to systematic errors above a complex urban terrain (Nordbo et al., 2012b). Spike removal was made based on

5 ~~the a~~ difference limit (Mammarella et al., 2016). Time lags between wind and scalar data were obtained by maximizing the cross-covariance function. For the CO and CO₂ measurements, mean time lags of 5.8 s and 7.0 s, respectively, were obtained. Finally, spectral corrections were applied. The low frequency losses for ~~both the~~ fluxes were corrected based on theoretical corrections (Rannik and Vesala, 1999), whereas the high-frequency losses were experimentally determined. Finally, the 30-min fluxes were quality checked for stationarity with a limit of 0.3 (Foken and Wichura, 1996), and the periods with $u_* < 0.2$

10 m s^{-1} were removed from further analysis. More details of the data post-processing can be found in Nordbo et al. (2012b). Data-The corresponding data coverages for CO and CO₂ fluxes were 54.0% and 61.9%, respectively. The random error and detection limit of CO flux were $0.23 \mu\text{g m}^{-2}\text{s}^{-1}$ and $0.16 \mu\text{g m}^{-2}\text{s}^{-1}$, respectively. The corresponding numbers for the CO₂ flux were $0.05 \mu\text{g m}^{-2}\text{s}^{-1}$ and $0.03 \mu\text{g m}^{-2}\text{s}^{-1}$, respectively.

2.2 VOC flux calculations

15 2.2.1 Disjunct eddy covariance method

In ~~the a~~ disjunct eddy covariance method (hereafter DEC), the flux is calculated using a discretized covariance:

$$\overline{w'c'} \approx \frac{1}{n} \sum_{i=1}^n w'(i - \lambda/\Delta t) c'(i), \quad (1)$$

where n is the number of measurements during the flux averaging time, Δt is ~~the a~~ sampling interval and λ is a lag time caused by sampling tubes (e.g. Rinne et al., 2001; Karl et al., 2002; Rinne and Ammann, 2012). The ~~fluxes measured by the DEC method suffer from same sources of systematic underestimation as the fluxes measured by the EC method, including high and low frequency losses (e.g. Moore, 1986; Horst, 1997). According to Horst (1997), the high frequency losses, α_{horst} , can be estimated using an equation-~~

20 ~~DEC method suffer from same sources of systematic underestimation as the fluxes measured by the EC method, including high and low frequency losses (e.g. Moore, 1986; Horst, 1997). According to Horst (1997), the high frequency losses, α_{horst} , can be estimated using an equation-~~

$$(\alpha_{\text{horst}})^{-1} = \frac{1}{1 + (2\pi f_m \tau)^\beta},$$

~~where τ is the response time of the system, $f_m = n_m \bar{u} / (z_m - d)$ and $\beta = 7/8$ and $\beta = 1$ in unstable and stable stratification, respectively. In here, \bar{u} is the mean horizontal wind, z_m the measurement height and d a zero displacement height. The parameter n_m has been observed to be constant in unstable stratification at the site ($n_m = 0.1$), and in stable stratification ($\zeta > 0$) having the following experimental, stability and wind direction dependent values (Järvi et al., 2009b):-~~

25 ~~where τ is the response time of the system, $f_m = n_m \bar{u} / (z_m - d)$ and $\beta = 7/8$ and $\beta = 1$ in unstable and stable stratification, respectively. In here, \bar{u} is the mean horizontal wind, z_m the measurement height and d a zero displacement height. The parameter n_m has been observed to be constant in unstable stratification at the site ($n_m = 0.1$), and in stable stratification ($\zeta > 0$) having the following experimental, stability and wind direction dependent values (Järvi et al., 2009b):-~~

$$n_m = \begin{cases} 0.1(1 + 2.54\zeta^{0.28}), & d = 13 \text{ m, (built)} \\ 0.1(1 + 0.96\zeta^{0.02}), & d = 8 \text{ m, (road)} \\ 0.1(1 + 2.00\zeta^{0.27}), & d = 6 \text{ m, (vegetation)} \end{cases}$$

~~where ζ is the stability parameter.~~

VOC fluxes were calculated for each 45-min-period according to Eq. (1) using 385 data points (600 data points between 26 June and 30 September 2016). Before the calculations, ~~a the~~ linear trend was removed from the concentration and wind measurements. In addition, the 2D rotation was applied to the wind vectors.

- 5 The PTR-MS and the wind data were recorded to separate computers, thus, lag times were shifting artificially as the computer clocks performed unequally. Therefore, we first determined lag times of m/z 37 (first water cluster, $\text{H}_3\text{O}^+\text{H}_2\text{O}$) for each data set between two calibrations. Then, a linear trend was removed from the lag times to cancel the artificial shift. After that, the shifted cross covariance functions were summed (as in Park et al., 2013), and an average lag-time was determined for each mass-to-charge ratio from the summed cross covariance functions. Finally, ~~a the~~ lag-time for each 45-min-period was determined by
- 10 using a ± 2.5 s lag time window around the previously determined mean lag-time ~~, and with~~ a smoothed maximum covariance method described ~~by Taipale et al. (2010), in Taipale et al. (2010).~~ The smoothed cross covariance functions were calculated using a running mean with an averaging period of ± 2.4 s. However, if the mean lag-time value was not found, the previous reliable mean lag-time value was used instead. We defined that ~~a the~~ mean lag-time was representative if a peak value of ~~a the~~ summed cross covariance function was higher than $3\sigma_{\text{tail}}$ where σ_{tail} is ~~the~~ mean standard deviation of the summed cross
- 15 covariance function tails. The standard deviations were calculated using a lag-time ~~windows window of~~ $\pm(180 - 200)$ s. If a certain mass-to-charge ratio showed no representative peak values during the whole period at all, its flux values were defined to be insignificant and the mass-to-charge ratio was disregarded from further study.

The lag times were allowed to vary slightly (± 2.5 s) around the mean lag-times because removing the linear trend potentially caused uncertainties. Moreover, changes in relative humidity might have led to changes in the lag times at least in the case of

20 methanol which is a water-soluble compound, even with heated inlet line. Thus, the fluxes could be underestimated if the constant lag-times were used (see supplementary material). However, the lag time window we used, was quite narrow, ± 2.5 s, to limit uncertainties ("mirroring effect") caused by the maximum covariance method connected to the fluxes near the detection limit (Langford et al., 2015). Also, one should note that in our case the maximum covariance was determined from the smoothed cross covariance function which already limits the possible overestimation of the measured DEC fluxes, and thus

25 the mirroring effect (Taipale et al., 2010). Some flux values could be slightly underestimated if the correct lag-time was outside of the ± 2.5 s window. Figure S1 shows a comparison of the fluxes that were calculated using a constant lag-time and the fluxes obtained in this study.

- ~~Constant~~ The fluxes measured by the DEC method suffer from same sources of systematic underestimation as the fluxes measured by the EC method, including the high and low frequency losses (e.g. Moore, 1986; Horst, 1997). According to
- 30 Horst (1997), the high frequency losses, α_{horst} , can be estimated using an equation

$$(\alpha_{\text{horst}})^{-1} = \frac{1}{1 + (2\pi f_m \tau)^\beta}, \quad (2)$$

where τ is the response time of the system, $f_m = n_m \bar{u} / (z_m - d)$ and $\beta = 7/8$ and $\beta = 1$ in unstable and stable stratification, respectively. In here, \bar{u} is the mean horizontal wind, z_m is the measurement height and d corresponds to the zero displacement height. The parameter n_m has been observed to be constant in the unstable stratification at the site ($n_m = 0.1$), and in the stable

stratification ($\zeta > 0$) having the following experimental, stability and wind direction dependent values (Järvi et al., 2009b):

$$n_m = \begin{cases} 0.1(1 + 2.54\zeta^{0.28}), & d = 13 \text{ m, (built)} \\ 0.1(1 + 0.96\zeta^{0.02}), & d = 8 \text{ m, (road)} \\ 0.1(1 + 2.00\zeta^{0.27}), & d = 6 \text{ m, (vegetation)} \end{cases} \quad (3)$$

where ζ is the stability parameter.

A constant response time of 1.0 s and Eq. (2) were used for the high-frequency flux corrections. The constant value was estimated based on the previous studies with PTR-MS (Ammann et al., 2006; Rantala et al., 2014; Schallhart et al., 2015) where the response time of the measurement setup was estimated ~~of being to be~~ around 1 s. However, the response time is probably compound dependent as e.g. methanol might have a dependence on the relative humidity (RH) ~~because it is a polar molecule due to its polarity and water solubility~~. The response time of water vapour has been observed to increase as a function of RH (e.g. Ibrom et al., 2007; Mammarella et al., 2009; Nordbo et al., 2012b) and this is likely true for methanol as well. In addition, the length of the sampling tube affects the response time as well but the effect is difficult to quantify without experimental data (Nordbo et al., 2013).

The correction factor α_{horst} ~~was on average 1.16 for the high frequency losses was 1.16 on average~~. Even though the use of the constant value of $\tau = 1.0$ s may lead to random uncertainties if the true response time varies temporally, this is likely to ~~have only only have~~ a small effect on the calculated fluxes. Also a systematic error of a few percentages is possible, if the actual average response time was smaller or higher. We can also note that the change of the flow rate from 20 to 40 l min⁻¹ had only a negligible effect on the attenuation as long as the flow is turbulent (see Nordbo et al., 2014).

In addition to the high frequency losses ~~and lag-time searching routines~~, the calculated flux values may also be biased by some other factors. For short-lived isoprene and monoterpenes (minimum lifetimes ca. 2 hours, see Hellén et al., 2012), the flux losses due to chemical degradation were estimated to be few percentages (see Rinne et al., 2012). However, these losses are difficult to compensate as they do depend on oxidant concentrations (mainly OH and O₃) and ~~the on~~ surface layer mixing. Thus, no corrections due to the chemical degradation were applied. All ~~flux values are also slightly underestimated as the flux values were slightly underestimated (< 3% based on the measured CO₂ fluxes) as the~~ low frequency corrections were left out due to noisy VOC spectra. Larger errors might be produced by calibration uncertainties that affect directly ~~on~~ the measured fluxes. All mass-to-charge ratios excluding *m/z* 47 (ethanol+formic acid) were directly calibrated ~~against a standard~~ in this study, ~~but according~~. According to Kajos et al. (2015), ~~concentrations of the concentrations of the~~ calibrated compounds may also be biased ~~due to unknown reasons. Flux. The flux~~ values of ethanol+formic acid should especially be considered with caution as the concentrations of *m/z* 47 signal ~~were determined from was scaled based on~~ transmission curves (see Taipale et al., 2008).

Periods when the anemometer or the PTR-MS were working improperly, were removed from the time series (Fig. 1). For example, the fluxes were not measured during summer 2013 due to a thunderstorm that broke the anemometer, and in the beginning of 2014, ~~when~~ the PTR-MS was serviced ~~in a laboratory~~. During some periods, signal levels did not behave normally but had for example a lot of spikes. ~~Thus those Those~~ periods were disregarded as well. To limit the underestimation of the absolute flux values caused by a weak mixing, the fluxes during which $u_* < 0.2 \text{ m s}^{-1}$ were ~~also~~ rejected from further analysis.

Other quality ~~controlling controls~~, such as filtering ~~the~~ flux data with ~~the~~ flux detection limits or with the stationarity criteria (Foken and Wichura, 1996), was not performed because applying these methods for the noisy DEC data would potentially bring other uncertainty sources. ~~For example, disregarding the fluxes below the detection limit would lead to an overestimation of the mean absolute flux values.~~ However, before calculating correlation coefficients between a ~~specific~~ VOC and another compound (CO, CO₂ or ~~a~~ another VOC), a percentage (1%) of the lowest and highest values were removed to avoid effect of possible outliers. Data coverages for ~~VOCs~~ VOC fluxes are listed in Table 2.

2.2.2 Identification of measured mass-to-charge ratios

Identifications of the measured mass-to-charge ratios are listed in Table 2. Most of the identifications are clear but there are some exceptions. First of all, p-cymene fragments to the same m/z 93 with toluene (Tani et al., 2003). ~~Therefore,~~ ~~therefore,~~ p-cymene may potentially have ~~had~~ an influence on the observed concentrations at m/z 93 as the used E/N -ratio, 135 Td, ~~caused probably can cause~~ fragmentation of p-cymene (Tani et al., 2003). However, Hellén et al. (2012) observed that ~~the~~ p-cymene concentrations at the SMEAR III site are low compared with the toluene concentrations, ~~being~~ around 9% ~~during in~~ July. Therefore, the major compound at m/z 93 was likely toluene, although p-cymene might have increased ~~flux the fluxes~~ at m/z 93 during warm days.

Anthropogenic furan (de Gouw and Warneke, 2007) ~~and cycloalkanes~~ had probably a major contribution on the measured m/z 69 concentrations between October and May ~~when as~~ isoprene concentrations at the site ~~have been are~~ reported to be small (around 5 – 30 ppt; Hellén et al., 2006, 2012). In our study, ~~the~~ mean m/z 69 concentrations between June and August were only ca. 60% larger than during ~~the~~ other seasons (Table 43), indicating ~~a~~ considerable influence of furan ~~and cycloalkanes~~ (e.g. cyclohexane, see Hellén et al., 2006 and Lee et al., 2006). Another important compound influencing ~~the~~ measurements at m/z 69 is methylbutenol (MBO) fragment (e.g. Karl et al., 2012). However, MBO is mostly emitted ~~from by~~ conifers (e.g. Guenther et al., 2012) that are rare near the SMEAR III station. Therefore, MBO should ~~have had only only have~~ a negligible effect on the concentration and fluxes measured at m/z 69.

Monoterpenes fragment to the m/z 81. The parental mass-to-charge ratio of ~~the~~ monoterpenes, m/z 137, had ~~a~~ low sensitivity during the study, and therefore, ~~the~~ monoterpene concentrations were calculated using m/z 81. For some reason ~~, the~~ monoterpene concentrations were only slightly higher during ~~June–August than during September–May (Table 4); thus, the summer than during the other seasons (Table 3).~~ ~~Therefore,~~ a contribution of other compounds than monoterpenes at m/z 81 ~~might have been can be~~ possible. On the other hand, Hellén et al. (2012) observed also considerable monoterpene concentrations at the site in winter, spring and fall, possibly due to anthropogenic sources.

Acetone and propanal are both measured at m/z 59 with the PTR-MS but Hellén et al. (2006) showed that the average propanal concentrations ~~are were~~ only around 5% compared with the average acetone concentrations in Helsinki during winter. Thus, most of the m/z 59 signal consisted probably of acetone. However, as propanal fluxes at the site are unknown, m/z 59 will still be referred as acetone+propanal.

Measurements at m/z 107 consisted of C₂-benzenes including, for example, o- and p+m-xylene and ethylbenzene. According to Hellén et al. (2012), major compounds measured at the site is p+m-xylene. Other important compounds reported are o-xylene

and ethylbenzene. Hellén et al. (2012) observed annual variation for those compounds with a ~~minima~~ minimum in March. In our study, ~~no considerable differences between June–August and September–May were observed~~ only small differences between the seasons were observed (Table 3). However, the measured concentrations in this study were quite close to the corresponding values ~~from in~~ from Hellén et al. (2012). For example, ~~the~~ the summed concentration of o-, p+m-xylene and ethylbenzene was ca. 0.16 ppb in July (Hellén et al., 2012) whereas in this study, a mean value from June–August was 0.23 ppb (Table 43).

~~Mass-to-charge~~ The mass-to-charge ratio 42 is connected with acetonitrile but Dunne et al. (2012) observed ~~that~~ that the signal might be partly contaminated by product ions formed in reactions with NO^+ and O_2^+ that exist as trace amounts inside the PTR-MS. However, ~~that this~~ that this effect was impossible to quantify in this study, ~~and~~ and thus, m/z 42 was assumed to consist of acetonitrile.

Generally, acetonitrile is used as a marker for biomass burning as it is released from those processes (e.g. Holzinger et al., 1999; De Gouw et al., 2003; Patokoski et al., 2015).

2.3 Estimating biogenic contribution of isoprene

~~The A~~ A well-known algorithm for isoprene emissions (E_{iso}) is written as

$$E_{\text{iso}} = E_{0,\text{synth}} C_T C_L, \quad (4)$$

where $E_{0,\text{synth}}$, C_T and C_L are the same as in the traditional isoprene algorithm (Guenther et al., 1991, 1993; Guenther, 1997). The shape of this algorithm is based on the light response curve of the electron transport activity (C_L) and on the temperature dependence of the protein activity (C_T). The emission potential, $E_{0,\text{synth}}$, describes the emission rate of isoprene at $T = 30^\circ\text{C}$ where T is the leaf temperature (the ambient temperature in this study).

The algorithm was used to identify possible biogenic isoprene emissions. For other compounds, such as methanol or monoterpenes, no empirical algorithms were applied.

3 Results and discussion

3.1 ~~Observed VOC~~ Seasonal behaviour of observed fluxes and ~~their general behaviour~~ concentrations

Significant fluxes were observed for methanol (m/z 33), acetaldehyde (m/z 45), ethanol+formic acid (m/z 47), acetone+propanal (m/z 59), isoprene+furan+cycloalkanes (m/z 69, later referred as iso.+fur.+cyc.), benzene (m/z 79), toluene (m/z 93), C₂-benzenes (m/z 107) and sum of monoterpenes (m/z 81). The fluxes of these compounds had also a diurnal cycle at least in one of the wind sectors (Fig. 3, Table 1). Correlation coefficients between VOC, CO, CO₂ fluxes and traffic rates are shown in Table A1.

Methyl *tert*-butyl ether (MTBE) and *tert*-Amyl methyl ether (TAME) are commonly connected to the vehicle exhaust emissions as the compounds were at least used to increase the octane number of gasoline (e.g. Hellén et al., 2006). MTBE and TAME were measured at their parental ions at m/z 89 and m/z 103, respectively. However, both mass-to-charge ratios showed no significant fluxes, and therefore, those measurements were excluded from further analysis. As the identification of these

mass-to-charge ratios was uncertain, both m/z 89 and m/z 103 are marked as *unknown* in Table 2. Formaldehyde, which was measured at m/z 31 showed no fluxes either; ~~therefore,~~ Therefore, m/z 31 was excluded from further analysis as well.

~~Fluxes of aromatic compounds (benzene, toluene,~~ All of the studied compounds except acetonitrile had significant fluxes during winter (Table 4), indicating anthropogenic sources. All compounds except acetonitrile, iso.+fur.+cyc. and monoterpenes
5 had also a significant difference between weekday and weekend values (Fig. 4) which is also a strong anthropogenic signal as many anthropogenic activities can expected to be lower during the weekend than during the weekdays.

~~The toluene and C₂-benzenes) did not show any seasonal variation during the measurement period–benzene fluxes showed statistically significant seasonal variation with a maximum in winter and a minimum in summer–autumn (Table 4). This was expected because and Fig. 5). However, the variations were rather small because the biogenic emissions of these compounds~~
10 ~~should be either small or negligible and anthropogenic emissions from traffic-, and the anthropogenic emissions are unlikely to have considerable seasonal variation. On the other hand large seasonal variations. Nevertheless, the traffic counts are were lower during June–August (Fig. 1) but the average aromatic fluxes had no statistically-. The average benzene fluxes had statistically no significant differences between September–May and June–August the seasons (Table 4). Nevertheless, benzene and Fig. 5). A ratio between the average toluene or C₂-benzene and benzene fluxes had no considerable seasonal trend either (Table A2).~~

15 The benzene and toluene concentrations had a clear annual trend with a minimum during June–August. This is a well understood pattern and it is partly caused by the different atmospheric lifetimes of these compounds between seasons (e.g. Hellén et al., 2012). ~~The ratio of aromatic~~ Of course, local sources may affect the observed concentration trend as well if the boundary layer height has a seasonal cycle. The concentrations of all aromatic compounds had also a diurnal cycle with a maximum during morning rush hours when the traffic related emissions were high and the atmospheric boundary layer was
20 still shallow after the night (Fig 6). The behaviour is similar compared with the CO and CO₂ concentrations.

A clear biogenic signal was observed for iso.+fur.+cyc. which had a large difference in both the fluxes and concentrations between winter and summer (Tables 4 – 3). Therefore, the fraction of terpenoid to the total VOC fluxes to total measured VOC fluxes had also variations as the terpenoid fluxes had a clear seasonal cycle was also higher in the summer than in the winter (Fig. 7).

25 ~~Methanol, acetone~~ The iso.+propanal and acetaldehyde had higher average fluxes during June–August compared with the other months ~~fur.+cyc. flux followed also well the ambient temperature (Fig. 8). The monoterpene fluxes were significantly higher during the summer but the average flux during the winter was considerable as well (Table 4), indicating other major sources than only the biogenic ones. Interestingly, both the monoterpene and iso.+fur.+cyc. concentrations peaked during morning rush hour (Fig. 6), indicating an anthropogenic contribution, most likely from traffic related sources.~~

30 Methanol had a higher average flux during spring and summer compared with winter and autumn (Table 4 and Fig. 5). Similarly, an average acetaldehyde flux from summer was around 100% larger compared with the winter value, which might indicate a significant biogenic contribution during the summer. For methanol and acetone, the largest difference between the average fluxes was interestingly between summer and autumn season. This cannot be explained by the biogenic emissions as the autumn values were smaller than the winter ones (Table 4) and Fig. 5), but it might be a result of changes in the non-traffic
35 related anthropogenic activity. On the other hand, the observed differences can be partly explained by wind directions: in

summer, 38% of the time the wind blew from the road sector ($40^{\circ} - 180^{\circ}$) whereas in autumn, the corresponding occurrence was only 24%.

The methanol, acetone and acetaldehyde (OVOCs) concentrations had also a seasonal cycle with a maximum in summer. However, those compounds showed no clear diurnal cycles, probably due to high ambient background concentrations compared with aromatic or terpenoid compounds (Table 3; Fig 6). However, the differences were rather small, indicating only minor biogenic emissions compared with the other sources. The ratio of the measured OVOC fluxes to the total measured VOC fluxes stayed stable, being 55–62% in all sectors 48–61% depending on the season (Fig. 7).

A clear biogenic signal was observed only for isoprene. The diurnal concentration level of acetonitrile stayed almost constant but the concentrations showed an annual trend with a maximum in summer (Table 3 and Fig. 5). However, this was probably related to advection from distant sources (e.g. Patokoski et al., 2015). Generally, the average acetonitrile fluxes were really small being still above the detection limits except in winter (Table 4; Fig. 5).

Both ethanol+formic acid fluxes and concentrations had significant differences between the seasons. However, as the ethanol+formic acid flux followed also well the ambient temperature, formic acid was not calibrated, the results should be taken as rough estimates. Nevertheless, the average ethanol+formic acid flux seemed to have a maximum in winter. Their concentration showed also a weak diurnal trend with minimum during early morning (Fig. 86).

3.2 VOC, CO fluxes and CO₂ emissions from different sources

To investigate the relative contributions different sources, the fluxes were analysed by wind sectors. The data was divided into three groups based on the local wind direction corresponding to built, road and vegetation dominated areas (Table 1 and Fig. 2). The measured flux value was defined to be, for example, from the road sector if less than 30% of the flux footprint area covered other than the road sector. Thus, the periods when wind blew close to a sector border, were rejected from further analysis. The total rejection rate was around 30%. The footprints were determined according to Kormann and Meixner (2001).

The CO flux was observed to have a clear diurnal cycle, and as expected, the highest emissions were detected from the road sector (Fig. 9) where the traffic emissions are at their highest. The measured CO fluxes from the road sector also correlated very well with both the corresponding CO₂ fluxes ($r = 0.69$, $p < 0.001$) and with the traffic rates ($r = 0.56$, $p < 0.001$, Fig. 10). The average and median CO and CO₂ fluxes and CO concentrations from April 3 – May 27 2014 are presented in Table 7. The ratio between the median CO and CO₂ fluxes was the lowest during night-time due to respiration of CO₂ from vegetation (Fig. 9). The highest flux values of both CO and CO₂ were observed during day-time. However, the rush hour peaks cannot be seen from the flux data. On the other hand, the traffic rates were only slightly higher during the rush hours compared with the other day-time values.

During the measurement period, the average CO flux from the traffic-road sector was ca. 0.46% compared with the corresponding CO₂ flux (Table 7). On the other hand, CO₂ had probably already experienced biogenic up-take between April and May 2014 (Järvi et al., 2012; Fig. 9; Table 7). Therefore, a better estimate for the flux ratio was taken

from Järvi et al. (2012) who estimated that the CO₂ emission rate from the road sector is 264 $\mu\text{g m}^{-2}\text{s}^{-1}(1000 \text{ veh h}^{-1})^{-1}$ ~~(which is based on wintertime data from 5 years)~~. In our study, the corresponding CO emission rate from traffic was 0.9 $\mu\text{g m}^{-2}\text{s}^{-1}(1000 \text{ veh h}^{-1})^{-1}$ which is ca. 0.34% compared with the corresponding emission rate of CO₂ in mass basis. Järvi et al. (2012) used data from a more narrow wind sector, 40–120°. However, ~~the~~ average CO fluxes had no considerable differences between ~~the~~ more narrow and the whole road sector, ~~thus, this had probably~~. Thus, this probably had only a minor effect on the results. The CO/CO₂ fraction ~~is was~~ smaller than in previous study conducted in Edinburgh by Famulari et al. (2010) who estimated that the traffic related CO emissions are 0.60% compared with the corresponding CO₂ emissions in Edinburgh (in mass basis). In that study, the CO/CO₂ flux ratio was also otherwise quite large, 1.36%. ~~Conversely, Popa et al. (2014) observed a ratio of 0.26% for CO~~ On the other hand, Harrison et al. (2012) found that the CO/CO₂ ~~concentrations (in mass basis) in a tunnel study which is quite close~~ flux fractions of 0.32% and 0.55% which are closer to the flux ratio ~~of our study, obtained in this study. Furthermore, the Edinburgh data set is many years older and the traffic related anthropogenic CO emissions have generally decreased during these years (e.g. Air quality in Europe – 2015 report, <http://www.eea.europa.eu/publications/air-quality-in-europe-2015>, accessed 2 May 2016).~~

Considerable CO fluxes were ~~also~~ observed from the built sector during afternoons (Fig. 9). Such ~~a~~ behaviour was not observed for ~~the~~ CO₂ during the same period (Fig. ~~10~~). ~~This may be due to 9~~. Domestic burning sources might explain part of the observed behaviour of the CO fluxes from the built sector. On the other hand, many car engines ~~that are started always are~~ always started in the afternoon (between ~~Monday-Friday~~ Monday and Friday) when people are leaving the university campus. Catalytic converters that oxidize CO to CO₂ may not work properly right after starting the engine (e.g. Farrauto and Heck, 1999) ~~leading to the high observed CO emissions. Unfortunately, the CO data set from the built sector was very limited~~ from weekends, ~~therefore~~. Therefore, the CO fluxes from ~~the~~ working days could not be compared with ~~the~~ CO fluxes from Saturday and Sunday. However, aromatic VOCs seem to ~~also~~ have a similar behaviour with increasing values during afternoon from the built sector (Fig. 3) which is somewhat expected as Reimann and Lewis (2007, p. 33) mentions that ~~the~~ VOC related "cold start emissions" are becoming more and more important. On the other hand, none of the aromatic compounds had a positive correlation with the CO flux, indicating different sources for CO and for the aromatic compounds.

25 ~~VOC emissions from different sources~~

~~Measured VOC fluxes were studied from all three sectors to estimate sources for VOCs. Based on an older study at the site According to a study by Hellén et al. (2006), traffic should be the traffic is the most important source for aromatic compounds the aromatic compounds in Helsinki with for example wood combusting explaining less than 1% of the detected benzene concentrations. However, the study by Hellén et al. (2006) was based on the chemical mass balance receptor model with the VOC concentrations. Thus, the footprint of their study is was larger than in our flux measurement based study.~~

Major work which is based on the flux measurements. The major emissions could originate also from ~~the~~ biogenic sources, at least in the case of isoprene and monoterpenes (Hellén et al., 2012). ~~Thus, isoprene~~ Therefore, summertime data of iso.+furanfur.+cyc., monoterpenes, and also OVOCs (methanol, acetone+propanal and acetaldehyde were analysed from two periods: June–August (assumed growing season) and September–May. The division is somewhat rough as many VOCs are also emitted from biogenic sources between September and May. However, these emissions are smaller than during June–August (Rantala et al., 2015) were

analysed more carefully. Conversely, the aromatic compounds were assumed to have no biogenic emissions, although benzenoid compounds might also originate from vegetation (Misztal et al., 2015).

Other In addition to the traffic, other anthropogenic VOC sources could potentially include wood combusting and solvent use. Industry is also a source for the VOCs but no industrial activities were located inside flux footprint areas. However, the solvent use might be a significant source for many compounds, especially in the built sector where the university buildings are located.

3.1.1 Traffic related emissions

Out of the measured compounds, methanol, acetaldehyde, ethanol, acetone, toluene, benzene, and C₂-benzenes are ingredients of gasoline (Watson et al., 2001; Niven, 2005; Caplain et al., 2006; Langford et al., 2009). Therefore, the traffic is potentially an important anthropogenic source for these compounds. In addition, many studies have shown traffic related isoprene emissions (Reimann et al., 2000; Borbon et al., 2001; Durana et al., 2006; Hellén et al., 2006, 2012). Hellén et al. (2012) also speculated that some of the monoterpene emissions could originate from traffic. Of course, the ingredients of gasoline probably do have variations between countries. In Finland, a popular 95E10 gasoline contains a significant amount of ethanol (< 10%) and methanol (< 3%).

In recent VOC flux studies at urban sites, the fluxes of some VOCs have correlated with traffic rates the traffic rates (Langford et al., 2009, 2010; Park et al., 2010; Valach et al., 2015) but this does not necessarily imply causality (Langford et al., 2009, 2010; Park et al., 2010; Valach et al., 2015). At SMEAR III, the traffic has been shown to be the most important source for CO₂ at from the road sector (Järvi et al., 2012) and the same seems to hold also for CO (Table 7). Therefore, the influence of the traffic on the VOC emissions was quantified by studying the measured VOC fluxes from this direction.

The difference between the average fluxes from the road sector and the other sectors was statistically significant (95% confidence intervals) for methanol, isoprene acetaldehyde, iso-furan, toluene fur+cyc., benzene and C₂-benzenes. However, benzene fluxes were so close to the detection limit that the differences between the sectors were insignificant.

All three studied aromatics (benzene, toluene and C₂-benzenes) were assumed to have same sources, thus, from now on these main source, the traffic. Therefore, the aromatic compounds are analysed together as an "aromatic flux" and they are later referred as the aromatic flux. However, especially toluene and C₂-benzenes are also released from solvents and paint related chemicals. These non-traffic related sources were studied by comparing the average toluene and C₂-benzene flux with the corresponding average benzene flux, as benzene was assumed to be emitted from the traffic related sources only. The ratios between the average toluene and benzene fluxes from the road, vegetation and built sector were around 2.6 ± 0.4 , 2.50 ± 0.7 and 3.70 ± 1.9 , respectively. The ratios indicate that toluene might have also evaporative sources. In previous studies, the exhaust emission ratio between toluene and benzene has been determined to be around 2 – 2.5 (e.g. Karl et al., 2009 and references therein) but the ratio depends on catalytical converters etc. (e.g. Rogers et al., 2006). Above an industrialized region in Mexico City where toluene had also other major sources in addition to traffic, Karl et al. (2009) found the ratio to be around 10–15. In this study, the corresponding ratios for benzene/C₂-benzenes were 0.32 ± 0.05 , 0.31 ± 0.09 and 0.30 ± 0.17 . In earlier studies

(e.g. Karl et al., 2009 and references therein), the exhaust emission ratio for those compounds have been observed to be around 0.4. Thus, both toluene and C₂-benzenes had probably also other than traffic related emissions in all the sectors. However, the possible sources for these non-traffic related emissions remained unknown. In the built sector, the evaporative emissions from the University buildings might explain part of the toluene and C₂-benzene flux.

5 The traffic rates and the aromatic fluxes had a significant correlation (~~$r = 0.39$~~ $r = 0.38$, $p < 0.001$, measurements between January 2013 and September 2014) from the road sector. The aromatic fluxes correlated even better with the measured CO fluxes (~~$r = 0.54$~~ $r = 0.50$, $p < 0.001$, measurements between April and May 2014). The significant correlation ~~of between the~~ aromatic VOC flux ~~with and the~~ CO flux indicates a common source ~~in from~~ incomplete combustion. As these both correlated in also with ~~the~~ traffic rates, the traffic is likely to be ~~a the~~ major source for aromatics.

10 To estimate the total emission of the aromatic compounds from ~~the~~ traffic, the aromatic fluxes were fitted against the traffic rates. A linear model between ~~the~~ traffic rates and ~~the~~ CO₂ emissions has been suggested, for example, ~~by in~~ Järvi et al. (2012). On the other hand, Langford et al. (2010) and Helfter et al. (2011) proposed an exponential fit for ~~the~~ VOC and CO₂ emissions. Helfter et al. (2011) mention many reasons for the exponential relationship, such as an increased fuel consumption at higher traffic rates. However, Järvi et al. (2012) did not observe ~~the~~ exponential behaviour between ~~the~~ CO₂ fluxes and ~~the~~ traffic rates at the site, ~~therefore,~~ ~~Therefore,~~ a linear model was also used in this study. Additionally, ~~an the~~ exponential relationship was tested but it brought no clear benefit compared with the linear model. The linear fit gave ~~$F_{\text{aro}} = (29 \pm 5) \cdot 10^{-3} \text{Tr} + 7 \pm 9$~~
15 ~~$F_{\text{aro}} = (28 \pm 5) \cdot 10^{-3} \text{Tr} + 10 \pm 9$~~ ng m⁻²s⁻¹, where F_{aro} is the flux of the aromatics (unit ng m⁻²s⁻¹) and Tr is the traffic rate (veh h⁻¹). Based on this model and the traffic rates measured in 2013, the aromatic emission from traffic was estimated to be ca. ~~1.21~~ 1.1 ± 0.2 g m⁻²yr⁻¹. ~~This if the intercept is assumed to be indicative other than traffic-related sources. The uncertainty estimate excludes possible errors related to the calibrations and to the traffic counts. Nevertheless, the value~~ 1.1 ± 0.2 g m⁻²yr⁻¹
20 is around 0.01% compared with the corresponding CO₂ emission from the road sector (in mass basis) that was estimated using a linear model provided by Järvi et al. (2012).

~~Methanol fluxes were also~~ ~~The methanol fluxes were~~ observed to correlate with the traffic rates (~~$r = 0.34$~~ $r = 0.32$, $p < 0.001$, Sep–May) and ~~with the~~ CO fluxes (~~$r = 0.34$~~ $r = 0.31$, $p = 0.001$, Apr–May 2014). ~~On the other hand, according in the road~~
25 ~~sector. According~~ to a linear fit, ~~the~~ methanol flux values were ~~still~~ around 20 ng m⁻²s⁻¹ or higher when the traffic rate was close to zero (Fig. 11) ~~which~~. ~~This~~ indicates that methanol had probably also other major sources ~~in the road sector than the~~ ~~traffic~~. This is also supported by the fact that ~~the~~ average methanol fluxes from weekend and weekdays were ~~almost equal quite~~ ~~close to each other~~ (Fig. 4), ~~although traffic rates are even though the traffic rates were~~ clearly larger during ~~the~~ weekdays (Fig. 9). However, we were not able to identify any clear ~~sources except possible additional sources to the traffic except~~ biogenic
30 emissions during summer. ~~Langford et al. (2010) found also~~ ~~To support our claim, Langford et al. (2010) found~~ that the traffic counts were able to explain only a part of the observed methanol fluxes but other methanol sources remained unknown in that study as well.

~~Other~~ ~~The other~~ oxygenated hydrocarbon fluxes correlated also with the traffic rates. ~~Ethanol~~ ~~The ethanol~~ + formic acid fluxes were somewhat noisy and mostly close to the detection limit (Table 4) but the correlation between the measured fluxes and
35 the traffic rates was still significant (~~$r = 0.20$~~ $r = 0.19$, $p < 0.001$, Jan 2013 – Sep 2014). However, no correlation between ~~the~~

ethanol+formic acid and CO fluxes was found. ~~Corresponding~~ The corresponding correlation coefficients for acetone+propanal were ~~0.24-0.23~~ ($p < 0.001$, traffic) and ~~0.42~~ (~~$p = 0.005$~~ $p < 0.001$, CO). The correlation between the acetaldehyde and CO ~~flux was 0.30~~ (~~$p = 0.004$~~ fluxes was 0.39 ($p < 0.001$)) and between the acetaldehyde flux and the traffic rates ~~0.31-0.30~~ ($p < 0.001$). ~~Methanol~~ The methanol, acetaldehyde and acetone+propanal fluxes had also considerable correlations with each other, indicating that these compounds had probably similar ~~non-traffic-related sources at~~ sources from the road sector. The correlation coefficients between the methanol and acetaldehyde fluxes and methanol and acetone+propanal fluxes were ~~0.44 and 0.37~~ 0.52 and 0.38, respectively ($p < 0.001$, measurements from Sep–May). The period between September and May was used instead of winter, i.e. non-growing season, to have a reasonable amount of data.

~~Isoprene~~ The iso.+furan fluxes that were fur.+cyc. fluxes measured during September–May had a weak but a significant correlation (~~$r = 0.24$~~ $r = 0.20$, $p < 0.001$) with the traffic rates (Fig. 11). Moreover, the average ~~isoprene iso.+furan fluxes were also positive during September–May~~ fur.+cyc. flux was positive during winter (Table 4), indicating that some ~~isoprene of the iso.+furan fluxes should fur.+cyc. fluxes~~ originate from anthropogenic sources. A correlation between ~~isoprene the iso.+furan fur.+cyc. fluxes~~ and the traffic rates has also been earlier observed by Valach et al. (2015). ~~Thus, the correlation found in this study seems reasonable.~~ A correlation between ~~isoprene the iso.+furan and fur.+cyc. and the~~ CO fluxes was significant ($r = 0.37$, $p < 0.001$) also indicating a traffic related source.

~~Monoterpene fluxes had no correlation with~~ However, one should note that isoprene is also emitted from biogenic sources and this component is difficult to distinguish from the measured fluxes. If the data from winter months was only used, no relation between iso.+fur.+cyc. fluxes and the traffic rates during September–May. In summer (Jun–Aug), the correlation coefficient between the monoterpene fluxes and was found. On the other hand, amount of data was also quite limited from those months (Table 4).

The monoterpene fluxes had only a weak correlation with the traffic rates ~~was significant, $r = 0.26$ ($p < 0.001$)~~ ($r = 0.14$, ~~but this $p = 0.001$~~). However, even the weak correlation might also have been a result of the increased biogenic emissions as they have a similar kind of diurnal cycle compared with the traffic rates. The biogenic influence would be possible to eliminate by dividing the monoterpene fluxes into different temperature classes, ~~however, but~~ the amount of data was too small for that kind of analysis. Thus, the possible monoterpene emissions from the traffic remained unknown, although the rush hour peak in the diurnal concentration cycle (Fig. 6) indicated traffic related emissions.

~~Acetonitrile~~ The acetonitrile fluxes had no correlation with the traffic rates. This was expected as the only considerable acetonitrile fluxes were observed from the built sector (Fig. 3). The acetonitrile emissions from the traffic should also be small compared to toluene or benzene emissions (e.g. Karl et al., 2009 and references therein).

Overall, the observed correlations were relatively low for all the VOCs. One explanation is that the fluxes were noisy, reducing therefore also the corresponding correlation coefficients. On the other hand, the low correlations may also indicate multiple sources for many of the VOCs, decreasing therefore the correlations between the fluxes and, for example, the traffic rates, and thus making the VOC source analysis very challenging.

3.1.2 Biogenic emissions

Nordbo et al. (2012a) observed that the urban CO₂ fluxes are clearly dependent on the fraction of vegetated land area in the flux footprint. Moreover, Järvi et al. (2012) observed that at our measurement site the vegetation sector is a sink for CO₂ during summer (see also Fig. 9). Thus, the biogenic VOC emissions could be expected to occur at the site. For isopreneiso.+furanfur.+cyc., the biogenic contribution was clear, and an anticorrelation ($r = -0.54, p < 0.001$) between the CO₂ and isopreneiso.+furanfur.+cyc. fluxes were observed from the vegetation sector during June–August. Isoprenethe summer. The iso.+furanfur.+cyc. fluxes were also affected by the ambient temperature with small fluxes at the small fluxes associated with the low temperatures (roughly $T < 10^{\circ}\text{C}$, Fig. 8). Also the methanol fluxes had a high anticorrelation with the carbon dioxide fluxes at from the vegetation sector between June and August ($r = -0.61, r = -0.59, p < 0.001$), indicating a biogenic source as well.

IsopreneThe iso.+furanfur.+cyc. fluxes were fitted against the empirical isoprene algorithm (Eq. 4) for each wind direction. to obtain the emission at standard conditions. Thus, the only free parameter in the fitting was the emission potential E_0 . It has been shown before that the emission potential of isoprene might have a seasonal cycle with a maximum during midsummer (e.g. in the case of aspen: Fuentes et al., 1999; see also Rantala et al., 2015). However, due to a lack of data points, the fitting was done for the whole summer period (Jun–Aug) only.

The emission potentials, $E_{0,\text{synth}}$, from each wind sector (Jun–Aug) for isoprene First, the fitting was done for each wind direction, but no considerable differences in the emission potentials between the wind directions were found. When all the data from the summer was used, the correlation between the measured fluxes and the calculated emissions (Fig. 12) was good ($r = 0.81$), indicating that most of the measured flux at m/z 69 originated from the biogenic isoprene emissions during the summer. On the other hand, the algorithm was unable to explain some higher iso.+furan are presented in fur.+cyc. flux values from the road sector (Fig. 12). These values might be related to random uncertainties but they might also be, for example, a result of the traffic related emissions.

The calculated emission potential ($E_0 = 125 \pm 5 \text{ ng m}^{-2}\text{s}^{-1}$) is roughly twice as high that has been measured above a pine dominated boreal forest in Hyytiälä, Southern Finland (Rantala et al., 2015), although the fraction of vegetation cover at SMEAR III is only 38–59%. However, this was expected as the urban vegetation consists of mostly broadleaved trees that are major isoprene emitters (e.g. Guenther et al., 2006). The emission potentials from each wind sector were close to each other, especially when considering differences in land use (Tables 1 and 5). In that sense, SMEAR-III can be considered as a horizontally homogeneous location from a point of isoprene flux measurements. On the other hand, the algorithm was unable to explain some higher isoprene On the other hand, one should note that the emission potentials were determined above a rather heterogeneous terrain with multiple tree species (e.g. Botanical garden). Thus, a direct comparison with the other studies should be avoided. More accurate analysis would be possible if dry leaf masses were known inside the flux footprint area. Unfortunately, this information was not available for this study. As a conclusion, the biogenic isoprene emissions explained around $80 \pm 5\%$ of the measured iso.+furan flux values from the road sector (Fig. 12). These values might be related to random uncertainties but they might also be, for example, a result of traffic related emissions. fur.cyc. flux in the summer (Table 6).

This estimate was calculated by comparing the average iso.+fur.cyc. flux at low temperatures (Fig. 8) with the average flux in the summer (Table 4).

Methanol, acetaldehyde and acetone are also emitted from the biogenic sources (e.g. Guenther et al., 2012), and the methanol fluxes from the vegetation sector were dependent on the ambient temperature. However, the (see supplementary material). The average methanol flux from the vegetation sector was still was around $30 \text{ ng m}^{-2}\text{s}^{-1}$ when temperature $T < 10^\circ\text{C}$ which indicates that the biogenic emissions can explain only a minor part of the measured methanol fluxes was less than 10°C indicating a biogenic contribution as the average flux was around $54 \text{ ng m}^{-2}\text{s}^{-1}$ in the summer (Table 4). For acetaldehyde and acetone+propanal the effect of the ambient temperature was even weaker.

As the biogenic OVOC emissions were difficult to distinguish from other exchange processes, such as traffic related emissions, the biogenic contribution for these compounds was estimated from the average flux values, the corresponding average fluxes when $T < 10^\circ\text{C}$ were around 9 and $14 \text{ ng m}^{-2}\text{s}^{-1}$, respectively. When comparing these values ($T < 10^\circ\text{C}$) to the average summer time fluxes (Table 4). Methanol fluxes were significantly larger during June–August than during September–May, indicating that biogenic sources could explain around 25% and taking to account the variation in data, the vegetation had a contribution of $42 \pm 8\%$, $26 \pm 8\%$ and $30 \pm 11\%$ for the methanol, acetaldehyde and acetone fluxes during the summer, respectively. Together, the biogenic emissions explained around 35% of the measured methanol fluxes during June–August (Table 4). This is, of course, only a rough estimate total OVOC flux during summer. These estimates are valid if anthropogenic emissions are assumed to be independent of the ambient temperature. Therefore, the estimates are only rough but still reasonable when comparing with, for example, measured biogenic methanol. For example, the measured biogenic OVOC emissions in Hyytiälä, Southern Finland, have been comparable (Rantala et al., 2015). Acetaldehyde and acetone+propanal had also significant differences between the average flux values from June–August and September–May. Those differences were around 20–30% indicating that the possible biogenic contribution for these compounds is quite small even during June–August.

Monoterpene fluxes were highly scattered (Fig. 3) and the fluxes were also clearly above zero when temperature $T < 10^\circ\text{C}$. The average monoterpene flux was around $7 \text{ ng m}^{-2}\text{s}^{-1}$ when temperature was $< 10^\circ\text{C}$ (Fig. 8) indicating, indicating that the significant monoterpene emissions originated from other sources than the biogenic ones. Therefore, no empirical emission algorithms were fitted against the monoterpene fluxes. Nevertheless, in June–August the average monoterpene flux was almost around twice as high, when compared with the average flux from September–May. The monoterpene fluxes were also dependent on the ambient temperature (Fig. 8). Therefore, biogenic contribution during June–August at the low temperatures ($T < 10^\circ\text{C}$; Table 4). Taking into account the variation in the data, the biogenic contribution was assumed to be around 40% $50 \pm 15\%$ of the value of the average monoterpene emissions in the summer. Overall, the anthropogenic emissions were estimated to be around 35% compared with the total monoterpene emissions, terpenoid (isoprene+monoterpenes) emission in the summer (Table 6).

3.1.3 Other VOC sources or sinks

Other The other potential sources of VOCs, mainly wood combustion and solvent use, were found to be difficult to identify. For example, quite large acetone+propanal emissions were observed from the built sector in the afternoon (Fig. 3), and the difference between the weekdays and weekend values was also statistically significant (95% confidence intervals, see Fig. 4).

These emissions might have been originating from the chemistry department near the site that uses acetone as a solvent. Recent studies (e.g. Wohlfahrt et al., 2015 and references therein; Rantala et al., 2015; Schallhart et al., 2015) have shown that deposition might have a significant role in the OVOC exchange in some ecosystems. However, clear signals of net deposition were not observed for any of the studied OVOCs.

- 5 Nevertheless, methanol, acetaldehyde and acetone+propanal ~~were observed to have emissions that were independent of both ambient temperature and emissions were observed and they did not depend on the ambient temperature or on the~~ traffic rates. ~~For methanol, these~~ The methanol emissions were around $20\text{--}45\text{ ng m}^{-2}\text{s}^{-1}$ from the road sector ~~when the traffic rate was close to zero~~ (Fig. 11) ~~which is correspondingly around 30–70 % compared with the average methanol flux (Table 4, Fig. 4). The offset~~. The intercept of the linear fit was larger during June–August than during September–May but the difference was statistically insignificant. Recent studies (e.g. Wohlfahrt et al., 2015 and references therein; Rantala et al., 2015; Schallhart et al., 2015) have shown that deposition might have also a significant role in OVOC exchange in some ecosystems. However, no clear signals of net deposition was observed for any of the studied OVOCs. Overall, non-traffic sources were estimated to explain around 50% ~~When the sum of OVOCs (excluding ethanol+formic acid) was fitted together against the traffic rates (Sep–May), the intercept was $28 \pm 22\text{ ng m}^{-2}\text{s}^{-1}$ whereas the corresponding average OVOC flux was around $82\text{ ng m}^{-2}\text{s}^{-1}$. If the intercept~~ is assumed to describe of a non-traffic anthropogenic flux, the ratio between the non-traffic related anthropogenic emissions and the total anthropogenic OVOC flux was 0.34 ± 0.27 . The ratios between the average benzene and the average OVOC fluxes had no considerable differences between the sectors, thus the given estimate represents the whole measurements site. Hence, the other anthropogenic sources than the traffic explained $35 \pm 25\%$ of the ~~anthropogenic OVOC emissions between September and May~~ total anthropogenic OVOC flux at the site (Table 6). This is, of course, a rough estimate, as the biogenic sources, traffic and other anthropogenic sources are difficult to distinguish from each other. Probably all of these sources have, for example, similar diurnal cycles with the minimum and maximum emissions during night and day, respectively.

Globally, ~~the~~ aromatic compounds have ~~also~~ other sources than traffic, such as solvent and petroleum use (Na et al., 2005; Srivastava et al., 2005; Langford et al., 2009). When considering an ~~offset of around 7~~ intercept of $10 \pm 9\text{ ng m}^{-2}\text{s}^{-1}$ of the linear fit between the aromatic fluxes and the traffic rates (Fig. 11), ~~emissions of the emissions of the~~ aromatic compounds from ~~the~~ non-traffic sources might ~~have also been possible play a role~~ at the SMEAR III. ~~Nevertheless, an influence of non-traffic sources was rather small. A ratio between the intercept and the average aromatic flux from the road sector was 0.18 ± 0.17 . Thus, the other sources than the traffic were estimated to explain $20 \pm 15\%$ of the measured aromatic fluxes (Table 6). Again, this represents the whole measurement site as the flux ratios between toluene or C₂-benzenes and benzene had no considerable differences between the sectors.~~

- 30 Isoprene ~~For the iso.+furan+had fur.+cyc. compounds,~~ small emissions around ~~2–5~~ $2\text{--}3\text{ ng m}^{-2}\text{s}^{-1}$ ~~were detected~~ (Fig. 8 and Table 4) ~~from other sources than biogenic ones originating from other than biogenic sources~~. They might be traffic-related as discussed above but they may also ~~originate come~~ from petroleum products (Langford et al., 2009). Nevertheless, the contribution of ~~other than biogenic isoprene~~ the iso.+furan emissions was small during June–August. ~~fur.+cyc. emissions from the anthropogenic sources was relatively small during summer, with a maximum around 15 – 25%. The estimate was calculated by comparing the average iso.+fur.+cyc. flux at $< 10^\circ\text{C}$ with the average iso.+fur.+cyc. flux between June and August. For~~

monoterpenes, the anthropogenic influence was stronger but no clear sources were identified. However, monoterpenes could originate from solvents as they are for example ingredients of various cleaning products.

Acetonitrile had significant emissions only from the built sector. This indicates that the major sources of acetonitrile are not traffic related, although Holzinger et al. (2001) found weak signals for the traffic related acetonitrile emissions, and Langford et al. (2010) measured the acetonitrile fluxes that correlated with the traffic rates. On the other hand, Langford et al. (2010) also mentioned that despite of the correlation, the acetonitrile sources were left unknown not known. In this study, a possible source for the acetonitrile could be wood combusting in the residential building area, which is located around 200–400 m from the site, and thus at the edge of the typical flux footprint area (see Ripamonti et al., 2013) and Fig. 2). On the other hand, for example Christian et al. (2010) mentioned that the acetonitrile emissions from wood combusting are small in comparison with the other biomass burning sources. In addition, acetonitrile is released from the solvents. Thus, this might explain the observed acetonitrile flux as well. This is supported by the observed correlation between the acetone and acetonitrile fluxes from the built sector (Table A1). However, the acetonitrile fluxes were mostly noisy and below the detection limit close to the detection limits (Table 4), making any final conclusions challenging.

3.2 Comparing Comparison of the results to with previous VOC studies

Generally, the measured VOC fluxes were much lower than those reported in the previous urban VOC flux studies (Fig. 13). For example, Velasco et al. (2005) measured an order of magnitude higher methanol, acetone+propanal, toluene and C₂-benzene fluxes in Mexico City compared with this study. Most of the previous measurements were done in the city centres while this study was done at the urban background site, which likely has a considerable effect on the magnitude of the VOC fluxes. For example, Reimann and Lewis (2007, p. 53) mentions that aromatic underlined the fact that the concentrations were lower in the suburban area of Zürich compared with the city centre.

For the measured CO₂ fluxes, intercity variations are also found to be considerable (Nordbo et al., 2012a). For example, Helfter et al. (2011) measured ca. five times higher CO₂ fluxes in London than Järvi et al. (2012) at SMEAR III (Fig. 13) in Helsinki. The variations in the carbon dioxide fluxes can be due to the intensity of the anthropogenic activity, the differences in differences in the heating systems (central, electrical, domestic gas, coal, oil or wood fired heating systems), the means types of public transport (electric buses and trams or diesel buses) etc. The relatively low VOC fluxes observed in this study are in line with the low carbon dioxide flux, both of which indicate relatively low anthropogenic intensity for an in the urban area. In this study, for example, the traffic related aromatic emissions were around 0.01% compared in comparison with the corresponding CO₂ emissions, and according to Valach et al. (2015), the aromatic VOC fluxes measured in London were around 0.025% compared with the corresponding average CO₂ fluxes (scaled from yearly CO₂ budget, see Helfter et al., 2011). Hence, the VOC flux to the CO₂ flux ratio is in the same order of magnitude, although there is almost a one order of magnitude difference between the absolute aromatic flux values.

Fraction A fraction of urban vegetation has a strong influence on a the CO₂ exchange (Nordbo et al., 2012a), thus a perfect correlation between the VOC and CO₂ fluxes cannot be expected. However, the larger CO₂ fluxes could indicate also larger VOC fluxes as both have common sources, such as traffic. In Figure 13 the average urban VOC fluxes reported in the literature

are plotted against the corresponding average CO₂ fluxes. ~~Lowest~~ The lowest average VOC and CO₂ fluxes were found in Helsinki (Fig. 13). On the other hand, the largest CO₂ fluxes were measured in London, although the largest VOC fluxes were measured in Mexico City. The large VOC fluxes in Mexico City can be due to much older vehicle fleet, fewer catalytic converters and poorer fuel quality in Mexico City than in the UK (Langford et al., 2009). The differences in the ambient
5 temperatures might also affect the evaporative emissions. In Mexico City, the ambient temperature varied diurnally between 10 and 25°C (Fast et al., 2007) whereas in London, the average temperature was around 13°C during the measurements. In Mexico City, the evaporative emissions of toluene were considerable as the ratio between the average toluene and the average benzene flux was around 8 (Velasco et al., 2009). Therefore, the CO₂-fluxes do not of course directly correlate with the VOC fluxes as VOCs are released also from other than the burning processes.

10 ~~VOC flux spectrum also~~ The VOC flux composition differed between the cities (Fig. 13). Benzene was the least emitted compound in all three studies which is an expected result ~~of a stemming from the~~ development of catalytic converters and changes in fuel composition ~~, as the~~ traffic related benzene emission have generally decreased dramatically (Reimann and Lewis, 2007, p. 33 and references therein). Otherwise, the VOC flux ~~spectra seem to be~~ composition is unique for each of the measurement location.

15 4 Conclusions

We present results from the first urban VOC flux measurements in a northern city with cold winters. Out of 13 measured mass-to-charge ratios, the fluxes were observed for ten ~~. These compounds have been observed to be emitted also in previous (m/z~~ 33, 42, 45, 47, 59, 69, 79, 81, 93 and 107). Previous published works have indicated the emissions of the same compounds in urban VOC flux studies ~~reported in literature~~. The different land use ~~forms~~ categories around the measurement site in different
20 wind directions enabled us to analyse the different sources of various compounds differentiating between the traffic, vegetation and residential sources.

The VOC fluxes varied as a function of season. Methanol had the highest fluxes ~~both in June–August and September–May. Other in all seasons. The other~~ OVOCs, toluene and C₂-benzenes fluxes were of the same magnitude with each other and had ~~no considerable differences~~ differences in the absolute flux values between winter and summer. ~~On the other hand, isoprene~~ The
25 iso.+furan.fur.+cyc. fluxes were clearly higher during ~~June–August than during September–May, indicating the the summer~~ than during the winter, indicating a major contribution of biogenic isoprene emissions.

All compounds with ~~detectable fluxes had the~~ detectable fluxes illustrated contributions from anthropogenic sources at the site. ~~Aromatic~~ The aromatic compounds originated mostly from the traffic whereas for ~~isoprene~~ the iso.+furan.fur.+cyc. fluxes, the anthropogenic influence was ~~only minor~~ less important. However, even ~~those small isoprene~~ the small iso.+furan fluxes can
30 have fur.+cyc. fluxes had a relatively large influence on ~~isoprene~~ the iso.+furan concentrations during fur.+cyc. concentrations during the winter when the biogenic emission is small. For monoterpenes, the anthropogenic influence was larger, being of similar magnitude with the biogenic emissions in summer. ~~Oxygenated~~ The oxygenated VOCs originated from the traffic, vegetation and unknown anthropogenic sources, which probably included solvent use at the University campus. Generally,

the magnitude of the traffic related OVOC emissions was estimated to be ~~similar to~~ slightly higher compared with other anthropogenic sources. ~~Biogenic activity had only a minor contribution in~~ However, estimating the exact fraction was found to be difficult and uncertainties were large. Even in the urban background site, the biogenic activity had a contribution to the total annual OVOC exchange. For methanol, the biogenic emissions explained ~~up to 25~~ around 40% of the measured flux values

5 during ~~June–August~~ the summer.

~~Measured~~ On one hand, the measured VOC fluxes were much lower than ~~has~~ have earlier been observed in the urban VOC flux studies. On the other hand, most of the earlier urban VOC flux studies have been carried out in dense city centres, such as in London, whereas this study was done ca. five kilometres from the Helsinki city centre in a semi-urban area. Moreover, ~~also~~ the CO₂ fluxes have been observed to be relatively low at SMEAR III compared with the other urban stations. However,

10 the variation of the CO₂ flux ~~does not fully~~ can only partly explain the variation in the VOC fluxes between the different urban areas.

The measured urban VOC fluxes ~~have showed~~ considerable variations between ~~different locations~~ the different cities both in quantity and in quality. Thus ~~a parameterization for a~~ a general parameterization for the VOC exchange in the urban areas may be challenging. However, links between the VOC emissions and CO₂ and the CO emission provide indication of the

15 processes which need to be described by ~~such parameterizations. For this~~ the parameterizations. To acquire this, a larger body of concomitant measurements of VOC, CO and CO₂ fluxes may be needed.

Appendix A

Table A1. Correlation coefficients from each wind sector between VOC, CO, CO₂ fluxes and the traffic rates (Tr, only from the road sector) using all available data (one percent of the highest and the lowest values were disregarded). Insignificant ($p > 0.05$) correlation coefficients are not shown in the Table. For the comparison, the correlation coefficient between the CO₂ fluxes and the traffic rates was calculated from the same period with the CO fluxes (Apr–May 2014).

Road sector													
	<i>m/z</i> 33	<i>m/z</i> 42	<i>m/z</i> 45	<i>m/z</i> 47	<i>m/z</i> 59	<i>m/z</i> 69	<i>m/z</i> 79	<i>m/z</i> 81	<i>m/z</i> 93	<i>m/z</i> 107	CO	CO ₂	Tr
<i>m/z</i> 33	1	–	0.52	0.31	0.38	0.33	0.29	0.21	0.3	0.33	0.31	0.31	0.30
<i>m/z</i> 42	–	1	–	–	–	0.12	–	–	–	–	–	–	–
<i>m/z</i> 45	0.52	–	1	0.32	0.44	0.44	0.31	0.13	0.33	0.35	0.39	0.33	0.30
<i>m/z</i> 47	0.31	–	0.32	1	0.14	0.08	0.23	0.13	0.23	0.25	–	0.37	0.19
<i>m/z</i> 59	0.38	–	0.44	0.14	1	0.31	0.23	0.19	0.24	0.34	0.42	0.15	0.23
<i>m/z</i> 69	0.33	0.12	0.44	0.08	0.31	1	0.19	0.19	0.24	0.19	0.37	–	0.30
<i>m/z</i> 79	0.29	–	0.31	0.23	0.23	0.19	1	–	0.26	0.25	0.35	0.21	0.17
<i>m/z</i> 81	0.21	–	0.13	0.13	0.19	0.19	–	1	0.13	0.19	–	0.11	0.14
<i>m/z</i> 93	0.3	–	0.33	0.23	0.24	0.24	0.26	0.13	1	0.38	0.37	0.37	0.30
<i>m/z</i> 107	0.33	–	0.35	0.25	0.34	0.19	0.25	0.19	0.38	1	0.44	0.38	0.32
CO	0.31	–	0.39	–	0.42	0.37	0.35	–	0.37	0.44	1	0.68	0.56
CO ₂	0.31	–	0.33	0.37	0.15	–	0.21	0.11	0.37	0.38	0.68	1	0.43
tr	0.30	–	0.30	0.19	0.23	0.30	0.17	0.14	0.30	0.32	0.56	0.43	1
Vegetation sector													
	<i>m/z</i> 33	<i>m/z</i> 42	<i>m/z</i> 45	<i>m/z</i> 47	<i>m/z</i> 59	<i>m/z</i> 69	<i>m/z</i> 79	<i>m/z</i> 81	<i>m/z</i> 93	<i>m/z</i> 107	CO	CO ₂	
<i>m/z</i> 33	1	0.1	0.55	0.29	0.37	0.34	0.14	0.23	0.23	0.21	0.28	-0.29	
<i>m/z</i> 42	0.1	1	–	0.08	0.09	–	–	–	–	0.09	–	–	
<i>m/z</i> 45	0.55	–	1	0.35	0.42	0.35	0.14	0.18	0.19	0.22	0.34	-0.12	
<i>m/z</i> 47	0.29	0.08	0.35	1	0.25	–	0.19	0.13	0.19	0.24	0.18	0.18	
<i>m/z</i> 59	0.37	0.09	0.42	0.25	1	0.25	0.18	0.17	0.19	0.18	0.39	-0.10	
<i>m/z</i> 69	0.34	–	0.35	–	0.25	1	–	0.13	–	0.18	–	-0.44	
<i>m/z</i> 79	0.14	–	0.14	0.19	0.18	–	1	0.08	0.13	0.14	–	–	
<i>m/z</i> 81	0.23	–	0.18	0.13	0.17	0.13	0.08	1	0.13	–	0.20	-0.17	
<i>m/z</i> 93	0.23	–	0.19	0.19	0.19	–	0.13	0.13	1	0.17	0.24	–	
<i>m/z</i> 107	0.21	0.09	0.22	0.24	0.18	0.18	0.14	–	0.17	1	0.22	0.09	
CO	0.28	–	0.34	0.18	0.39	–	–	0.2	0.24	0.22	1	0.28	
CO ₂	-0.29	–	-0.12	0.18	-0.10	-0.44	–	-0.17	–	0.09	0.28	1	
Built sector													
	<i>m/z</i> 33	<i>m/z</i> 42	<i>m/z</i> 45	<i>m/z</i> 47	<i>m/z</i> 59	<i>m/z</i> 69	<i>m/z</i> 79	<i>m/z</i> 81	<i>m/z</i> 93	<i>m/z</i> 107	CO	CO ₂	
<i>m/z</i> 33	1	0.21	0.45	0.37	0.30	0.27	–	0.24	0.32	–	–	–	
<i>m/z</i> 42	0.21	1	0.35	–	0.40	–	–	–	0.19	0.21	–	–	
<i>m/z</i> 45	0.45	0.35	1	0.48	0.25	0.19	–	–	0.26	–	–	–	
<i>m/z</i> 47	0.37	–	0.48	1	0.22	–	0.33	–	0.35	–	–	–	
<i>m/z</i> 59	0.30	0.40	0.25	0.22	1	0.18	0.27	0.18	0.32	–	0.75	–	
<i>m/z</i> 69	0.27	–	0.19	–	0.18	1	0.33	–	0.38	0.19	–	-0.32	
<i>m/z</i> 79	–	–	–	0.33	0.27	0.33	1	–	0.23	–	–	–	
<i>m/z</i> 81	0.24	–	–	–	0.18	–	–	1	–	–	–	–	
<i>m/z</i> 93	0.32	0.19	0.26	0.35	0.32	0.38	0.23	–	1	0.4	–	–	
<i>m/z</i> 107	–	0.21	–	–	–	0.19	–	–	0.40	1	–	–	
CO	–	0.52	0.60	0.55	0.53	–	–	–	–	–	1	0.49	
CO ₂	–	–	–	–	–	-0.32	–	–	–	–	0.49	1	

Table A2. The average VOC fluxes from the different seasons compared with the corresponding benzene fluxes (Table 4). The values in the parenthesis represent 95% confidence intervals.

	<i>m/z</i> 33	<i>m/z</i> 42	<i>m/z</i> 45	<i>m/z</i> 47	<i>m/z</i> 59	<i>m/z</i> 69	<i>m/z</i> 79	<i>m/z</i> 81	<i>m/z</i> 93	<i>m/z</i> 107
Jan 2013–Sep 2014	8.2 (±1.0)	0.13 (±0.03)	1.9 (±0.2)	4.0 (±0.5)	3.0 (±0.4)	1.5 (±0.2)	1	2.0 (±0.3)	2.6 (±0.3)	3.0 (±0.4)
Winter	4.8 (±1.9)	–	0.7 (±0.3)	6.3 (±2.3)	2.4 (±0.9)	0.3 (±0.2)	1	1.2 (±0.6)	2.7 (±0.9)	3.4 (±1.2)
Spring	9.1 (±1.7)	0.20 (±0.05)	1.9 (±0.4)	4.6 (±1.0)	2.9 (±0.6)	0.9 (±0.2)	1	1.6 (±0.4)	2.4 (±0.5)	2.9 (±0.6)
Summer	11.2 (±2.0)	0.13 (±0.05)	2.4 (±0.4)	3.0 (±0.7)	4.3 (±0.8)	3.0 (±0.6)	1	2.9 (±0.6)	2.7 (±0.5)	2.9 (±0.6)
Autumn	6.0 (±1.8)	0.18 (±0.08)	2.2 (±0.7)	3.8 (±1.2)	2.6 (±0.9)	1.8 (±0.6)	1	2.3 (±1.0)	2.4 (±1.1)	2.7 (±1.2)

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Table 1. The table presents three sectors around the measurement site and the fraction of vegetation of each sector (f_x , see Järvi et al., 2014). The average CO₂ flux values (in carbon basis) were taken from Järvi et al. (2012).

	f_{paved}	f_{build}	f_{veg}	Annual CO ₂ emissions [gC m ⁻²] (five-year average)
All	0.36	0.15	0.49	1760
Built (320–40°)	0.42	0.20	0.38	
Road (40–180°)	0.39	0.15	0.46	3500
Vegetation (180–320°)	0.30	0.11	0.59	870

Table 2. The [list of compounds for which the fluxes were determined for](#). The compound names and the formulas listed below in third and fourth column, respectively, are estimates for the measured mass-to-charge ratios (see e.g. de Gouw and Warneke, 2007). The second column shows whether a sensitivity was determined directly from the calibration or from a transmission curve (i.e. *calculated*), and which compounds were used in the calibrations. [LoD shows the average limit of detection for 0.5 s measurement \(\$1.96\sigma\$ \)](#). [Note that \$m/z\$ 89 and \$m/z\$ 103 were measured only during 27.6.27 June – 27.8.2014.27 August 2014](#). Due to software problems, some data were lost. Those gaps are marked by superscripts *a* and *b* that correspond to the lost periods [between](#) 27 June–9 July 2014 and [between](#) 27 August–30 September, respectively. The [second](#) final column shows [the flux](#) data coverages (~~flux-values~~) for each [of the](#) compound from the whole period January 2013–September 2014.

[m/z]	Calibration compound	Compound	Chemical formula	Data coverage [%]	LoD [ppt]
31 ^a	<i>calculated</i>	formaldehyde	CH ₂ O	–	~
33 ^a	methanol	methanol	CH ₄ O	32.2	397
42 ^a	acetonitrile	acetonitrile, alkane products	C ₂ H ₃ N	32.4	35
45 ^a	acetaldehyde	acetaldehyde	C ₂ H ₄ O	32.6	141
47 ^a	<i>calculated</i>	ethanol, formic acid	C ₂ H ₆ O, CH ₂ O ₂	32.9	~
59 ^a	acetone	acetone, propanal	C ₃ H ₆ O	37.0	71
69 ^a	isoprene	isoprene, furan, cycloalkanes	C ₅ H ₈	32.1	105
79 ^b	benzene	benzene	C ₆ H ₆	32.8	60
81 ^b	α -pinene	monoterpene fragments		28.5	120
89 ^b	<i>calculated</i>	<i>unknown</i>	–	–	~
93 ^b	toluene	toluene	C ₇ H ₈	31.7	295
103 ^b	<i>calculated</i>	<i>unknown</i>	–	–	~
107 ^b	m-xylene,o-xylene	C ₂ -benzenes	C ₈ H ₁₀	30.9	197
137 ^b	α -pinene	monoterpenes	C ₁₀ H ₁₆	–	~

Table 3. Average and median concentrations for each measured VOC compound excluding m/z 31, m/z 89 and m/z 103. The error estimates of the average values were calculated using the equation $1.96 \cdot \sigma_{\text{voc}} / \sqrt{N}$, where σ_{voc} is the standard deviation of the VOC time series and N the number of data points. Lower and upper quartiles are given in parenthesis after the median values, and the 95% quantile is shown as well. One percent of the lowest and the highest values were disregarded from the time series to avoid effect of possible outliers.

	methanol	acetonitrile	acetaldehyde	ethanol+formic acid	acetone+propanal	iso.+fur.+cyc.	benzene	monoterpenes	toluene	C ₂ -benzenes
	VOC concentration [ppb]									
Jan 2013–Sep 2014										
mean	3.28 (±0.09)	0.10 (±0.00)	0.59 (±0.01)	1.05 (±0.04)	1.45 (±0.03)	0.10 (±0.00)	0.19 (±0.01)	0.14 (±0.00)	0.20 (±0.01)	0.22 (±0.01)
median	2.58 (1.61...4.57)	0.09 (0.07...0.13)	0.51 (0.36...0.76)	0.71 (0.41...1.22)	1.30 (0.85...1.89)	0.08 (0.05...0.14)	0.13 (0.08...0.25)	0.12 (0.08...0.17)	0.14 (0.05...0.28)	0.18 (0.12...0.29)
95%	7.66	0.19	1.20	4.07	2.97	0.27	0.52	0.28	0.63	0.52
N	2415	2431	2451	2477	2779	2412	2462	2139	2383	2319
Winter										
mean	1.33 (±0.11)	0.06 (±0.00)	0.49 (±0.03)	1.01 (±0.08)	0.89 (±0.05)	0.07 (±0.00)	0.45 (±0.02)	0.13 (±0.01)	0.36 (±0.02)	0.30 (±0.02)
median	1.13 (0.79...1.67)	0.06 (0.05...0.08)	0.43 (0.34...0.60)	0.82 (0.60...1.26)	0.79 (0.60...1.11)	0.06 (0.04...0.08)	0.44 (0.34...0.57)	0.12 (0.09...0.15)	0.32 (0.21...0.45)	0.26 (0.18...0.38)
95%	2.78	0.10	0.91	2.26	1.71	0.13	0.72	0.29	0.70	0.66
N	176	199	207	203	354	203	357	203	380	371
Spring										
mean	3.05 (±0.15)	0.09 (±0.00)	0.59 (±0.02)	0.75 (±0.04)	1.28 (±0.04)	0.09 (±0.00)	0.18 (±0.01)	0.12 (±0.00)	0.15 (±0.01)	0.18 (±0.01)
median	2.18 (1.46...3.81)	0.08 (0.06...0.11)	0.53 (0.40...0.73)	0.65 (0.35...1.00)	1.08 (0.83...1.58)	0.08 (0.05...0.11)	0.15 (0.10...0.23)	0.11 (0.08...0.15)	0.12 (0.06...0.19)	0.15 (0.11...0.22)
95%	8.20	0.15	1.10	1.92	2.61	0.19	0.41	0.22	0.45	0.41
N	874	876	905	891	915	879	892	853	892	859
Summer										
mean	4.27 (±0.17)	0.12 (±0.00)	0.60 (±0.02)	1.15 (±0.07)	1.88 (±0.05)	0.14 (±0.01)	0.11 (±0.00)	0.15 (±0.01)	0.12 (±0.01)	0.23 (±0.01)
median	3.88 (2.40...5.70)	0.12 (0.09...0.15)	0.50 (0.35...0.79)	0.79 (0.52...1.40)	1.70 (1.24...2.42)	0.12 (0.07...0.18)	0.09 (0.06...0.14)	0.13 (0.09...0.18)	0.08 (0.02...0.18)	0.19 (0.13...0.29)
95%	8.56	0.21	1.22	4.00	3.54	0.32	0.26	0.29	0.44	0.50
N	748	751	756	778	863	743	938	823	826	823
Autumn										
mean	2.95 (±0.13)	0.11 (±0.00)	0.62 (±0.03)	1.36 (±0.13)	1.41 (±0.05)	0.10 (±0.01)	0.13 (±0.01)	0.16 (±0.01)	0.35 (±0.04)	0.25 (±0.02)
median	2.58 (1.62...3.96)	0.11 (0.06...0.15)	0.50 (0.29...0.92)	0.60 (0.26...1.65)	1.46 (0.67...1.91)	0.06 (0.04...0.14)	0.10 (0.07...0.16)	0.14 (0.09...0.21)	0.30 (0.08...0.5)	0.21 (0.10...0.35)
95%	5.81	0.19	1.29	4.36	2.64	0.28	0.31	0.36	1.03	0.62
N	617	605	583	605	647	587	275	260	285	266

Table 4. The average and median fluxes for each measured VOC compound excluding m/z 31, m/z 89 and m/z 103. The error estimates of the average values were calculated using the equation $1.96 \cdot \sigma_{\text{VOC}} / \sqrt{N}$, where σ_{VOC} is the standard deviation of the VOC time series and N number of data points. The lower and upper quartiles are given in parenthesis after the median values. One percent of the lowest and the highest values were disregarded from the time series to avoid effect of possible outliers. The mean detection limits ($\overline{\text{LoD}}$) were calculated as $\overline{\text{LoD}} = 1/N \sum \text{LoD}^2$ (Valach et al., 2015) where single detection limits, LoD, were defined to be $1.96\sigma_{\text{ccf}}$ where σ_{ccf} is the standard deviation of cross covariance tails (Taipale et al., 2010). The acetonitrile flux was below $\overline{\text{LoD}}$ in the winter.

	methanol	acetonitrile	acetaldehyde	ethanol+formic acid	acetone+propanal	iso.+fur.+cyc.	benzene	monoterpenes	toluene	C ₂ -benzenes
	VOC flux [ng m ⁻² s ⁻¹]									
Jan 2013–Sep 2014										
mean	44.9 (±2.5)	0.7 (±0.1)	10.1 (±0.6)	21.9 (±1.7)	16.7 (±1.1)	8.0 (±0.6)	5.5 (±0.6)	10.9 (±1.2)	14.1 (±1.1)	16.4 (±1.4)
median	29.4 (10.4...62.2)	0.7 (-1.2...2.2)	8.3 (2.4...16.7)	16.5 (-0.8...35.2)	11.6 (2.1...25.9)	5.5 (-0.7...14)	4.6 (-2.2...11.2)	11.0 (-5.7...25.6)	11.4 (-1.3...26)	14.6 (-3.7...33.0)
LoD	1.2	0.1	0.5	1.0	0.7	0.3	0.5	0.9	0.7	1.0
N	2021	2034	2050	2066	2311	2018	2090	1820	2029	1983
Winter										
mean	35.5 (±7.9)	–	5.0 (±1.3)	46.4 (±8.8)	17.4 (±3)	2.4 (±1.4)	7.3 (±2.3)	8.5 (±3.4)	19.6 (±3.1)	24.6 (±4.0)
median	16.4 (4.8...42.4)	–	5.1 (-0.6...9.7)	26.7 (8.2...69.9)	11.6 (3.0...27)	2.4 (-1.9...5.7)	5.9 (-6.3...20.6)	8.1 (-4.5...19.7)	15.5 (1.3...35.2)	23.3 (0.9...43.8)
LoD	3.0	0.3	1.3	4.0	2.5	1.0	2.2	3.5	2.5	3.5
N	178	–	185	179	327	182	315	181	328	324
Spring										
mean	52.1 (±4.7)	0.9 (±0.2)	10.7 (±1.1)	26.2 (±3.3)	16.4 (±1.8)	4.9 (±0.8)	5.7 (±1.0)	8.9 (±2.0)	13.9 (±1.9)	16.5 (±2.4)
median	31.8 (10.6...75.5)	0.8 (-1.3...2.5)	8.3 (1.7...18.6)	18.4 (-2.2...43)	11.2 (1.1...25.9)	3.8 (-2.6...11.3)	5.0 (-2.7...12.2)	8.4 (-11.5...26.4)	11.7 (-4.0...27.3)	15.2 (-5.4...33.7)
LoD	2.3	0.2	1.1	2.0	1.3	0.6	0.8	1.6	1.1	1.7
N	758	765	775	765	789	762	775	731	778	755
Summer										
mean	54.2 (±4.5)	0.6 (±0.2)	11.8 (±1.0)	14.7 (±2.2)	20.6 (±2.1)	14.3 (±1.4)	4.8 (±0.8)	14.1 (±1.8)	13.2 (±1.5)	14.0 (±1.9)
median	39.1 (15.7...76.0)	0.8 (-1.1...2.0)	9.4 (3.9...18.1)	14.1 (-2.4...29.3)	15.0 (4.4...30.2)	9.1 (2.1...22.6)	4.0 (-1.1...9.3)	12.8 (0.4...26.1)	10.8 (2.6...22.0)	13.1 (-2.4...29.4)
LoD	2.3	0.1	0.6	1.2	1.2	0.7	0.5	1.4	0.9	1.5
N	623	622	626	643	710	608	782	689	688	688
Autumn										
mean	24.4 (±2.5)	0.7 (±0.3)	9.0 (±1.0)	15.6 (±2.5)	10.8 (±2.1)	7.3 (±1.0)	4.1 (±1.2)	9.3 (±3.0)	10.0 (±3.6)	11.2 (±3.5)
median	21.4 (6.3...42.6)	0.7 (-1.1...2.2)	8.4 (2.7...14.3)	14.6 (-1.5...31.2)	7.4 (-1.2...17.9)	5.8 (-0.1...12.6)	4.1 (-1.4...8.5)	9.6 (-6.0...25.8)	7.0 (-6.6...22.0)	8.5 (-7.3...26.9)
LoD	1.8	0.1	0.4	1.2	0.9	0.4	0.7	1.8	3.0	2.0
N	462	465	464	479	485	466	218	219	235	216

Table 7. Statistics of the measured CO and CO₂ fluxes and CO concentrations from each surface-cover-wind sector (3 Apr – 27 May 2014). The error estimates of the average values were calculated using the equation $1.96 \cdot \sigma / \sqrt{N}$, where σ is the standard deviation of the CO or CO₂ time series and N the number of data points. The lower and upper quartiles are given in parenthesis after the median values.

	All	Built	Road	Vegetation
<hr/>				
	CO flux [$\mu\text{g m}^{-2}\text{s}^{-1}$]			
mean	0.69±0.05	0.57±0.11	1.46±0.15	0.35±0.03
median	0.36 (0.11 – 0.86)	0.37 (0.22–0.75)	1.18 (0.54 – 2.08)	0.26 (0.10 – 0.48)
	CO ₂ flux [$\mu\text{g m}^{-2}\text{s}^{-1}$]			
mean	138±9	157±34	282±27	71±9
median	111 (57 – 198)	123 (68–177)	257 (135 – 378)	80 (31 – 123)
	CO concentration [ppb]			
mean	146.5±1.0	152.7±5.6	152.6±1.9	143.1±1.1
median	142.0 (133.8 – 155.9)	141.2 (132.8–164.4)	148.2 (138.7–161.4)	139.2 (131.8 – 151.9)

Table 6. The estimated contributions (%) of the aromatic and biogenic sources for the OVOCs (methanol+acetaldehyde+acetone), aromatics (benzene+toluene+C₂-benzenes) and terpenoids (iso.+fur.+cyc.+monoterpenes). One should note that furan and cycloalkanes may affect also to the contributions of the terpenoids. For the terpenoids, separating the different anthropogenic sources was not possible. In the case of OVOCs and aromatics, the ratio between the traffic related and the other anthropogenic emissions was assumed to have constant annual cycle.

	OVOCs [%]	aromatics [%]	terpenoids [%]
<hr/>			
	Winter		
Traffic	65 ± 25	80 ± 15	–
Other anthropogenic sources	35 ± 25	20 ± 15	–
Total anthropogenic	100	100	100
Total biogenic	0	0	0
	Summer		
Traffic	42 ± 16	80 ± 15	–
Other anthropogenic sources	23 ± 16	20 ± 15	–
Total anthropogenic	65 ± 6	100	35 ± 8
Total biogenic	35 ± 6	0	65 ± 8

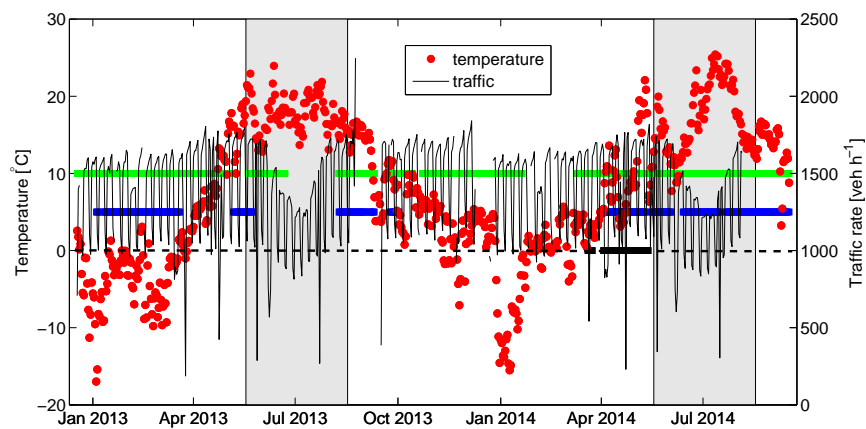


Figure 1. Daily averages of the ambient temperatures and traffic rates. The data coverages of the PTR-MS (VOCs), Li-Cor 7000 (CO_2) and LGR (CO) measurements are marked by blue, green and black lines, respectively. The grey shaded areas show periods between June–August. The black dashed line represents the zero line of the ambient temperature.

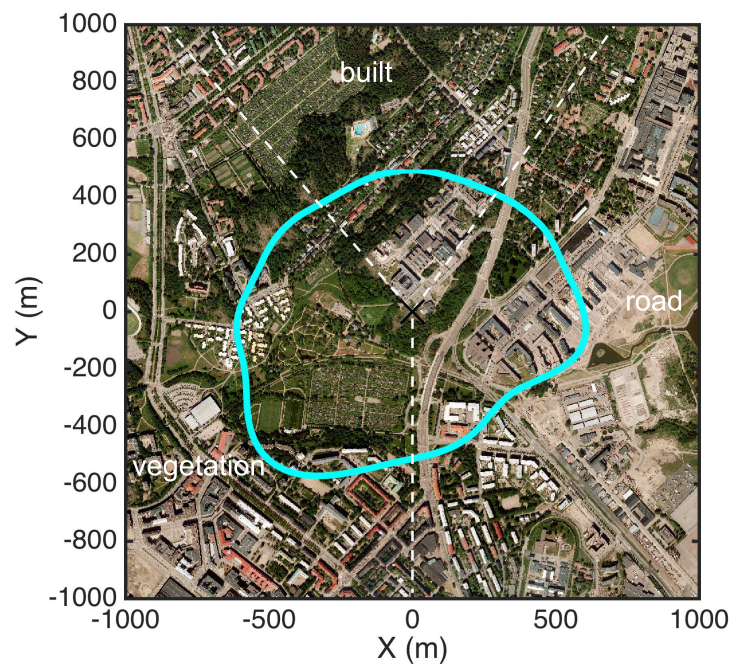


Figure 2. ~~Aerial~~ The aerial photograph of the SMEAR III station (©Kaupunkimittausosasto, Helsinki, 2011). The measurement tower is marked with a black cross. ~~White~~ The white dashed lines represent different sectors (built, vegetation, road) ~~whereas a white~~ The turquoise solid ~~lines border the botanical garden~~ line shows borders of cumulative 80% flux footprint (Kormann and Meixner, 2001).

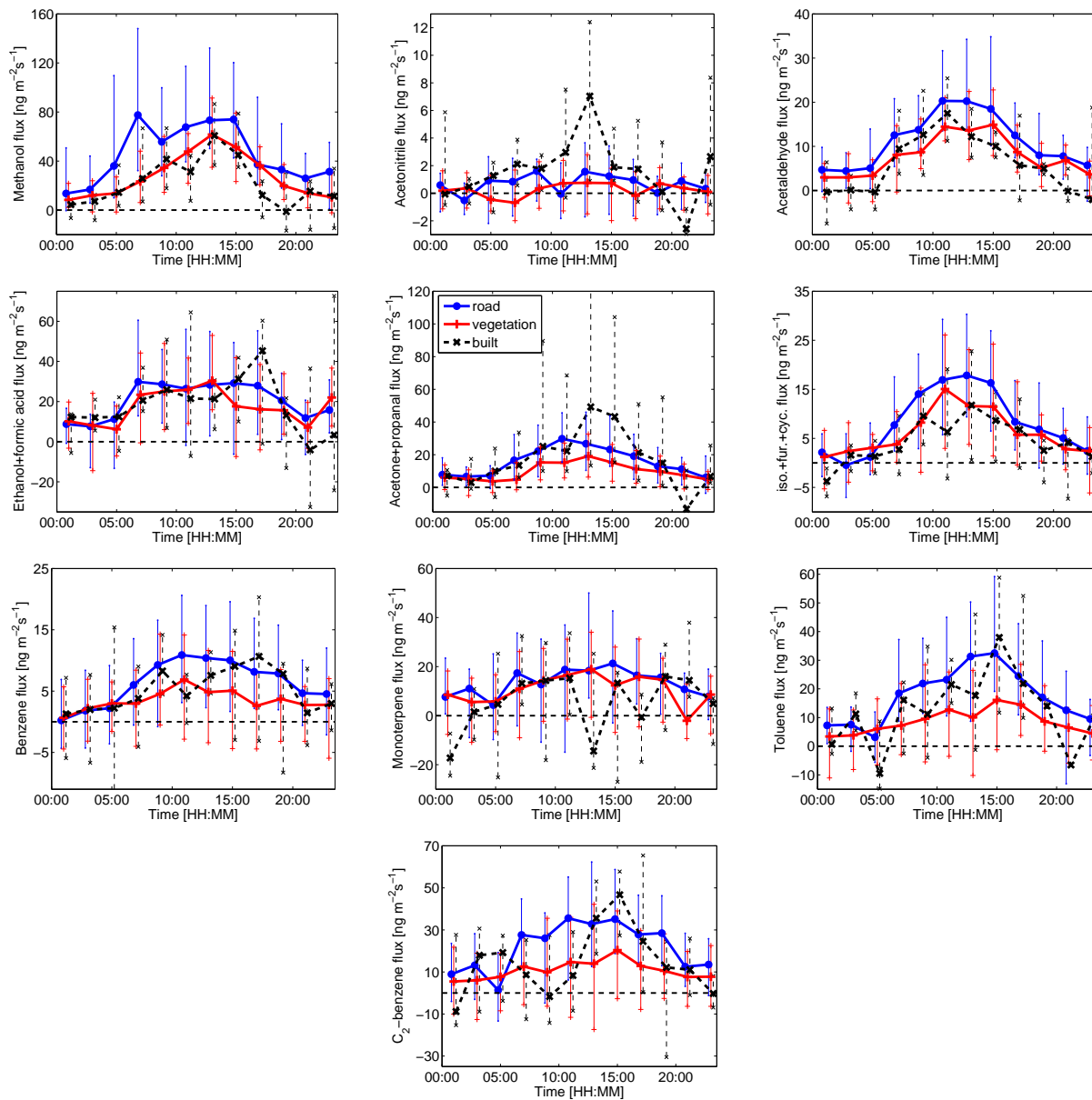


Figure 3. Median diurnal VOC fluxes from the three sectors for each of the compound excluding m/z 31, m/z 89 and m/z 103 (Jan 2013 – Sep 2014). Blue circles, red crosses and black crosses correspond to the road sector, the vegetation sector and the built sector, respectively. Vertical lines show the lower and upper quartiles (25% and 75%). Due to sensible-scaling, one upper quartile value is not shown in the m/z 59 acetone+propanal figure.

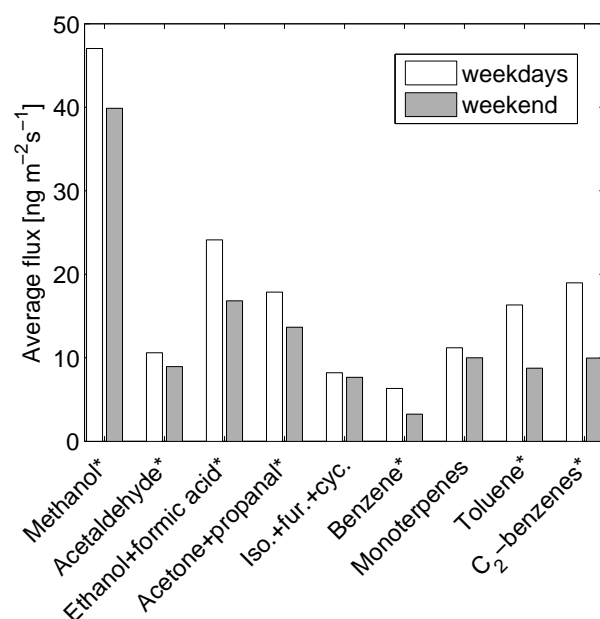


Figure 4. The average fluxes for each of the VOCs (excluding acetonitrile) from Saturday+Sunday and from weekdays (Jan 2013 – Sep 2014). The white and the grey bars show the average fluxes during the weekdays and Saturday+Sunday, respectively. The asterisks in the x-axes show if the differences between the average week and the average weekend fluxes were statistically significant. The uncertainties of the average fluxes were calculated using the equation $\pm 1.96\sigma_{\text{VOC}}/\sqrt{N}$, where σ_{VOC} is the standard deviation of a VOC flux time series and N the number of data points.

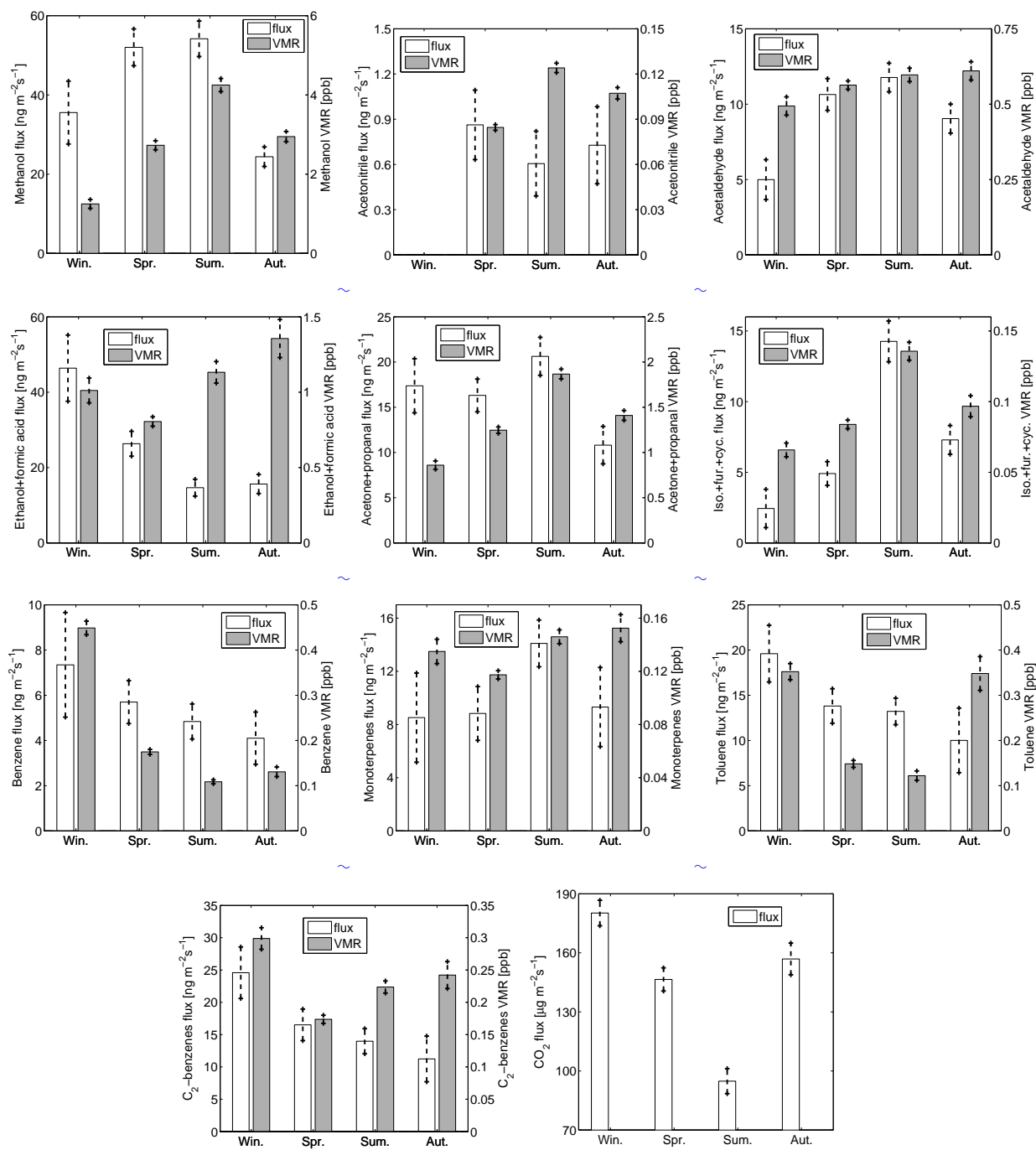


Figure 5. Fractions of measured OVOC. The mean seasonal flux and concentration (methanol, acetaldehyde, acetone+propanal VMR); aromatic values for the VOCs (benzene, toluene, α -benzenes) Tables 4 and terpenoid (isoprene+furan, monoterpenes) fluxes from each sector in June–August and September–May. The vertical lines show the 95% confidence intervals. The seasonal cycle of the CO₂ flux is shown for a comparison. However, the longer gaps without the PTR-MS measurements (in mass-basis) Fig. Ethanol+formic acid was left out 1), were removed also from the analysis as its concentrations were not directly calibrated corresponding CO₂ data.

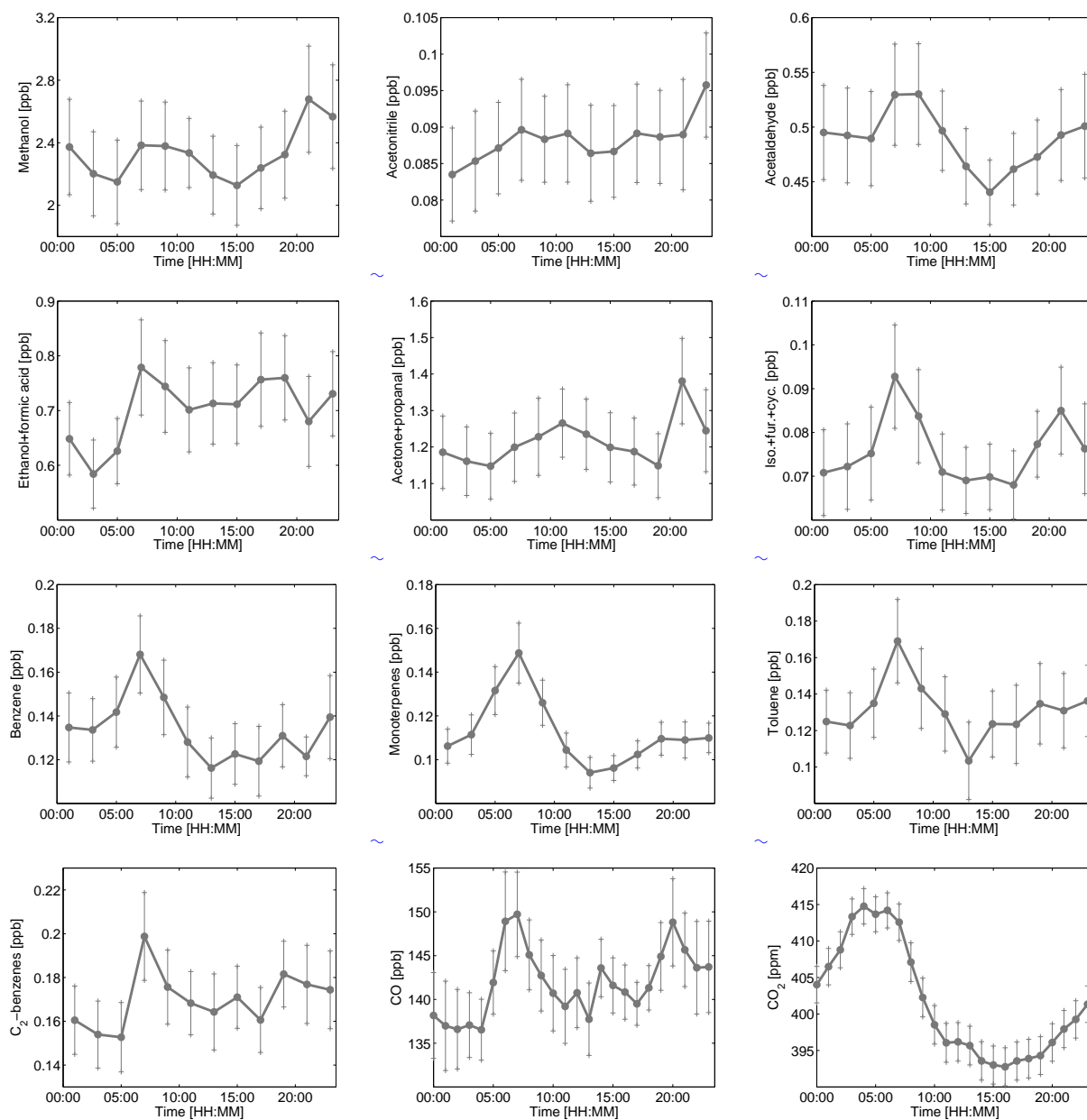


Figure 6. The median diurnal VOC, CO and CO₂ volume mixing ratios for each compound. The vertical lines show the 95% confidence intervals. The VOC and CO₂ data is between January 2013 and September 2014. However, times corresponding to the longer gaps in the PTR-MS data (Fig. 1), were removed also from the CO₂ data. The CO data is from April – May 2014.

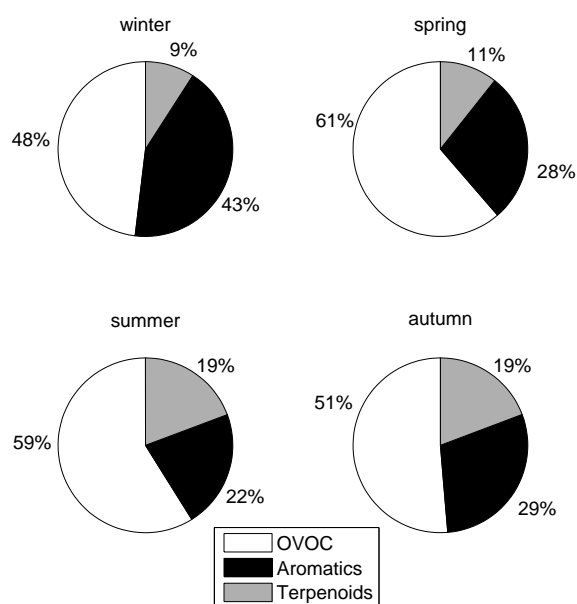


Figure 7. The fractions of the measured OVOC (methanol, acetaldehyde, acetone+propanal), aromatic (benzene, toluene, C_2 -benzenes) and terpenoid (isoprene+furan+cycloalkanes, monoterpenes) fluxes from each season (in mass basis). Ethanol+formic acid was left out from the analysis as its concentrations were not directly calibrated.

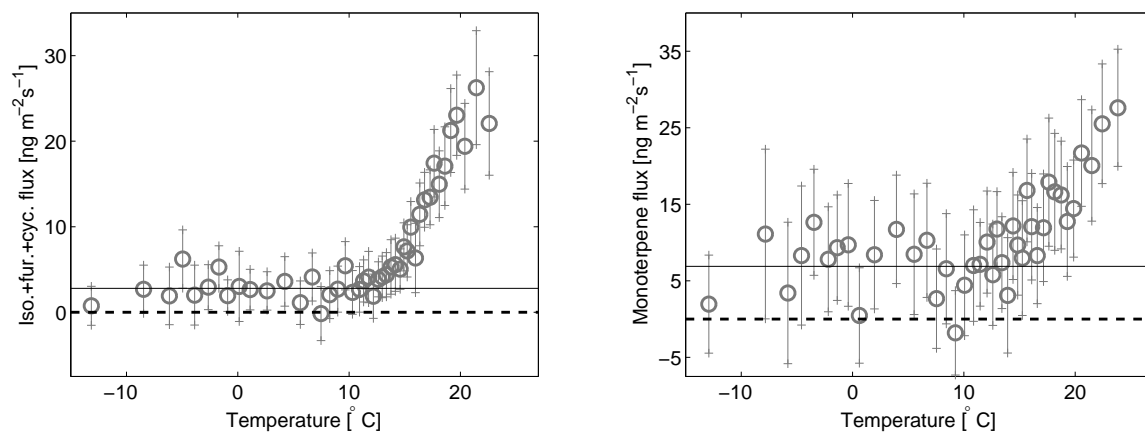


Figure 8. Bin-averaged isopreneThe bin-averaged iso.+furan-fur+cyc. ($n=15$, m/z 69 $n=45$) and monoterpene ($n=15$, m/z 81 $n=45$) fluxes as a function of the ambient temperature from the three sectors (January 2013 – Sep 2014). SolidThe solid and dashed lines show the average fluxes in the range of $T < 10^\circ\text{C}$ and zero lines, respectively.

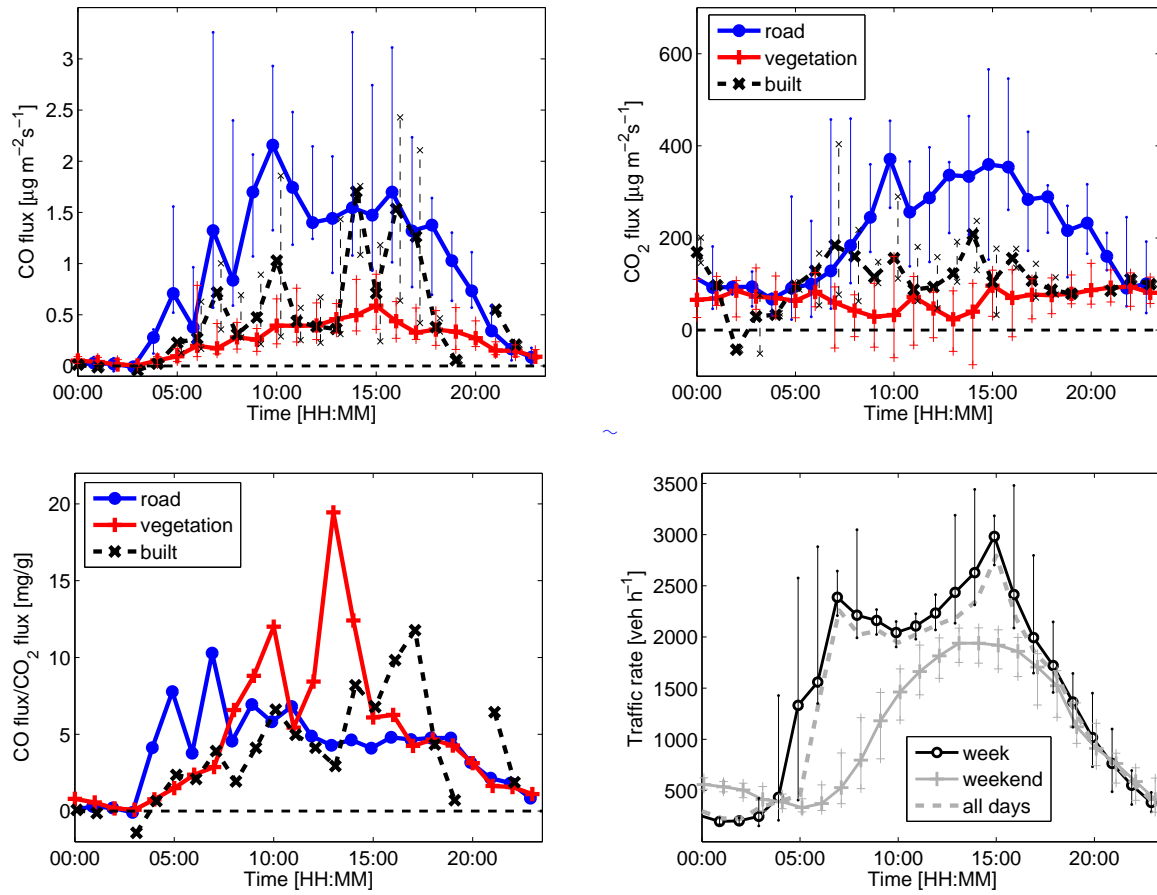
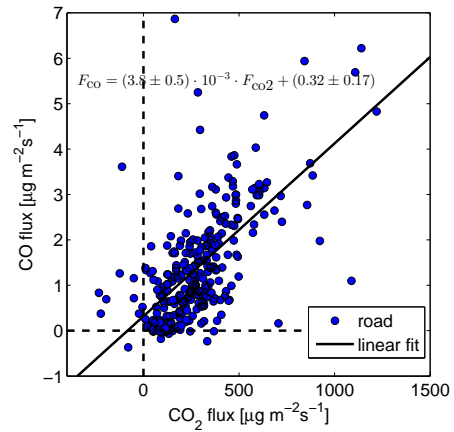
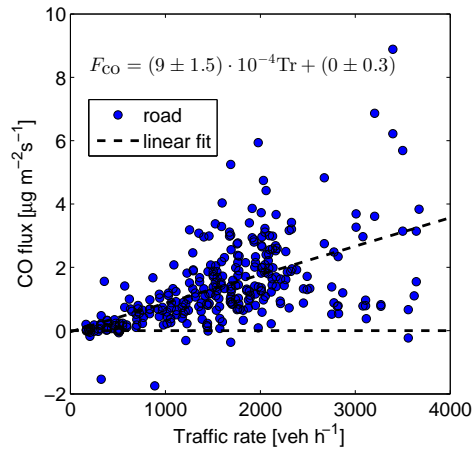


Figure 9. The two topmost figures present the hourly median diurnal fluxes of CO and CO₂ from the three sectors for and (3 Apr – 27 May 2014). The blue circles, red crosses and black crosses correspond to the road sector, the vegetation sector and the built sector, respectively. The vertical lines show the 25 and 75 quartiles. The lowest ratios between the median CO and CO₂ fluxes are shown in the figure show in the left corner. The figure in the right corner depicts the median diurnal cycles of the traffic rates from Saturday+Sunday, weekdays, and all days (Jan 2013 – Sep 2014). The vertical lines show the lower and upper quartiles for the weekend and week day values. The CO₂ flux is positive during night-time due to biogenic respiration (Järvi et al., 2012).



CO-fluxes

against traffic rates (upper figure) and fluxes (lower figure) from the road sector (measured during April–May 2014).

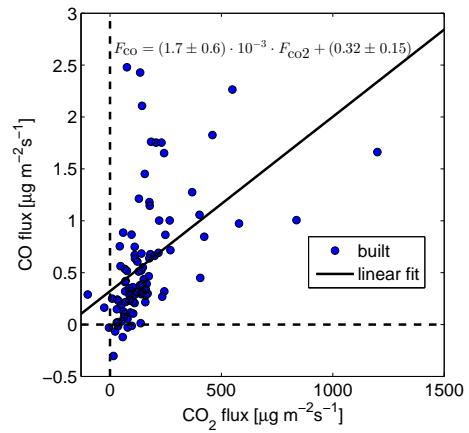
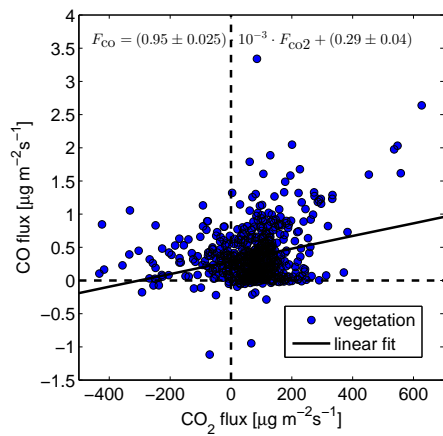


Figure 10. The CO fluxes against the traffic rates and the CO_2 fluxes from the road, vegetation and built sector (measured during April–May 2014).

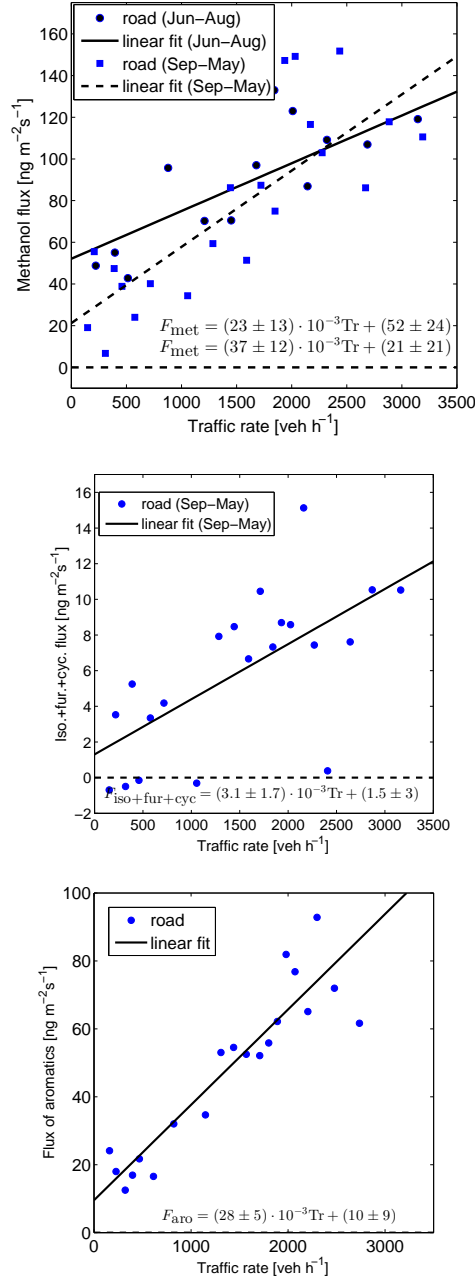


Figure 11. Traffic rates against the methanol (m/z 33, bin-averages, $n = 15$), isoprene+iso.+furan+fur.+cyc. (m/z 69, bin-averages, $n = 15$) and aromatic fluxes (m/z 107benzene+toluene+C₂-benzenes, bin-averages, $n = 30$) from the road section. A. The linear correlations between the methanol, isoprene+iso.+furan+fur.+cyc. and aromatic fluxes and the traffic rates were 0.28–0.24 (Jun–Aug)/0.34–0.32 (Sep–May), 0.24–0.20 and 0.39–0.38, respectively ($p < 0.001$).

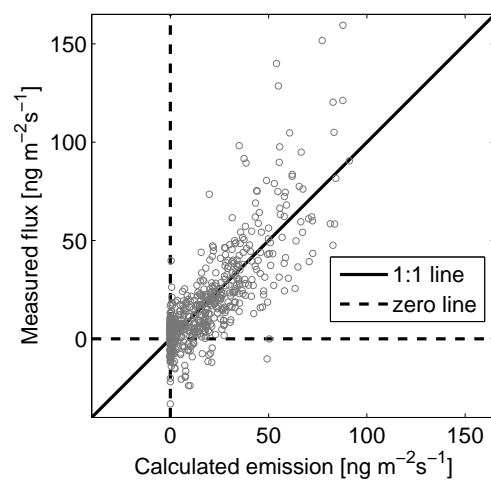


Figure 12. The measured iso.+fur.+cyc. fluxes vs. the calculated isoprene emissions (Eq. 4) from summer (Jun–Aug) data.

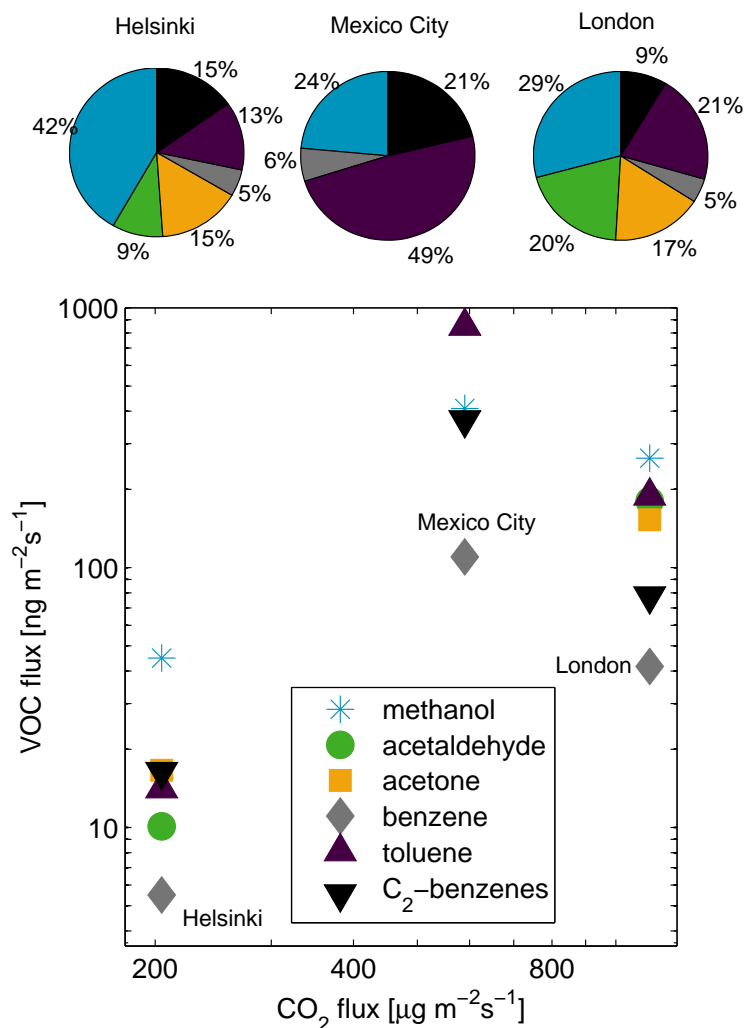


Figure 13. ~~Selected~~The selected VOC fluxes as a function of CO₂ fluxes from Helsinki, London and Mexico City (note the logarithmic scale). The average CO₂ and VOC fluxes ~~of~~for Helsinki are taken from Järvi et al. (2012) (scaled from the annual average) and this study, respectively. The corresponding average values ~~of~~for London are from Helfter et al. (2011) (scaled from the annual average) and Langford et al. (2010). All the values ~~of~~for Mexico City are from the MILAGRO/MCMA-2006 campaign (Velasco et al., 2009). ~~Pie~~The pie diagrams show the corresponding fractions of each compound.

Influence of lag-time determination on flux values

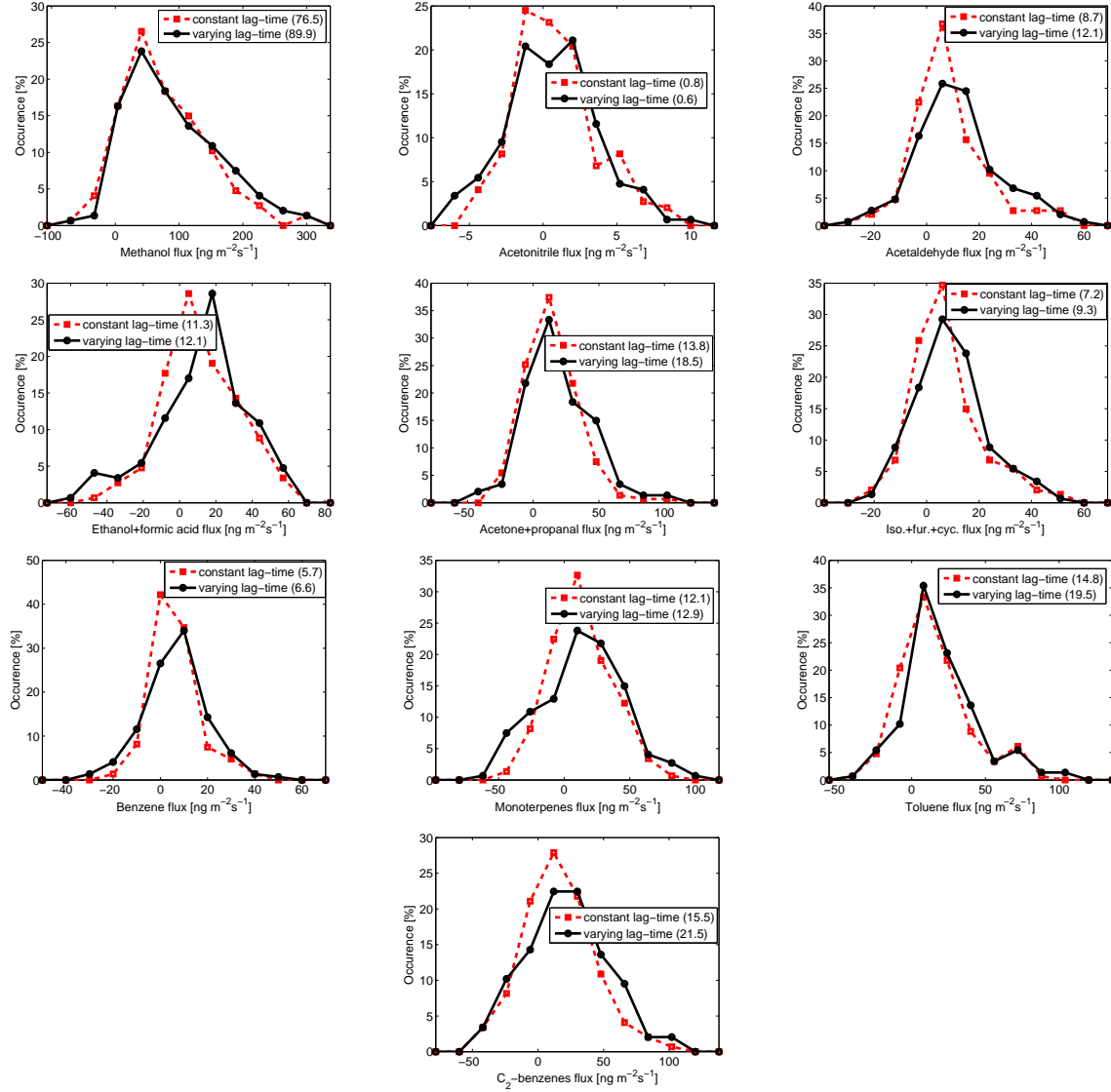


Figure S1: Flux distributions with constant lag-times (red) and varying lag-times (black). The numbers in the legends represent the mean fluxes (unit $\text{ng m}^{-2}\text{s}^{-1}$). The distributions were calculated from a period between 21 May and 4 July 2013 (147 data points).

Fluxes as a function of wind direction

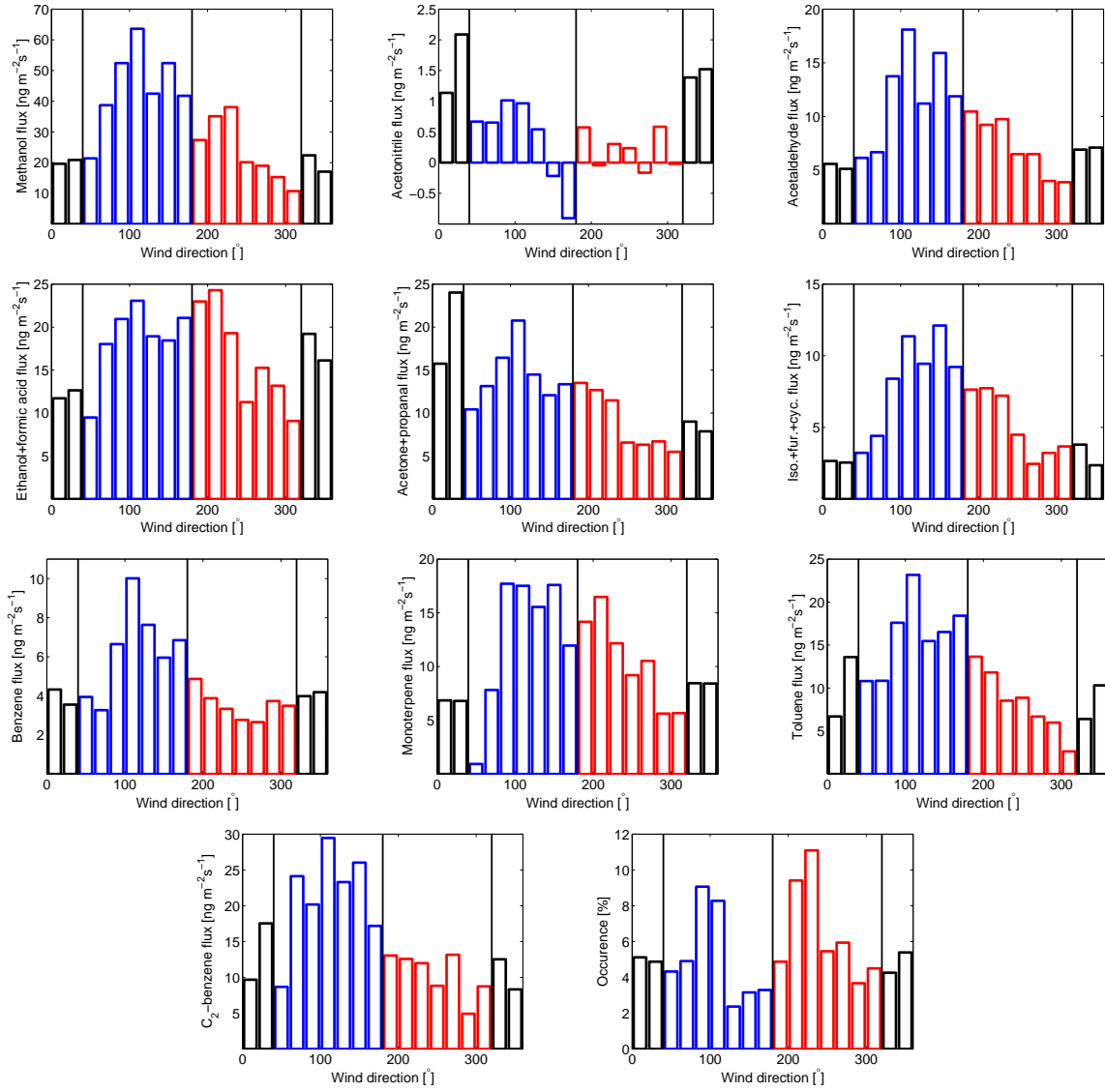


Figure S2: The median fluxes (Jan 2013 – Sep 2014) as a function of the local wind direction (20° interval). Black, blue and red bar edges describe the built, road and vegetation sector, respectively. The final figure shows the histogram of the wind direction.

OVOC fluxes as a function of the ambient temperature

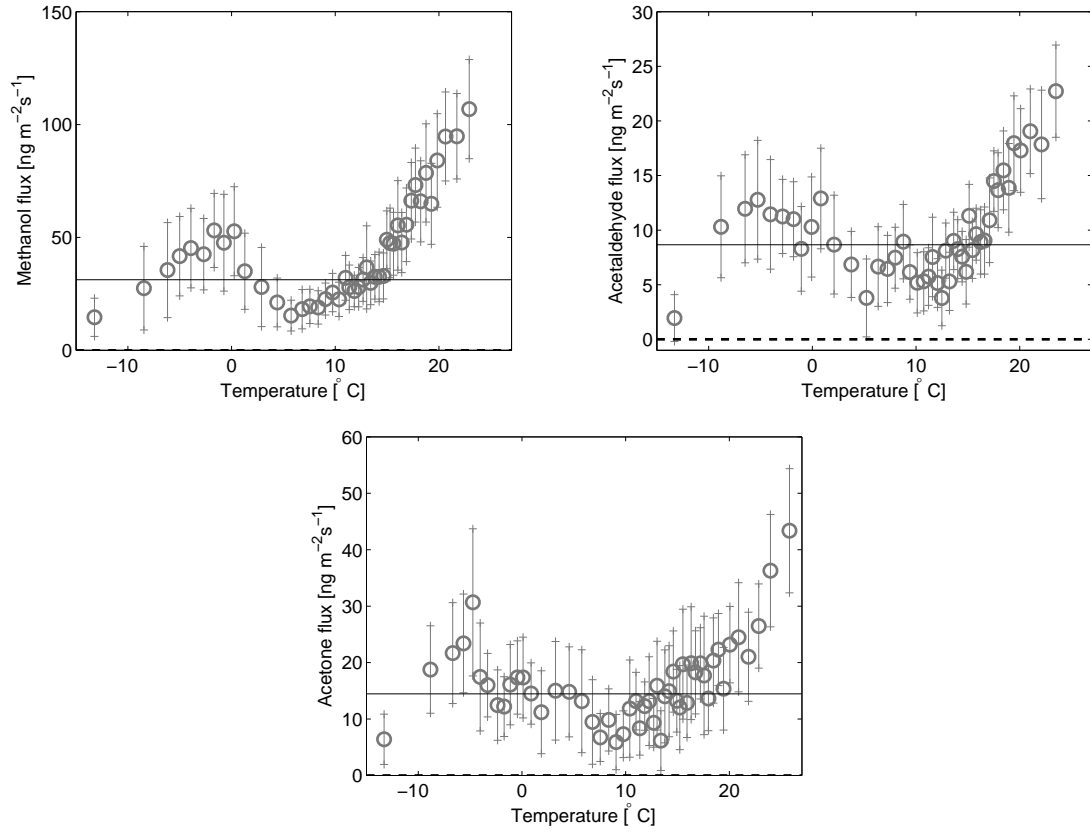


Figure S3: Bin-averaged methanol ($n = 45$), acetaldehyde ($n = 45$) and acetone ($n = 45$) fluxes as a function of the ambient temperature (January 2013 – Sep 2014). The solid lines show the average fluxes in the range of $T < 10^\circ\text{C}$.