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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Anthropogenic and biogenic influence on VOC fluxes at an urban background site in Helsinki, Finland" *by* P. Rantala et al.

Anonymous Referee #1

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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

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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 is 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.

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

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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.

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?

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

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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.

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 (ng g-1 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).

Minor Corrections:

In the main text you discuss the fluxes and concentrations using the specific names

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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.

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.

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

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

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

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.

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

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

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

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

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?

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

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

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

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.

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

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

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.

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

Page 31: Figure 3 please add the y axis zero line 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.

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.

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.

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