

## ***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 #2**

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#### General Comments:

This paper describes >1.5 year long-term flux measurements of VOC, CO and CO<sub>2</sub> 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 CO<sub>2</sub> 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

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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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> should be included and not be shown in a separate chapter.

2 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.

3 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 CO<sub>2</sub> 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.

4 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.

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

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actual measurements and not with optimized SEM voltages?

- page 3 line 25: Does the zero air generator change the humidity? Background measurements at a different humidity can produce significant artifacts.
- page 3 line 31-32: How much does the uncertain zero air measurement add to the uncertainty, please be specific.
- page 4 line 9: Also for CO and CO<sub>2</sub> measurements it would be good to add the precision and uncertainties.
- page 4 line 16 and page 5 line 11: Why did you use different averaging times for CO and CO<sub>2</sub> with 30 min compared to the VOCs with 45 min?
- page 5 line 13: Was there a reason not to use something like a time server synchronization program?
- page 5 line 14: Was m37 the highest flux, higher than methanol? Is that why m37 was used for the time lag calculation?
- page 6 line 31: Are those data coverages for flux measurements or do those include the mixing ratio measurements?
- 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.
- page 7 line 19: Are those anthropogenic monoterpene likely from the sector “solvents and other products” or more traffic related?
- page 7 line 33: Mention here that acetonitrile is often used as a tracer for biomass burning.
- page 8 line 6: Often biogenic inventories do not represent urban environments well, please explain where you get the E<sub>0,synth</sub> values for the measurement location from

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and what your confidence in this value is.

- 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?

- 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.

- page 9 line 19-23: I think it is problematic to compare CO/CO<sub>2</sub> 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/CO<sub>2</sub> enhancement ratios.

- 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.

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- page 10 line 9: Why did you choose Sep-May and not Dec-Feb? Shouldn't that give you a better contrast?
- 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.
- 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 extent C2-aromatics have large non traffic related sources such as solvents, paints and paint thinners. This should be mentioned here.
- 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  $1.2 \pm 0.2$  g/m<sup>2</sup>/yr correct? Looking at the error estimate in the equation two lines above, this seems low?
- 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.
- 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.
- page 11 lines 29-34: Here I am wondering again, if cycloalkanes are contributing to the signal on mass 69.
- page 12 line 21: The isoprene emissions, at least for the road and vegetation sectors, are of the same magnitude, but the CO<sub>2</sub> emissions look very different. There is a very clear signature of CO<sub>2</sub> uptake in the vegetation sector, and therefore one would expect

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to have similar CO<sub>2</sub> uptake in the road sector and as a result the anthropogenic CO<sub>2</sub> 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?

- 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.

- 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.

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

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

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

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.

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