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***Interactive comment on* “Seasonal trends in concentrations and fluxes of volatile organic compounds above central London” by A. C. Valach et al.**

Anonymous Referee #2

Received and published: 1 June 2015

Valach et al. present results of turbulent flux measurements of selected volatile organic compounds over a central district of London. The disjunct eddy covariance method was used with an instrumented tower at the King College monitoring site. The application of the flux method is properly described in the manuscript and in general, the data analysis is correct.

Although the results do not provide any new finding, in particular for the case of London, the manuscript fills the requirements to be published in Atmospheric Chemistry and Physics. This type of measurements is still scarce in urban ecosystems. Two major and a number of minor issues need to be addressed before publication.

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Major comments:

1) The suitability of the King College site for monitoring turbulent fluxes needs further assessment. The land cover is very heterogeneous and the buildings morphology does not seem to contribute for measuring fluxes by eddy covariance. The street canyon formed by the own building where the measurements were conducted may enhance the accumulation of freshly emitted VOCs below the urban canopy, particularly during periods of stable atmospheric conditions at night and winter.

2) For eddy covariance flux measurements samples are usually collected at 10 Hz (15,000 samples in a period of 25 min). The sampling rate when using the disjunct eddy covariance method is slower. However, a sampling rate of 5.5 sec (273 samples in a period of 25 min) as that used here seems to be extremely slow. The statistical uncertainty of the fluxes caused by a longer time resolution needs to be evaluated. The CO₂ flux data discussed in section 3.2.2 may help to assess this issue.

Specific comments:

P6602, L17. G95 algorithm?

P6603, L12. . . .use a “bottom-up” approach based on activity data and emission factors
....

P6603, L22. This reviewer has serious concerns on the methodology used by Park et al., 2010 & 2011.

P6603, L29. Define PTR-MS.

P6604, L11. Check symbols of seconds, minutes, inches, etc. throughout the text.

P6604, L16. Update classification based on Stewart & Oke (2012).

P6604, Section. 2.1. Add fractions of the plan area cover (i.e., building, roads, vegetation, water bodies, etc.).

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P6605, L13. Although in following paragraphs the averaging process is described, in a few words mention why periods of 25 min were used instead of periods of 30 min. Periods of 30 min are usually used when measuring fluxes over urban surfaces.

P6605, L16-18. Note that emissions in cities respond strongly to human activities, and the behaviour of these follows the local time and not the UTC.

P6606, L-15-20. Why were data of m/z 33 and m/z 121 not included?

P6607, L2. Check that all variables are written with italic fonts.

P6607, Eq. 1. Fix the fluctuations' symbols.

P6609, Eq. 1. This equation is unreadable.

P6609, L20. Ergodicity is a rare/exotic term to indicate that the buildings height and morphology in the monitored district were quite variable. From Wikipedia: "The term ergodic is used to describe a dynamical system which has the same behaviour averaged over time as averaged over the space of all the system's states. In physics the term is used to imply that a system satisfies the ergodic hypothesis of thermodynamics."

P6610, L7. Do not begin sentences with numbers or acronyms.

P6612, L5-10. If daily mean fluxes are presented, it would be better to use units of $\text{kg km}^{-2} \text{ day}^{-1}$.

P6612, L14-15. ... lifetimes and widespread origin including anthropogenic and biogenic sources and photochemistry ...

P6613, L5-7. It may only be true for London and other UK cities.

P6614, L23-24. Explain how advected air masses rich in methanol and acetone might affect the local boundary layer meteorology.

P6615, L11-12. Is there an important potential emission source (e.g. petrol station) at the west of the flux tower?

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P6617, L3-6. Was turfgrass considered?

P6617, L21. . . . for fluxes indicated (What?) . . .

P6617, L22. Provide examples of such species.

P6617, L21-25. This paragraph is difficult to read.

P6618, Section 3.2.1. A figure showing scatter plots of benzene versus toluene would be helpful.

P6618, L10. IQR?

P6618, L14-24. Zavala et al. (2006), Rogers et al. (2006), Velasco et al. (2007) and Karl et al. (2009) reported benzene to toluene ratios for Mexico City. The vehicular fleet and industry from both cities are expected to be considerably different, as well as the benzene to toluene ratio.

P6621, L20-22. If this was true, the reported fluxes would not be representative of the monitored district. The measurement height together with the data quality assurance suggests that the flux measurements were properly conducted at the inertial sublayer, where the turbulence and fluxes are relatively homogenous.

P6622, L7-27. This discussion is long and difficult to follow.

P6623, L11. The London Emissions Inventory (LAEI) and the Atmospheric Emissions Inventories (NAEI) . . .

P6623, Section 3.4. Do NAEI and LAEI provide data on the spatial and temporal distribution of the estimated emissions?

P6624, L6. SNAP?

P6625, L15-17. The article does not discuss the suitability of the King College for turbulent flux measurements. If its suitability has been previously analysed, include the corresponding references.

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P6636, Fig. 1. The green marker is difficult to find. Make it larger.

P6636, Fig. 1. It would be helpful to see the estimated footprint overlaid on the map.

P6637, Fig. 2. There is no need of mixing weekdays and weekend's fluxes in one profile. For some species, such as C2-benzenes and toluene, the difference is considerable. Show only the variability (i.e. confidence interval) of weekdays or weekends.

P6637, Fig. 2. For panels in section (b) select scales that help to visualize the diurnal characteristics. For example, the scale for benzene should go from 0.20 to 0.40 ppb, instead from 0.00 to 0.45 ppb.

P6638, Fig. 3. Check the linear regression of panel (E).

P6639, Fig. 4. What do the bar charts represent? Do they show the mean daily flux/mixing ratio for each monitored month?

P6640, Fig. 5. Too many dashed lines in the scatter plots. They are confusing.

P6640, Fig. 5. OLS?

P6640, Fig. 5. Describe first the panels at the left and then the panels at the right.

P6641, Fig. 6. Scatter plots between fluxes would be more interesting.

References

Stewart, I.D., Oke, T.R., 2012. Local climate zones for urban temperature studies. *Bull. Am. Meteorol. Soc.* 93, 1879e1900.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 6601, 2015.

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