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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Fluxes and concentrations of volatile organic compounds above central London, UK" *by* B. Langford et al.

**Anonymous Referee #2**

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Langford et al. present a set of disjunct eddy covariance flux measurements of selected volatile organic compounds (VOCs) measured by Proton Transfer Reaction – Mass Spectrometry (PTR-MS) over central London. The origin of the measured fluxes is investigated using traffic counts and parallel flux measurements of CO. The annual emissions of the monitored compounds were estimated through a parameterization of the observed fluxes with the vehicular activity, and were compared to the emissions reported in the official emissions inventory. The results must be of interest to the atmospheric community, in particular to researchers studying urban pollution. However, the high altitude above the urban surface at which the measurements were conducted raises serious concerns regarding to the representativeness and distribution of the observed fluxes.

Main comments

Usually, ground flux measurements are conducted at the top of mast or scaffolding towers between two and four times higher than the average height of the roughness elements (see the Urban Flux Network, http://www.geog.ubc.ca/urbanflux/index.html) with the aim to be in the constant flux layer and observe fluxes from a spatial scale (10ˆ2 - 10ˆ4) of similar size to the cells in gridded emissions inventories. In this case the flux measurements were conducted at 200 m above ground, more than 13 times the average height of the surrounding buildings (page 17305, line 26). At this height many of the measured fluxes might not be representative of the ground fluxes, in particular during stable conditions at nighttime and cloudy days. The authors recognize that in some nights the measurements were de-coupled from the inertial sublayer (page17308, line 20) and were not representative of the ground fluxes. However, it is not clear how those periods were identified, neither if they were removed for further analysis. The estimation of the boundary layer height using a model, which cannot estimate heights below 250 m is useless to determine measurement periods de-coupled from the inertial sublayer. An alternative model needs to be used to determine those periods. Also the routine radio-sounding from the closer airport may be used.

Following the rule-of-thumb that says that typically the observed fluxes correspond to footprints between 100 and 300 times the measurement height (Grimmond and Oke, 1999), footprints between 18.5 and 55.5 km might be expected from the Telecom tower (considering a measurement height of 185 m, zm = ztower – z0). Using a simple footprint model (Hsieh et al., 2000) and Zm / L = 1 for stable conditions, it was found that the fetch (80% of the flux) might extend up to 77.7 km. For unstable conditions (Zm / L = -1) it was found a similar fetch to that reported in the manuscript (page 17305, line 27). However, the extended footprints might jeopardize the identification of emission sources. During long periods of the day, the measured fluxes might include fluxes from the whole city and beyond its boundaries. The authors need to calculate the footprint for a wider range of atmospheric conditions, and explain how the periods with very long



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footprints were considered for further analysis, in particular for the comparison with the emissions inventory.

The disjunct eddy covariance technique does not allow an inspection of the spectra and cospectra of the measured variables. However, the parallel flux measurements of CO and CO2 by the traditional eddy covariance method might be used to investigate the influence of the measurement system in the attenuation of the turbulent signal. The massive Telecom tower might have a significant influence on the turbulence pattern.

As suggested in the section describing the ratios between VOC and CO (page 17311, line 15), the chemical degradation might have an important impact on the measured fluxes because of the height at which the measurements were conducted. It is necessary to asses the sensitivity of the VOC fluxes to chemistry, in particular the isoprene fluxes, since isoprene is a very reactive VOC. This can be done applying a transport model coupled with a simple chemical mechanism, such as the model proposed by Rinne et al. (2007). The life time of the measured species under the chemical conditions of the atmosphere of London needs to be clearly longer than the time consumed by an air parcel to reach the top of the flux tower.

Both, ambient concentrations and fluxes need to be analyzed in terms of wind direction. Currently the manuscript does not consider the wind direction in the results discussion. For example, winds blowing from the north might be related to higher VOC fluxes and concentrations due to the presence of a large number of important roadways in that direction. In the same context, the Regents Park located $\sim$1 km from the Telecom tower might produce larger fluxes of isoprene due the biogenic emissions when the wind blows from the northwest direction. For the ambient concentration discussion is necessary to keep in mind that concentrations depends on emission patterns, meteorology and chemical processes, while the fluxes depend mainly on the emissions and a few meteorological variables.

It is not completely clear how the comparison between the measured fluxes and es-



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timated emissions in the official emissions inventory was conducted. The only information provided of the emissions inventory is the grid scale; nothing is said about the temporal and seasonal distributions. Does the emissions inventory provide hourly, daily or annually emissions of anthropogenic and natural sources? How many species include? Certainly, more information regarding to the emissions inventory is required, as well as an explanation of the method used to extract the VOC emissions from the grid cells. Finally, if the parameterization used to evaluate the emissions inventory represents only a "snap-shot" of the annual emissions and considering that the seasonal changes in the VOC emissions are significant, a direct comparison of the measured fluxes with the emissions estimated for a day of October in the emissions inventory might be more appropriate.

Specific and technical comments

1) Page 17299, line 13: Amman et al. (2006) reports water vapor fluxes and not fluxes of biogenic VOC as indicated in the text.

2) Page 17299, line 17: Please define a suitable elevation above street level to perform eddy covariance measurements.

3) Page 17299, line 17: To reduce the impact of the surface heterogeneity, variability on the emissions distribution and effects of advection, the eddy covariance measurements are limited to fairly uniform urban areas in terms of topography and patterns of buildings, roads, emission sources and vegetation.

4) Page 17299, line 3: Instead of "emission estimates" better use "fluxes". Emissions refer only to upward fluxes. A downward flux is called deposition.

5) Page 17300, line 3: Which were the prevalent meteorological conditions during the field study?

6) Page 17300, line 5: In two lines indicate the main objectives of the REPARTEE project. Not all readers are familiar with it, in addition that (Dall'Oslo et al., 2009) is still



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under preparation.

7) Page 17300, line 12: Please indicate the average height of the surrounding buildings.

8) Page 17300, line 13: Please indicate the land cover fraction of buildings, vegetation and impervious ground of the monitored district, at least during daytime under convective conditions ($\sim$4.7 km).

9) Page 17301, line 7: Which was the eleventh monitored mass? Only 10 masses are indicated in the text.

10) Page 17301, line 12: Indicate that m/z 107 (C8-aromatics) includes the three xylone isomers and benzaldehyde, in addition to ethylbenzene.

11) Page 17302, line 5: Please provide more details of the flux post-processing. Was the Web correction applied? What about the presence of possible trends in the 30-min series, were they eliminated using a low pass filter?

12) Page 17305, line 1: Was the same fraction of rejected periods due to stationarity and limit of detection for all the monitored species?

13) Page 17305, line 5: Which were the criteria to consider a data period of high or low quality?

14) Page 17306, line 8: In addition to the evolution of the boundary layer and emission patterns, the ambient concentration of any pollutant depends also on wind transport and chemical processes. The finding that the highest VOC concentrations were observed for oxygenated species shows the importance of the photochemistry in the VOC levels in the atmosphere of London.

15) Page 17306, line 13: How does the diurnal profile of CO compare to the diurnal profiles of VOCs?

16) Page 17307, line 8: Is the benzene to toluene ratio in units of ppbv/ppbv or ppbC/ppbC?



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17) Page 17307, line 9: Is there any reason for this significant increment in the benzene to toluene ratio?

18) Page 17307, line 16: Were the canister samples collected also at 200 m of height?

19) Page 17308, line 9: If this statement is true, one of the basic assumptions of the eddy covariance technique is not fulfilled. The monitored footprint must be homogeneous in terms of topography and emission sources to avoid interferences by advection.

20) Page 17308, line 19: Please indicate for all the times within the text if they are referred to UTC or local time? Because of the strong relationship between VOC fluxes and anthropogenic activities, it might be better to use local time.

21) Page 17308, line 23: According to Fig. 5, the boundary layer height passed from $\sim$600 m at midnight m $\sim$400 m at noon, being always above the measurement height.

22) Page 17309, line 18: Please define “cold starts”.

23) Page 17310, line 16: Define the acronym HGV.

24) Page 17310, line 27: Provide examples of other major toluene sources.

25) Page 17311, line 5: The units of ppvb-1/ppbv-1 are not clear. They must be ppbv of VOC /ppbv of CO

26) Page 17311, line 8: Change etheylbenzene by C2-benzenes. See comment 10.

27) Page 17312, line 9: Was the flux analysis in terms of traffic activity restricted to periods with north winds?

28) Page 17313, line 14: Which are those potential sources of methanol?

29) Page 17313, line 17: It is true that the biogenic emissions of isoprene depend on ambient temperature and solar radiation, but there are other parameters which might be also important under certain conditions, such as the plant phonology, relative hu-



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midity, pollution and water stress, etc. (see Guenther et al., 2006).

30) Page 17315, line 7: Which footprint area was used to extract the emissions from the emissions inventory?

31) Page 17315, line 8: Which of the measured VOCs are not reported in the emissions inventory?

32) Page 17315, line 11: The statement that the flux estimates are larger than NAEI estimates in all cases is not true. According to Fig. 9 the benzene emissions in the emissions inventory are larger than the emissions estimated in this work.

33) Page 17315, line 19: (Polson et al., 2009) is missing in the reference section.

34) Page 17313, line 20: According to the references Famulari et al. (2009) report NOx fluxes.

35) Page 17316, line 7: The statement that the traffic contribution to the VOC fluxes changes from season to season was not demonstrated in this study.

36) Page 17323, Table 2: It will be good to include the $\pm 1$ standard deviation of the 24-h flux averages listed in this table to have an idea of the day to day variability. The average toluene flux reported by Karl et al. (2009) is $14.1 \pm 4.0$ mg m-2 h-1.

37) Page 17323, Table 2: The VOC fluxes inside of a city vary according to the emissions sources in each neighborhood. For example the fluxes reported by Karl et al. (2009) correspond to the industrial sector of Mexico City, while the fluxes reported by Velasco et al. (2009) correspond to a busy residential neighborhood. To give a better idea of the average fluxes measured in previous studies it will be good to add a column to indicate the type of monitored district in each study.

References

Grimmond, C. S. B., Oke, T. R.: Aerodynamic properties of urban areas derived from analysis of surface form, J. App. Meteor., 38, 1262–1292, 1999.



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Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys. 6, 3181-3210, 2006.

Hsieh, C. I., Katul, G., and Chi, T.: An approximate analytical model for footprint estimation of scalar fluxes in thermally stratified atmospheric flows, Adv. Water Resour., 23, 765– 772, 2000.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellen, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, Atmos. Chem. Phys. 7, 3361-3372, 2007.

Please also note the Supplement to this comment.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17297, 2009.