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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mixing ratios and eddy covariance flux measurements of volatileorganic compounds from an urban canopy (Manchester, UK)" *by* B. Langford et al.

Anonymous Referee #1

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General comments

This work presents eddy covariance flux measurements of VOCs above a city applying two different flux measurement methods. VOC flux measurements above urban areas are still scarce and EC flux intercomparisons are particularly valuable, so the topics are certainly of interest for the readership of this journal. The paper is well-written, but I have some methodical concerns on the VOC measurements and on the flux calculations which are adressed in the specific comments below. Part of the discussion needs to be relativized or be phrased more carefully if the methodical limitations are considered appropriately.

Specific comments

Abstract

Last sentence: Rephrase or omit (see coment to section 3.3)

Introduction

When introducing the disjunct sampling eddy covariance technique, the authors should include a reference to the pioneers of DEC for VOCs (Rinne et al., 2001; Warneke et al., 2002).
Page 248, lines 29f. The statement in its current absolute form is wrong. The vDEC results in more data points per averaging period, but on the other hand, the uncertainty of each single concentration measurement may be greater, because of the shorter integration time. Please clarify.

Methods

Page 250, lines 8ff:
It is relevant to also know the height of the mast relative to the third level of the roof and the horizontal position of the mast (surface area of the roof, distance of mast to edge of roof).
Page 251, lines 1f:
In the context of flux measurement discussions, the description ”standard PTR-M” is not sufficient, since there are various types of the Ionicon instrument available with important differences in dimensions and materials of the drift tube, inlet system etc. that affect the total residence time of the analyte and hence the effective response time. It is ok to refer the reader to more detailed descriptions, but at least the characteristics determining time response and information on sensitivities (normalized cps/ppb and cps/ppb) should be added here, since they are important to judge the quality of the flux measurements.
Page 251, line 19: Replace”always” (mostly, typically).

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Page 251, lines 24f:
Transmission is indeed an important parameter if VOC concentrations are determined by calculation. But it is not the residence time of the ions in the drift tube, but the transmission efficiencies of the ions. It is also important to note how the transmission curve was determined, e.g. whether it was determined experimentally, from calibration gases or whether a default curve from the manufacturer was used. Even when transmission curves are determined carefully, determining VOC concentrations by such a calculation results in uncertainties as large as a factor of two (de Gouw and Warneke, 2007 and references therein). A statement about the uncertainty of the measurements is needed here.
Page 252, lines 14 ff and figure1:
The short dwell times for the vDEC measurements raise some questions and make it necessary to add information about the sensitivity (see comment above). If we assume a typical sensitivity of 10-20 normalized cps/ppb for benzene and 10 mio cps of H_3O^+ ions, an ambient concentration of 1 ppb will result in 100-200 cps. As shown in table 1, the average benzene concentration was 0.1 ppb. Therefore it seems evident that the benzene signal measured with only 20ms dwell time is affected by limited counting statistics. As benzene fluxes are prominently discussed in this work, the authors should explain in detail, how this will influence the presented results.
Page 253, line 18:
A time resolution of 0.5 seconds means that fluctuations up to 1 Hz can be resolved, not 2 Hz.
Page 254, equation 1:
As the correction for carry-over is not an exact correction, it would be interesting to illustrate the effect of this correction in the results section, i.e. show both corrected and uncorrected fluxes at least for some of the data.
Page 255, lines 5f:
The determination of the time lag is obviously a key step in the calculation. If fluxes are small, and in particular with the reduced number of data points in case of the DEC

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measurement, a clear maximum in the cross correlation may not always appear. Where such periods discarded or how was the lag determined under such circumstances?
Page 255:
The authors mention ”standard error” of the fluxes in the results section. As the error of a flux measurement is not trivial, a description of these errors must be added here.
Page 255, lines 23f:
It would be helpful for the interpretation of Figure 8, if the data omission is clarified: Does fig.8 only include hours where both DEC and vDEC data were available?

Results and Discussion

3.1. VOC Concentrations
Page 258, isoprene results:
The authors speculate that biogenic isoprene from outside the city could have reached the measurement site. What about trees within the city? Are there any parks nearby (even if the inventory shows no isoprene emissions!)?
Figure 6 cannot be interpreted without additional information. How was the temperature controlled fraction of isoprene calculated? What is the purpose of the second (dashed) trendline? If the authors assume this non-linear trend, the expected temp.controlled isoprene fraction at 30° would be higher than 32%.
Page 260, figure 7: It would be helpful to also show temperature in this plot. The discussion of the benzene/toluene ratio is interesting, but interpreting the ratio of 0.67 as indicator of advection of aged air masses seems rather speculative considering that primary exhaust emissions can be as high as 0.8. It appears that the variation in the ratio can mainly be explained by temperature, i.e. as a consequence of the OH concentration dependency on temperature.
Page 260, lines 22f: Maybe it is a combination of the shorter lifetime of acetaldehyde and its removal by oxidation and photolysis (probably strongly correlated with temperature) that cause a less prominent temp.dependency as compared to acetone.

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3.2. VOC fluxes

Page 261: General comment to figure 8: The comparison of averaged daily fluxes requires some additional information for interpreting the agreement of the two measurement techniques. What do the standard errors represent here: Is it simply stdev/(sqroot of n) or does it somehow include the uncertainty of the flux measurements (see comment above)?

Page 261, line 22: There is no two peak trend in panel E.

Page 262, lines 10f: Correlation plots would be helpful.

Page 262, line 17: Please specify ”absolute error”.

Page 263, lines 1-15: As nicely shown by the simulation of the heat fluxes, the disjunct sampling cannot explain the differences between the two systems. In this context, the effect of the applied carry-over correction should also be presented.

The tendency of the differences to be inversely proportional to the concentrations suggests that DEC does not underestimate, but that vDEC overestimates the fluxes! As the authors correctly concluded, the dwell time for benzene was too short. The discussion should be extended and it should be explained why this could result in an overestimate of fluxes (e.g. counting statistics leading to more noise in the flux signal and if fluxes are determined by searching for maxima in the covariance function then this might introduce systematic overestimation)

3.3. Comparison of measured benzene fluxes with NAEI estimates

Page 263, line 20:

After concluding that the vDEC measurement was close to the detection limit due to a too short dwell time, it seems more appropriate to use the DEC measurements which did not suffer from this limitation.

Page 264, lines 10 f:

The comparison of the average flux during a 15-day measurement period with the annual emission from an inventory is obviously problematic in various aspects. First, it is unclear what data from the inventory were used, i.e. how was the information from the

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footprint calculations used for the selection of the emissions from the inventory? Figure 9 indicates that only the length of the fetch was used. However, given the typically considerable spatial variation of emissions in urban areas, it seems more important to consider the influence of wind direction on the footprint. Secondly, the authors mention themselves that the linear extrapolation of the average fluxes during 15 days in summer for computing annual emissions is an arguable assumption. Does the NAEI inventory not have any temporal resolution that would make it possible to make a more direct comparison with summer emission estimates? Thirdly, the absolute values of concentrations measured by a non-calibrated PTR-MS have a considerable uncertainty (see also comment to methods section).

As it stands now, the comparison of the measured benzene fluxes with that of the inventory can be misunderstood. It could as well be concluded that, given all the uncertainties, the measurements prove that the emissions of the inventory are in the right ballpark. Therefore the comparison should either be omitted or be significantly extended. The latter would obviously be very valuable for further improvements of the inventory.

Technical corrections

Page 248, line 7: The cited paper was published in 2004.
Page 261, line 16: Fig. 8.

References:

J.H.I. Rinne, et al., Disjunct eddy covariance technique for trace gas flux measurements, Geophys. Res. Letters 28(2001), pp. 3139-3142.

C. Warneke et al., Disjunct eddy covariance measurements of oxygenated VOC fluxes from an Alfalfa field before and after cutting, J. Geophys. Res. 107(2002), p. 10.1029/2001JD000594.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 245, 2008.