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Atmospheric
Chemistry
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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.

B. Langford et al.

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We would like to thank all the reviewers for their helpful comments and constructive criticism, which after addressing we feel have helped to make this manuscript much stronger. In particular we are grateful to reviewer 1 whose comments prompted us to re-evaluate our data analysis strategy, focusing particularly on the cross-correlation function. In our re-analysis we used longer time windows in our CC function (0 to 30 s (vDEC) and 0 to 80 s (DEC)) and found we had been missing the true maximum and consequently had thus underestimated the flux. This has now been changed and we now find we have a much closer agreement between the two measurement systems. With the closer agreement, some of the points raised by the referees are not so relevant anymore and we have indicated this in the reply. Also, as a consequence of this, we have placed more emphasis on the flux side of the paper and removed some of the discussion of mixing ratios.

Reviewer 1

Specific comments:

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

AR: After re-analysis of the data and inclusion of further VOC emission estimates from the NAEI the section has been re-phrased to "The observed fluxes were up-scaled to give city wide emission estimates for each compound and the results compared to estimates made by the National Atmospheric Emission Inventory (NAEI) for the same flux footprint. Fluxes of toluene and benzene compared most closely differing by approximately 50%, while in contrast the oxygenated fluxes were found to be between 3.6 and 6.3 times larger than the annual average predicted by the NAEI."

RC: 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).

AC: Section 1, paragraph 4 "More recently a second technique, disjunct eddy covariance (DEC) (Rinne et al., 2001; Warneke et al., 2002), has been developed for "relaxed" flux measurement."

RC: 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.

AC: The information on the concentration is similar as the PTRMS spends a similar fraction of time on each m/z in the two modes, even though each individual measurement is less certain. However, with shorter dwell times, more wind data enters the calculation and concentration measurements reflect a larger number of eddies. Thus,

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overall statistical representativeness is improved in the vDEC approach. We have clarified this in the text and Section 1, paragraph 7 line 9 now reads "Furthermore, analysis times are shorter than in DEC, allowing more data points to be collected during each averaging period and reducing the statistical uncertainty associated with the use of a discontinuous time series by averaging over a larger number of eddy motions. However, shorter dwell times can lead to increased random error in individual concentration measurements, therefore a balance must be found between analysis times and measurement frequency."

RC: 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)

AR: The section has now been changed to (Section 2.1, paragraph 2, line 4): "The roof of the substation was used as the foundation for a 15 m mast which was fitted to the north west facing wall and instrumented with a sonic anemometer (Solent Research R3, Gill Instruments Ltd, Lymington, Hants, U.K.) and Teflon gas inlet line (1/2" OD; 0.38" ID)".

RC: Page 251, lines 1f: In the context of flux measurement discussions, the description "standard PTR-MS" 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.

AR: We agree that the description of the PTR-MS could have been more detailed. To this end section 2.2 line 5 has been changed to "The PTR-MS used was a standard model, containing two turbo molecular pumps, a 9.6 cm long drift tube (stainless steel rings) and heated silico steel inlet which drew air at a rate of 0.15 l min-1" and section 2.2, paragraph 3 now states "During the measurement period drift tube parameters such as pressue, temperature and voltage were held constant at 2 mbar, 45 oC and 600 V respectively to give an E/N ratio of approximately 125 Td. The primary ion count ranged between 2.2 and 3.6 Œ 106 with an average of 2.8 Œ 106. The reagent ions ranged between 1.07 - 2.62 Œ 105 with a mean of 1.69 Œ 105 which represented 6 % of the primary ion signal. Average normalised counts ranged between 3 (benzene) and 72 (methanol) with instrument sensitivities in the range of 4.3 (isoprene) to 13.26 (benzene) ncps ppbv-1."

RC: Page 251, line 19: Replace "always" (mostly, typically).

AR: "always" was changed to "typically"

RC: 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.

AR: The transmission curve was calculated experimentally using VOC standards of methanol, acetaldehyde, acetone, isoprene, methylethylketone, benzene, xylene, mesitylene, camphor and sevoflurane. Full details of the method used can be found in Wilkinson 2006. Although the transmission was determined carefully we recognise that this can still result in large uncertainties. We have recognised this fact in the revised text and included the reference from de Gouw and Warneke, 2007. Section 2.2, paragraph 4 was changed to "A VOC gas standard was not available for on-site calibra-

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tion of the PTR-MS, hence mixing ratios were calculated using the instrument specific transmission coefficients and reaction times taken from Zhao and Zhang (2004). The transmission coefficients were calculated experimentally under laboratory conditions using a range of gas standards and the method used has been described in detail by Wilkinson (2006). Despite the careful calculation of coefficients, previous studies (de Gouw and Warneke, 2007) have suggested mixing ratios calculated using this approach can have large systematic errors, therefore some systematic bias in mixing ratios cannot be ruled out here. It should be noted that a systematic offset in the VOC mixing ratio due to the instrument background will not affect the measured fluxes."

RC: 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 H3O+ 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.

AR: The reviewer is correct that the short dwell times chosen for the vDEC setup may not have been ideal and probably resulted in limited counting statistics. The revised manuscript now contains discussion on this subject, including how limited counting statistics are likely to influence the flux. Section 3.2, paragraph 9 now reads "Counting statistics cause uncertainty in the flux and the error is inversely proportional to N0.5, where N is the total number of ion counts during a (25 minute) flux averaging period (Fairall, 1984). N remains similar, independent of whether a concentration is measured frequently with a short dwell time, or less often with a longer dwell time, except for the increased relative dead time associated with switching between m/z more rapidly. However, reducing the error associated with individual count rates on the raw DEC and

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vDEC data points is important as it can impact upon the cross-correlation function used to calculate delta t and may thus affect the overall precision of the flux measurement. When the random error is high, the cross-correlation becomes noisier and more difficult to interpret, reducing the measurement precision. By looking for the time lag that maximises the cross correlation, fluxes may be systematically biased towards extreme values, which would be more important the noisier the time-series and the smaller the flux (i.e. during night-time). Calculating the flux limit of detection by taking the standard deviation of the covariance function at distances far from the true lag would help to eliminate such periods in the future. It should be noted that, where a constant time-lag can be used, a systematic bias should not occur."

RC: Page 253, line 18: A time resolution of 0.5 seconds means that fluctuations up to 1 Hz can be resolved, not 2 Hz.

AR: The reviewer is correct and the section has been altered accordingly. Section 3.2, paragraph 10, line 1 "Some of this difference can be explained by the faster response time of the DEC system, which could resolve turbulent fluctuations of up to 1 Hz as apposed to 0.5 Hz for the vDEC system."

RC: 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.

AR: The presented DEC fluxes now include both uncorrected and corrected results with regression plots for both shown in figure 6.

RC: 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 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?

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AR: Lagtimes were chosen automatically by the LabVIEW program used to process the data. In each covariance function the program searched for the maximum value inside the given time window. As the reviewer points out, this protocol may result in a systematic overestimation of the flux as false maximums may be selected when the noise of the CC function exceeds the flux signal. We have included some discussion on this and suggest that in the future flux LOD are used to filter out such periods. Section 3.2, paragraph 9, line 6 now reads "However, reducing the error associated with individual count rates on the raw DEC and vDEC data points is important as it can impact upon the cross-correlation function used to calculate ∆t and thus affects the overall precision of the flux measurement. When the random error is high, the cross-correlation becomes noisy and difficult to interpret, reducing the measurement precision. This problem is exacerbated at night-time when ambient concentrations are at their lowest and may result in vDEC fluxes being overestimated as the peak may not exceed the general noise of the cross-correlation. Calculating the flux limit of detection by taking the standard deviation of the covariance function at distances far from the true lag would help to eliminate such periods in the future."

RC: 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.

AR:The standard error was used here to give the reader an idea of the day-to-day variation of VOC fluxes during the campaign. We agree that error bands associated with flux measurements are often sizable and warrant some discussion here. As the data presented in this paper focuses on two techniques whose primary difference is the rate of sampling (delta x) we choose to look at the errors associated with the choice of sampling interval as described by Karl et al (2002) and Lenschow et al (1994). If we take integral time scales (lws) to be in the range of 10 to 20 s, our averaging period (T) to be 1500 s and our sampling interval to be 0.2 s and 12 s respectively for the vDEC and DEC techniques, flux errors due to disjunct sampling are $<$ 1% for the

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vDEC technique and between 6 and 13% for the DEC mode. At this comparably high measurement location, errors associated due to variations in geophysical variability are a much larger source of error to the flux estimates. The errors associated with both unstable and neutral conditions were calculated following the method of Wesley & Hart (1985) and were found to be 47% and 61% respectively. In order to reduce this error to 20% the averaging period would need to be extended to ˜2.5 h potentially introducing non stationarities and severely reducing the resolution of the flux data.

This discussion has been added to the manuscript (section 3.2).

RC: 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?

AR: This is correct, data used in this figure only includes hours where both systems were operational. Section 3.2, line 2, now reads "Data included in the averages were selected from time periods where measurements from both systems were available."

RC: 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!)?

AR: The section detailing discussion of biogenic isoprene has been omitted, therefore these comments no longer apply to the manuscript. However, there are no areas of parkland and very few trees within the flux footprint.

RC: 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%.

AR: This section was omitted from the revised manuscript.

RC: 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.

AR: We agree with the reviewer that the discussion presented was slightly speculative. Therefore the discussion of this section has been shortened considerably, concluding that the elevated ratio may relate to either an older air may or simply an increased removal rate corresponding to higher temperatures and more OH. Section 3.1, paragraph 8, line 8 now states "In the present study the average B/T ratio was approximately 0.57 (Fig. 5), suggesting the observed concentrations were typically originating from sources close to the measurement site. However, during the period of elevated temperatures (9th - 12th of June), the ratio increased to an average 0.67, which suggests either slightly older, photochemically processed, air was being advected from outside of the city or that the removal rate of toluene increased due to higher concentrations of the OH radical corresponding to the increase in temperature or both."

RC: 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.

AR: We thank the reviewer for their suggestion and have changed the last sentence in section 3.1 to read "Furthermore, the shorter atmospheric lifetime of acetaldehyde which is removed by oxidation and photolysis (both likely to be strongly correlated with temperature) may also contribute to the less prominent temperature dependency."

RC: 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 com-

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ment above)?

AR: The standard error is as the reviewer suggests stdev/(sqroot of n). This has been clarified in the manuscript. Section 3.2, paragraph 6, line 3 "Despite the indirect nature of the comparison, the two flux measurement systems showed good agreement, with measured fluxes falling within the range of the standard error (sd/sqrt(n)) of hourly fluxes".

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

AR: This figure has changed so this comment is no longer relevant

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

AR: Correlation plots have been added to figure 6 for each mass, showing both corrected and uncorrected DEC fluxes.

RC: Page 262, line 17: Please specify "absolute error".

AR: This term has now been removed from the text.

RC: 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)

AR: After the re-analysis of the data the difference between the two systems is much less, but DEC fluxes are still lower than vDEC fluxes. As the reviewer points out this dif-

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ference is partly due to the effect of limited counting statistics for the vDEC approach, leading to an overestimation of the flux, particularly at night when concentrations are at their lowest. However, most of the difference is explained by the carryover between DEC samples. To this end we have included both corrected and uncorrected DEC fluxes with regression plots for each in figure 6. In addition we have added discussion of limited counting statistics and the effect this has on the vDEC fluxes. Section 3.2, paragraph 8, line 3 now addresses each of these points "The correction increases the amplitude of the PTR-MS data and consequently gives larger flux values as can be seen in Fig 6. After the correction was applied the average offset between the two systems was reduced to less than 7%. Despite this correction, DECcorr values remained lower than vDEC fluxes at night-time. This is thought to relate to the very short dwell times chosen for the vDEC method which can result in limited counting statistics. Counting statistics cause uncertainty in the flux and the error is inversely proportional to N0.5, where N is the total number of ion counts during a (25 minute) flux averaging period (Fairall, 1984). N remains similar, independent of whether a concentration is measured frequently with a short dwell time, or less often with a longer dwell time, except for the increased relative dead time associated with switching between m/z more rapidly. However, reducing the error associated with individual count rates on the raw DEC and vDEC data points is important as it can impact upon the cross-correlation function used to calculate delta t and may thus affect the overall precision of the flux measurement. When the random error is high, the cross-correlation becomes noisier and more difficult to interpret, reducing the measurement precision. By looking for the time lag that maximises the cross correlation, fluxes may be systematically biased towards extreme values, which would be more important the noisier the time-series and the smaller the flux (i.e. during night-time). Calculating the flux limit of detection by taking the standard deviation of the covariance function at distances far from the true lag would help to eliminate such periods in the future. It should be noted that, where a constant time-lag can be used, a systematic bias should not occur."

RC: 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.

AR: Values from the DECcorr technique are now used instead of those collected by vDEC.

RC: 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 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.

AR: In the revised manuscript we have included a more detailed explanation of how the footprint analysis was used to generate an emission estimate for the NAEI. As the reviewer points out, spatial variability of emissions in the urban environment is considerable, therefore a revised emission estimate has been calculated which has been weighted for wind direction. Regrettably the NAEI does not provide emission estimates at a temporal resolution lower than 1 year, therefore a more direct comparison was not possible. Section 3.3, paragraph 2, line 13 now includes "A circular flux footprint (radius = Xr) was then superimposed over a map of NAEI grid squares and the entrained grids averaged using a weighting factor to account for the wind direction during the measurement period."

Technical corrections: RC:Page 248, line 7: The cited paper was published in 2004.

AR: The year has been changed.

RC: Page 261, line 16: Fig. 8. AR: changed to Fig 8.

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

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