

Interactive comment on “Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK)” by B. Langford et al.

B. Langford et al.

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Reviewer 3

RC: P248, line9 Quadrupole mass analyzers are not new and have been employed in GC based VOC analysis for decades, so this sentence sounded odd to me. What is new is "real time in-situ" VOC sensors using chemical ionization as the detection principle.

AR: We would agree that quadrupole mass analysers are not new, yet we would argue that there application for VOC flux measurements is relatively new (past ~8 years).

RC: P248, line16. The term duty cycle has a specific and very different definition that

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the one employed here. A simple fix is to replace duty cycle with scan cycle. The duty cycle would be the fraction of time spent measuring mass *i* over the total scan cycle time. I suggest replacing this usage of duty throughout your paper.

AR: The term duty cycle has been replaced with scan cycle as suggested by the reviewer.

Section 1, paragraph 6, line 1 "The quadrupole mass spectrometer in the PTR-MS can be programmed to scan over a small suite of masses in what is termed a scan cycle."

RC: P251, line 1. A small point but the "standard PTR-MS" isn't descriptive enough. Can you give the model type and perhaps a description of the inlet type? Was this a new instrument? In the last couple of years the inlet design has been much improved so that the sample lines are passivated steel tubing and are heated.

AR: We agree that our description of the PTR-MS could have been more detailed. Therefore we have expanded the method section to give a full description of the PTR used, including details on drift tube type, turbo pumps and inlet type.

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"

RC: P251, line 21. In an urban area I wouldnt pre-suppose that the only mass interferent for isoprene would be furan. You should perhaps note the comparison of isoprene between PTR-MS and GC by Kuster et al ., EST, 2004 that shows pretty poor agreement for mixing ratios below 1 ppbv. Perhaps there are other urban PTR-MS vs. GC comparisons that can cited to convince that m69 in urban areas is really isoprene.

AR: We fully accept that in the urban environment where emitted VOCs are numerous it is wrong to presume furan as the only interference at mass 69. Therefore we have increased our discussion of this point and stressed that within the urban environment other compounds may be detected at this amu. Please see our response to reviewer 2

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who raised a similar point.

RC: P251, line 24. The discussion of PTR-MS calibration needs to be cleared up. You have confused reaction time with ion transmission efficiency (transmission numbers in your paper). How was the ion transmission efficiency determined? If this was not known what are the uncertainties of your calculated mixing ratios?

AR: As the reviewer points out, we confused transmission efficiency with reaction time. This mistake has been corrected. 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 calibration 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 be associated with large systematic errors, therefore some systematic bias in mixing ratios cannot be ruled out here. Nevertheless, it should be noted that a systematic offset in the VOC mixing ratio will not affect the measured fluxes."

RC: What was your average reagent ion (m21) count rate and what was the percentage of m37?

AR: Section 2.2, paragraph 3 now states "During the measurement period drift tube parameters such as pressure, temperature and voltage were held constant at 2 mbar,

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45 oC and 600 V respectively to give an E/N ratio of approximately 125 Td. The primary ion count ranged between 2.2 to 3.6 E6 with an average of 2.8 E6. The reagent ions ranged between 1.07 to 2.62 E5 with a mean of 1.69 E5 which represented 6 % of the primary ion signal."

RC: What were your calculated sensitivities?

AR: section 2.2, paragraph 3, line 6 "Average normalised counts ranged between 3 (benzene) and 72 (methanol) ncps with instrument sensitivities in the range of 4.3 (isoprene) and 13.26 (benzene) (ncps/ppbv)."

RC: A better parameterization of ion-molecule rate constants is from Su (J. Phys. Chem., 89, 555, 1988). The issue is do thermal rate constants accurately describe the ion molecule reaction in the drift tube for the more polar organics. Better to calibrate with external standards.

AR: We fully agree that it is best to calibrate the PTR-MS using external gas standards, however on this occasion, due to the measurement location this was not an option.

RC: You do not mention how background count rates were determined. Were background counts rates (determined by sampling clean zero air) subtracted from the ambient data?

AR: Our platinum catalyst was not available at the time of measurement, therefore online monitoring of the instrument background could not take place. Instead, typical background counts for each mass (for the same PTR-MS running with the same optimization) were subtracted. We accept that this approach is not ideal as some studies have shown the background to fluctuate with variations in sample air humidity. While this may cause some additional uncertainty on measured VOC mixing ratios, a systematic background offset will not affect the flux measurements.

RC: p. 252. You mention that scans were performed. It would be valuable and interesting to show an average of these mass scans to see what your urban air looked like

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(raw signal counts vs m/z).

AR: We agree that the scans taken of urban air are interesting; there are plans to present this data along with scans from other urban campaigns elsewhere.

RC: p. 255. Were quality control tests done to check for stationarity?

AR: Normal stationarity tests of eddy covariance data (i.e. ogives in the frequency domain) are not available to disjunct data due to the differing time resolution of c and w . The only stationary test available to disjunct data is that suggested by Foken (1996) where the 30 minute flux is disaggregated into 5 minute blocks and the average of these compared to the 30 minute flux. Unfortunately, due to the low number of data points collected over 25 mins by the DEC technique, results obtained for 5 minute fluxes are unlikely to be statistically valid, therefore no stationarity tests were applied to this data set.

RC: P256. line 27. The use of the adjective "strong" to characterize an r^2 value of 0.24 seems excessive.

AR: The reviewer is correct, however, since the re analysis of the data this comment no longer applies.

RC: P257, line 16. Can you explain why a change in wind direction would produce a spike? Are you saying there were local sources producing a high concentration plume?

AR: Yes, for example, some wind vectors contain busy roads such as Oxford Road, whereas others only contain smaller side streets where traffic activity is limited.

RC: P258, line 1. The slope through the isoprene vs. benzene plot is more informative regarding the source. You have more isoprene than benzene by factor of 3. Does fuel sold in Manchester really contain isoprene, does the fuel really contain 3 times more isoprene than benzene? For gasoline sold in the US (of which I know something about) there is very little isoprene compared to other C5 alkenes, and it is much less abundant than benzene. Isoprene and benzene are also formed in the combustion process but

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roadway emissions also show low isoprene compared to benzene. In Figure 6 why not show the molar ratio found in gasoline and roadway emissions that reflect UK fuel composition?

AC: Due to the uncertainties associated with an uncalibrated PTR-MS and potential interferences at m/z 69, the detailed discussion of isoprene and benzene mixing ratios has been omitted from the revised manuscript.

RC: One oak tree near your site may have a strong influence on local isoprene. What trees were nearby? What does a plot of $\ln(\text{isoprene})$ versus temperature look like? Isoprene emission and ambient concentrations display an exponential dependence on temperature. How was the temperature controlled fraction of isoprene determined?

AR: See comment above. Manchester has no areas of urban parkland and there were no oak trees near the measurement location.

RC: P261. The differences in the emissions rates as a function of time of day are interesting. In Figure 4 you have shown that acetone and toluene have a reasonable linear positive correlation (perhaps 2 trend lines) suggesting a common source and variability driven by emission rate strength and dilution. The diel emissions plot however shows the acetone emission rate maximizing during the toluene afternoon minima. Some discussion on how these temporal differences in emission rates impact ambient correlations would be valuable.

AR: As the data have been reprocessed and the trend in data has changed, particularly for toluene, we believe these comments are no longer relevant to the data presented in the revised manuscript.

RC: If benzene and toluene have similar sources why are their diel emissions patterns so different (no afternoon emission minima in benzene)?

AR: Again, after reprocessing of the data benzene and toluene now show very similar trends therefore we feel this comment is no longer relevant.

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RC: Wouldnt emissions rates be greatest for benzene and toluene in the morning when there is concentrated traffic from morning rush hour, or does vehicle traffic peak in the afternoon? Please elaborate.

AR: This point has been addressed in response to a similar point raised by reviewer 2
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RC: What was the inner diameter of the 1/2" OD tubing used as sampling line of the DEC system?

AR: The main inlet tubing had an inside diameter of approximately 0.38 inch. This has been added to the text.

RC: What was the limiting factor for the rate of evacuation, the efficiency of the pump or the flow resistance of the tubing between the pump and the ISR?

AR: The limiting factor was the performance of the pump.

Section 2.3.2, paragraph 2, line 2 was changed to "The time taken to evacuate the canister, 12 s, was determined by the efficiency of the pump and proved to be the limiting factor in determining the length of time between sampling."

RC: What were the dimensions of the evacuation tube?

AR: The evacuation pump was OD 1/4" PFA tubing and approximately 2 m in length.

RC: The correction Equation (1) corrects for the average reduction of the fluxes due to the carryover but the authors should also estimate how the carryover affects the accuracy of the fluxes.

AR: In the revised manuscript we now present results for corrected and uncorrected DEC fluxes in figure 6.

RC: The time needed to fill the ISR is more than double than in the systems previously presented in the literature (Rinne et al., 2000; 2001; 2007; Warneke et al., 2002; Grab-

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mer et al., 2004). Is this due to the flow resistance of the sample valve or the sample tube?

AR: As you point out, the time to fill the ISR is longer than in previous studies. During a previous deployment over a grassland field where air was sampled directly the time to fill the ISR was also 0.5 s, therefore it must be concluded that the slower grab sample time is due to flow resistance from the valve. This point has been added to Section 2.3.2, paragraph 2, line 4 "By contrast, the time taken to fully pressurise the ISRs, 0.5 s, proved to be the limiting factor in determining sampling times. This value is more than double that of previous studies (Grabmer et al 2004; Rinne et al., 2000; 2001; Warneke et al., 2002) and is thought to occur as a consequence of the flow resistance of the sample tube."

RC: There is some confusion on the defining the high frequency response of the system. Firstly, authors state on page 253, lines 15 to 18, that due to the effective response time of 0.5 s of the DES it can resolve turbulent fluctuations up to 2 Hz. This is incorrect. As two samples per period are needed to resolve any variation the frequencies resolved by 0.5 s sampling are up to 1 Hz. The same error is repeated at least in page 262 lines 20 to 23.

AR: We thank the reviewer for pointing out our mistake, which we have now corrected.

RC: The use of 20 ms dwell time does not necessarily mean that the response time of the measurement would be 20 ms. Due to the mixing in the sample line and most importantly in the reaction tube of the PTRMS the response time can be significantly longer than this. Depending on the type of the PTRMS this may vary. For the newer instruments with three turbomolecular pumps and smaller reaction tube the manufacturer states the response time to be <200 ms. Thus 200 ms can be taken as a conservative estimate. However the older PTRMS instruments have response times over one second. Therefore the authors should give more detailed information on their "standard" PTR-MS and revise their high frequency loss calculations.

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AR: The reviewer is again correct, that the chosen dwell time is not the same as the instrument response time. As our PTR-MS was the older model we have concluded the response time for the vDEC system was ~ 1 s and hence lower than that of the DEC system.

Section 2.3.2, paragraph 2, line 8 was changed to "This considered, the overall effective response time of the DFS setup is about 0.5 s, which is sufficient to resolve turbulent fluctuations of up to 1 Hz. In comparison, the effective response time of the vDEC system, which is limited by the response time of the PTR-MS and not sample integration time, was approximately 1 s. Therefore, despite the shorter dwell time used in vDEC (20 ms) the effective response time was longer than in DEC, allowing turbulent fluctuations of up to 0.5 Hz to be resolved. At a measurement height of 95 m the portion of the total flux carried in the sub 1 s range is negligible (estimated from Horst, 1997) and therefore no explicit corrections were applied. Simulations, using the sensible heat flux data, indicate that on average 5% of the heat flux were carried by frequencies between 0.5 and 1 Hz. The effect is discussed below."

RC: The sampling interval in any DES method does not need to be shorter than the integral time scale of the turbulence for reasonably good flux measurement as stated in page 248, line 4-7. This issue has been studied by simulations and field comparisons by e.g. Lenschow et al., (1994), Rinne et al., (2000; 2007), and Bosveld and Beljaars, (2001). For sample intervals longer than the integral timescale, the uncertainty induced by the DES is simply a function of the standard deviation of the product $w'c'$ and number of samples utilized for flux calculation (e.g. Rinne et al., 2007). Thus the increase in the flux integration time can be used to compensate the longer sample interval.

AR: The text has now been altered to read (section 1, paragraph 4, line 8) "The discontinuous dataset generated can be used to give high precision flux information, which is numerically similar to the EC approach, but with reduced statistics (Grabmer et al., 2004)."

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RC: The longer sample interval of the DEC as compared to vDEC is not inherent feature of this method (Page 248, lines 28- 29). It could be also possible to construct sampler with short sample interval and in some cases the measurement cycle of the mass spectrometer may be considerably longer than the one used in this paper.

AR: Although longer sampling intervals are not an inherent feature of the DEC approach, it is a potential benefit, especially for slower sensors than the PTR-MS.

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