

## ***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.***

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The paper presents interesting measurements of VOCs fluxes and mixing ratios above an urban area. My comments are related mainly on the DEC method and technical details presented in the paper and I do not comment the concentration measurements or the validity of the up-scaling.

The set-up with ISRs filled from a sample line is advantageous in using the DEC with grab samplers to measure VOC fluxes above high canopies. This may, however, be the reason for a couple of shortcomings of the system, as pointed out below.

1) The relatively high carry-over is partly caused by the reduction of the pressure in

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the sample line. What was the inner diameter of the 1/2" OD tubing used as sampling line of the DEC system? Even more important than the reduction of the sample line pressure is the relatively high pressure of the evacuated ISR (250 mb). This pressure in the evacuated ISR was considerably higher than for the systems presented previously in the literature (Rinne et al., 2000; 2001; 2007; Warneke et al., 2002; Grabmer et al., 2004). 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? What were the dimensions of the evacuation tube? Even a couple of meters of 1/4" OD tubing can have a significant flow resistance lengthening the evacuation time considerably. 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.

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

There is some confusion on the defining the high frequency response of the system. Firstly, authors state on page 253, lines 15-18, 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 20-23.

Secondly, 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 PTR-MS the response time can be significantly longer than this. Depending on the type of the PTR-MS 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

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a conservative estimate. However the older PTR-MS 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.

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.

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.

Clarification of these issues would make the methodological description of the paper much stronger and point out the critical details of the measurement system. I would also help to avoid some confusion of the reader.

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