Atmos. Chem. Phys. Discuss., 8, S207–S210, 2008
www.atmos-chem-phys-discuss.net/8/S207/2008/

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 #3

Received and published: 15 February 2008

General comments

This paper presents results for VOC flux measurements from an urban area using two different methodologies. A PTR-MS instrument was used to make fast VOC measurements. There are very few measurements of urban VOC fluxes. The comparison between the two methods to better understand the methodological uncertainties are valuable to the APCD readership. While the paper in general is well written, there are a number of PTR-MS technical points that need to be more fully discussed or re-phrased. Some of the data interpretation wasn't clear. These are noted in the specific comments below.

Specific comments

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.

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

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.

P251, line 21. In an urban area I wouldn't 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.

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?

What was your average reagent ion (m21) count rate and what was the percentage of m37? What were your calculated sensitivities?

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

ACPD

8, S207–S210, 2008

external standards.

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?

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 (raw signal counts vs m/z).

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

P256. line 27. The use of the adjective "strong" to characterize an r2 value of 0.24 seems excessive. If these relationships are linear then emission rate variability and variable dilution are driving the dynamic range.

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?

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 x 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 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?

One oak tree near your site may have a strong influence on local isoprene. What trees were nearby? What does a plot of ln(isoprene) versus temperature look like? Isoprene emission and ambient concentrations display an exponential dependence on temperature.

ACPD

8, S207–S210, 2008

How was the temperature controlled fraction of isoprene determined?

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.

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

Wouldn't 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.

Technical Corrections

p251. It is Zhao not Zaho.

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