

Interactive
Comment

Interactive comment on “Airborne determination of the temporo-spatial distribution of benzene, toluene, nitrogen oxides and ozone in the boundary layer across Greater London, UK” by M. D Shaw et al.

M. D Shaw et al.

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1.1 I feel the authors have missed an opportunity to look at the evolution of the London plume in flights 7-10 where the flight track is parallel to the wind direction. Surely these data provide a unique opportunity to compare concentrations of ozone and its precursors both up and downstream of London from which an approximate emission estimate can be derived and compared to NAEI emission estimates? In my mind an analysis of this sort would offer far more scientific value than reporting the city cross

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section concentrations. At the very least it would be interesting to see how the T/B ratios change as the London plume evolves.

1.2 This was not the focus of the research flights, hence they were not designed to monitor plume evolution. Please refer to response 3.2. The measurement of plume evolution should be carried out by perpendicularly transecting the plume at different distances from the emission source (Hopkins et al., 2009). Without perpendicular transects, flying only parallel with the mean wind direction can create unknowns in the data interpretation as it's difficult to know the width of the plume which can lead to the potential of sampling different point sources/other plumes.

We have not calculated emission estimates from these flights as we consider the errors would be too large. Again our flights were not designed for a mass balance calculation as described by Hopkins et al (2009), i.e. we did not spend enough time flying upwind and downwind of Greater London. Our flights were focussed over Greater London where we expected VOC and NO_x emissions would be highest.

Hopkins, J. R., Evans, M. J., Lee, J. D., Lewis, A. C., Marsham, J., McQuaid, J., Parker, D. J., Stewart, D. J., Reeves, C. E., and Purvis, R. M.: Direct estimates of emissions from the megacity of Lagos, *Atmospheric Chemistry and Physics*, 9, 8471-8477, 2009.

1.3 As a result of this comment, and due to the comments of reviewer 3 we have removed all discussion of flights 7-10 from this manuscript.

2.1 Page 27338, line 3, change "is" to "are"

2.2/2.3 Corrected

3.1 Page 27338, line 7. In the context of ground level ozone and its precursors I am curious as to why you focus on benzene and toluene and not for example isoprene which has a greater ozone forming potential. A short sentence to justify your choice of compounds is warranted. Furthermore, why do you limit the number of VOCs you measure to just two compounds surely you could have increased your duty cycle without

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compromising the spatial resolution of the data?

3.2 The primary focus of this project was to calculate highly spatially resolved (1km) VOC and NO_x Eddy covariance fluxes across greater London from an airborne platform, only mixing ratio data is presented here. EC flux data will be made available in later publications. In order to obtain VOC mixing ratio data with a PTR-QMS suitable for virtually disjunct Eddy covariance flux calculation requires a minimum quadrupole ion dwell time of 0.2 secs per VOC at a total acquisition rate of approx 2Hz. Hence only 2 compounds could be scanned for simultaneously. Benzene and Toluene were chosen as their emissions within urban regions are dominated by anthropogenic sources, and their measured ratios can be used to indicate the emission source type (e.g. vehicular, Industrial).

3.3 The following text has been added “with a view to identify dominant emission sources in the region using measured toluene to benzene (T/B) concentration ratios”
Pg 4 lines 13-14.

4.1 Page 27341, line 6, change to “...adding a small flow..”

4.2/4.3 Changed

5.1 Page 27341, line 14, Please could you clarify the rate at which data were acquired and used in the paper. Earlier we are told they it was 10 Hz but here it suggests it is 1 Hz.

5.2/5.3 NO and NO₂ data was acquired at 10Hz (for the purposes of Eddy Covariance flux calculations see response 3.2), however it has been averaged to 1Hz in this work as we are only looking at concentrations. This is now made clear in the text, Pg 6 lines 28-29.

6.1 Page 27341, line 2, change to “setup”

6.2/6.3 Corrected

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7.1 Page 27343, line 9. Please could you clarify your use of the humidity controlled zero air. Did you modulate the zero air humidity to reflect ambient RH conditions or did you calibrate over a range of RH to assess the effect on instrument sensitivity?

7.2 Zero air Humidity was calibrated over a range of RH% (0,20,40,60 and 80% RH each in triplicate) to assess the effect on PTRMS sensitivity. The normalisation of both benzene and toluene icps against the primary icps takes into account changing ambient humidity as described in Warneke et al 2001.

Warneke, C., Van der Veen, C., Luxembourg, S., De Gouw, J., and Kok, A.: Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: calibration, humidity dependence, and field intercomparison, International Journal of Mass Spectrometry, 207, 167-182, 2001.

7.3 The following has been added to Pg 8 lines 17-22, "Zero air humidity was calibrated over 20 -80% RH in triplicate to assess humidity effects on sensitivity during the campaign. Benzene and toluene, do not react with the hydrated hydronium ions generated at higher ambient air humidity within the PTRMS drift tube(Warneke et al., 2001). To account for this humidity dependent PTRMS sensitivity toward benzene and toluene, these compounds were normalised against the hydronium ion counts only."

8.1 Page 27343, line 19. Please include the inner diameter of the tube – this is the value that actually matters.

8.2/8.3 Inner tube diameter now added to discussion. Pg 8 lines 31-33 now read "During flights, ambient air was sampled from the forward facing isokinetic inlet along a heated (70°C) 5 m $\frac{1}{4}$ " Teflon (PFA) tube (0.21" ID) pumped by a stainless steel diaphragm pump (Millipore) at a flow-rate of 22L min⁻¹."

9.1 Page 27345, line 9. I am pleased to see you have taken the time to compare the PTRMS measurements with the GC-FID WAS samples. This always provides additional confidence in the reported measurements. I see the benzene bias is half of that

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reported by Jobson et al., 2010 at 8%. This potentially reflects the differing operating conditions of the two instruments, with less fragmentation in your system operating at 110 Td as opposed to theirs operating at 145 Td. The agreement for toluene is slightly less convincing with the PTR-MS underestimating by $\sim 20\%$. This warrants some further comment. Can you suggest why the disagreement is so large? Finally, a 20 % negative bias on the toluene concentrations and an 8% bias on the benzene measurements will undoubtedly have a significant impact on the T/B ratios reported which the authors should also comment on.

9.2/9.3 It is unclear why the PTR-MS exhibited such a negative bias toward ambient toluene concentrations, the only explanation that we can provide is that perhaps this comparison is influenced by the small sample size used for the PTR-MS vs WAS GC-FID comparison (benzene $n=4$, Toluene $n=6$). However, it is important to point out that the PTR-MS vs WAS GC-FID comparisons for toluene and benzene were technically within the calculated measurement uncertainty of PTR-MS alone. As stated on pg 8, lines 25-27 “Calculated uncertainties for the PTRMS during the campaign were 16 ± 5 and 21 ± 9 % for benzene and toluene respectively, calculated using the standard deviation of linear regression (S_m) of pre-flight calibrations”. Also on page 8 lines 8-10, “Inter-comparison of the two sampling methods showed excellent agreement within measurement uncertainty”.

Using the variance formula method of uncertainty propagation produces a PTRMS vs GCFID Toluene/Benzene concentration ratio total uncertainty of 30%. For a WAS-FID vs PTR/MS derived T/B ratio of $(1.08/0.79) \times 1.8 = 2.5 \pm 0.75$ ppbv ppbv⁻¹, hence the ratios are equivalent within the calculated uncertainties.

10.1 Page 27349, line 11. It would be interesting to see the same plot for a different flight leg (R6) where the wind direction and hence LHA plume are slightly shifted. This might help separate the influence of local emissions from the LHA plume.

10.2/10.3 Additional plots for NO_x, toluene and benzene during RF 1 (approx. 360m

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agl) have now been added to figure 6. The mean wind direction during RF 1 was slightly shifted when compared to the mean wind direction observed during RF 5. This has helped to visually separate the influence of localised emissions from the LHA plume. During both RF1 and RF5, NO_x mixing ratios approximately doubled (approx. 15 - 30 ppbv) on entering the LHA plume whereas toluene and benzene only showed a negligible increase in mixing ratios. Refer to figure 1 attached.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 27335, 2014.

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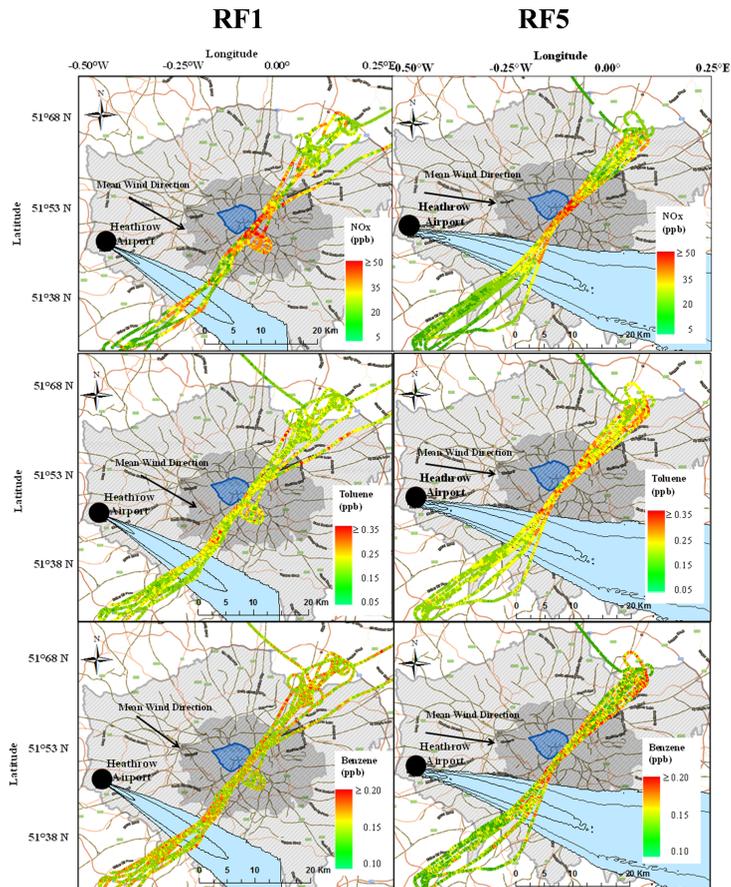


Fig. 1.

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