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Atmospheric Chemistry and Physics Discussions

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.

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1.1 As a general comment, I found several of the figures difficult to read, particularly Fig 2 and 8. Larger markers and perhaps some colour would help the reader to interpret these figures more easily.

1.2/1.3 Figures 2 and 8 adjusted. Marker size increased and marker colour added. See attached figures 1 and 2.

2.1 p. 27337, line 6. Is there a more recent reference you could use to describe emission sources for anthropogenic VOCs? note marked changes in VOC emissions on decadal scales for Los Angeles and London;a 31-year old reference may not be relevant here.

2.2/2.3 3 references added to manuscript. Langford et al 2010 and Karl et al 2009. Karl, T., Apel, E., Hodzic, A., Riemer, D., Blake, D., and Wiedinmyer, C.: Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity, Atmos. Chem. Phys, 9, 271-285, 2009.

Langford, B., Misztal, P., Nemitz, E., Davison, B., Helfter, C., Pugh, T., MacKenzie, A., and Hewitt, C.: Fluxes and concentrations of volatile organic compounds from a South-East Asian tropical rainforest, 2010, 4293, p. 27337, line 12. ". . . about 50% of NOx is thought to be derived from vehicles,"

Lee, J., Helfter, C., Purvis, R., Beavers, S., Carslaw, D., Lewis, A., Moller, S., Nemitz, E., and Tremper, A.: Measurement NOx fluxes from a tall tower above central London, UK and comparison with emissions inventories. , Environ. Sci. Technol. DOI: 10.1021/es5049072, 2015.

3.1 p. 27337, line 28. "However, these networks only measure mixing ratios . . ." Please describe what other measurements these networks should provide.

3.2/3.3 Pg 3 lines 30-33 now reads "However, measurements from these networks suffer from the limitations of being made at relatively few sites and so may not be representative of mixing ratios over larger spatial scales".

4.1 p. 27339, line 17. "Parallel wind directions allow us to assess the horizontal advection and dispersion of pollutants across the city and their transport to suburban and rural regions." Was this done in the following text? I didn't see much discussion of RFs 7-10 beyond Tables 1 and 2. Perhaps these flights could be removed from the manuscript if they are not part of the discussion section.

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4.2/4.3 Agreed flights RF 7-10 have been removed from the manuscript.

5.1 p. 27341, line 12. “Typically calibrations are carried out at the beginning and end of a flight, with sensitivities and conversion efficiency Interpolated between the two and applied to all data.” Was the data corrected for O3 and H2O (titration of NO and quenching of NO2 excited state, respectively)? Any idea how important those effects would have been to your set of sampling conditions?

5.2 Data was not corrected for H2O or O3, however, we actually humidify the sample flows so that any changes in ambient humidity to do affect instrument sensitivity.

5.3 Changes in O3 are of minor importance and will have an effect of <0.5% on instrument sensitivity under the conditions experience on these flights. Pg 6 lines 22-30 now read "The conversion efficiency of the NO2 converter was measured during each calibration by gas phase titration of the NO to NO2 by addition of O3. NO2 mixing ratio data is corrected for using the measured 90% photolytic conversion efficiency. In flight calibrations were always carried out above the boundary layer, thus ensuring low and stable background levels of NOx. Typically calibrations are carried out at the beginning and end of a flight, with sensitivities and conversion efficiency interpolated between the two and applied to all data. In this work, the 10Hz data has been averaged to 1Hz, with Ddetection limits for the 1Hz data were being $\sim$75pptv for NO and 100pptv for NO2 with approximate total errors at 1ppbv being 10 and 15% for NO and NO2 respectively."

6.1 p. 27341, line 18. “Ozone was quantified in-situ, using a Thermo Scientific 49i . ..” Is this instrument sufficiently fast to compare with other measurements?

6.2/6.3 We feel the 4 second averaging from this instrument (which is the instrument’s fastest acquisition rate) is suitable for comparing to the 1s averaged data from the other instruments. Ozone was only compared to the faster data over diurnal or vertical profile averages, meaning there was always a significant number of overlapping points.

7.1 p. 27343, line 11. “. . . 6-8 normalised ion counts per second (ncps) . . .” Please

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describe how the data is normalized - which ion(s) are used for normalization?

7.2 As described previously (Warneke et al., 2001), generally a humidity dependent PTRMS sensitivity can be expected for two classes of compounds. These are substances, such as benzene and toluene, that do not react with the hydrated hydronium ions and substances with a proton affinity close to water, such as formaldehyde. To account for this humidity dependent PTRMS sensitivity toward benzene and toluene, these compounds were normalised against the hydronium ion counts only.

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 text has been added to pg 8 lines 19-22: “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 p. 27346, line 3. “. . . increasing the NOx oxidation rate leading to decreased NO2 and increased O3 (Pudasainee et al., 2010].” The authors of the cited work describe increased NO2 photolysis leading to decreased NO2 and increased O3. Oxidation of NOx could imply conversion of NOx to further oxidized species (e.g. HNO3). Also, the authors discuss Ox (NO2 + O3) later in the manuscript (Figure 7) with regards to RF 1.I wonder if a discussion of Ox here for RFs 2-6 would help to distinguish between O3 titration and production.

8.2/8.3 We have re-written this paragraph to clarify pg 11 lines 1-8: “Variations in O3 mixing ratio are generally attributed to photochemical production in the mixing layer with some contribution from entrainment from the free troposphere. In London, the low O3 morning mixing ratios were attributed to the destruction of O3 by rapid titration with NO,

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which is emitted during the morning rush hour and highest during the morning. As the day progresses, sunlight intensity becomes higher increasing the radical concentration and hence NO to NO2oxidation rate from the reaction of NO with peroxy radicals. Subsequent photolysis of NO2 leading to increased O3 throughout the day, with this rate of O3 production being a function of NOx and VOC levels and well as sunlight intensity."

9.1 p. 27347, line 27. "These T/B ratios are similar to the average T/B concentration ratio of 1.8 ± 0.3 ppbv ppbv-1 observed within inner London in this study," The supplementary material indicates that the PTR/WAS-FID intercomparisons for benzene and toluene were 1.08 and 0.79, respectively. By my math, this would yield a WAS-FID derived T/B ratio of (1.08/0.79) x 1.8 = 2.5 ppbv ppbv-1. This would be slightly higher than the range of values reported by the ground sites. Do the ground sites use GC-FID? Are the ratios equivalent within uncertainties (I've not bothered to propagate the uncertainties here)?

9.2/9.3 The ground sites are part of the London Air Quality network using GC/FID for online vOC determination. The PTRMS/WAS-FID comparisons are discrete comparisons made by comparing real-time insitu PTRMS measurements against whole air canister samples (1-2 per flight) which were analysed using a dedicated laboratory GC-FID (York University).

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) x 1.8 = 2.5± 0.75 ppbv ppbv-1, hence the ratios are equivalent within uncertainties.

10.1 p. 27348, line 11. "This trimodal distribution between benzene, toluene and NO2 . . ." I don't think this is a tri-modal distribution, but rather these three species have significant covariance. A tri-modal distribution would be a population having three maxima over some range (e.g. particle concentration as a function of diameter, with

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nucleation, accumulation and coarse modes).

10.2/10.3 We agree. This has now been adjusted throughout the manuscript.

11.1 p. 27348, line 16. "Figure 5 also suggests a secondary source contribution to toluene that is not shared with NO2 or benzene . . ." Is there any toluene source indicated in the NAEI that can reconcile the observed plume of toluene?

11.2/11.3 There is no specific toluene emission data available for the NAEI (2012). However, upon analysis of benzene and total VOC emission (NAEI 2012) using ArcGIS, no point sources were evident within the region.

12.1 p. 27350, lines 1-19. "VOC and NOx emissions from airports . . ." This paragraph would be more appropriate in the introduction of the paper, as it presents a discussion of the literature rather than of the authors' work. Also, please provide a reference for the first sentence of the cited paragraph.

12.2/12.3 We agree. The sentence has been moved to the Introduction section and the first paragraph has now been cited (Carslaw et al., 2006).

Carslaw, D. C., Beevers, S. D., Ropkins, K., and Bell, M. C.: Detecting and quantifying aircraft and other on-airport contributions to ambient nitrogen oxides in the vicinity of a large international airport, Atmospheric Environment, 40, 5424-5434, 2006.

13.1 p. 27352, line 15. "However, Ox mixing ratios are substantially reduced at ground levellikely due to enhanced O3 titration with NO . . ." I don't understand how enhanced O3 titration by NO would perturb the Ox mixing ratio, as O3 +NO yields NO2 (+ O2), and Ox is the sum of NO2 and O3. Why wouldn't Ox be expected to be conserved here?

13.2/13.3 We agree and have corrected this error.Pg 16 lines 12 -14 now reads "However, Ox mixing ratios are substantially reduced at ground level possibly due to enhanced deposition in proximity to the surface".

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14.1 p. 27353, line 28. “However, recent developments in diesel emission technology . .” I found this section of the discussion intriguing. Could an evaluation of weekday vsweekend mixing ratios provide some information to tease out effects from diesel emissions(e.g. Pollack et al., 2012, doi:10.1029/2011JD016772)? I’m not sure if there’senough flight data for this, but the ground sites may prove useful here.

14.2/14.3 We agree that in principal this would be an intriguing idea. However detailed traffic density and fleet composition at weekdays and weekends within Greater London would be required. Also we only have very limited flight data, with only a single flight made within the weekend period making a weekday vs weekend comparison tenuous. Ground data could be used for such an analysis but we feel that such an analysis would go beyond the scope of this manuscript.

15.1 p. 27355, line 12. “The reason these VOCs correlate well with NO2, but not NO is possibly because of the ubiquity of diesel vehicles in London.” I’m not sure the discussion provided sufficient evidence for this statement in the conclusions. The authors twice state “however the measured NO/NO2 concentration ratio at 360 m.a.g.l. is likely to be dominated by photochemistry rather than emission sources (Atkinson et al., 2000).” I can’t see how this statement can be reconciled with the sentence above, without further analysis and interpretation of the data (e.g., considering periods of high and low diesel traffic emissions).

15.2/15.3 We agree and retract the statement “The reason these VOCs correlate well with NO2, but not NO is possibly because of the ubiquity of diesel vehicles in London.” Replaced with “As the measured NO/NO2 concentration ratio at 360 m.a.g.l. is likely to be dominated by photochemistry rather than emission sources, VOCs correlate well with NO2 but not NO due to its longer atmospheric lifetime (Atkinson et al., 2000)”.

16.1 p. 27338, line 18. “. . . none pressurised aircraft . . .” Change to “. . . non-pressurised aircraft . . .”

16.2 Corrected.

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17.1 p. 27338, p. 23. ". . . maximum range of 2400 km (5 hr at 500 kg)." I don't understand the parenthetical comment – to what does the 500 kg refer? Sorry if this is obvious to others.

17.2 Parenthetical comment removed

18.1 p. 27339, line 2. "Figure 1a shows all flight legs . . ." There is no "a" or "b" in Figure 1 (Figure text refers to top and bottom).

18.2/18.3 Figure caption changed to "Figure 1a: top map showing all NERC Dornier-228 flights overlaid on UK transport map. Figure 1b: bottom map showing total flight legs across Greater London. Grey area; Greater London boundary, black area; inner London boundary, blue area; London CCZ. "

19.1 p. 27341, line 6. ". . . by adding a small a flow . . ." change to ". . . by adding a small flow . . ."

19.2 Corrected

20.1 p. 27342, line 8. ". . . the inlet flow (50-500 STP sccm)" change to ". . . the inlet flow (50-500 sccm)"

20.2 Corrected

21.1 p. 27345, line 27. "O3 mixing ratios were superficially anti-correlated to NOx . . ." Is'superficially' necessary here?

21.2 "Superficially" removed

22.1 p. 27347, line 26. ". . . showed T/B ratios of 1.6 (1.3-2.0) ppbv ppbv-1 . . ." Please define the meaning of the numbers in parentheses.

22.2 Corrected. Pg 12 lines 23-26 now read "showed average T/B ratios of 1.6±0.3 ppbv ppbv-1 and 1.8±0.3 ppbv ppbv-1 respectively"

23.1 p. 27362. Table 1, RF2 is shown having an April flight date. Is this correct?

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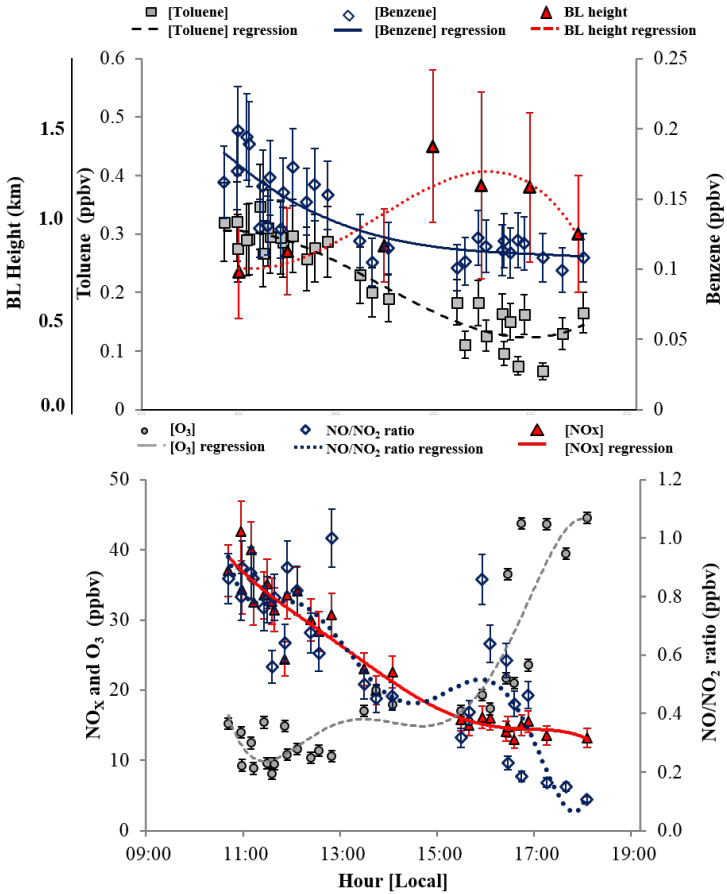

Fig. 1.

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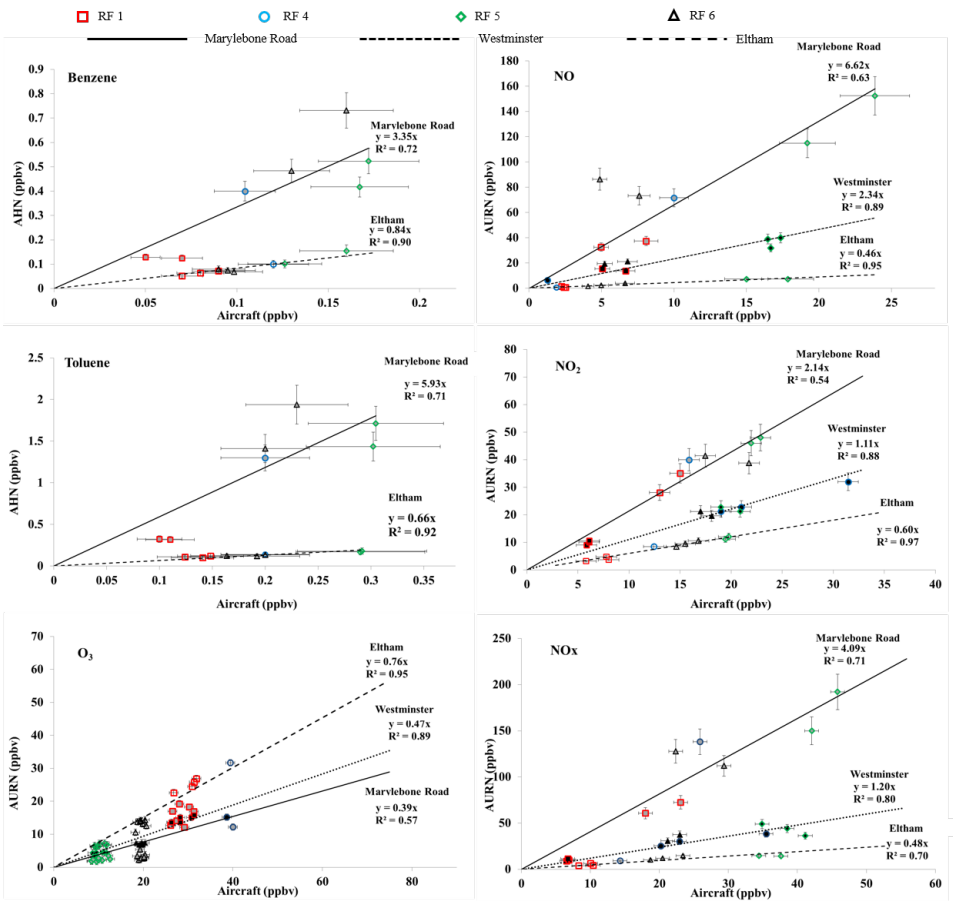

Fig. 2.

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