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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.

Anonymous Referee #3

Received and published: 25 December 2014

This manuscript reports on recent airborne measurements of ozone, oxides of nitrogen, benzene and toluene above London during early summer of 2013. The authors provide detailed description of the instrumental methods used to collect their dataset along with a consideration of measurement uncertainties. They also consider observed NO/NO₂ and toluene/benzene ratios to investigate the impacts of direct local emissions, transport and photochemistry during the day. The manuscript is well organized and written and should be accepted for publication with minor revision. I've added both specific and technical comments below.

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

Specific Comments

p. 27337, line 6. Is there a more recent reference you could use to describe emission sources for anthropogenic VOCs? Warneke et al. [2012] (doi:10.1029/2012JD017899) note marked changes in VOC emissions on decadal scales for Los Angeles and London; a 31-year old reference may not be relevant here.

p. 27337, line 12. “. . . about 50% of NO_x is thought to be derived from vehicles,” Please provide a reference here.

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

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.

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?

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

p. 27343, line 11. “. . . 6-8 normalised ion counts per second (ncps) . . .” Please describe how the data is normalized - which ion(s) are used for normalization?

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p. 27346, line 3. “. . . increasing the NO_x 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 NO_x could imply conversion of NO_x 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.

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 $(1.08/0.79) \times 1.8 = 2.5$ 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)? How do your observed ratios compare to the NAEI, rather than just the ground sites?

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 nucleation, accumulation and coarse modes).

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?

p. 27350, lines 1-19. “VOC and NO_x 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

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the first sentence of the cited paragraph.

p. 27352, line 15. “However, Ox mixing ratios are substantially reduced at ground level likely 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?

p. 27353, line 28. “However, recent developments in diesel emission technology . . .” I found this section of the discussion intriguing. Could an evaluation of weekday vs weekend 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’s enough flight data for this, but the ground sites may prove useful here.

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 “[h]owever 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).

Technical Corrections

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

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.

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)

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p. 27341, line 6. “. . . by adding a small a flow . . .” change to “. . . by adding a small flow . . .”

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

p. 27345, line 27. “O3 mixing ratios were superficially anti-correlated to NOx . . .” Is ‘superficially’ necessary here?

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.

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

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

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